Doctoral Dissertation

Laboratory and *in-situ* Investigations of Methane Bubble Occurrence and Ebullition in Peatland

湿原におけるメタンバブルの存在と噴出に関する室内実験および現地観測研究

Takeshi TOKIDA
常田　岳志

Laboratory of Soil Physics & Soil Hydrology
Depatment of Biological & Environmental Engineering
Graduate School of Agricultural & Life Sciences
The University of Tokyo

March, 2007

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Chapter1

Introduction

1.1 Global Significance of CH_4 Emissions from Peatlands

The historical record of CH_4 abundance obtained from Antarctica ice core have shown that CH_4 concentrations had never exceeded 773 ppb during the past 650,000 years (Spahni et al. [2005]). During the past several centuries, atmospheric CH_4 concentration has increased from pre-industrial level of ~700 ppb to 1783 ppb (2004) as evidenced by CH_4 content in trapped bubbles in ice cores and firn (Etheridge et al. [1998]). This makes CH_4 account for around 20% (0.48 W m^{-2}) of the total radiative forcing (2.43 W m^{-2}) (Houghton et al. [2001]). In contrast to the abundance-based radiative forcing estimates, an emission-based estimate has shown that CH_4 may contribute more (~0.8-0.9 W m^{-2}) to the radiative forcing when considering all the indirect effects (Shindell et al. [2005]). Production of tropospheric ozone in the presence of NOx (0.2 W m^{-2}) and photochemically-formed stratospheric water vapor (0.1 W m^{-2}) are the most notable indirect effects. The overall forcing is equivalent to 61% of the forcing from CO_2.

Although it is clear that human-induced emissions are responsible for the excess CH_4 burden, natural wetlands are likely to be the single largest source of atmospheric CH_4 (Houghton et al. [2001]). However, there is a large uncertainty in wetlands emissions, with estimates ranging from ~100 to 240 Tg yr^{-1} (Fung et al. [1991], Bartlett and Harriss [1993], Hein et al. [1997], Cao et al. [1998], Houweling et al. [1999], Mikaloff Fletcher et al. [2004]).

Although year-to-year variability had been believed to be negligible, recent studies showed global CH_4 efflux has a significant inter-annual variation (Dlugokencky et al. [2003]). *Bousquet et al.* [2006] have suggested that about 70% of the variations over the past two decades are attributable to the fluctuation of CH_4 emission from natural wetlands caused by climatic fluctuations. They also reported that a possible rise in anthropogenic emissions may have been masked by a reduction in wetland emissions caused by negative precipitation anomalies in recent years. In the light of global significance of wetlands CH_4 source, it is imperative that we understand the processes determining the production, consumption, transport and emission of CH_4 in natural wetlands. Understanding wetland CH_4 dynamics may contribute to constrain the estimates of the other source strengths, which may ultimately help to establish mitigation strategies of CH_4 emissions from human activities.

In this study, I have investigated the mechanisms of CH_4 emission from a Japanese peatland, called Bibai mire. Peatland is one of the categories of natural wetlands and covers more than half of the total wetlands area in the world (Matthews and Fung [1987], Aselmann and Crutzen [1989]). Most peatlnads exist in high latitude of northern hemisphere and may constitute about one-third of the world's total wetland emissions (Matthews [2000]). Because the high latitude regions are expected to receive the most pronounced change in climate due to albedo feedbacks involving snow and sea ice (Holland and Bitz [2003], Chapin III et al. [2005]) and subsequent changes in ecosystems (e.g. Gorham [1991]), understanding the processes controlling CH_4 emissions from northern peatlands is a highly important issue.

1.2 Objectives of This Study

Accurate observation of CH_4 exchange between the peat and the atmosphere is one of the fundamental bases for any efforts to improve our knowledge of CH_4 emissions from peatlands. At present, most of the estimates of CH_4 emissions from peatlands are based on infrequent, temporally discontinuous ground-based flux measurements. Weekly to monthly measurement intervals have been widely adopted. Efforts have been made to extrapolate the measured emission rates to seasonal amounts of CH_4 emission using relevant biogeochemical measurements of water table positions, peat temperatures, and other variables with the assumption that the flux was stationary for the period between the measurements (e.g. Dise et al. [1993], Frolking and Crill [1994], Kettunen et al. [2000]). However, temporal variation of CH_4 flux in the shorter time scales has not commonly been measured, presumably because diffusion of dissolved CH_4 or releases of CH_4 through aquatic plants, which might have small temporal variability are believed to be the main transport mechanisms to the atmosphere (Kettunen et al. [2000]).

It has conventionally been thought that wetland soils are saturated below the water table and that CH_4 exists in a dissolved state. However, in the context of investigating the cause of the anomalously small hydraulic conductivity of peat, a new conceptual model has recently been proposed; the low hydraulic conductivity may be attributable to the occlusion of pores by gas bubbles, mainly of CH_4 (Mathur and Lévesque [1985], Dinel et al. [1988], Brown et al. [1989], Buttler et al. [1991]). Suppose there is a unit volume of peat and you have interest in the mass of gas in it. You may wonder whether gas may exist in gas-phase and/or in liquid phase. Figure 1.1 shows mole fraction of gas in gas-phase to the total gas (= gas-phase gas + dissolved-phase gas) as a function of ratio of air content to water content. This relation can be calculated from ideal gas law combined with Henry's law. Because of its very low solubility, mole fraction of CH_4 in gas phase dramatically increase with increasing air content. Even when ratio of air content to water content is only 0.05, more than 60% of CH_4 exists in the gas phase, exhibiting a sharp contrast to CO_2 which is a rather soluble gas species. Hence, if the occurrence of CH_4-containing bubbles in peat is confirmed, it is plausible that most CH_4 exists in the bubbles (not in dissolved form) and a considerable portion of CH_4 emitted to the atmosphere might be via release of bubbles, i.e. ebullition. As ebullition seems highly variable in space and time, widely-used flux measurement scheme may not be able to capture the ebullition events. Hence, there seems an urgent need to improve our understandings about the volume, composition, and distributions of the bubbles as well as the factors that may cause the ebullition.

The objective of this study is to investigate occurrence of CH_4 bubbles and their possible ebullition in peatland. In particular in the following chapters of the thesis the following research questions are addressed:

Chapter 2: Occurrence of gaseous-phase CH_4 in waterlogged peat was investigated by using a newly-designed gas sampler and measuring gas-phase content below the water table level. Vertical distribution of the volume of the bubbles and mixing ratio of CH_4 in the bubbles were measured and the state of CH_4 in a waterlogged peat was quantified.

Chapter 3: A long-term (more than a year) mesocosm experiment was conducted using an intact peat core sample. In this experiment, the peat core was subjected to natural air pressure fluctuations while the temperature and water table were controlled and kept constant. This experimental design aimed at investigating the effect of atmospheric pressure fluctuation on CH_4 ebullition from peat to the atmosphere.

Chapter 4: A 90-hour field study was carried out in high-summer season to determine the CH_4 ebullition rate from peat soil into the atmosphere in the field and to identify factors that control the processes of CH_4 ebullition. We measured the air pressure, water table, and peat temperature as potential determinants of the ebullition. Theoretical considerations followed by numerical computations were also performed to isolate and quantify the effect of the individual factors on the ebullition.

Chapter 5: Intensive CH_4 flux measurements were conducted during a period of spring thaw to determine whether or not a sudden change in CH_4 emission rates occurs. In order to obtain better understanding of the mechanisms of the possible CH_4 ebullition during spring-thaw, CH_4 release into the atmosphere and stored CH_4 in near-surface peat trapped during winter were simultaneously investigated.

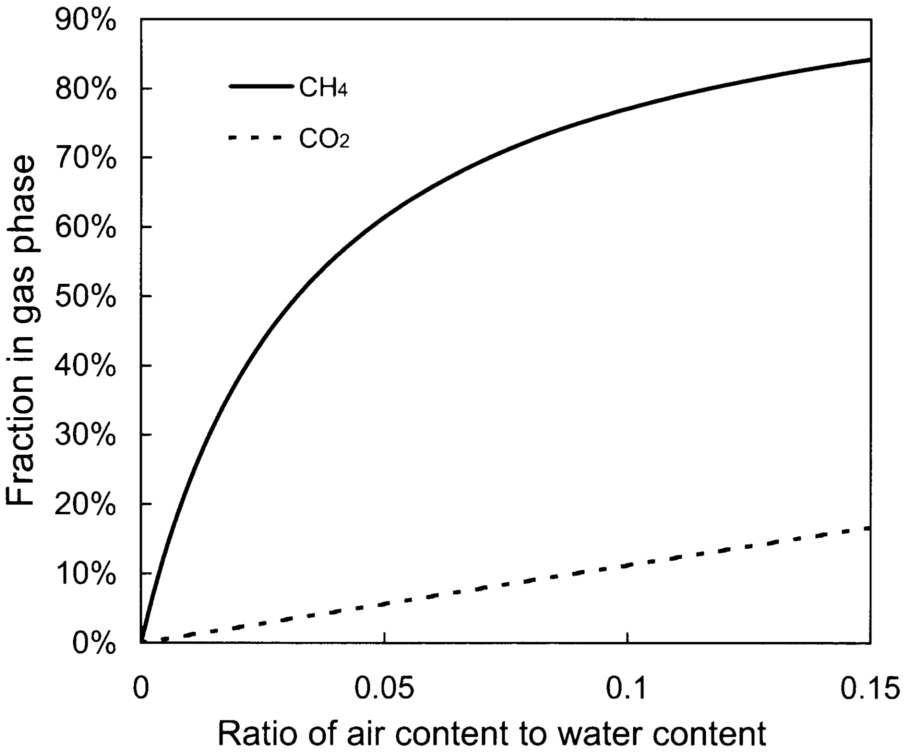

Figure1.1 Mole fraction of gas in gas-phase to the total gas (= gas-phase gas + dissolved-phase gas) as a function of ratio of air content to water content in a unit volume of peat.

Chapter2

In situ Accumulation of Methane Bubbles in a Natural Wetland Soil

In this chapter, occurrence of gaseous-phase CH_4 in waterlogged peat was investigated by using a newly-designed gas sampler and by measuring gas-phase content below the water table. Vertical distributions of the volume of the bubbles were measured, mixing ratio of methane therein were determined, and thus the state of methane in a waterlogged peat were described.

T. Tokida, T. Miyazaki, M. Mizoguchi and K. Seki.
European Journal of Soil Science, 56:389-395, 2005.

2.1 Summary

Natural wetlands are a significant source of atmospheric methane, an important greenhouse gas. Compared with numerous papers on measurements of methane emission from natural wetland surfaces, there are few reports on methane configuration and distribution within wetland soil profiles. By using a newly designed gas sampler, we succeeded in collecting free-phase gas from beneath the water table down to 120 cm in a peat soil. The volumetric percentage of methane in the gas phase increased with depth and was generally more than

50% beneath the zone within which the water table fluctuates. The fractional volume of the gas phase in the peat beneath the water table was estimated to be from 0 to 19% with significant variation with depth, suggesting uneven distribution of gas bubbles. Using the volume ratio of the gas and liquid phases and methane concentration in the gas phase, as well as assuming that methane was in equilibrium (based on Henry's Law between the two phases), we calculated that ~60% of the methane accumulates in the form of bubbles. These results suggest the importance of ebullition in methane emission, which might be a major cause for the reportedly large variation of methane emission in both space and time. Most importantly, our results show the need to consider gaseous-phase methane for understanding the mechanisms of production, transport and emission mechanisms of methane in wetlands, which has been overlooked to date.

2.2 Introduction

Natural wetlands are a significant source of methane to the atmosphere (Matthews and Fung [1987], Fung et al. [1991], Bartlett and Harriss [1993], Hein et al. [1997]). Net methane emission rate is a complex function of processes that regulate the production, oxidation and transport of the gas to the atmosphere (e.g. Bartlett and Harriss [1993]). Various kinds of biogeochemical factors affect emission, and there has been much work to find key factors responsible for the large variations in both space and time of the emissions (e.g. Harriss et al. [1982], Shurpali et al. [1993], Whiting and Chanton [1993], Christensen et al. [2003]).

In contrast to the numerous papers on measurements of methane emission from the land surface, stored methane within wetland soils has attracted little attention. However, precise knowledge of the configuration and distribution of the methane within soils is essential for understanding methane dynamics in wetland ecosystems. A fundamental question now arises: does the methane in waterlogged peat exist in a gaseous phase as bubbles, or in the dissolved state in the liquid phase?

Conventional wisdom maintains that wetland soils are saturated below the water table, and methane has been thought to exist in a dissolved state. In contrast, in investigating the cause of the anomalously small hydraulic conductivity of catotelm peat, *Mathur and Lévesque* [1985] developed a new conceptual model in which the hydraulic conductivities were attributed to the occlusion of pores by gas bubbles generated by anaerobic respiration and fermentation. There is support for this concept and subjective evidence for the presence of gaseous-phase methane in some field studies (Dinel et al. [1988], Brown et al. [1989], Buttler et al. [1991]). The first quantitative work, in which the volume of the bubbles and the amount of methane in the bubbles were measured, was probably that of *Reynolds et al.* [1992]. They did a column experiment using 'grab' samples from a Canadian raised bog, and they showed that the gaseous phase, in which methane seems to be the main constituent, does exist in a 'saturated' column with water. *Beckwith and Baird* [2001] did a similar experiment using undisturbed peat cores at more realistic temperatures and found that the volumetric gas content increased up to 16% as biogenic gas bubbles, especially methane, accumulated in the peat matrix.

In situ quantification of the volume and composition of the bubbles is much more difficult than measurement in the laboratory presumably because trapped free-phase gas below the water table can easily escape to the atmosphere with little change in ambient pressure, or by mechanical disturbance. There appear to be no reports on the composition of the gas bubbles stored in peat, and only two studies have presented in situ measurement data to estimate the volume of the gas beneath the water table by a non-destructive approach. *Fechner-Levy and Hemond* [1996] used the magnitude of the buoyancy response to changes in atmospheric pressure in a floating bog in Massachusetts and determined the amount of the gas trapped in the peat matrix to be 8-15% by volume. By using hydraulic-head data in a raised bog in northern Minnesota, *Rosenberry et al.* [2003] estimated the gas content to be 9% or 13%, depending on their two types of assumptions regarding the distribution and method of confinement of the gas. Methodologies used in the two studies, however, can be applied to calculate depth-averaged values, indicating the need to establish a new approach that takes vertical distribution of the gas into consideration.

Here we report results of in situ direct gas sampling, the determination of methane content in the bubbles, and estimation of the volume of the gaseous-phase profile in a Japanese peatland, which gives quantitative information on the state of methane in a waterlogged peat.

2.3 Study Site

Our study site is the Bibai 50-ha peat bog, in Hokkaido, Japan (141°48'E, 43°19'N). In the past, there were about 60,000 ha of peatlands in this region. Now, almost all of this bog has vanished as a result of land reclamation since 1950. Surrounded by drainage ditches and farmland, the site has gradually dried up, allowing the invasion of bamboo (*Sasa palmata*) and low shrubs, while the *Sphagnum* community, which was spread all over the surface in 1960, has decreased and now occupies only about 1 ha. We report here the results obtained from the wettest area where *Sphagnum* spp. dominate. The peat from the surface to a depth of ~2.7 m consists mainly of moderately decomposed *Sphagnum* mixed with some sedge sediments, with a volcanic ash layer at 30 cm depth (Kondo et al. [1997]). Below this, purple moor grass (*Moliniopsis japonica*) and reed (*Phragmites communis*) sediments accumulate to approximately 4 m depth (Miyaji et al. [1995]). The mean annual temperature is 7.1°C and the mean annual precipitation is 1153 mm over the past 20 years.

2.4 Methods

2.4.1 Gas Sampling Equipment

Our gas sampling equipment consisted of a metallic probe, a vacuum gauge, and a 60-cm^3 syringe (Figure 2.1). Basically, sampling is achieved by sucking the gas from the peat with the syringe after the probe is inserted into the peat layers.

The probe consists of a hollow tube (8 mm outside diameter and 7 mm inside diameter) with a 5.5-mm diameter rod inside it. Before the probe is inserted into the peat, the tip of the probe is plugged with wet paper or clay and the inside evacuated with the syringe to avoid air contamination during the insertion. After the probe has been installed, one removes the plug at the desired sampling depth by pushing the rod down. This rod is slightly bent so as not to fall under its own weight. However, it can easily be moved up and down by finger pressure on the flexible plastic tube.

Gas samplings were made at intervals of 10 cm down to 120 cm relative to the peat surface in August and October 2002 and October 2003 at the same site, referred to as 'Site A'. To avoid the influence of disturbance caused by sampling at a specific depth on the next sampling, the sampling positions were shifted at regular intervals on the circumference of a circle of 1.5 m radius.

2.4.2 Procedure for Gas Sampling and Analysis

We present the procedure for sampling and analyses as a series of instructions.

1. Plug the tip of the probe (Figure 2.1) with wet paper or clay. Connect the 60-cm^3 syringe to the stopcock and evacuate the inside of the equipment to minimize air contamination. Close the stopcock and detach the syringe. Repeat this operation two or three times so that the internal pressure in the probe, as indicated by the pressure gauge, is < 5 kPa. Determine the quantity of remaining atmospheric air from the internal pressure and the volume of the probe (20 cm^3 excluding the syringe volume).
2. Insert the probe vertically into the peat with the internal pressure kept small until the tip reaches the desired sampling depth. Remove the plug by pushing down the movable rod.
3. Again connect the empty syringe to the probe and sample the gas. Allow sufficient time, usually less than 15 s, for the pressure in the syringe to equal atmospheric pressure. Record separately the volumes of water and gas collected in the syringe. Disconnect the syringe from the stopcock, attach a needle to the syringe and inject the collected gas into a sealed, pre-evacuated 5-cm^3 vial for storage and transfer.
4. Analyse the gas in the vial by flame ionization gas chromatography to quantify the

methane concentration.

5. Correct the gas composition data to remove the effect of the residual atmospheric air (step 1).

2.4.3 Gas Content Measurement

We estimated the gas contents in October 2002 and October 2003 at three sites (A, B, C), including the gas sampling site (Site A), along an east-west transect at intervals of 50 m. There were small differences in vegetation type and water table position relative to the peat surface among the three sites.

To estimate the volumetric gas content by difference, we measured volumetric water content combined with previous measurement of the solid fraction (Kasubuchi et al. [1994]). A soil-moisture probe (Profile Probe type PR1 100 cm version, Delta-T Devices) with sensors at 10, 20, 30, 40, 60 and 100 cm depths was used to measure the water content of the undisturbed profile at intervals of 10 cm to 100 cm depth. We obtained data at 70, 80 and 90 cm by re-using the 100-cm sensor in 10-cm increments.

In October 2002, the gas content profile was estimated at one point per site. In October 2003, to assess the variation of the gas content within a site, we measured such profiles at three points 30 cm apart from each other per site.

2.4.4 Measurement of Water Table Level and Temperature Profile

The height of the water table at Site A was measured and recorded automatically by the 'Diver' (Van Essen Instruments, The Netherlands) every 3 hours from 1 July 2002 to 26 October 2003. The temperature profiles at Site A were measured on each field investigation date with a digital thermometer at 10-cm intervals from the peat surface to 100 cm to determine the Henry's Law constant of methane at each depth.

2.5 Resuts and Discussion

2.5.1 Presence of Gas Bubbles below the Water Table

By using the gas sampling equipment, we succeeded in sampling from the peat below the water table which, at Site A, was at 11.2 cm and 10.8 cm on 23 August and 18 October in 2002, respectively, and at the surface on 25 October in 2003 (Figure 2.2). Figure 2.3 shows the volumes of gas collected in the 60-cm^3 syringe from the surface zone down to 120 cm depth in the peat.

There were three cases in this sampling. The first case (Case 1), observed in the shallow layers, was that the syringe filled with water only, indicating that there were no or few gas bubbles adjacent to the probe. The second case (Case 2, the most commonly observed pattern) was that the syringe was filled with both gas and water. To our surprise, in the other case (Case 3), the syringe was completely filled with gas. This was observed mainly at depths of 90 and 100 cm but also occasionally in shallower layers. In some samplings in Case 3, the whole equipment was completely filled with gas as soon as suction was applied, with no water drawn into the probe. This response indicates -without doubt- the presence of large, continuous gas pockets with a volume greater than $80\,\mathrm{cm}^3$ ($60\,\mathrm{cm}^3 + 20\,\mathrm{cm}^3$: syringe + the other parts of the equipment) at the sampling depths.

In Case 2 and in some instances in Case 3, both water and gas were taken into the probe simultaneously, and the water tended to remain in the probe without entering the syringe for the following reason. When pore water and trapped gas are taken into the probe, water rises with the pressure gradient, while the gas bubbles rise inside the water-filled probe due to their buoyancy as well as with the pressure gradient. As a result, the gas moves faster than the water, and consequently, the gas:water ratio in the syringe is expected to be greater than that in the peat layer. Therefore, the volume of gas collected (Figure 2.3) should not be regarded as the volume ratio of the gas phase in the peat layer; rather it simply indicates the relative amount of gas bubbles in the vicinity of the probe.

Although the aim of the sampling is to extract the gaseous phase, the suction applied by the syringe might release gas from the liquid phase. To evaluate the possibility of such an evolution, we did a supplementary experiment as follows. First, tap water was exposed to the atmosphere so that the dissolved gas in the water was allowed to equilibrate with it. Then the water was extracted in a similar way as in the field. This gave $1.2 \pm 0.4\,\mathrm{cm}^3$ (mean ± standard error; n=3) of gas in the 60-cm^3 syringe. The solubilities of the major constituents of the atmosphere, N_2 and O_2, and of methane, which is expected to be one of the main gas species in waterlogged peat, are 0.016, 0.031 and $0.033\,\mathrm{m}^3\,\mathrm{m}^{-3}$, respectively, at 20°C (National-Astronomical-Observatory [2002]). So it is plausible to consider that if the volume of the gas collected in the syringe is substantially larger than $1.2\,\mathrm{cm}^3$ then the gas must have originally existed as the gaseous phase. Because, in Cases 2 and 3, the volume of gas collected (Figure 2.3) far exceeded the amount that could have been generated from the liquid phase, we can safely say that the gas sampled had originally existed in the gas phase in the peat.

Thus, we regard Figure 2.3 as evidence of substantial amounts of gas bubbles in this waterlogged peatland. Our newly designed sampling equipment is thus useful when we need to sample in such a way as not to change the relative composition of the gas phase. To determine the volume ratio of gas phase in the peat layer, additional independent measurement is required.

2.5.2 Gas Content below the Water Table

Table 2.1 shows the depth profile of the volumetric gas content beneath the water table. We measured the water content profile and estimated the volumetric gas content by subtracting the solid and liquid content from the whole volume. The solid content was 3-3.5% by volume down to 100 cm except in the layer around 30 cm where we found volcanic ash (Kasubuchi et al. [1994]). In October 2002, we estimated the volumetric gas content at one point per site. In October 2003, we measured such profiles at three points 30 cm apart from each other per site.

In October 2002, gas contents were estimated to be from 0 to 17% by volume, with fluctuations with depth > 10% without a coherent trend. Also, depth-averaged gas contents at each site ranged from 7.2 to 12.9%.

In October 2003, volumetric gas contents were estimated to be 0-19%. Variations among the three positions at each site (Table 2.1, in parentheses) were generally smaller than the measurement errors, and so we could not detect spatial heterogeneity within sites. Unlike in 2002, depth-averaged gas contents at the three sites seemed comparable with each other. The gas content profiles showed clear trends with depth; the average gas contents from 60 to 100 cm (14.7-15.5%) were considerably larger than those in the upper layers (3.1-4.2%).

Thus, the existence of a gaseous phase beneath the water table was clearly demonstrated by Table 2.1, as was also shown in the discussions of Figure 2.3, even though the measurement errors were relatively large. The larger gas contents at 70-100 cm depth are particularly notable. Comparison of the profiles in October 2002 and October 2003 suggests that the gas contents might change with time, especially in the shallower layers.

2.5.3 Methane Concentration in Gas Bubbles

Figure 2.4 shows the vertical profile of methane concentration at Site A on 23 August and 18 October in 2002, and on 26 October in 2003. Each point shows the methane concentration in the gas phase that was collected beneath the water table.

Methane concentration increased with depth down to 50-60 cm on every sampling date (Figure 2.4). Large differences between the dates are attributed to the fluctuation of the water table (Figure 2.2) by which the boundary between production and oxidation of methane is affected (Beckmann and Lloyd [2001]). There were relatively small variations at 40-50 cm depth, suggesting that the effect of fluctuation in the water table could reach as low as 20 cm below the lowest level.

There was little temporal variation below 60 cm depth, indicating that methane concentration in the gas phase was kept constant below the level of impact of the low water table. These results accord with those of a dissolved methane profile in a Scottish peatland (Clymo and Pearce [1995]). Decreased methane concentration at around 80 cm depth implies an earlier steep drawdown of the water table. Greater concentrations between 50 and 60 cm as opposed to greater depths might be caused by greater production of methane in near-surface layers (Brown [1998], Van den Pol-van Dasselaar and Oenema [1999]) after the water table has recovered.

These results, as well as the facts that the normal water table fluctuation is limited down to 35 cm and that the peat is 4 m thick (Miyaji et al. [1995]), strongly suggest that methane consistently is a major constituent of the bubbles in deep layers.

2.5.4 Amount of Methane in the Gas Bubbles and in the Dissolved State

We calculated the amount of methane at Site A both in the gaseous phase and dissolved in the liquid phase using the volume ratio of the gas and liquid phases and methane concentration data in the gas phase. In this paper, we assume that methane was in equilibrium between the two phases according to Henry's Law. This assumption seems reasonable, since a slow change in methane content in the waterlogged soil, inferred in Figure 2.4, might allow enough time for methane to achieve equilibrium between the gaseous and liquid phases. We assume further that the pressure in the bubbles was the sum of atmospheric and hydrostatic pressure.

We calculated that the proportion of methane existing as the bubbles to the total (dissolved + bubble) was 33-67% in 2002 and 51-83% in 2003 (Table 2.2). These results contrast with the conventional assumption that methane exists in solution beneath the water table; our best estimates of the amount of methane down to 1m depth were 2.2-3.2 times larger than those calculated under an assumption that there is no gasphase (Table 2.2). Our results thus indicate that a significant fraction of methane exists in the gaseous state, rather than in the dissolved form, even below the water table. Our results further indicate that in deep peat layers considerable amounts of methane bubbles seem to be trapped, forming a substantial methane reservoir (Brown et al. [1989]).

Most previous reports on biogeochemical processes of methane in wetland soils have expected methane to be dissolved. For example, studies designed to determine depth distributions of the methane production below the surface (Clymo and Pearce [1995], Blodau and Moore [2003]) took no account of methane bubbles beneath the water table. However, our results clearly show the need to quantify the amount of methane in the gaseous phase even below the water table, especially where a mass-balance approach is required.

2.5.5 Implications for Methane Emission

Our results offer some insights when considering methane emissions from wetlands. Methane reaches the atmosphere by three processes: molecular diffusion of dissolved methane, transport through plants, and ebullition (bubbling). Our results show the importance of ebullition in emission. Release of gas bubbles due to buoyancy presumably occurs when the stored gas volume exceeds some critical value (Beckwith and Baird [2001]). For this reason, it is likely that methane release by ebullition occurs discontinuously. Large methane fluxes associated with factors causing an increase in gas volumes in peats, such as a drop in water table or atmospheric pressure (Shurpali et al. [1993]), support this conjecture. Ebullition might also take place through discrete channels that are distributed non-uniformly in peatlands. Therefore, the commonly observed variation in methane flux in space and time from wetlands might well be explained by ebullition. We suggest that further studies on production, transport in soil and release of methane bubbles at the soil-atmosphere interface, with emphasis on spatial and temporal variation, are necessary for the precise estimation of methane fluxes from wetlands.

2.6 Conclusions

In situ volumetric gas profiles beneath the water table in peat, and methane concentrations in the gas phase at each depth, were quantified for the first time. To our surprise, ~60% of the methane accumulates in the form of bubbles, not in the dissolved form. The volume ratio of the gas was estimated to be from 0 to 19%, with significant variation with depth. These results indicate the importance of ebullition in methane emission mechanisms, and can explain the reported large spatial and temporal variability of the emissions of methane from natural wetlands.

2.7 Acknowledgments

We thank the National Agricultural Research Center for Hokkaido Region for access to the research field.

Table2.1 Depth profile of volumetric gas content (%) beneath the water table

Depth below the peat surface (cm)	Site A		Site B		Site C		Measurement error of sensor[a]
	Oct. 2002[b]	Oct. 2003[c]	Oct. 2002[b]	Oct. 2003[c]	Oct. 2002[b]	Oct. 2003[c]	
20	9.6	3.0 (2.5)	13.9	1.5 (0.2)	-[d]	5.2 (3.2)	1.7
30	8.7	3.8 (2.3)	13.7	8.6 (1.9)	6	4.5 (1.7)	1.9
40	9.7	4.2 (4.4)	17.0	3.5 (1.0)	7.8	7.8 (4.0)	2.6
50	3.6	2.6 (2.6)	14.9	1.8 (1.6)	4.8	1.8 (2.0)	2.5
60	3.9	1.9 (2.2)	9.8	0.0 (0.1)	0.1	1.7 (2.7)	2.5
70	8.3	15.4 (0.7)	11.5	15.5 (0.3)	11.9	12.2 (5.3)	3.9
80	9.7	18.1 (1.2)	12.9	15.7 (0.4)	14.8	15.3 (2.0)	3.9
90	4.4	17.7 (1.0)	14.9	17.7 (1.9)	9.9	19.1 (4.7)	3.9
100	-[d]	8.1 (7.4)	7.1	13.3 (3.8)	10.1	12.2 (4.3)	3.9
Average	7.2	8.3	12.9	8.6	8.2	8.9	
Depth of the water table (cm)	10.2	0	0.8	0	7.5	0	

[a] Standard deviations from calibration curves of Profile Probe outputs (each sensor) against volumetric water content. [b] Value of single measurement. [c] Mean of the three measurements with standard deviation in parentheses. [d] Not measured due to temporary failure of the equipment.

Table2.2 Amount of methane (g CH_4 m^{-2}) in the gas bubbles and in dissolved state down to 1 m from the peat surface at Site A. Fractions of methane in each phase to the total (%) are shown in parentheses.

	Best estimates			95% lower limit			95% upper limit			Amount of potential dissolution[a]
Date	Dissolved	Bubble	Total	Dissolved	Bubble	Total	Dissolved	Bubble	Total	Dissolved
Oct. 2002	8.5 (42)	12 (58)	20	8.8 (67)	4.3 (33)	13	8.3 (33)	17 (67)	25	9
Oct. 2003	9.5 (28)	24 (72)	34	10.1 (49)	10.4 (51)	21	8.8 (17)	42 (83)	51	11

[a] Calculated under the assumption that the peat pore is saturated with respect to water.

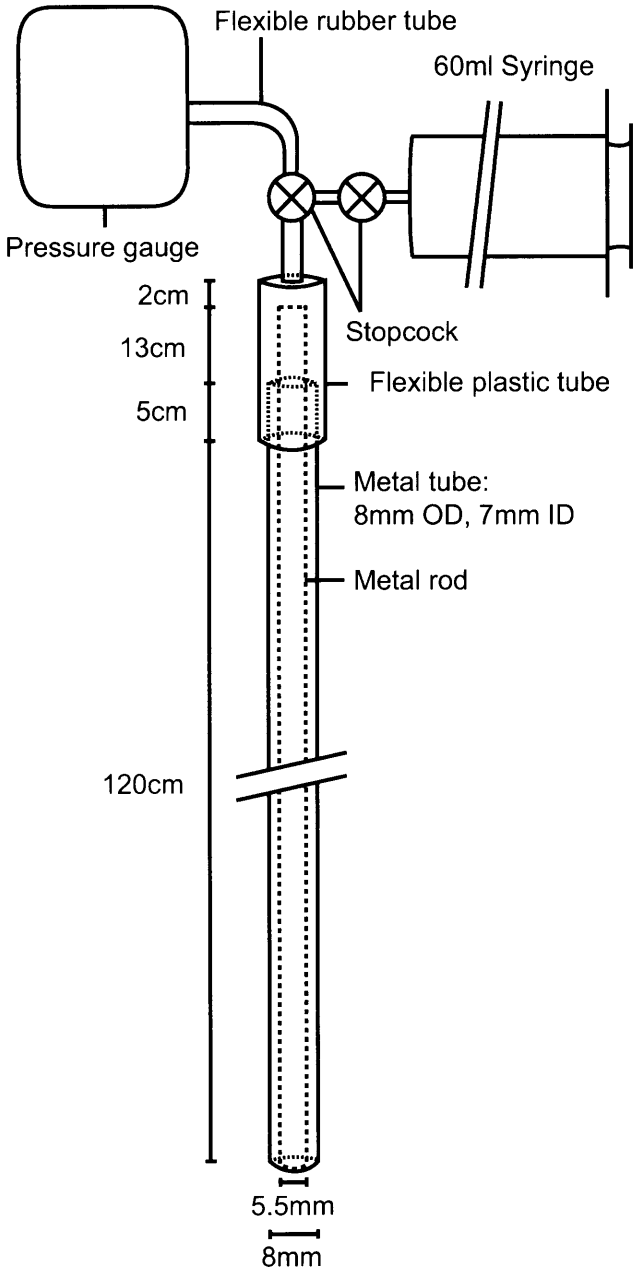

Figure2.1 A newly designed gas sampling apparatus.

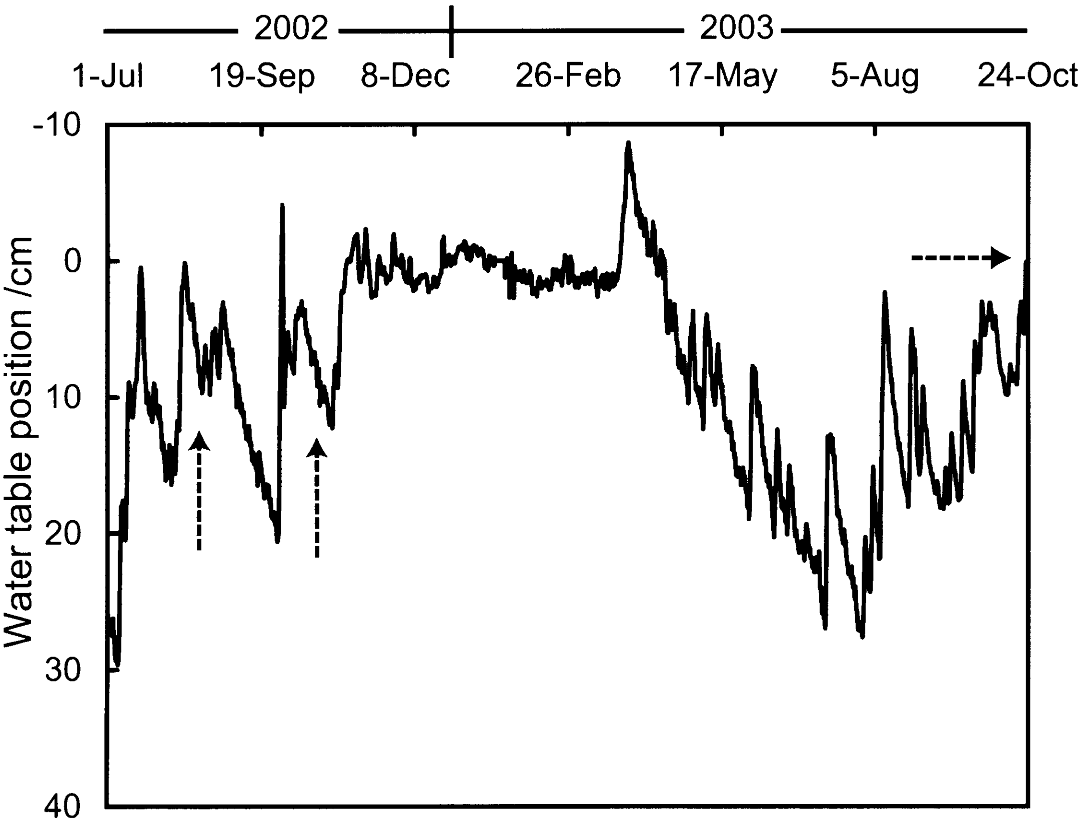

Figure2.2 Water table position relative to the peat surface at Site A. The positive value indicates depth beneath the peat surface. Field study dates are indicated by three arrows.

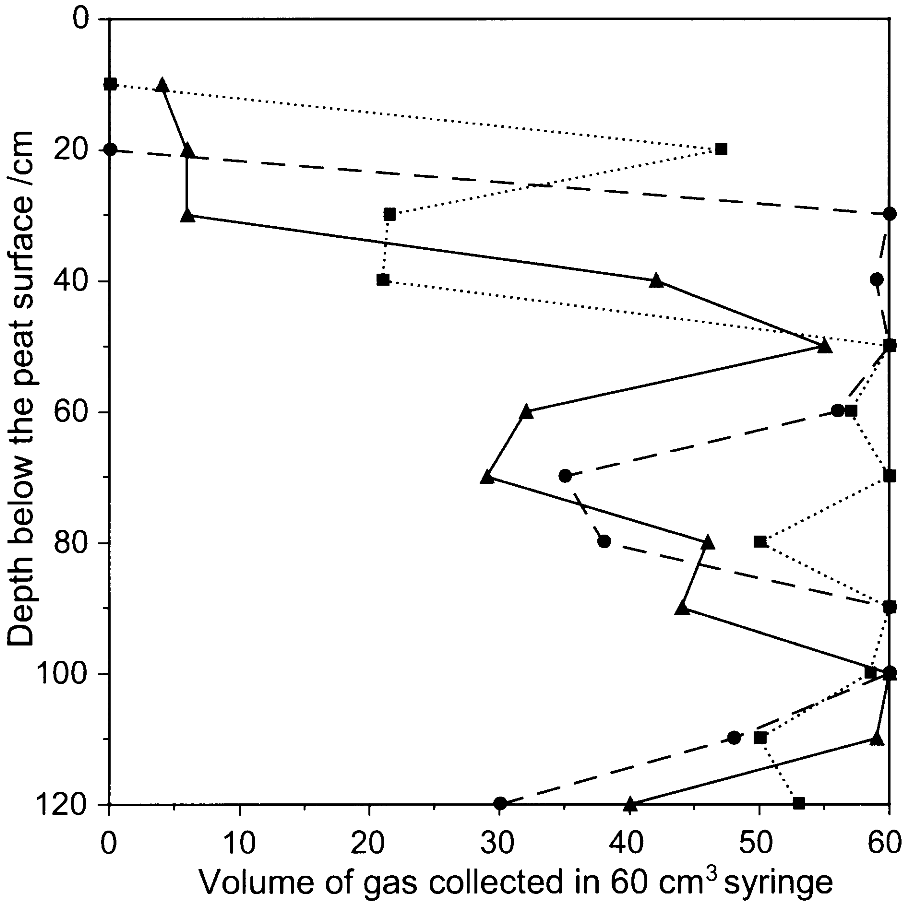

Figure2.3 Volume of gas collected in the 60-cm^3 syringe at Site A. ■, 23 August 2002; ●, 18 October 2002; ▲, 26 October 2003.

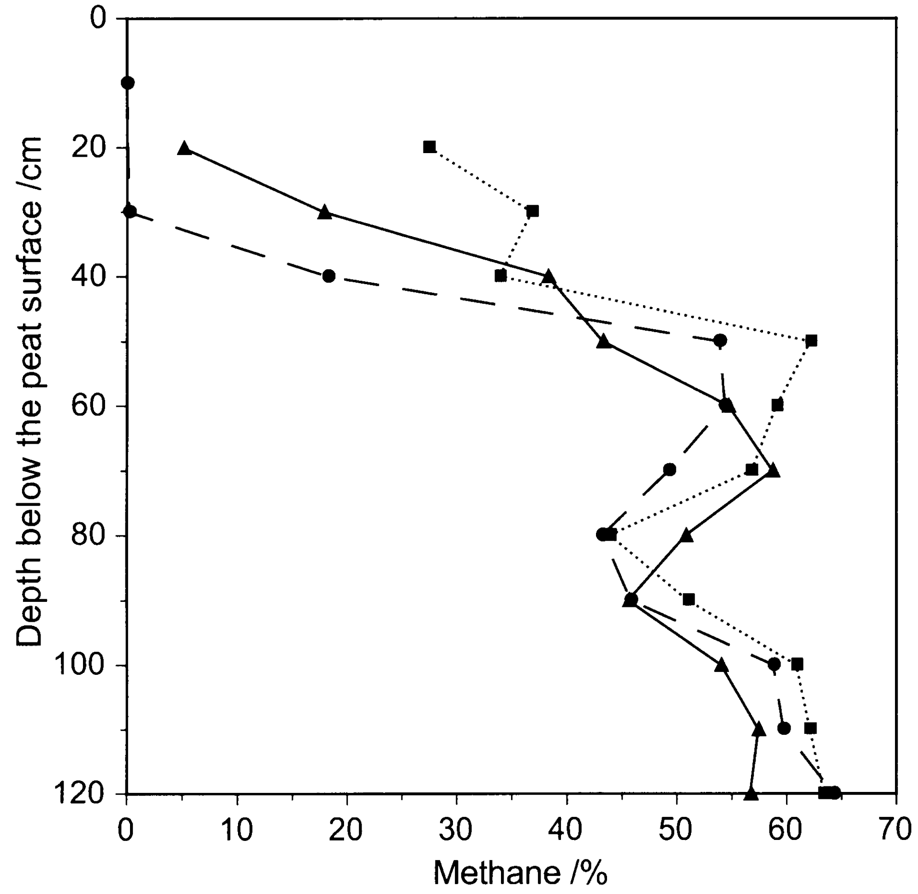

Figure2.4 Vertical profile of methane concentration at Site A. Methane is expressed as a percentage of gas sampled from the peat beneath the water table. ■, 23 August 2002; ●, 18 October 2002; ▲, 26 October 2003.

Chapter3

Ebullition of Methane from Peat with Falling Atmospheric Pressure

A long-term (more than a year) mesocosm experiment was conducted using an intact peat column. In this experiment, the sample was subjected to natural air pressure fluctuations while the temperature and water table were controlled and kept constant. This experimental design aimed at investigating the effect of atmospheric pressure fluctuation on CH_4 ebullition from peat to the atmosphere.

T. Tokida, T. Miyazaki, M. Mizoguchi.
Geophysical Research Letters, 32, L13823, doi:10.1029/2005GL022949. 2005.

3.1 Summary

Recent works on CH_4 emissions from peatlands have demonstrated that ebullition can be a more important emission pathway than it has been thought. However, knowledge of its features and associated environmental factors is still very limited. In this study, we investigated the quantitative relationship between the amount of CH_4 emitted via ebullition and changes in the atmospheric pressure through a laboratory experiment. During the flux measurement period, ebullition was recorded almost exclusively in air-pressure-declining phases. The in-

creased volume of the gas bubbles due to reduction in atmospheric pressure and the amount of released gas bubbles revealed a strong linear relation, suggesting that *in situ* CH_4 emissions via ebullition can be estimated from this correlation. Our results clearly showed that atmospheric pressure can be one of the most important factors to control CH_4 emissions from peatlands and that ebullition can be the main transport mechanism during the pressure-falling phase.

3.2 Introduction

Because most previous reports on biogeochemical processes of CH_4 in peatland have assumed CH_4 to be in dissolved state (Clymo and Pearce [1995]), it has been generally believed that diffusion of dissolved CH_4 is the main transport mechanism to the atmosphere and that episodic ebullition of CH_4-containing bubbles does not commonly occur (Windsor et al. [1992], Arah and Stephen [1998], Kettunen [2003]). However, our recent work on CH_4 in peatland has demonstrated that peat soil is not saturated with respect to water even below the water table due to the existence of CH_4-containing gas bubbles (Tokida et al. [2005a]), suggesting the importance of the ebullition of CH_4 emission mechanisms.

To date, few studies have estimated the amount of ebullitive CH_4 flux. *Glaser et al.* [2004] interpreted the topographic oscillations of the peat surface as a result of CH_4 ebullitions from a deep layer, which may contain a large amount of gas bubbles (Romanowicz et al. [1995]), and estimated the amount of CH_4 released via ebullition using changes in the peat-pore pressure and volume of the peat. These studies proposed that several tens of grams of CH_4 per square meters could be released in a single ebullition event. *Baird et al.* [2004] conducted laboratory incubation experiments and showed that the ebullition of CH_4 from near-surface *sphagnum* peat can occur if the volume of biogenic gas bubbles in waterlogged peat exceeds some critical value. Their results also suggested that the ebullition could be as important mechanism as the diffusion of dissolved CH_4. These previous reports clearly illustrate that ebullition is a more important emission pathway than had previously been thought. However, quantitative understanding of its features is still very limited due to the lack of simultaneous direct measurements of ebullition and the factors that may affect it.

Among various potential parameters, which may trigger CH_4 ebullition, barometric pressure is possibly one of the most important factors because a drop in atmospheric pressure may lead to gas generation from solution and the enlargement of the volume of the gas phase (Fechner-Levy and Hemond [1996]). Moreover, in freshwater lake environments, a correlation has been observed between low air pressure and increased rates of CH_4 emissions (Mattson and Likens [1990], Casper et al. [2000]), suggesting that CH_4 emission from peatlands is also influenced by changing atmospheric pressure. In this study, we examined the quantitative relationship between air pressure change and the amount of CH_4 emitted via ebullition through a laboratory experiment with an intact peat sample.

3.3 Experimental Design

We investigated CH_4 ebullition in an intact peat sample, 20 cm in diameter and about 57 cm in length, collected in an acrylic cylinder (20 cm i. d., 60 cm in length) from a 50-hectare small peat bog located in Hokkaido, Japan (141°48'E, 43°19'N). The mean annual temperature of the site is 7.1°C, and the mean annual precipitation has been 1,153 mm in the past 20 years. The vegetation of the sample, consisting primarily of *Sphagnum* mosses and minor numbers of *Moliniopsis japonica*, was left intact. The peat from the surface to a depth of ~28 cm consists mainly of moderately decomposed *Sphagnum*. Below this, sedge and *Sphagnum* accumulate with a volcanic ash layer at ~48 cm depth. Further descriptions of the study site can be seen in *Tokida et al.* [2005a].

The collected peat sample was stored in a large container with *in situ* water to avoid oxic degradation and transferred to the laboratory. The incubation of the peat column was started on December 2, 2003. Distilled water was continuously supplied through a Mariotte tank to make up for the loss of water due to evapotranspiration and sampling required for analysis. Therefore, the water table was adjusted to 6 cm below the *Sphagnum* surface with < 1 cm fluctuations. The peat sample was maintained at 20°C, and the vegetation was exposed to a 12 hour light/dark cycle with a light intensity of 150 μmol m^{-2} s^{-1}. The sides of the column were covered with aluminum foil to prevent light penetration. Ambient atmospheric pressure was measured and recorded by the 'Diver' pressure gauge (Van Essen Instruments, The Netherlands).

CH_4 flux measurements were made using an ordinary closed-chamber method (non-steady-state) at four independent periods starting at days 366, 378, 399, and 408 after the onset of incubation. In this study, we tried to isolate the effect of air pressure change alone from other potential factors, among which the trapped gas-phase volume in the peat can be the most important determinant of CH_4 ebullition (Baird et al. [2004]). As in the past peat incubation experiments, which suggested that an increase in the volume of trapped gas would level off in less than 100 days of incubation (Beckwith and Baird [2001], Baird et al. [2004]), the amount of the stored gas should have already plateaued and had little effect on the difference in the CH_4 flux. The duration of each flux measurement was approximately 60 hours, in which an intensive sampling scheme (at intervals of 1-3 hours) was adopted with the chamber placement for 20 minutes in order to identify the expected episodic, short-time bubbling of CH_4 from the peat matrix to the atmosphere. The CH_4 flux was calculated from a linear trend of CH_4 concentration measured at 0, 3, 7, and 20 minutes after the chamber placement. When ebullitive emissions occurred, a sudden jump of the headspace CH_4 concentration was commonly observed, rendering the slope of the CH_4 concentration calculated by the linear fitting to be unrepresentative of the measurement period. Thus, in these cases, we assumed that a difference in concentrations at 0 and 20 minutes divided by the time of 20 minutes was the rate of CH_4 emission for the corresponding measurement period.

To measure the dissolved CH_4 and CO_2 concentration profiles, pore water samplers consisting of an unglazed pipe (2.35 mm outer diameter and 1.45 mm inner diameter) fitted with a three-way stopcock were horizontally inserted at 1-cm intervals down to 18 cm and at 2-cm intervals below that to a depth of 54 cm. A 0.6 ml of pore water was collected from each sampler and injected into a 5-ml vial. A Shimadzu gas chromatograph (GC-14A) was used to measure the CH_4 (FID) and CO_2 (TCD) concentration in the gas phase of the vial. The original dissolved concentration was reconstructed using the headspace concentrations, the volumes of the headspace and the water phase, and Henry's law. Measurements were conducted on days 359, 375, 393, and 414. We assumed that dissolved gases were in equilibrium between the liquid and the gas phases according to Henry's Law constant (National-Astronomical-Observatory [2002]).

3.4 Results

The concentration of dissolved CH_4 showed significant variation with depth. However, the concentrations of neither dissolved CH_4 or CO_2 at each depth varied significantly with time (Figure 3.1). In addition, the depth-averaged concentration showed little variation with time, 45.1% (SD=0.9%) for CH_4 and 12.1% (SD=0.4%) for CO_2 on average. Therefore, we hereafter assume that the averaged CH_4 and CO_2 concentrations in the bubbles were 45% and 12%, respectively, and the other 43% was N_2 throughout the flux measurement period. Because the water vapor fraction was small compared to other gas species, we decided to ignore it.

Figure 3.2 shows the time course of cumulative methane fluxes and changes in the atmospheric pressure. During the four flux measurement periods, five air-pressure-reduction phases occurred (Figure 3.2). In Figure 3.2-a, the pressure-declining phase was divided into phases 1 and 2 and treated separately because of the clear difference in the pressure-reduction rate. Apart from the base flux which was the slope of gradual increase in cumulative flux, episodic ebullition of CH_4 was recorded in all pressure-declining phases. In contrast, during the non-pressure-reduction phases, ebullitive emissions were scarcely observed. A tremendous release of CH_4 was observed with an acute drop in air pressure (Figure 3.2-a). All these results strongly indicate that the CH_4 ebullition was induced due to the drop in atmospheric pressure.

Table 3.1 summarizes the cumulative CH_4 flux and relative contribution of the ebullitive and non-ebullitive flux (= base flux) during the pressure-reduction phases. Non-ebullitive CH_4 fluxes were similar to commonly observed field data measuring diffusive CH_4 emissions (e.g., Roulet et al. [1994]). The amount of ebullition in terms of the volume of CH_4-containing gas bubbles was calculated by assuming that bubbles were released equally from the entire peat profile. Ebullition accounted for a major fraction of the total flux in all the pressure-reduction phases.

3.5 Discussion

To quantitatively understand the relationship between lowering of air pressure and the CH_4 ebullition, we estimated the amount of increased gas bubbles due to the reduction in barometric pressure as described below. Under the assumption that dissolved gases in the liquid phase rapidly equilibrate with gas bubbles as the atmospheric pressure changes, the pressure-volume relationship is shown to be

$$\frac{\mathrm{d}V_g}{\mathrm{d}P_i} = -\frac{V_g}{P_i} - \frac{V_w}{\mathrm{H_i}P_i} = -\frac{C_i}{P_i^2} \tag{3.1}$$

where V_g is the volume of the gas, V_w is the volume of water in which V_g occurs as bubbles, P_i is the partial pressure of gas species i, $\mathrm{H_i}$ is the dimensionless Henry's law constant for gas i, and C_i is defined to be $P_i(V_g + \frac{V_w}{\mathrm{H_i}})$ (after Fechner-Levy and Hemond [1996]). It is noteworthy that C_i does not change with P_i. The integration of Equation (3.1) with respect to V_g from V_{g1} to V_{g2} and P_i from P_{i1} to P_{i2} yields the following simultaneous equation for each gas species,

$$\Delta V_g = V_{g2} - V_{g1} = C_i\left[\frac{1}{P_{i2}} - \frac{1}{P_{i1}}\right] \tag{3.2}$$

where subscripts 1 and 2 indicate the time at the beginning and at the end of the pressure-declining phase, respectively. We can obtain the increased gas volume ΔV_g and partial pressure of each gas P_{i2} by solving Equation (3.2) on the condition that $\sum P_{i2}$ is the total pressure at the end of the pressure-declining phase. Equation (3.2) assumes that no bubble emission occurs during the pressure-declining phase, thus, it may somewhat overestimate the increased volume of the gas phase. However, because the amount of ebullition is much smaller compared to the existing gas volume, this assumption is a reasonable approximation.

We calculated the increased gas volume (ΔV_g) in the five pressure-reduction phases by solving Equation (3.2). The initial partial pressures of each gas in the bubbles (P_{i1}) were determined by multiplying the atmospheric pressure by each gas concentration, 45% for CH_4, 12% for CO_2, and 43% for N_2. The initial volumetric gas content (V_{g1}) was assumed to be 12%, which is the median of the existing typical data of the gas content in waterlogged peat. Calculations of ΔV_g under different assumptions of V_{g1}, with the maximum literature value of 16% (Beckwith and Baird [2001], Baird et al. [2004]) and the minimum of 8% (Tokida et al. [2005a]), were also made.

Regardless of the assumed V_{g1} values, we found a strong linear relation between the increased gas volume calculated by Equation (3.2) and the amount of released gas bubbles (Table 3.1) (Figure 3.3). A positive x-intercept suggests that ebullition may occur only after some drop in atmospheric pressure. This is consistent with our intuition that, due to the possible increase in air pressure prior to the reduction phase, the volumetric gas content at the beginning of the pressure lowering was, to some extent, less than the threshold value beyond which buoyancy forces cause bubbles to escape. After the initiation of ebullition, it is natural to consider that the amount of released bubbles would be proportional to the increased gas volume in the peat. Indeed, in our calculation, the slope of the linear regression would be unity when V_{g1} is set to be 10.7%. Hence, the linear regression is considered to properly describe the quantitative nature of ebullition from the peat to the atmosphere.

These results and discussions as well as a close agreement between our results and field observations of *Glaser et al.* [2004] clearly revealed that atmospheric pressure can be one of the most important factors to control CH_4 emissions from peatlands and that ebullition can be the main transport mechanism during the pressure-falling phase. In addition, our results may raise some questions about the reliability of reported field data. It is very likely that scientists take field measurements in good weather and avoid less desirable conditions, such as wind or rain. This would lead to reports of field data obtained in primarily stable atmospheric pressure regimes. Since CH_4 flux when the air pressure is dropping may be less frequently measured, it is possible that smaller CH_4 emission rates were preferentially reported, resulting in an underestimation of the extrapolated annual CH_4 flux from peatlands. Because ebullition occurs discontinuously in both space and time, it seems very difficult for conventional flux measurement methods to accurately quantify ebullitive CH_4 emissions in the field. We, thus, finally suggest that the utilization of the linear relationship shown in Figure 3.3 can be a good way to estimate *in situ* CH_4 emissions via ebullition.

3.6 Acknowledgments

We thank Hiromi Imoto for his technical assistance with our experiments, Katsutoshi Seki for his perceptive comments to improve the manuscript, and Osamu Nagata and Michio Yasuda (the National Agricultural Research Center for Hokkaido Region) for kindly giving permission to take peat samples from the research field. We also thank Michinao Kojima, Ken Takeuchi, and Shoichiro Hamamoto for their assistance in the flux measurements. This research was partially supported by a Grant-in-Aid for Scientific Research (DC1 16-11631) by the Japan Society for the Promotion of Science.

Table3.1 Cumulative CH_4 emission in the five pressure-reduction phases.

	Phase No.				
	1	2	3	4	5
Length of time /hours	34.6	10.2	40.7	17.1	20.0
Non-ebullition /mg m^{-2}	66	26	86	27	24
Ebullition /mg m^{-2}	261	523	187	54	122
Ebullition[a] /ml $column^{-1}$	27.4	54.9	19.6	5.7	12.8
Contribution of ebullition	80 %	95 %	68 %	67 %	83 %

[a]Expressed as volume of CH_4-containing gas bubbles.

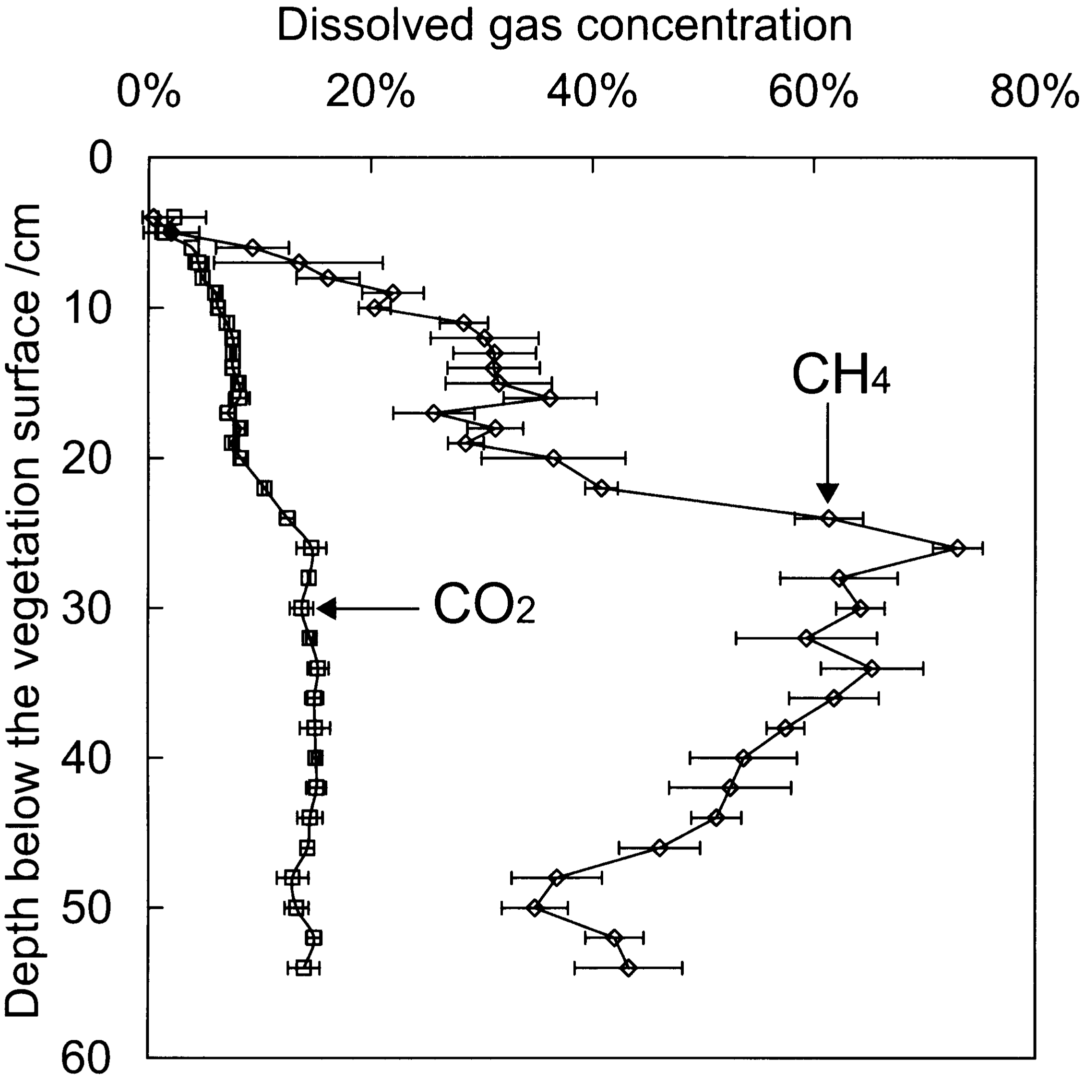

Figure3.1 Averaged dissolved CH_4 and CO_2 concentration profile measured on days 359, 375, 393, and 414. Bars indicate the standard deviation for each depth.

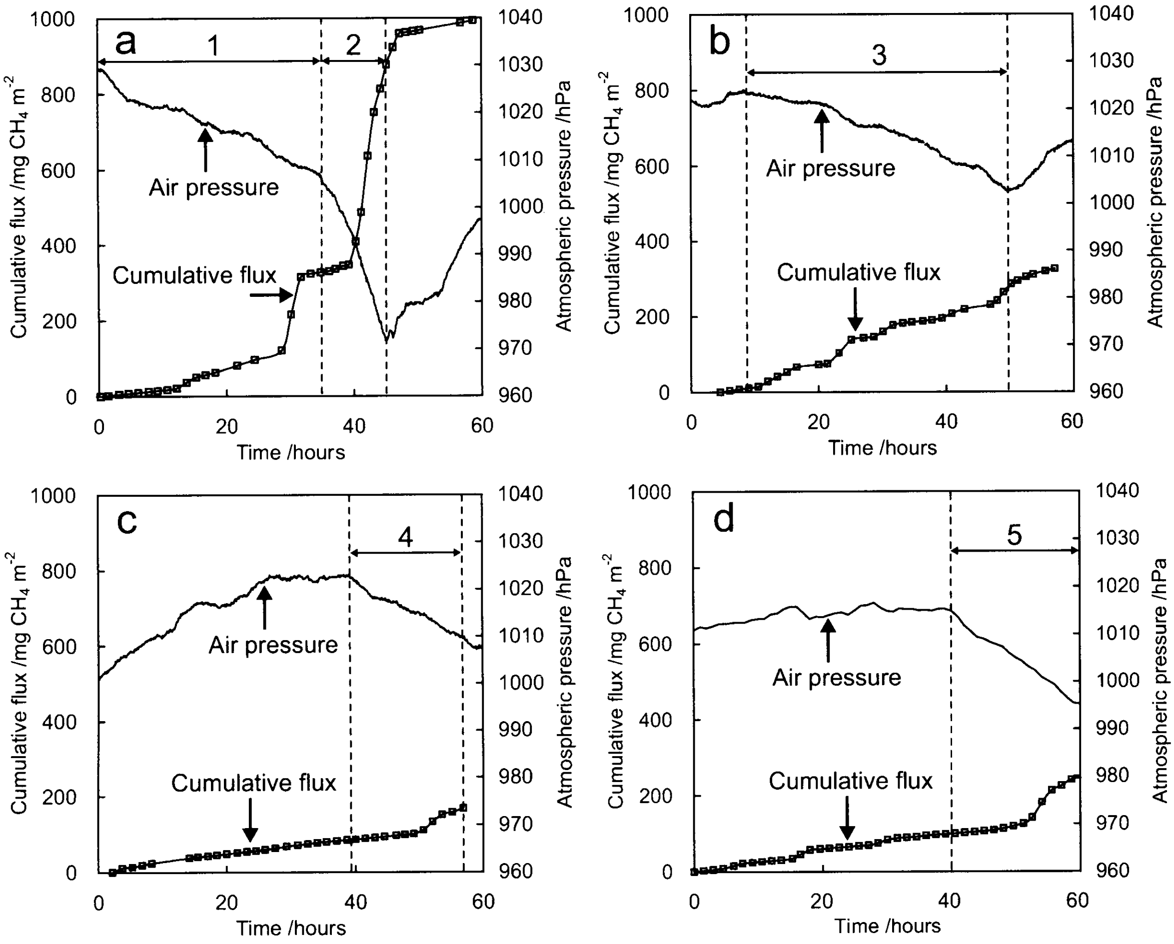

Figure3.2 Cumulative methane flux and change in atmospheric pressure starting at days 366 (a), 378 (b), 399(c), and 408(d). Each pressure-reduction phase was labeled with numbers (1-5). The timing of the flux measurement by a closed chamber is indicated by open squares.

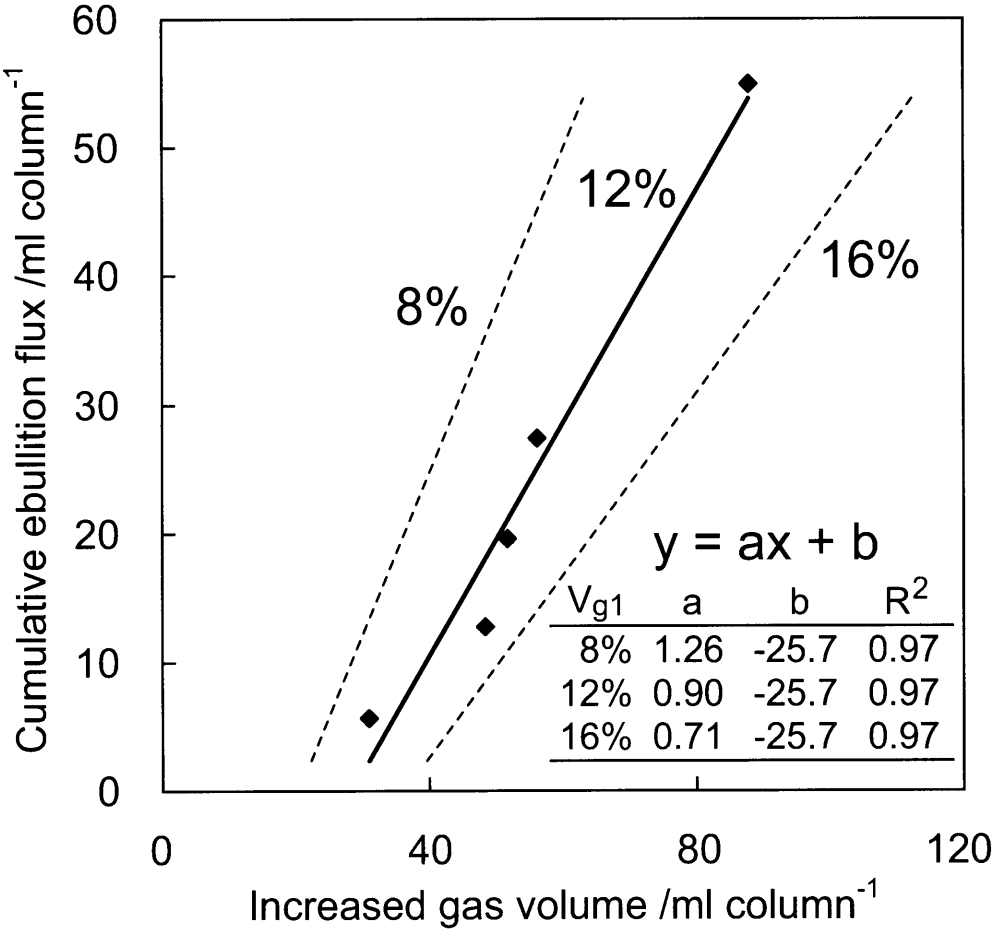

Figure3.3 Relationship between the increased gas volume obtained by solving Equation (2) and the observed cumulative ebullition flux (shown in Table 1) during the five pressure-reduction phases. Three linear regression lines are calculated under different assumptions of V_{g1} (8%, 12%, and 16%). The plotted data is calculated under the assumption of V_{g1} = 12%.

Chapter4

Falling Atmospheric Pressure as a Trigger for Methane Ebullition from Peatland

In this chapter, results of a 90-hour field study was presented. This field investigation was carried out in high-summer season to determine CH_4 ebullition into the atmosphere from peat soil in the field condition and to identify the determinant of CH_4 ebullition. We measured the air pressure, water table, and peat temperature as potential factors to control the ebullition. Theoretical considerations followed by numerical computations were also performed to isolate and quantify the individual effect of the factors on the ebullition.

T. Tokida, T. Miyazaki, M. Mizoguchi, O. Nagata, F. Takakai, A. Kagemoto, and R. Hatano.
Global Biogeochemical Cycles, in press

4.1 Summary

Peatlands are widely regarded as a significant source of atmospheric CH_4, a potent greenhouse gas. At present, most of the information on environmental emissions of CH_4 comes from infrequent, temporally discontinuous ground-based flux measurements. Enormous ef-

forts have been made to extrapolate measured emission rates to establish seasonal or annual averages using relevant biogeochemical factors, such as water table positions or peat temperatures, by assuming that the flux was stationary during a substantial non-sampling period. However, this assumption has not been explicitly verified, and little is known about the continuous variation of the CH_4 flux in a timescale of individual flux measurement. In this study, we show an abrupt change in the CH_4 emission rate associated with falling atmospheric pressure. We found that the CH_4 flux can change by two orders of magnitude within a matter of tens of minutes due to the release of free-phase CH_4 triggered by a drop in air pressure. The contribution of the ebullition to the total CH_4 flux during the measurements was significant (50-64%). These results clearly indicated that field campaigns must be designed to cover this rapid temporal variability caused by ebullition, which may be especially important in intemperate weather. Process-based CH_4 emission models should also be modified to include air pressure as a key factor for the control of ebullient CH_4 release from peatland.

4.2 Introduction

Natural wetlands, with more than half of their geographical area covered with peat-rich ecosystems (Matthews and Fung [1987], Aselmann and Crutzen [1989]), are likely to be the single largest natural source of atmospheric CH_4 (Matthews [2000], Mikaloff Fletcher et al. [2004]). Although recent findings indicate that living terrestrial vegetation is a significant source of atmospheric CH_4 (Keppler et al. [2006]) and that source categories may need to be reclassified, it is important to continue studying the processes governing the production of CH_4 in anoxic peat layers in wetlands and its eventual release.

Once produced in the waterlogged peat sediment, CH_4 can be emitted into the atmosphere through any of the three following pathways (Chanton [2005]): diffusion of dissolved CH_4 along the concentration gradient, transport via the aerenchyma of vascular plants, or release of CH_4-containing gas bubbles, i.e., ebullition. Diffusive CH_4 emission occurs wherever a CH_4 concentration gradient exists. The diffusion of dissolved CH_4 may be the dominant pathway in *Sphagnum*-dominated peatlands (Romanowicz et al. [1995], Chasar et al. [2000], Frenzel and Karofeld [2000]). CH_4 produced in anoxic soils can also be transported through the roots and aerenchymatous tissues of emergent vegetation; in this way, plants serve as direct conduits to the atmosphere.

Compared to diffusive transport and plant-mediated emission, ebullition appears to have attracted less attention, presumably because most previous reports on the biogeochemical processes of CH_4 in peatlands have assumed CH_4 to be in a dissolved state (e.g. Clymo and Pearce [1995], Blodau et al. [2004]). Consequently, it has been generally believed that diffusion of dissolved CH_4 or/and plant-mediated release are responsible for the majority of the total emissions and that the episodic ebullition of CH_4-containing bubbles does not commonly occur (Windsor et al. [1992], Arah and Stephen [1998], Kettunen [2003]). However, recent studies on CH_4 in peatlands have demonstrated that peat soil is not saturated with respect to water even below the water table due to the existence of gas bubbles that contain a high concentration of CH_4 (Comas et al. [2005a,b], Tokida et al. [2005a]), suggesting the importance of ebullition in CH_4 emission mechanisms. Overall, at present, there is some controversy over the occurrence of ebullition itself as well as its significance as a mechanism for CH_4 transport from peat to the atmosphere.

Because of its episodic behavior, the ebullitive CH_4 flux from the peat surface is difficult to quantify. To date, few studies have looked at ebullition. Those that have, have used indirect field methods or laboratory incubations of peat samples. *Glaser et al.* [2004], for example, interpreted the topographic oscillations of the peat surface as a result of CH_4 ebullitions from a deep layer and estimated the amount of CH_4 released via ebullition using changes in the peat pore-water pressure and volume of the peat. They proposed that several tens of grams of CH_4 per square meter could be released in a single ebullition event, a value that exceeded the annual average value measured with chambers. *Baird et al.* [2004] conducted laboratory incubation experiments and showed that the ebullition of CH_4 can occur from near-surface *Sphagnum* peat and that ebullition was as important as diffusion. These previous reports clearly illustrate that ebullition is a more important emission mechanism than had previously been thought.

Among various potential parameters, that may trigger CH_4 ebullition, barometric pressure is possibly one of the most important factors because a drop in atmospheric pressure may lead to gas generation from solution and the enlargement of the volume of the gas phase (Fechner-Levy and Hemond [1996]). In freshwater lake environments, a correlation between low air pressure and increased rates of CH_4 emissions has been observed (Mattson and Likens [1990], Casper et al. [2000], Engle and Melack [2000]), suggesting that CH_4 emission from peatlands are also influenced by changing atmospheric pressure. Recently, a laboratory experiment was conducted using an intact peat core, in which the experimental setup was subjected to natural air pressure fluctuations while the temperature and water table were controlled and kept constant (Tokida et al. [2005b]). The experiment indicated that a reduction in barometric pressure can cause a sudden release of CH_4 bubbles from the peat core. Moreover, it demonstrated that ebullition can be the main transport mechanism during the pressure-falling phase.

In this paper, we present the results of a 90-hour field study that was carried out to determine CH_4 ebullition from peat soil to the atmosphere in the field conditions, and to identify the factors that control the ebullition. We measured the air pressure, water table, and peat temperature as potential factors that control ebullition. Direct gas sampling and analysis of the gas were also conducted to confirm the existence of bubbles and relate ebullition to CH_4 bubbles that accumulated below the water table level.

4.3 Materials and Methods

4.3.1 Study Area

The study site is an ombrotrophic peatland located in Bibai, Hokkaido, northern Japan (141°48'E, 43°19'N). Peatlands began forming in this region in 4000-5000 YBP, and had increased to 60,000 ha in this region until the late 19th century. However, as a result of an extensive land reclamation project, mainly soil dressing, almost all of these peatland have vanished and at present only 50 ha of peatland is preserved. Surrounded by drainage ditches and farmland, the 50 ha has gradually dried up, allowing the invasion of bamboo (*Sasa palmata*) and low shrubs, while the *Sphagnum* community, which was a dominant species all over the surface in 1960, has decreased and now occupies only about 1 ha. The peat from the surface to a depth of ~2.7 m consists mainly of moderately decomposed *Sphagnum* mixed with some sedge sediments, with a volcanic ash layer at 30 cm in depth (Kondo et al. [1997]). Below this, purple moor grass (*Moliniopsis japonica*) and reed (*Phragmites communis*) sediments occur to approximately 4 m depth (Miyaji et al. [1995]). Over the past 20 years, the mean annual temperature has been 7.2 ± 0.6 (mean ± SD) °C, and the mean annual precipitation has been 1170 ± 124 (mean ± SD) mm.

In this study, we selected the wettest area, where the original *Sphagnum* vegetation is preserved. Other than mosses, *Moliniopsis japonica*, *Carex omiana*, *Carex middendorffi*, *Eriophorum vaginatum*, *Rhynchospora alba* and *Rhynchospora fauriei* are included in the vegetation (Nagata et al. [2005], Takakai et al. [2005]). Methane flux and water table level measurements as well as direct gas sampling were made at two plots (31.2 m apart), which, hereafter, are referred to as plots A and B. Changes in the water table position during the study period were measured with the "Diver" pressure gauge (Van Essen Instruments). Period of the measurements were from July 14, 2005, at 15:00 to July 18 at 8:30. In this study, information about possible fluctuations in the peat surface levels [Glaser et al. [2004], Strack et al. [2005]] was not available and the water table positions were expressed relative to the peat surface (Figure 4.1). In general, the water table position at the two plots showed decreasing trends, except for that at the end of the field campaign, in which 8.5 mm of precipitation was recorded. The atmospheric pressure was monitored at one location (several meters away from plot A) with the "Baro" pressure gauge (Van Essen Instruments) every 15 minutes.

4.3.2 CH_4 Flux Measurement

The CH_4 flux from the peat surface to the atmosphere was measured simultaneously at plots A and B, in which an intensive measurement scheme (at 1.5-2-hour intervals) was adopted in order to identify the expected short-time bubbling release of CH_4. A static chamber technique, one chamber on each plot, was used to measure the CH_4 flux (Hutchinson and Livingston [2002]). An open bottomed acrylic chamber (~0.054 m^3 in volume) was placed on a previously installed collar. The collar enclosed an area of 900 cm^2 and was inserted into the ground to a depth of 15 cm. The chamber was fitted into a water-filled groove on the collar, enabling an air tight seal between the headspace air and surrounding atmosphere. Boardwalks leading to the two plots were constructed to minimize disturbance.

In order to transmit the ambient air pressure change into the headspace of the chamber, a flexible plastic bag, which was open to the atmosphere via a plastic tube, was placed inside the chamber. The chamber was also equipped with a thermometer and an air sampling tube through silicone rubber plugs installed in the openings at the top of the chamber. When the chamber was set into the water-filled groove on the collar, the openings remained open to avoid pressurizing the chamber air, which has the potential to cause a large measurement error (Hutchinson and Livingston [2001]). Five ml of internal air was collected at 0, 4, 12, and 30 minutes after the deployment of the chamber through the air sampling port and injected in a pre-evacuated vial. A Shimadzu gas chromatograph (GC-14A) equipped with a flame ionization detector was used to determine the CH_4 concentration of the sample.

The CH_4 flux was calculated using the effective chamber volume, the temperature of air in the chamber, the ambient atmospheric pressure (=chamber pressure), and the slope of the CH_4 concentration against time. When ebullition occurred, a sudden jump of the headspace CH_4 concentration was commonly observed (Tokida et al. [2005b]), rendering the slope of the CH_4 concentration calculated by the linear fitting unrepresentative of the measurement period. Thus, in these cases, the difference in the concentrations at 0 and 30 minutes divided by the time of 30 minutes was considered to be the rate of CH_4 emission for the corresponding period.

4.3.3 Gas Sampling From Beneath The Water Table

Free-phase gas below the water table level was directly collected using a gas sampling equipment (Tokida et al. [2005a]) at 10-cm intervals down to 90 cm. The collected gas sample was injected into a pre-evacuated 5 ml vial and transferred to the laboratory. Because CH_4, CO_2, and N_2 have been shown to be the main components of the gas phase in waterlogged peat sediments (Buttler et al. [1991], Shannon et al. [1996]), we analyzed the collected gas for CH_4 and CO_2 and assumed the other fraction to be N_2. A Shimadzu gas chromatograph (GC-14A) equipped with a thermal conductivity detector was used for CO_2 analysis, and a flame ionization detector was used for CH_4 analysis.

4.3.4 Peat Temperature

The temperature profiles at 10-cm intervals were obtained with thermocouples and recorded in a CR-10X (Campbell Scientific, Inc.) at plot A. We assumed plot B had an identical profile. During the field campaign, water table was lowered (Figure 4.1) and there was an unsaturated moss layer, which has low thermal conductivity (van der Molen and Wijmstra [1994]). In such a condition, the diurnal temperature fluctuation is insignificant below the water table level where CH_4 exists (Puranen et al. [1999]). Therefore we ignored the diurnal cycle and estimated the average temperature and increasing temperature trend during the study period due to an annual cycle by linearly fitting the peat temperature against time (Table 4.1).

4.3.5 Estimation of Changing Gas Volume below the Water Table

It has been suggested that the release of gas bubbles occurs when the volume of the bubbles exceeds some threshold beyond which the buoyancy forces cause the bubbles to escape into the atmosphere (e.g. Tokida et al. [2005b]). The effects of changing atmospheric pressure, peat temperature, and water table level on the change in the gas content can be evaluated by using a mass balance approach, as described below. The total mass of a gas species, i, at a specific depth beneath the water table level, C_i, is shown to be

$$C_i = \frac{P_i^{t1} V_g^{t1}}{RT^{t1}} + \frac{P_i^{t1} V_w}{H_i^{t1} RT^{t1}} \tag{4.1}$$

where P_i is the partial pressure of gas species i, V_g is the volume of the gas, V_w is the volume of water in which V_g occurs as bubbles, H_i is the dimensionless Henry's law constant for gas i, R is the universal gas constant, and T is the temperature (Fechner-Levy and Hemond [1996]). The superscript $t1$ denotes "time 1," representing the beginning of the field study. Recent studies concerning biogenic bubbles in peat sediments have suggested that the value of the gas content below the water table is approximately 10% of the total peat volume (Fechner-Levy and Hemond [1996], Rosenberry et al. [2003], Tokida et al. [2005a]). We adopted this value as V_g^{t1} throughout the peat profile. V_w can be estimated by subtracting the V_g and solid content from the whole volume. Because a previous study showed the volumetric solid content to be slightly less than 5% down to the 1.2 m depth at this site (Kasubuchi et al. [1994]), V_w was estimated to be approximately 85% in volume. Because a small change in V_w has little influence on the outcome of the calculation, we treated V_w as a constant. The initial partial pressure of each gas in the bubbles (P_i^{t1}) can be determined by multiplying the total pressure (air pressure + hydrostatic pressure) by the mixing ratio of each gas in the bubbles (Figure 4.2). Here, we assumed that N_2 was the single component of the gas bubbles except for CH_4 and CO_2. When the gas compositions were not available due to a lack of gas samples, they were estimated by linear interpolations. In the following calculations, we further assume that there was no production, consumption, or release of any gas species during the intended time period. Under these assumptions, C_i does not change with time because of the law of mass conservation. At an arbitrary time ($t2$), the partial pressure of gas species i can be calculated by transforming equation (4.1) and can be expressed using C_i as follows (equation (4.2)).

$$P_i^{t2} = C_i R T^{t2} \left[V_g^{t2} + \frac{V_w}{H_i^{t2}} \right]^{-1} \tag{4.2}$$

Because we have assumed the existence of three gas species (CH_4, CO_2, and N_2) in the bubbles, we have a simultaneous equation consisting of the three gas species.

$$\begin{aligned} P_{CH_4}^{t2} &= C_{CH_4} R T^{t2} \left[V_g^{t2} + \frac{V_w}{H_{CH_4}^{t2}} \right]^{-1} \\ P_{CO_2}^{t2} &= C_{CO_2} R T^{t2} \left[V_g^{t2} + \frac{V_w}{H_{CO_2}^{t2}} \right]^{-1} \\ P_{N_2}^{t2} &= C_{N_2} R T^{t2} \left[V_g^{t2} + \frac{V_w}{H_{N_2}^{t2}} \right]^{-1} \end{aligned} \tag{4.3}$$

Solving the simultaneous equation (4.3) on the condition that$\sum P_i^{t2}$ is the sum of the atmospheric pressure and hydrostatic pressure at $t2$ will provide a new bubble size (V_g^{t2}) and partial pressure of each gas species (P_i^{t2}). To obtain the changing profile of V_g^{t2} with time, a series of equation (4.3) was established by shifting $t2$ at intervals of 15 minutes and substituting the temperature (calculated from Table 4.1), atmospheric pressure (Figure 4.3), and hydrostatic pressure (Figure 4.1) at the corresponding time. The temperature dependency of H_i was taken into consideration on the basis of the solubility data (Wilhelm et al. [1977], Battino [1982], Clever and Young [1987]). The change in the gas content was estimated at every 10 cm in depth. The Scilab software package was used to solve the equation consecutively.

In addition to estimating the change in gas content by all of the three parameters, we carried out three different calculations by changing only one variable while treating the others as constants when solving the equation (4.3). For example, in one calculation, the temperature was treated as a variable, while the other factors were regarded as constants. This manipulation was aimed at isolating and quantifying the individual effect of these variables on the change in the gas volume.

4.4 Results and Discussion

4.4.1 CH_4 Flux and Atmospheric Pressure

Figure 4.3 shows the time course of the CH_4 flux and atmospheric pressure at plots A (Figure 4.3-a) and B (Figure 4.3-b). Apart from the base flux (1.06 ± 0.31 mg CH_4 m^{-2} h^{-1} for plot A and 0.85 ± 0.22 CH_4 m^{-2} h^{-1} for plot B, mean ± SD), episodic CH_4 emissions were clearly identified at the two plots. These episodic CH_4 releases were almost always associated with declining air pressure. No other mechanism, except for the ebullition of bubbles, can explain the sudden increases in the CH_4 emission rates. Free-phase gas was directly collected from beneath the water table and CH_4 was a major constituent of the gas phase (Figure 4.2). Thus, the existence of free-phase CH_4 was confirmed, supporting the idea that upward migration and eventual rupture of the bubbles at the water-air interface caused the large CH_4 episodic emissions during the field survey.

Both the frequency and magnitude of the ebullition varied between the plots, indicating the spatial heterogeneity of this emission mechanism. Towards the end of the campaign, extremely large CH_4 bursts were observed at both plots after a continuous drop in barometric pressure (Figure 4.3). This remarkable CH_4 flush provided clear evidence that the rates of CH_4 emission can vary by two orders of magnitude within a matter of minutes or hours. The contribution of the ebullition events to the total CH_4 release was significant: 64% at plot A and 50% at plot B. Considering that the total chamber deployment time covered less than one-third of the whole study period, absolute values of the contribution of ebullition fluxes to the total CH_4 emissions may not be accurate. Hence, our results should be considered simply to indicate the importance of ebullition as the dominant emission mechanism during the pressure-falling phase.

4.4.2 Atmospheric Pressure Reduction as a Trigger for CH_4 Ebullition

To test the hypothesis that air pressure played the dominant role in determining the timing and the magnitude of CH_4 ebullition during the field campaign, we evaluated the effect of changing atmospheric pressure, peat temperature, water table level, and all the variables on the volumetric gas content. From Figure 4.4, it is clear that all ebullition events occurred during or shortly after the gas content increased as a result of a reduction in the air pressure. No correlations were found between the timing of the ebullition and the gas content change caused by any of the other factors. In addition, when considering the entire measurement period, the effects of the decreasing atmospheric pressure alone accounted for most of the increase in volumetric gas content: 69% at plot A and 75% at plot B. These results clearly demonstrate that the modulation of atmospheric pressure played the prominent role in controlling the volume of accumulated gas and that reductions in air pressure triggered bubbling releases of CH_4 into the atmosphere.

The results obtained in this short-term study are probably applicable on a large scale. The water table level in peatland ecosystems often has a seasonal variation, showing gradual decrease during fair weather and sudden rise during rainy periods (Zhang et al. [2002], Kellner et al. [2004]). As a result, in terms of the frequency, reductions in the level of the water table may have limited effects on the pressure regime, and thus, on changes in gas volume and subsequent ebullitions from peatlands.

When the water table is located substantially below the peat surface (i.e. below 10 cm), the temperature may also be considered as a less important factor than the barometric pressure because fluctuations in the diurnal temperature below the level of the water table are scarce or non-existent owing to the low thermal conductivity of the unsaturated moss layer (van der Molen and Wijmstra [1994]). While stored gas bubbles are always subjected to the annual temperature cycle, a more rapid and periodical fluctuation may allow for atmospheric pressure to have a greater effect in determining the episodic ebullition events. On the other hand, where the water table is close to the surface (i.e. within 10 cm), diurnal fluctuations occur in the shallow waterlogged peat layer and could be important even in a time scale of minutes to days. Future work is needed on how diurnal temperature fluctuations affect the volume of the gas bubbles and eventual ebullition under the shallow water-table conditions.

Regardless of the water table position, peat temperature and associated changes in the CH_4 production rate (e.g. Dunfield et al. [1993]) may become important when considering longer periods of time. For example, ebullition may be absent during the cooling peat temperature phase, even under severe air pressure reductions, due to a lack of sufficient CH_4 production for the formation and growth of CH_4-containing bubbles (Walter and Heimann [2000]). The contraction of the bubbles according to the ideal gas law and repartitioning of CH_4 as a result of increased solubility may also suppress the bubbling release (Fechner-Levy and Hemond [1996]).

4.4.3 Implications for Flux Measurements and a Wetland CH_4 Emission Model

The very large temporal variability of CH_4 emissions found as a result of the frequent sampling (Figure 4.3) clearly revealed that continuous flux measurements are required to obtain accurate emission estimates. Most seasonal flux estimates have been hitherto based on weekly (e.g. Bellisario et al. [1999]) or less frequent measurements (e.g. Windsor et al. [1992]) using apparent relationships between CH_4 emissions and relevant environmental factors, such as water table levels or peat temperature (e.g. Frolking and Crill [1994]). Since these parameters do not include short-term variations, it is plausible that the estimates may not be accurate.

In most chamber studies, the CH_4 flux was calculated by linear regression of the chamber concentrations, and the resulting flux was not adopted when R^2 failed to reach a certain criterion, with typical values ranging from 0.80 to 0.95 (e.g. Christensen et al. [1995], Panikov and Dedysh [2000]). This procedure for the flux calculation is based on the assumption that diffusion and/or plant-mediated transport is the dominant pathway and that omission of ebullitive CH_4 release, which results in a non-linear increase in the concentration inside the chamber, does not have significant consequences regarding the total CH_4 emission rates (Kettunen et al. [2000]). However, our results suggest that an arbitrary exclusion of apparently unnatural chamber concentration data from the series of flux data might induce serious error and lead to underestimation of temporally extrapolated CH_4 emissions from peatlands.

Recently, the eddy-covariance method was used in pioneering studies in order to conduct near-continuous and spatially integrated flux measurements that are representative of relatively larger areas (e.g. Hargreaves and Fowler [1998], Shurpali and Verma [1998]). The eddy-covariance methods, however, require a stationary concentration of target gas over the averaging time (Foken and Wichura [1996]), which, in most studies, is 30 minutes. Since ebullition is a short-lived phenomenon that may only last for several minutes, the CH_4 concentration in the air during ebullition may not meet this time requirement. Moreover, horizontal homogeneity of the gas concentrations, which is another requirement of this method, may not be satisfied if bubbling release occurs through discrete channels from the surface of peatlands. Although flux measurements were conducted at only two plots, the results are consistent with there being high spatial variability (Figure 4.3), but more data are needed to confirm the degree of spatial variability. If spatial variability is shown to be pronounced, it may not be possible to use the eddy covariance method to estimate ebullition fluxes.

The results of this study have important implications regarding the design of field studies and of wetland CH_4 models as well. Scientists may take field measurements in good weather and avoid less desirable conditions, such as wind or rain. While episodic fluxes were occasionally recorded (Windsor et al. [1992], Frolking and Crill [1994]), good conditions would result in reports of field data obtained in primarily stable atmospheric pressure regimes and less frequent measurements over the pressure-reduction phases. Therefore, smaller CH_4 emission rates might have been preferentially reported, resulting in an underestimation of the temporally-extrapolated CH_4 flux from peatlands. Some process-based wetland CH_4 models

(Walter and Heimann [2000], Zhang et al. [2002]) have adopted CH_4 ebullition as one of the emission mechanisms; however, none of them has adopted atmospheric pressure as a controlling factor. We, thus, suggest that a reassessment of the design of flux measurements over the course of field studies, as well as a reconsideration of wetland CH_4 emission models, is necessary.

4.5 Conclusions

1. The very frequent sampling regime adopted in this study provides clear evidence that ebullition represents an important mechanism of CH_4 emission from peatlands and that it occurs as episodic events.
2. During periods when ebullition occurs, ebullition may account for more than half of the total emission of CH_4 from the peatland.
3. Theoretical calculations followed by numerical computations confirmed the idea that fluctuations in the atmospheric pressure played a dominant role in determining the timing and magnitude of the ebullition events. This implies that field campaign in intemperate weather may be critically important.
4. Process-based CH_4 emission models should be modified to include air pressure as a key factor for the control of CH_4 release via ebullition from peatlands.

4.6 Acknowledgments

We thank K. Suzuki, Y. Ishihama, and T. Endo for their help with the flux measurements and M. Mano for his valuable comments regarding applicability of the micrometeorological technique for measuring ebullition flux. A.J. Baird and two anonymous reviewers provided insightful comments for improving the manuscript. This research was partially supported by a Grant-in-Aid for Scientific Research (DC1 16-11631) by the Japan Society for the Promotion of Science.

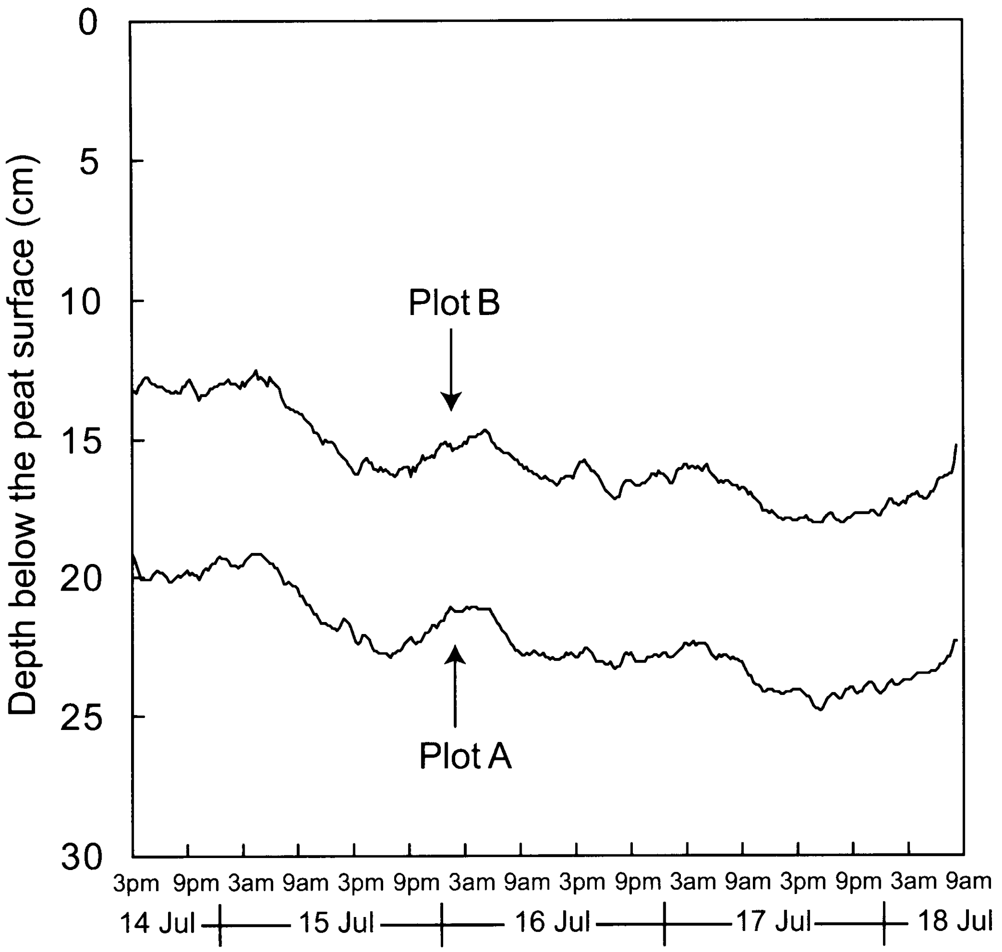

Figure4.1 Time series of the water table position relative to the peat surface. During the study period, 8.5 mm of precipitation was recorded from 7:15 to 9:00 on 18 July.

Table4.1 Averaged peat temperature profile and temperature elevation rate during the flux measurement period

Depth (cm)	30	40	50	60	70	80
Averaged temperature (°C)	18.8	17.7	16.7	15.9	14.9	14.1
Elevation rate (°C d^{-1})	0.24	0.2	0.15	0.11	0.07	0.05

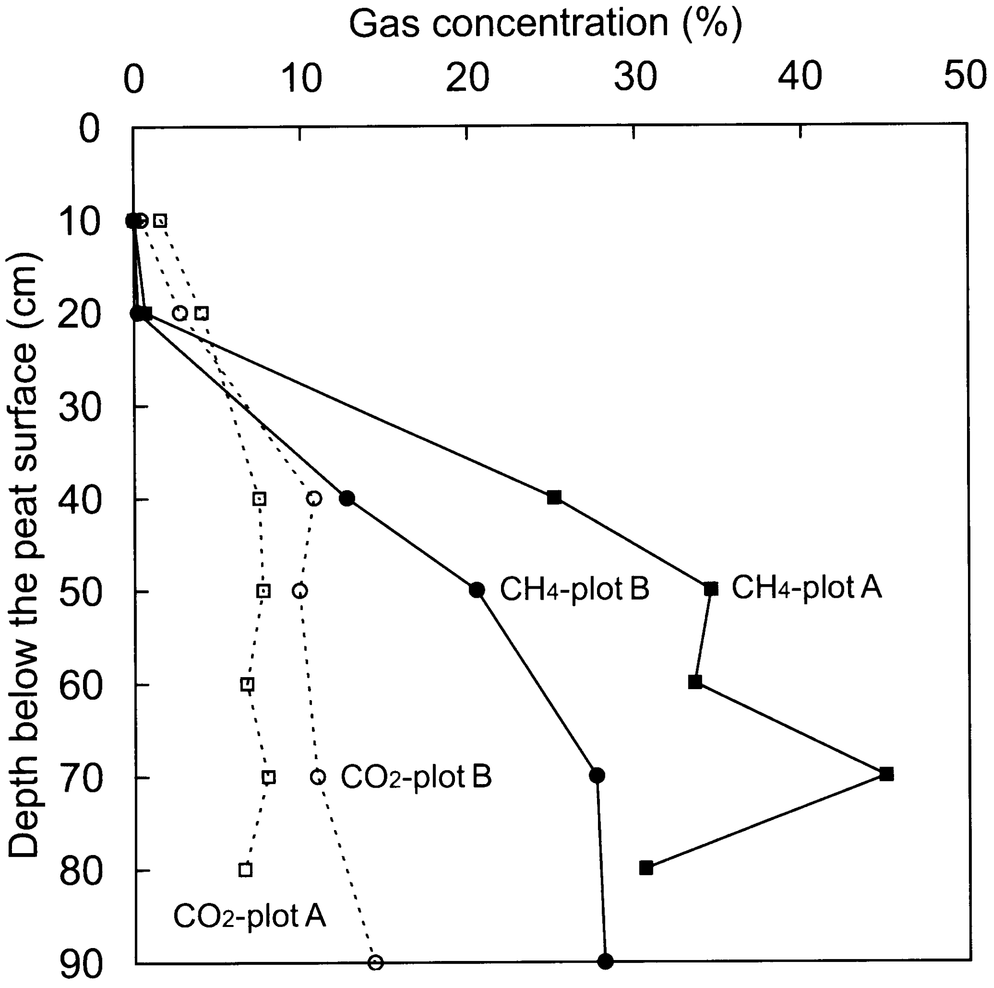

Figure4.2 Depth profile of the CH_4 (■ plot A, ● plot B) and CO_2 (□ plot A, ○ plot B) concentration expressed as the mixing ratio of the total gas. Gas samples were collected at an early stage of the field campaign (on 14 or 15 July, 2005). Samples at depths of 10 cm and 20 cm were collected from an unsaturated zone. Bubbles were collected from depths of 40 cm and deeper. Gas samples were not collected from the depths without symbols.

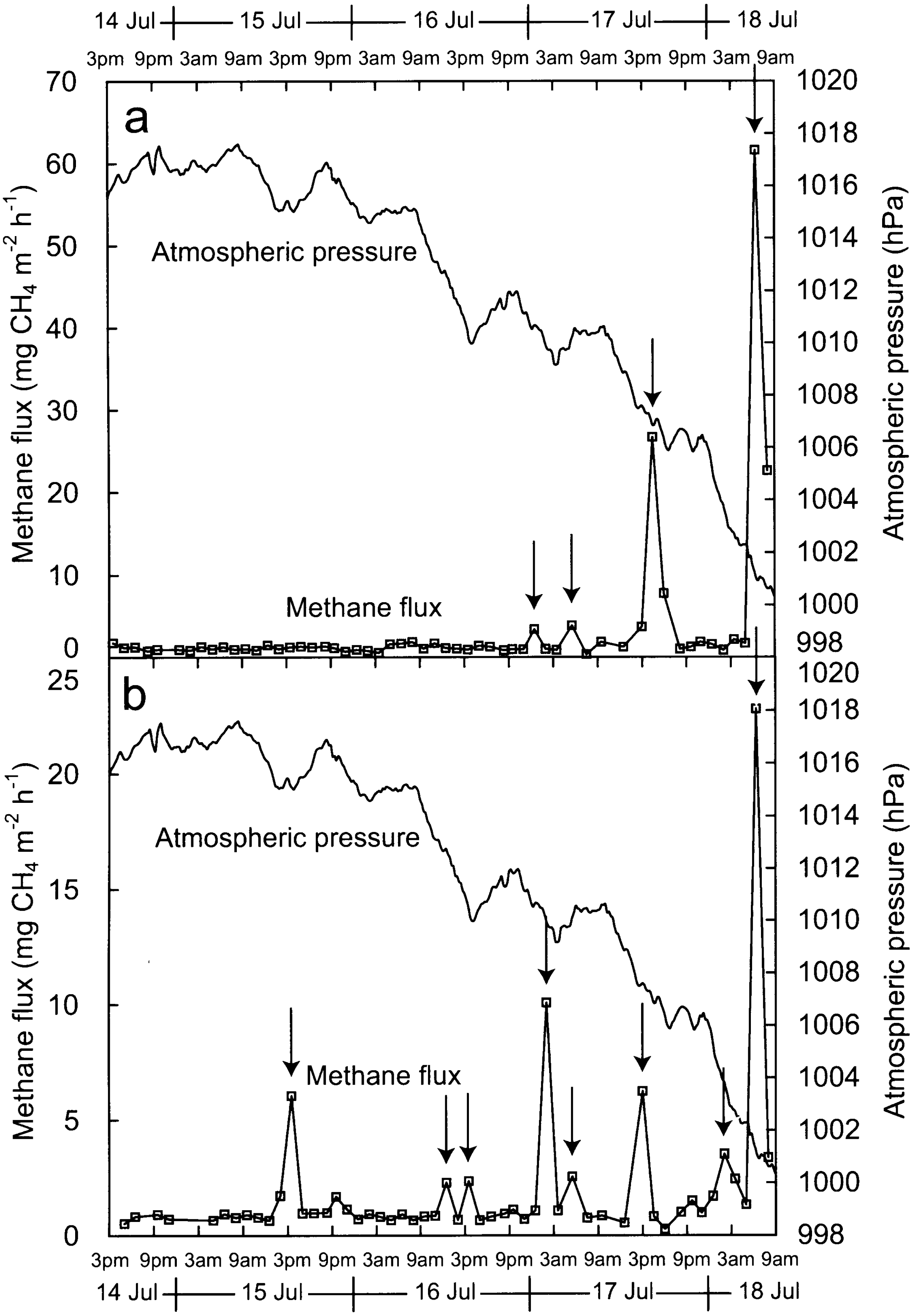

Figure4.3 Time series of CH_4 flux and atmospheric pressure at plots A (a) and B (b). The timing of the flux measurement is indicated by open squares. The vertical arrows indicate episodic fluxes, which are significantly greater ($P < 0.05$, by one-tailed t-test) than the other emission rates. The difference in the scale of CH_4 flux between a and b is noteworthy.

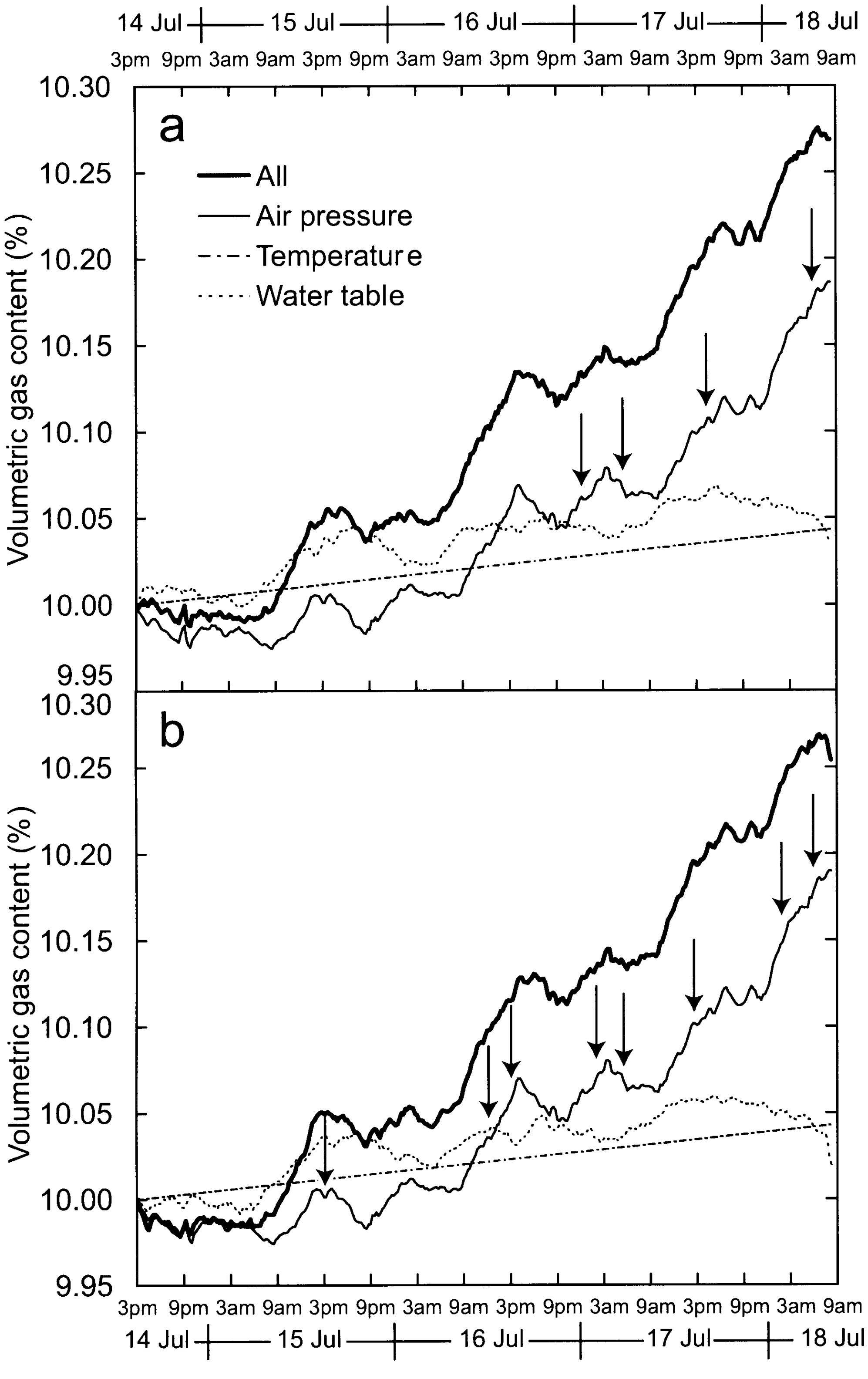

Figure4.4 Effect of changing atmospheric pressure, peat temperature, water table level, and all the variables on the volumetric gas content from the water table level to a depth of 80 cm at plot A (a) and plot B (b). The timing of episodic emissions is indicated by vertical arrows. The volumetric gas content is shown as a weighted mean with the abundance of CH_4 in the bubbles.

Chapter5

Episodic Release of Methane Bubbles from Peatland during Spring Thaw

Results of a one-week field campaign is presented in this chapter. In the field investigation, more than 50 times of chamber deployment on top of the snow cover was carried out and continued over 165 hours until the surface snow and underlying ice layer had completely thawed. This intensive sampling strategy aimed at investigating a possible sudden change in CH_4 emission rates at the moment of spring thaw in northern peatland.

T. Tokida, M. Mizoguchi, T. Miyazaki, A. Kagemoto, O. Nagata, R. Hatano

submitted to Chemosphere

5.1 Summary

Methane (CH_4) flux into the atmosphere during spring thaw has been investigated in a small ombrotrophic peatland (141°48'E, 43°19'N, Japan) using the conventional chamber method. More than 50 times of chamber deployment on top of the snow cover was carried out and continued over 165 hours until the surface snow and underlying ice cover on top of the peat layer had completely thawed. Methane emission was almost absent at the presence of snow cover. At the very moment the surface ice cover thawed, a large CH_4 flush (> 10 mg CH_4 m^{-2} h^{-1}) was recorded, which was on the same order of magnitude as episodic ebullition previously observed in high-summer season. Subsequent emissions showed a gradual decreasing trend with daily peaks appearing in the morning. Gas bubbles trapped in the ice layer on top of the waterlogged peat were preliminary analyzed for the volumetric percentage in the total ice volume as well as their composition of gas species. We found out that the bubbles occupied about 3.2% in volume and that the mixing ratio of CH_4 in the bubbles was about 20%. The abundance of the bubble-form CH_4 was likely to be sufficient to explain the observed episodic CH_4 release during the thaw. This study shows CH_4 emission during thaw season has great temporal variability, and it occurs as episodic release of bubble-form CH_4 stored in the frozen layer. Omission of the episodic release of stored CH_4 during the spring thaw results in underestimation of annual CH_4 emissions as well as misunderstanding of seasonal CH_4 dynamics. The results also imply the possibility that gas-phase CH_4 may play an important role not only in the growing season but also in the cold season CH_4 dynamics in northern peatlands.

5.2 Introduction

Natural wetlands are likely to be the single largest source of atmospheric CH_4, a potent greenhouse gas that accounts for about 20% of the total radiative forcing (Houghton et al. [2001]). Northern peatlands probably contribute more than one-third of the world's total wetland emissions (Matthews [2000]). Methane emission rates from peatlands have been shown to have a large temporal variability at various time scales. It appears that year-to-year variability had been believed to be negligible. However, a recent study indicated northern peatlands do have inter-annual variation which may be attributable to fluctuations in climatic factors, such as annual average temperature or the amount of precipitation (Bousquet et al. [2006]). Very large temporal variability at timescales of minutes to days could be caused by ebullition, i.e. release of CH_4-containing bubbles that occurs as episodic events (Baird et al. [2004], Glaser et al. [2004]). Fluctuations in atmospheric pressure were shown to be one of the dominant factors controlling the timing and magnitude of the ebullition (Tokida et al. [2005b, 2007, in press]).

Compared with the inter-annual or the short-term temporal variability, more efforts have been made to understand the seasonal change in CH_4 emission rates. Attempts to explain the inter-seasonal variability by linking it with various environmental factors, such as water table level or peat temperature (e.g. Frolking and Crill [1994]), have been made mainly during the growing season, often excluding non-growing season presumably because of logistical difficulty. Some reports, however, have shown that cold-season CH_4 release represents a non-negligible portion in annual CH_4 budget (Dise [1992], Melloh and Crill [1996], Panikov and Dedysh [2000], Nagata et al. [2005]). This view is supported by non-zero CH_4 production at low temperature (Wagner et al. [2003]) including subzero temperature (Panikov and Dedysh [2000]).

In most northern peatlands, it is clear that drastic changes in physical environments, including melting of snow and near-surface frozen peat, take place during the spring thaw in relatively short periods of time, invoking a corresponding sudden change in CH_4 emission rates. However, field investigations have been, so far, seldom conducted during the thawing moment. We are aware of only one study (Hargreaves et al. [2001]) which conducted intensive measurements during the whole spring thaw period. *Hargreaves et al.* [2001] measured CH_4 emissions from a Finnish aapa mire for approximately one month using eddy covariance method and showed a very high hour-to-hour temporal variability while the ice layer melted. The magnitude of the peak CH_4 emission rates were 2 to 3 times the rates observed during the summer season, which enables total spring-thaw emissions (only 20 to 30 days) to account for 11% of the annual emissions. They attributed the pulse of CH_4 to the release of CH_4-containing bubbles observed from holes and cracks in the ice layer. However, lack of quantitative information regarding stored CH_4 in and below the ice layer made it difficult to comprehend the whole picture of CH_4 dynamics during the period of winter-spring transition.

In this paper, in order to obtain better understanding of the mechanisms of the possible CH_4 ebullition during spring-thaw, CH_4 release into the atmosphere and stored CH_4 in near-surface peat trapped during winter were simultaneously investigated.

5.3 Materials and Methods

5.3.1 Study Site

The study site is a small ombrotrophic peatland located within the Ishikari-river basin in Hokkaido, northern Japan (141°48'E, 43°19'N). The most evident climatological feature in this region is heavy snowfall. The average total snow fall recorded at Iwamizawa Meteorological Station, 13.5 km from the site, was 750 cm per year during 1953-2005. Other meteorological data can be obtained from the nearest meteorological station (4.5 km): the average maximum snow depth was 116 ± 21 (mean ± SD) cm, average annual temperature of 7.1 ± 0.6 (mean ± SD) °C and winter minimum of -6.8 °C occurring in January. The mean annual precipitation was 1153 ± 153 (mean ± SD) mm including snowfall of about 300 mm between 1983 and 2005. Average temperatures are below freezing for the months of December through March, averaging -4.6 °C, while the mean daily highest temperature were above 0 °C even in the midwinter (4.4 °C in January and 3.8 °C in February). This indicates that midwinter thaws may occur in any winter months.

Because the thick snow layer serves as a thermal insulator, the temperature of underlying peat may be kept much higher than that in the air throughout the snow-covering period. Peat temperature monitored over the 1999-2000 winter season at the same *Sphagnum* site clearly showed that temperature at the snow-peat interface was almost zero °C and that the temperature at 5 cm depth was positive throughout the winter (Fig. 5.1). This indicates that the entire peat column is not frozen at all or even if it freezes, the depth of freezing is just limited within a couple of cm from the surface. It has also been shown that due to the continuous supply of melted snow, the peat is entirely waterlogged during winter and at thawing periods the surface may be submerged with several cm of water (Tokida et al. [2005a]).

We report here the results obtained from two plots, designated as plots A and B (31.2 m apart), where *Sphagnum* spp. dominate. The second dominant plant is *Moliniopsis japonica* at plot A and *Carex* spp. at plot B. High-moor peat consisting mainly of *Sphagnum*, *Carex middendorffii* and *Vaccinium oxycoccus* occurs from the surface to a depth of ~2.7m (Kondo et al. [1997]). Plots A and B are the same as those used in a flux survey conducted in July 2005 (Tokida et al. [2007, in press]), and identical to " point A" and "point C" in a study of *Nagata et al.* [2005] as well as two of the five sampling points in a study conducted by *Takakai et al.* [2005].

5.3.2 Methane Flux Measurement

The CH_4 flux was measured from the afternoon of April 13, 2006, to the morning of April 20. A static chamber technique, one chamber on each plot, was used to measure the CH_4 flux (Hutchinson and Livingston [2002]). An intensive sampling scheme, in which more than 50 times measurements over the 165 hours of the field survey, was adopted in order to identify the expected short-time change in CH_4 flux. Minimum and maximum chamber deployment time were 10 minutes and 3 hours, respectively and the total temporal coverage of the chamber deployments to the whole study period were 26% and 23% for plots A and B, respectively. An open bottomed acrylic chamber, 0.054 m^3 in volume and 900 cm^2 of basal area, was placed on a previously installed collar and sealed from the atmosphere with water for conditions of no snow. The chamber was placed on top of the snow and the headspace volume was corrected for snow within the chamber during the snow-cover period. The chamber was equipped with a thermometer and an air sampling tube through silicone rubber plugs installed in the openings at the top of the chamber. For each flux measurement, four samples (10 ml per sample) of internal air were taken at intervals through the air sampling port and injected in a pre-evacuated vial. A Shimadzu gas chromatograph (GC-14A) equipped with a flame ionization detector (FID) was used to determine the CH_4 concentration of the sample. The CH_4 flux was calculated using the effective chamber volume, the temperature of air in the chamber, the ambient air pressure measured with "Baro" pressure gauge (Van Essen Instruments) and slope of the CH_4 concentration against time. Slopes that were not significantly different from "zero" (by t-test, $p = 0.10$) were considered to be 0, i.e. no flux.

5.3.3 Quantification of Volume of the Bubbles in the Ice Layer

When the snow cover disappeared, ice layer appeared on top of waterlogged peat, and small gas bubbles (several mm in diameter) were trapped in the ice layer (Fig. 5.2-a). In order to quantify the mass of CH_4 trapped in these bubbles, we tried to estimate the (i) volume fraction of the gas bubbles in the ice (=total volume of these gas bubbles : volume of the ice in which bubbles occur) and (ii) mixing ratio of CH_4 in the bubbles. Once the volume fraction and the concentration of CH_4 were determined, the abundance of CH_4 trapped as bubbles (S) can be described as:

$$S = V_{bubble} \times C \times T_{ice} \tag{5.1}$$

where V_{bubble} is volume fraction of bubble in the ice, C is the concentration of CH_4 in the bubble and T_{ice} is the thickness of the ice.

5.3.3.1 Volume fraction

First, area ratio of the bubbles to the total surface area (A_{bubble}) was estimated by image analysis with Scion Image (Scion Corporation), assuming each bubble can be approximated by an individual ellipse (Fig. 5.2-b). We also assumed that the bubbles were spherical and the diameter of the each bubble was equal to the average length of the major and minor axes and that the thickness of the ice was identical to the diameter of the largest bubble. Under these assumptions, the volume fraction of bubbles (V_{bubble}) may be described by,

$$V_{bubble} = A_{bubble} \times \frac{\sum_i^n V_s}{\sum_i^n V_c} = A_{bubble} \times \frac{\sum_i^n \frac{4}{3}\pi r_i^3}{\sum_i^n \pi a_i b_i \times 2max(r_i)} \tag{5.2}$$

where A_{bubble} is the area ratio of the bubbles to the total surface area shown in Fig. 5.2), n is the total number of the bubbles, V_s is the spherical volume of the bubble, V_c is the volume of a cylindrical column the diameter of which is identical to the bubble inside it and the thickness is the same as that of the ice, a_i is the major axis of the bubble i, b_i is the minor axis of the bubble i and r_i is the average of a_i and b_i.

5.3.3.2 Gas composition

It was very difficult to collect the small gas bubbles (Fig. 5.2-a) to be used for gas composition analysis. Alternatively, gas samples were directly taken by syringe and needle from rather large gas pools trapped under the floating ice layer (Fig. 5.3) where ‘ ice-water-peat’ stratification existed. Such gas pools were ubiquitous and two of them located several meters away from plot A were taken. Positive temperature of the peat layer (Fig. 5.4) appeared to unfreeze the overlying ice layer and thus considered to be the main reason for this stratification. Lateral flow of melted snow might also contribute to the melting of the ice layer from the bottom upward. In such conditions the entrapped bubbles may gather as the ice being melted, forming a rather large gas pool trapped below the floating ice (Fig. 5.3). The collected gas samples were injected into a 5-ml vial and transferred to the laboratory for analysis. Mixing ratios of CO_2 and O_2 as well as CH_4 were analyzed with a Shimadzu gas chromatograph (GC-14A) equipped with a thermal conductivity detector (for CO_2), and a flame inonization detector(for CH_4).

5.3.4 Dissolved CH_4 and Dissolved Inorganic Carbon (DIC) Concentrations

Profiles of dissolved CH_4 and dissolved inorganic carbon (DIC) concentrations were measured on April 19 and 20 when the snow cover completely vanished. In this site, DIC is virtually identical to dissolved CO_2, because pH of the peat pore-water is ~4-5 (Kondo et al. [1997]). Pore water samplers consisting of a stainless pipe (2.35 mm o.d. and 1.45 mm i.d.) fitted with a Tygon® tube and a three-way stopcock were vertically inserted from the surface to depths of 3, 5, 7, 10, 18 and 25 cm with two samples per each depth. Peat pore-water were collected at depths of 30 to 80 cm, one sample per each depth, at intervals of 10 cm using another sampler that was originally used to sample gas bubbles below the water table level in the same site (Tokida et al. [2005a]). One should note that because each sample did not have the same sampling location, the profiles should be considered to include horizontal heterogeneity. About 1 ml of pore water was collected two times (on April 19 and 20) from the shallower zone (3 to 25 cm) using a 5 ml syringe. Samples were collected just one time (either on April 19 or 20) from depths of 30 to 80 cm. All the samples were injected into pre-evacuated 5-ml vials through a microfilter (0.2 μm, mixed cellulose ester, Toyo Roshi Kaisha, Ltd.). When injected into the vial, 5 μl of 5 M HCl solution was added to prevent biological decomposition of CH_4 and DIC. For the analysis of the gas phase of the vial, the same GC system was used as that for quantifying gas composition in the bubbles. The original dissolved concentration was reconstructed using the headspace concentrations, volumes of the headspace and the water phase, and Henry's law, assuming that the dissolved gases were in equilibrium between the liquid and the gas phases according to Henry's Law constant (Wilhelm et al. [1977], Clever and Young [1987]). At depths of 70 and 80 cm in plot A, only gas sample were available, indicating the existence of large gas pockets (Tokida et al. [2005a]). Therefore, we analyzed the composition of the gas and converted it into the equilibrated dissolved concentration. Temperature profiles needed to estimate the Henry's law constant were measured by thermocouples and recorded in CR-10X (Campbell Scientific, Inc.).

In addition to the profile measurements, time course of dissolved CH_4 and DIC concentrations just below the snow cover were measured. The same sampler as for the profile measurements was inserted from the snow surface to a certain depth and the occurrence of water at the tip of the probe was checked by giving suction through a syringe. If no water was sampled, then the sampler was pushed slightly deeper and the existence of water was examined again. This procedure was repeated until water was collected. After the melting of snow, both plots had several cm of standing water. It should be noted that because each sample had different sampling locations, the profile should be subjected to horizontal heterogeneity.

5.4 Results and Discussion

5.4.1 Methane Flux during Snow-covering Period

Flux measurements were began on April 13 when the surface was still covered with c. 20 cm of snow. Methane flux was almost absent from April 13 to 16 (Fig. 5.5). By April 16, the granular snow had vanished, leaving an apparently continuous ice layer spreading over the peat surface. Temperature profiles measured on April 13 (Fig. 5.4) clearly showed that negative temperature was limited down to the ice-peat boundary, indicating that the peat layer did not freeze during the winter as in the case of 1999-2000 shown in Fig. 5.1. Melting of snow occurred during the daytime but thaw water refroze during the night. Concurrent diurnal fluctuation in water table level was observed, i.e. it rose during the daytime due to the supply of melting water and declined as thawing temporally ceased during the night. However, the water table never dropped below the level of peat surface.

5.4.2 Episodic CH_4 Emission Associated with Release of Entrapped Bubbles in the Ice Layer

The sudden and the largest CH_4 release during the entire field campaign, 25.3 and 6.5 mg CH_4 m^{-2} h^{-1} for plots A and B, respectively, was observed on the morning of April 17 accompanied by the melting of the surface ice layer (Fig. 5.5). We have found that many bubbles trapped in the ice (Fig. 5.2) were directly released into the atmosphere as the ice melted (See supplemental material: Animation 1). Very high concentration of CH_4, a value 5 orders of magnitude higher than the atmospheric level, strongly suggests that the release of accumulated bubbles was responsible for the observed CH_4 flush. At plot A, emission of CH_4 returned to the level of snow-covering period after about 2 days of significant emissions. Although the observed peak flux at plot B was smaller compared to that of plot A, subsequent CH_4 emission remained relatively high (Fig. 5.5).

To confirm the hypothesis that the major contributor of CH_4 released during the thaw was gaseous-phase CH_4 trapped in the ice layer, the amount of trapped CH_4 must be related to that of released CH_4 into the atmosphere. From the image analysis, volume fraction of the bubbles in the ice was estimated to be 3.2%. This is similar to the value of bubble-filled pore space found in permafrost (Calmels and Allard [2004]). By using equation (5.1), the abundance of CH_4 trapped in the ice was estimated to be 132 mg CH_4 m^{-2}, assuming that the thickness of the ice layer was 3 cm, which might be a conservative guess based on field observations. As for cumulative CH_4 emissions, integration of the observed flux with time gave estimates of 107 and 150 mg CH_4 m^{-2} from plots A and B, respectively, during our 165 hours of field campaign. Considering the high temporal variability as shown in Fig. 5.5, our sampling frequency while two orders of magnitude more frequent than previous chamber studies, might be barely sufficient to account for this variation. Also, it should be recognized that the integrated fluxes might be underestimated because there is a high degree of possibility of more pronounced CH_4 peak occurring but not being captured especially on April 17 when the chamber deployment was often impossible due to strong wind. Nevertheless, striking similarity between the abundance of bubble-form CH_4 and the cumulative CH_4 emissions strongly indicates that the release of the entrapped bubbles was the dominant emission mechanism during the thaw.

5.4.3 Diurnal Variation of CH_4 Flux with Freeze-thaw Cycle

After the remarkable CH_4 flush on the morning of April 17, CH_4 flux showed a downward trend with a consistent pattern of diurnal variation, showing a peak in the morning on both plots from April 18 onwards (Fig. 5.5). Melting of the ice layer ended by the evening of April 17 at plot A, and it continued until the noon of April 18 at plot B. However, a cycle of nocturnal freezing and subsequent morning thaw continued for the rest of the field campaign. The diurnal change was associated with the freeze-thaw cycles in the surface water, suggesting the ice layer presented during the night may have acted as a physical barrier to prevent CH_4 from emitting into the atmosphere and in the next morning, the trapped CH_4 would be released as soon as the ice thawed. Diurnal variation of CH_4 flux during thaw season was also observed at a Swedish subarctic mire (Friborg et al. [1997]), suggesting that this is a common characteristic seen in many northern peatlands at early spring. We suggest that instead of adhering to the rather demanding flux measurements, investigations of change in CH_4 storage before- and after- spring thaw in the surface zone will provide valuable information for quantifying the abundance of CH_4 which can be released during spring thaw.

5.4.4 Possible Mechanisms Explaining High CH_4 Concentration in the Bubbles Trapped in the Ice Layer

Very high concentration of CH_4 together with distinctly different mixing ratios of CO_2 and O_2 from those in the atmosphere was clearly observed in the bubbles trapped in the surface ice (Table 5.1). It is obvious that the CH_4 in the bubbles were supplied from anoxic layer suitable for CH_4 production and had been trapped until the ice thawed. Concentration of CH_4 in the bubbles can be compared to that in the sub-ice water when converted into the corresponding equilibrium concentration in dissolved state. Obviously, the equilibrium concentration (492 μM, see Table 5.1) was significantly higher than the sub-ice water concentration (Fig. 5.6-a, April 14-16), suggesting that diffusion of dissolved CH_4 may not be able to contribute to the CH_4 accumulation in the ice layer. Conversely, it is more likely that the dissolution of entrapped CH_4 into the surface water during ice melt caused the increase in the CH_4 concentration during April 16-18 (Fig. 5.6-a).

Processes capable of explaining the high CH_4 concentration in the ice layer may include (i) upward migration of CH_4-containing bubbles through peat matrix from the deeper layers to the surface zone and (ii) physical containment of the bubbles into ice by freezing of the surface water. Profiles of pore water concentrations measured immediately after the snow melt are shown in Fig. 5.7 for CH_4 and in Fig. 5.8 for DIC. Methane concentration generally increased with depth and was high enough at depths deeper than 30-40 cm to account for the observed concentration in the ice-layer bubbles (Fig. 5.7 a-c). However, mechanisms responsible for the upward movement of the bubbles as well as the incorporation of them in the ice layer are uncertain. Moreover, in contrast to CH_4, CO_2 ($\approx$ DIC) concentration in the bubbles appeared to be similar to the sub-ice water concentration (Fig. 5.6-b, Fig. 5.8 d-f) and significantly lower than that at the deeper depths (Fig. 5.8 a-c), making our conjecture more questionable. Dissolution of CO_2, which is a highly soluble gas, into the surface water while trapped beneath the floating ice (Fig. 5.3) could cause decrease in the concentration, however, no exact explanation can be given to this point.

5.4.5 Some Implications for Cold Season CH_4 Abundance in Peat

Considering the few numbers of samples and the several assumptions used in the calculation, our estimates of the abundance of trapped CH_4 in the ice should be recognized as preliminary results. Much more should be known to quantitatively determine the significance of CH_4 accumulation within and below the frozen layer and importance of subsequent episodic CH_4 evasion during spring thaw. However, in situ observation of pronounced CH_4 accumulation in the ice itself is a clear evidence of cold season CH_4 storage and strongly supports the validity of previous conjectures that episodic CH_4 emission during thaw was attributed to the release of stored CH_4 in the upper frozen layers (Moore and Knowles [1990], Windsor et al. [1992], Friborg et al. [1997], Hargreaves et al. [2001]).

It is clear that the majority of northern peatlands is exposed to lower temperatures and receives less snow compared to our study site, resulting in the existence of frozen layer in the shallow peat zone during winter. Significant CH_4 accumulation in peat pore water, e.g. up to 1.1 mM in a temperate poor fen, has been observed (Dise [1992], Melloh and Crill [1996]). The results obtained in this study in conjunction with these previous reports imply that gas-phase CH_4 accumulation could occur not only within the frozen layer but also below the frozen layer. Considering the low solubility of CH_4 (about a thirtieth of CO_2), if occurrence of bubbles is prevalent the abundance of CH_4 in the entire peat profile during winter might be substantially larger than had previously been estimated. Recently, a series of papers has indicated the importance of the free-phase CH_4 as the main CH_4 inventory in peat even below the water table level (e.g. Fechner-Levy and Hemond [1996], Rosenberry et al. [2003], Tokida et al. [2005a]). However these investigations have been limited to the growing seasons. Our results imply that the gas-phase CH_4 may play an important role also in cold season CH_4 dynamics in northern peatlands.

5.5 Conclusions

1. Large CH_4 emissions associated with melting of the surface ice layer occurred as a result of release of entrapped bubbles found in the ice layer. Preliminary analysis showed that the bubbles contained 20% CH_4 and occupied 3.2% of the total ice volume.
2. Great temporal variability in CH_4 flux was found during spring thaw and may include diurnal variation associated with the freeze-thaw cycle of the surface water.

3. Upward migration of CH_4-containing bubbles from the deep layers to the surface zone and subsequent containment of the bubbles due to the freezing of surface water appeared to explain the high CH_4 concentration in the bubbles, although the mechanisms responsible for these processes are still not fully understood.
4. If the existence of bubbles within and beneath the frozen layer is found to be pronounced, gas-phase CH_4 is likely to play an important role not only during the growing season but also in the cold season CH_4 dynamics in northern peatlands.

5.6 Acknowledgments

I. Yamamuro identified the plants at the study sites. We thank T. Endo, K. Suzuki, M. Kajiura and F. Takakai for their help with the field survey. This research has been partially supported by a Grant-in-Aid for Scientific Research (DC1 16-11631) by the Japan Society for the Promotion of Science.

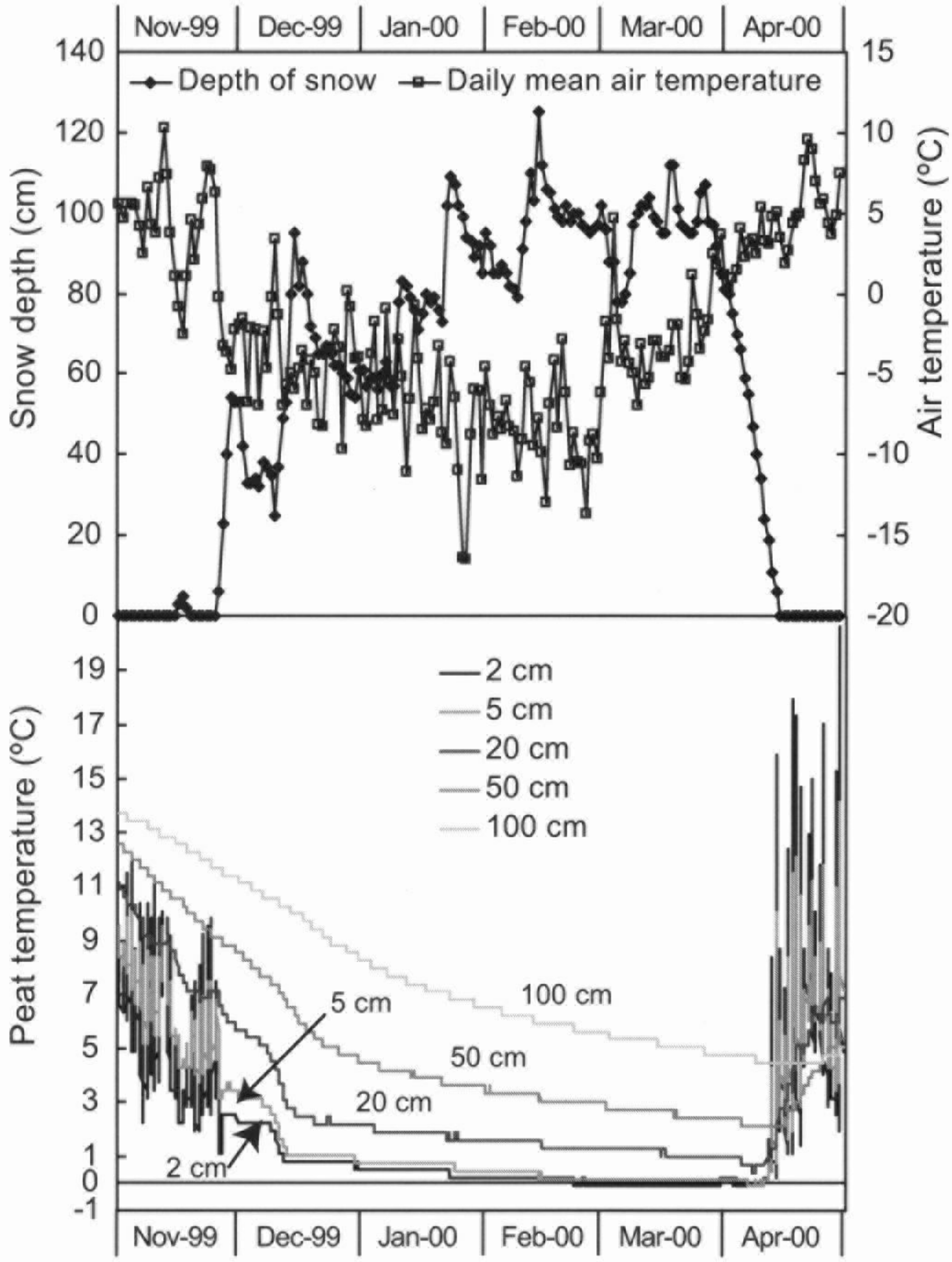

Figure5.1 Snow depth, daily mean air temperature and peat temperature from November 1999 to the end of April 2000. Snow depth and the daily mean air temperature were recorded at the nearest meteorological station, 4.5 km from the study site.

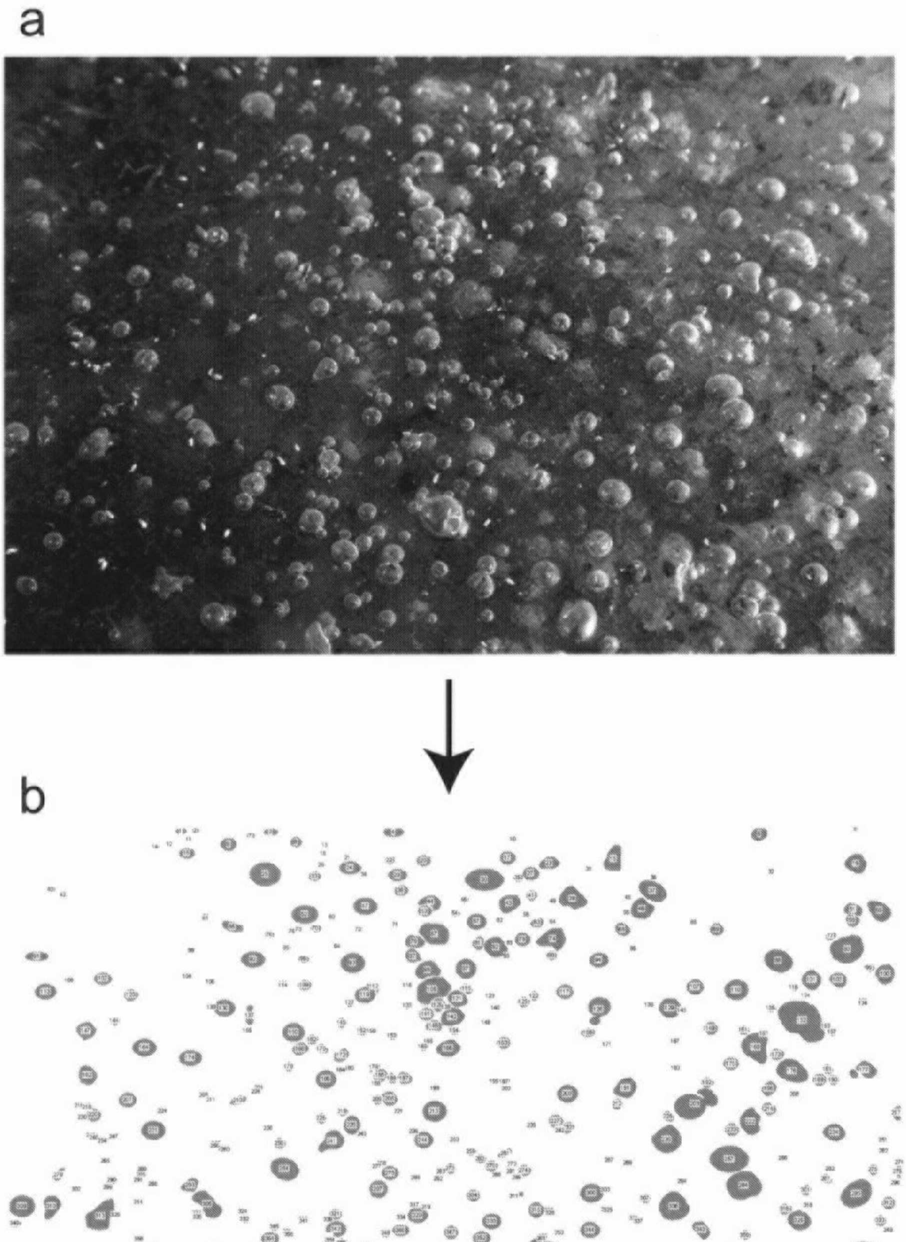

Figure5.2 A picture of bubbles stored in the ice layer between the snow and the peat layer taken on April 14. The maximum bubble diameter was approximately 1 cm. b. The areas of the bubbles were detected and quantified by Scion Image based on an assumption that all the bubbles can be approximated by ellipses.

Table5.1 Gas concentration of bubbles trapped in ice layer on top of peat

Sample #	CH_4[a] %	CO_2[a] %	O_2[a] %	CH_4-water[b] μM	CO_2-water[b] μM
1	13.8	0.33	11.3	353	253
2	24.6	0.30	8.4	630	228
Average	19.2	0.31	9.8	492	241
Atmosphere[c]	1.8 ppm	0.038	21		

[a] Expressed as a mixing ratio of the total gas.

[b] Corresponding dissolved gas concentration equilibrated with gaseous-phase gas at 0 °C.

[c] Gas composition in the atmosphere for comparison.

Figure5.3 Direct sampling of gaseous-phase gas (white portion) trapped between the ice and the underlying water layer conducted on April 17. The collected gas were injected in to vials and transferred to the laboratory for analysis.

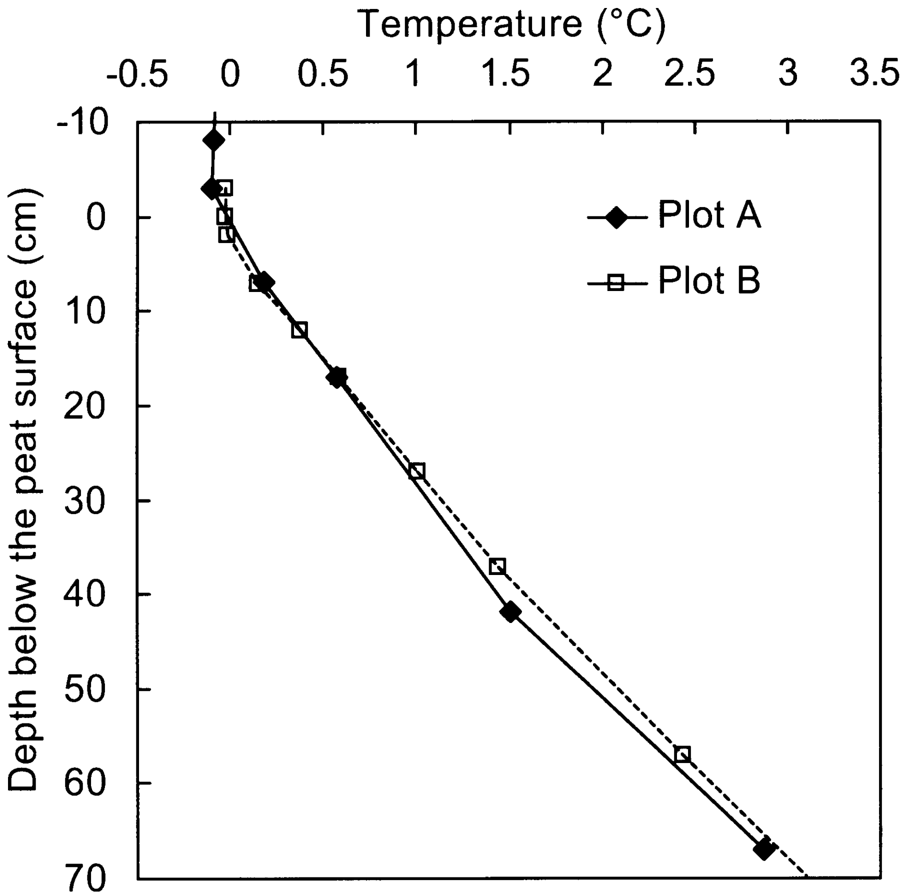

Figure5.4 Temperature profiles measured on April 13 for plots A and B. Negative temperatures were recorded only above the surface of the peat.

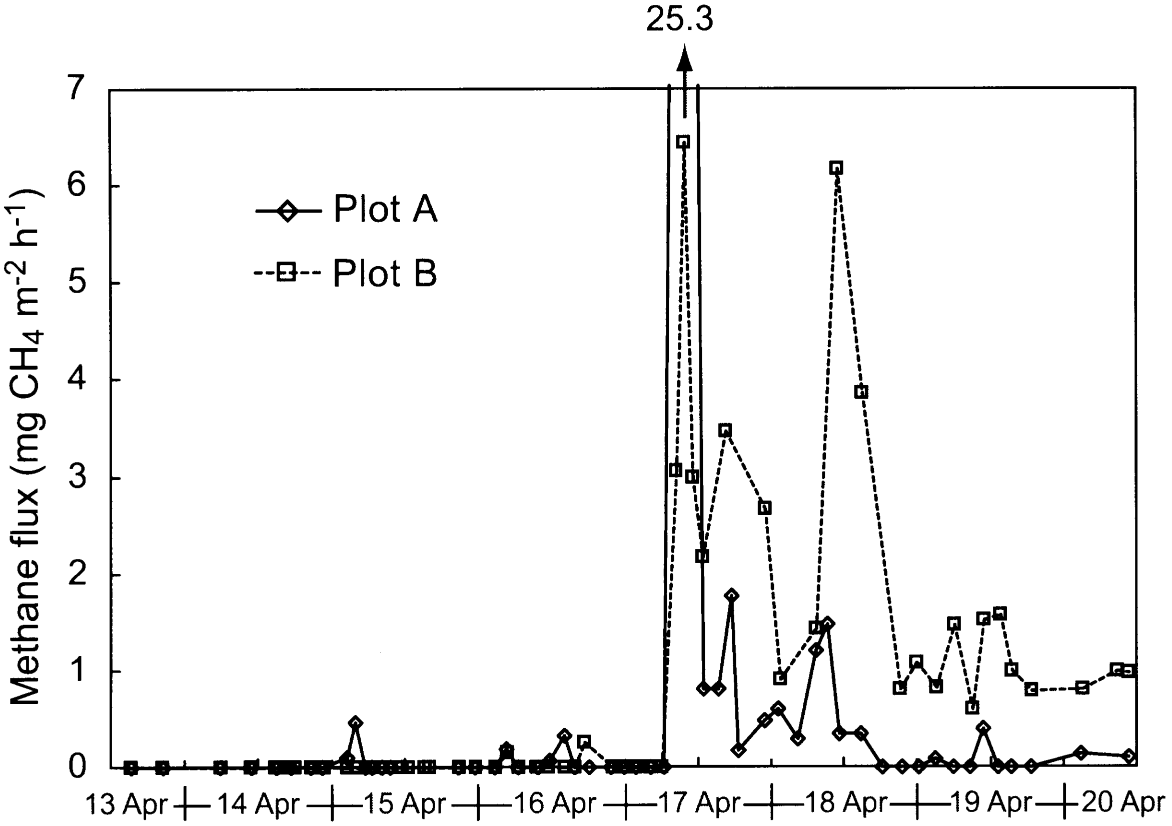

Figure5.5 Methane flux from either snow cover, standing water or peat surface from 13 April to 20 April, 2006 at plots A and B. Symbols indicate the timing of the chamber measurements.

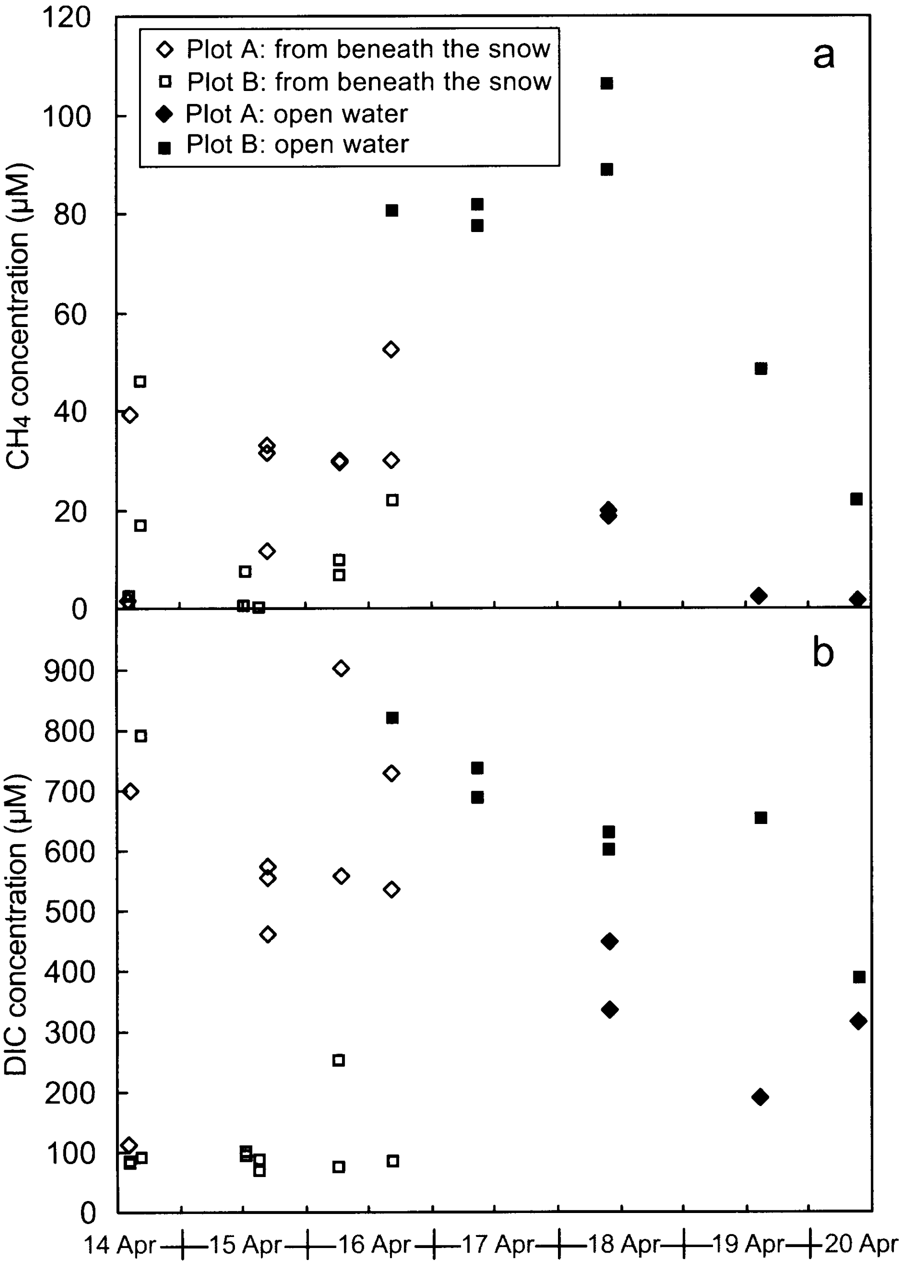

Figure5.6 Dissolved CH_4 (a) and DIC (b) concentration of the surface water. Open symbols represent water samples from beneath the snow cover and solid colored symbols indicate the samples of open water.

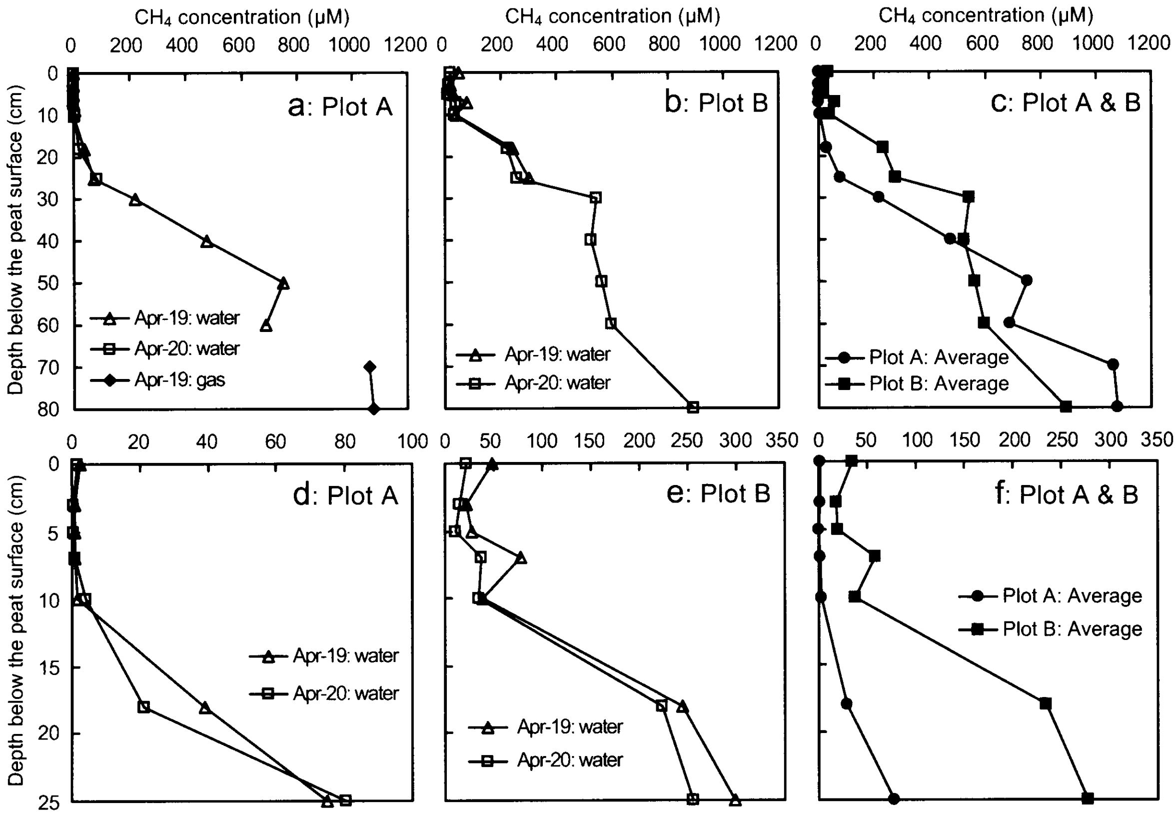

Figure5.7 Profiles of dissolved CH_4 concentration from surface water to a depth of 80 cm (a, b, c) and close-ups of surface zone (d, e, f). Water table was located at or slightly above the peat surface. Data from 0 to 25 cm depths is an average of two samples, while those from 30 to 80 cm are a result of single sample. The average profiles (c, f) showed means of two sampling dates if available.

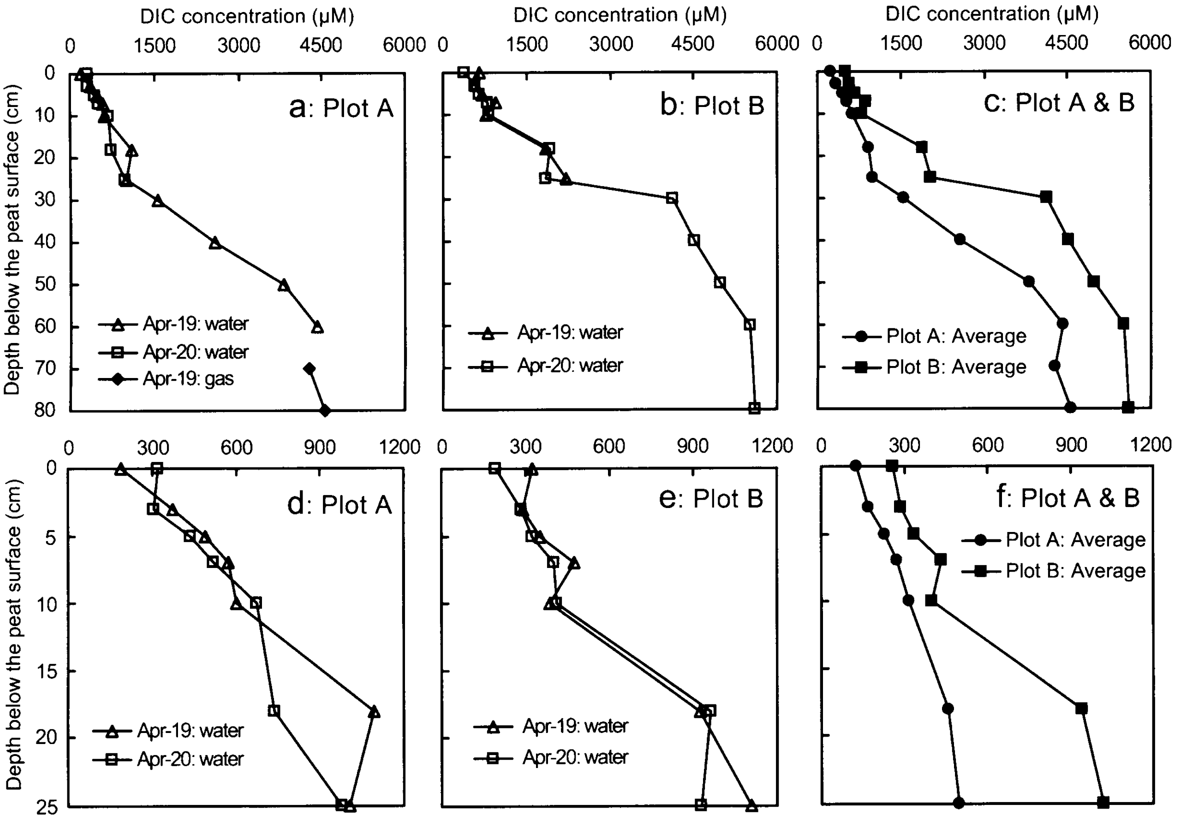

Figure5.8 Profiles of DIC concentration from surface water to a depth of 80 cm (a, b, c) and close-ups of surface zone (d, e, f). The data and the representation method are identical to those for CH_4 (see captions of Fig. 5.7.

Chapter6

General Discussion, Outlook and Conclusions of this Dissertation

6.1 Spatio-temporal Variability of Entrapped Gas in Peat and its Ebullition to the Atmosphere

This research provides some answers to the state of CH_4 in waterlogged peat (Chapter 2), causes of CH_4 ebullition and its importance relative to the other transport modes (Chapter 3 and 4) and points to potential importance of gas bubble release during spring thaw period (Chapter 5). Much more, however, should be known in order to attain the whole picture of the gas-phase CH_4 dynamics in peatlands. The most challenging problem, but probably the most important issue to be solved, is the spatio-temporal variability of entrapped gas volume in peat and its ebullition to the atmosphere.

6.1.1 Temporal Variability in Trapped Gas Volume and Ebullition

Entrapped gas volume in peat is a function of CH_4 production rate, solubility of gases in the gas-phase, pressure regimes, and other biogeochemical and physical processes affecting the changes in mass or composition of the free-phase gas, such as migration of bubbles, consumption of CH_4 by methanotrophs. Because all the processes are more or less temperature dependent, volume of free-phase gas must change in relation to diurnal or seasonal temperature cycle. Fluctuations in water table level and atmospheric pressure can also affect the volume through changing the pressure regime.

I have measured "snapshots" of gas volume profiles and shown that the volume fraction of the gas phase may differ between years even in the same season (Chapter 2). For investigating the changes in the gas volume with time and factors that may affect it, continuous measurements system is required. Monitoring of the entrapped gas volume by determining change in volumetric water content by a moisture sensor (Campbell Scientific CS 615 with probe length of 30 cm, Campbell Scientific Inc., Loga, Utah, USA) has been made in a Canadian peatland, showing a gradual increase during the growing season (Kellner et al. [2005], Strack et al. [2005]). Abrupt change of ~2% over the period of day has also been observed at some sites (Strack et al. [2006]) which might be relevant to the ebullition releases. A problem, however, lies in that due to the uncertainty arising from the calibration (between sensor output and volumetric water content) and unignorable inter-probe variation, only changes in the gas content but not the absolute gas content could be measured. Uncertainties associated with soil moisture sensor were also recognized in the present study, which resulted in nonnegligible measurement error (Chapter 2). Utilization of the magnitude of the buoyancy response to changes in atmospheric pressure (Fechner-Levy and Hemond [1996]) is one of the promising options for the continuous monitoring of the volume of the gas phase, although this approach cannot address issues of the vertical distribution of the gas volume. Innovative improvement of existing methodologies or development of new techniques, that enables continuous measurements of trapped free-phase gas and composition of the gas species in it, is indispensable but remain as a challenging problem.

I have presented direct evidences that fluctuations in atmospheric pressure can be the dominant factor to control ebullition events at time scale of minutes to several days, (Chapter 3 and 4). Due to the occurrence of ebullition, rates of CH_4 evasion into the atmosphere can vary by over two order of magnitude within a matter of minutes to hours (Chapter 4). These results are consistent with recent studies which also suggest that episodes of low atmospheric pressure triggers ebullition events as buoyancy increases in response to greater bubble volume (Rosenberry et al. [2003], Glaser et al. [2004], Kellner et al. [2004, 2005], Strack et al. [2005]). *Rosenberry et al.* [2003] observed overpressuring within peat up to 35 cm of water head above the water table at 2 m depth and sudden decrease in pressure which they inferred was the result of episodic movements of the gas bubbles. Because pressure pertubations were of very short duration and might occur within several minutes, ebullition seems a short-lived but frequently occurring phenomenon (Rosenberry et al. [2006]). *Strack et al.* [2005] also observed pressure spikes in short durations and suggested that small scale release of gas bubbles were occurring very frequently, at least several times a day, and proposed a "constant bubbling" hypothesis, which is in line with the results of the present thesis. To confirm or discard this hypothesis needs longer-time near-continuous flux data that may be obtained by an automated closed chamber method or micrometeorological flux measurement techniques. Generally speaking, chamber techniques may be preferable for process studies because they have well-defined basal area needed to relate observed fluxes with possible factors that may control them.

It is now widely accepted that ebullition occurs when buoyancy force causes bubbles escape into the atmosphere when the volume of the bubbles overcomes a threshold value. Therefore, from a mechanistic point of view, each ebullition event should be related to an increase in the gas volume and thus reductions in atmospheric pressure or water table level, production of CH_4, or any combinations of them are the potential candidates of trigger responsible for the episodic bubbling release. I quantitatively evaluated the relative contributions of the potential factors and found that drop in atmospheric pressure can be the dominant controller in a mesocosm laboratory experiment up to a period of 60 hours (Chapter 3) or *in situ* conditions up to 90 hours (Chapter 4). For longer periods of time, however, cumulative ebullition flux seems to exhibit a good correlation with the amount of cumulative CH_4 production for the corresponding period of time. Because rates of CH_4 production depends primarily on temperature (e.g. Dunfield et al. [1993]), it is reasonable that combination of changes in atmospheric pressure and temperature can better explain the variation of ebullition events (Kellner et al. [2006]).

CH_4 production also depends on the substrate availability, hence, "apparent" relationship between ebullitive CH_4 release and microbial substrate availability combined with temperature may exist in seasonal or annual time scale (Christensen et al. [2003]). Further investigations on the time-scale dependency of the dominant factors or "hierarchy" of temporal variation in CH_4 flux may need greater attention and would significantly improve the knowledge of wetland CH_4 cycles. It should be noted that ebullition during the thawing season should be treated separately because the mechanisms responsible for the ebullition in this season seems very different from those in the growing season (Chapter 5).

6.1.2 Spatial Variability in Trapped Gas Volume and Ebullition

Issues of spatial variability may have been more problematic and challenging than those of temporal variation due to lack of appropriate techniques to cover larger scale measurements. However, in recent years, efforts have begun to understand distribution and configuration of bubbles in the peat and their escape into the atmosphere.

As for trapped gas volume within peat, by using profile type moisture soil moisture sensor, I measured vertical distributions of trapped gas volume (Chapter 2). *Comas et al.* [2005a] used a surface-based and borehole-based ground penetrating radar (GPR) tests, showing this technique has considerable promise in quantifying three dimensional gas distribution at multiple scales ranging from a couple of meters to wetland-wide scales.

In the present study, I have measured CH_4 ebullition at two *Sphagnum* dominated plots simultaneously, showing that ebullitions do not necessarily occur simultaneously, although a continuous severe drop in air pressure can trigger synchronous large ebullitions (Chapter 4). Studies using the surface level fluctuations to infer the timing and magnitude of the ebullition have also suggested spatial heterogeneity of the ebullition (Glaser et al. [2004], Strack et al. [2006]). However, methodologies used in these studies are strictly limited to small scale measurements, making it difficult to understand the scale in which each ebullition occurs. Moreover, relating the areal distribution of gas volume in peat to areal distribution of gas release from the peat surface, which requires simultaneous measurements of trapped gas within peat and its release into the atmosphere, remain as a challenging task.

6.2 Processes Responsible for Upward Migration of Bubbles through Peat

I found volume of trapped gas in peat may control the timing and magnitude of the ebullition. It is not known, however, whether or not preferential pathways are present and serve as conduits for ensuing bubble release (Baird et al. [2004], Rosenberry et al. [2006]). To answer this question may require knowledge of the size and configuration of the bubbles trapped in peat as well as information about the structure, geometry and mechanical properties of peat at appropriate spatial scales.

Amos and Mayer [2006] conducted sand column experiments and measured dissolved gas concentrations, showing that rapid transport of CH_4 vertically through at rates several times faster than the bromide tracer and the more soluble gas CO_2, indicating that ebullition is the main transport mechanism for CH_4. Similar experiments using peat medium would help to improve understandings of physical mechanisms responsible for the bubble migration through peat. Comparison of undisturbed and disturbed peat sample may provide insights into the occurrence or absence of the preferential pathway of escaping bubbles.

Further work is also needed on the ratio of ebullitive release to the other transport modes. Some previous studies provided ratio of ebullition to diffusive release, indicating significantly greater contribution of ebullition (Romanowicz et al. [1995], Baird et al. [2004]). Also important is the dependence of individual pathways on vegetation type, because some plants have shown to act as a direct conduit of the trapped bubbles into the atmosphere, hence, plant-mediated transport and ebullition may have a trade-off relationship. These investigations seems very helpful to construct or improve physically-based CH_4 emission models that is needed to predict future CH_4 emission strengths from peatlands in relation to environmental changes.

6.3 Linkages between Trapped Gas and Peatland Hydrology

This thesis has been done in the context of greenhouse gas emissions and thus CH_4 bubbles trapped within peat have been investigated in relation to ebullitive CH_4 release into the atmosphere. However, from an eco-hydrological point of view, trapped bubbles have been shown to have significant impact on peatland hydrology, including anomalously low hydraulic conductivity (Reynolds et al. [1992], Shiozawa et al. [1995], Beckwith and Baird [2001], Baird and Waldron [2003]), alternation of local flow paths by developing overpressuring zones (Rosenberry et al. [2003], Glaser et al. [2004], Kellner et al. [2004, 2005], Strack et al. [2005, 2006]) which in turn has significant biogeochemical impacts in peatland ecosystems. More comprehensive review about linkages between trapped gas and peatland hydrology can bee seen elsewhere (Rosenberry et al. [2006]).

6.4 Conclusions

The main conclusions of the study are:

1. *In situ* volumetric gas profiles and CH_4 concentrations in the gas phase beneath the water table level were quantified, showing the occurrence of CH_4 bubbles in waterlogged peat soil.
2. Approximately 60-70% of CH_4 stored in water-logged peat from the surface to a depth of 1 m was found to exist as gas-phase gas (30-40% were in dissolved state).
3. The very frequent flux sampling regime adopted in the field study provided a clear evidence that ebullition represents an important mechanism of CH_4 emission from peatland and that it occurs as episodic events.

4. Theoretical calculations followed by numerical computations confirmed our hypothesis that fluctuations in the atmospheric pressure play a dominant role in determining the timing and magnitude of the ebullition events.
5. Field campaigns must be designed to cover the rapid temporal variability caused by ebullition, which may be especially important under intemperate weather.
6. Because existing CH_4 flux data may not capture ebullition events or ebullitions were not considered significant, widely-accepted process-based models might have been tested against erroneous data. Also, our findings may reveal the need to revise the model itself, i.e., air pressure should be included as a key factor for the control of CH_4 release via ebullition.
7. Large CH_4 emissions associated with melting of the surface ice layer occurred as a result of release of entrapped bubbles found in the ice layer, suggesting that the gas-phase CH_4 is play an important role not only during the growing season but also in the cold season CH_4 dynamics in northern peatlands.

References

R. T. Amos and K. U. Mayer. Investigating ebullition in a sand column using dissolved gas analysis and reactive transport modeling. *Environ. Sci. Technol.*, 40:5361–5367, 2006. doi: 10.1021/es0602501.

J. R. M. Arah and K. D. Stephen. A model of the processes leading to methane emission from peatland. *Atmos. Environ.*, 32:3257–3264, 1998.

I. Aselmann and P. J. Crutzen. Global distribution of natural freshwater wetlands and rice paddies, their net primary productivity, seasonality and possible methane emissions. *J. Atmos. Chem.*, 8:307–358, 1989.

A. J. Baird and S. Waldron. Shallow horizontal groundwater flow in peatlands is reduced by bacteriogenic gas production. *Geophys. Res. Lett.*, 30:2043, 2003. doi: 10.1029/2003GL018233.

A. J. Baird, C. W. Beckwith, S. Waldron, and J. M. Waddington. Ebullition of methane-containing gas bubbles from near-surface *Sphagnum* peat. *Geophys. Res. Lett.*, 31:L21505, 2004. doi: 10.1029/2004GL021157.

K. B. Bartlett and R. C. Harriss. Review and assessment of methane emissions from wetlands. *Chemosphere*, 26:261–320, 1993.

R. Battino, editor. *IUPAC Solubility Data Series, Vol. 10, Nitrogen and Air.* Pergamon, Oxford, 1982.

M. Beckmann and D. Lloyd. Mass spectrometric monitoring of gases (CO_2, CH_4, O_2) in a mesotrophic peat core from Koppåaras Mire, Sweden. *Global Change Biol.*, 7:171–180, 2001.

C. W. Beckwith and A. J. Baird. Effect of biogenic gas bubbles on water flow through poorly decomposed blanket peat. *Water Resour. Res.*, 37:551–558, 2001.

L. M. Bellisario, J. L. Bubier, T. R. Moore, and J. P. Chanton. Controls on CH_4 emissions from a northern peatland. *Global Biogeochem. Cycles*, 13:81–91, 1999.

C. Blodau and T. R. Moore. Experimental response of peatland carbon dynamics to a water table fluctuation. *Aquat. Sci.*, 65:47–62, 2003.

C. Blodau, N. Basiliko, and T. R. Moore. Carbon turnover in peatland mesocosms exposed to different water table levels. *Biogeochemistry*, 67:331–351, 2004.

P. Bousquet, P. Ciais, J. B. Miller, E. J. Dlugokencky, D. A. Hauglustaine, C. Prigent, G. R. Van der Werf, P. Peylin, E.-G. Brunke, C. Carouge, R. L. Langenfelds, J. Lathiè, F. Papa, M. Ramonet, M. Schmidt, L. P. Steele, S. C. Tyler, and J. White. Contribution of anthropogenic and natural sources to atmospheric methane variability. *Nature*, 443: 439–443, 2006. doi: 10.1038/nature05132.

A. Brown, S. P. Mathur, and D. J. Kushner. An ombrotrophic bog as a methane reservoir. *Global Biogeochem. Cycles*, 3:205–213, 1989.

D. A. Brown. Gas production from an ombrotrophic bog - effect of climate change on microbial ecology. *Climatic Change*, 40:277–284, 1998.

A. J. Buttler, H. Dinel, M. Lévesque, and S. P. Mathur. The relation between movement of subsurface water and gaseous methane in a basin bog with a novel instrument. *Can. J. Soil Sci.*, 71:427–438, 1991.

F. Calmels and M. Allard. Ice segregation and gas distribution in permafrost using tomodensitometric analysis. *Permafrost Periglac. Process.*, 15:367–378, 2004.

M. Cao, K. Gregson, and S. Marshall. Global methane emission from wetlands and its sensitivity to climate change. *Atmos. Environ.*, 32:3293–3299, 1998.

P. Casper, S. C. Maberly, G. H. Hall, and B. J. Finlay. Fluxes of methane and carbon dioxide from a small productive lake to the atmosphere. *Biogeochemistry*, 49:1–19, 2000.

J. P. Chanton. The effect of gas transport on the isotope signature of methane in wetlands.

Org. Geochem., 36:753–768, 2005.

F. S. Chapin III, M. Sturm, M. C. Serreze, J. P. McFadden, J. R. Key, A. H. Lloyd, A. D. McGuire, T. S. Rupp, A. H. Lynch, J. P. Schimeland J. Beringer, W. L. Chapman, H. E. Epstein, E. S. Euskirchen, L. D. Hinzman, G. Jia, C.-L. Ping, K. D. Tape, C. D. C. Thompson, D. A. Walker, and J. M. Welker. Role of land-surface changes in arctic summer warming. *Science*, 310, 2005. doi: 10.1126/science.1117368.

L. S. Chasar, J. P. Chanton, P. H. Glaser, and D. I. Siegel. Methane concentration and stable isotope distribution as evidence of rhizosphereic processes: Comparison of a fen and bog in the Glacial Lake Agassiz Peatland complex. *Ann. Bot.*, 86:655–663, 2000.

T. R. Christensen, S. Jonasson, T. V. Callaghan, and M. Havstrom. Spatial variation in high-latitude methane flux along a transect across Siberian and European tundra environments. *J. Geophys. Res.*, 100:21035–21045, 1995.

T. R. Christensen, A. Ekberg, L. Strom, M. Mastepanov, N. Panikov, M. Oquist, B. H. Svensson, H. Nykanen, P. J. Martikainen, and H. Oskarsson. Factors controlling large scale variations in methane emissions from wetlands. *Geophys. Res. Lett.*, 30: 10.1029/2002GL016848, 2003.

H. L. Clever and C. L. Young, editors. *IUPAC Solubility Data Series, Vol. 27/28, Methane.* Pergamon, Oxford, 1987.

R. S. Clymo and D. M. E. Pearce. Methane and carbon dioxide production in, transport through, and efflux from a peatland. *Philos. Trans. R. Soc. London, Ser. A*, 350:249–259, 1995.

X. Comas, L. Slater, and A. Reeve. Spatial variability in biogenic gas accumulations in peat soils is revealed by ground penetrating radar (GPR). *Geophys. Res. Lett.*, 32:L08401, 2005a. doi: 10.1029/2004GL022297.

X. Comas, L. Slater, and A. Reeve. Geophysical and hydrological evaluation of two bog complexes in a northern peatland: Implications for the distribution of biogenic gases at the basin scale. *Global Biogeochem. Cycles*, 19:GB4023, 2005b. doi: 10.1029/2005GB002582.

H. Dinel, S. P. Mathur, A. Brown, and M. Lévesque. A field study of the effect of depth on methane production in peatland waters: Equipment and preliminary results. *J. Ecol.*, 76: 1083–1091, 1988.

N. B. Dise. Winter fluxes of methane from Minnesota peatlands. *Biogeochemistry*, 17:71–83, 1992.

N. B. Dise, E. Gorham, and E. S. Verry. Environmental factors controlling methane emissions from peatlands in northern Minnesota. *J. Geophys. Res.*, 98:10583–10594, 1993.

E. J. Dlugokencky, S. Houweling, L. Bruhwiler, K. A. Masarie, P. M. Lang, J. B. Miller, and P. P. Tans. Atmospheric methane levels off: Temporary pause or a new steady-state? *Geophys. Res. Lett.*, 30:1992, 2003. doi: 10.1029/2003GL018126.

P. Dunfield, R. Knowles, R. Dumont, and T. R. Moore. Methane production and consumption in temperate and subarctic peat soils: Response to temperature and pH. *Soil Biol. Biochem.*, 25:321–326, 1993.

D. Engle and J. M. Melack. Methane emissions from an Amazon floodplain lake: Enhanced release during episodic mixing and during falling water. *Biogeochemistry*, 51:71–90, 2000.

D. M. Etheridge, L. P. Steele, R. J. Francey, and R. L. Langenfelds. Atmospheric methane between 1000 AD and present: Evidence of anthropogenic emissions and climatic variability. *J. Geophys. Res.*, 103:15979–15993, 1998.

E. J. Fechner-Levy and H. F. Hemond. Trapped methane volume and potential effects on methane ebullition in a northern peatland. *Limnol. Oceanogr.*, 41:1375–1383, 1996.

Th. Foken and B. Wichura. Tools for quality assessment of surface-based flux measurements. *Agr. Forest Meteorol.*, 78:83–105, 1996.

P. Frenzel and E. Karofeld. CH_4 emission from a hollow-ridge complex in a raised bog: The role of CH_4 production and oxidation. *Biogeochemistry*, 51:91–112, 2000.

T. Friborg, T. R. Christensen, and H. Søgaard. Rapid response of greenhouse gas emission to early spring thaw in a subarctic mire as shown by micrometeorological techniques. *Geophys. Res. Lett.*, 24:3061–3064, 1997.

S. Frolking and P. Crill. Climate controls on temporal variability of methane flux from a poor fen in southeastern New Hampshire: Measurement and modeling. *Global Biogeochem. Cycles*, 8:385–397, 1994.

I. Fung, J. John, J. Lerner, E. Matthews, M. Prather, L. P. Steele, and P. J. Fraser. Three-dimensional model synthesis of the global methane cycle. *J. Geophys. Res.*, 96:13033–13065, 1991.

P. H. Glaser, J. P. Chanton, P. Morin, D. O. Rosenberry, D. I. Siegel, O. Ruud, L. I. Chasar, and A. S. Reeve. Surface deformations as indicators of deep ebullition fluxes in a large northern peatland. *Global Biogeochem. Cycles*, 18:GB1003, 2004. doi: 10.1029/2003GB002069.

E. Gorham. Northern peatlands: Role in the carbon cycle and probable responses to climatic warming. *Ecol. Appl.*, 1:182–195, 1991.

K. J. Hargreaves and D. Fowler. Quantifying the effects of water table and soil temperature on the emission of methane from peat wetland at the field scale. *Atmos. Environ.*, 32: 3275–3282, 1998.

K. J. Hargreaves, D. Fowler, C. E. R. Pitcairn, and M. Aurela. Annual methane emission from Finnish mires estimated from eddy covariance campaign measurements. *Theor. Appl. Climatol.*, 70:203–213, 2001.

R. C. Harriss, D. I. Sebacher, and F. P. Day Jr. Methane flux in the Great Dismal Swamp. *Nature*, 297:673–674, 1982.

R. Hein, P. J. Crutzen, and M. Heimann. An inverse modeling approach to investigate the global atmospheric methane cycle. *Global Biogeochem. Cycles*, 11:43–76, 1997.

M. M. Holland and C. M. Bitz. Polar amplification of climate change in coupled models. *Clim. Dyn.*, 21:221–232, 2003. doi: 10.1007/s00382-003-0332-6.

J. T. Houghton, Y. Ding, D. J. Griggs, M. Noguer, P. J. van der Linden, X. Dai, K. Maskell, and C. A. Johnson, editors. *Intergovernmental Panel on Climate Change: Climate Change 2001: The Scientific Basis*. Cambridge Univ. Press, Cambridge, UK, 2001.

S. Houweling, T. Kaminski, F. Dentener, J. Lelieveld, and M. Heimann. Inverse modeling of methane sources and sinks using the adjoint of a global transport model. *J. Geophys. Res.*, 104:26137–26160, 1999.

G. L. Hutchinson and G. P. Livingston. Soil-Atmosphere Gas Exchange. In J. H. Dane and G. C. Topp, editors, *Methods of Soil Analysis: Part4 Physical Methods*, pages 1159–1182. Soil Science Society of America, Madison, 2002.

G. L. Hutchinson and G. P. Livingston. Vents and seals in non-steady-state chambers used for measuring gas exchange between soil and the atmosphere. *Eur. J. Soil Sci.*, 52:675–682, 2001.

T. Kasubuchi, N. Miyaji, K. Kohyama, and S. Yanagiya. The water conditions ofthe Bibai Wetland and the investigation of its conservation method. *Jpn. J. Soil Sci. Plant Nutr.*, 65: 326–333, 1994.

E. Kellner, J. S. Price, and J. M. Waddington. Pressure variations in peat as a result of gas bubble dynamics. *Hydrol. Process.*, 18:2599–2605, 2004. doi: 10.1002/hyp.5650.

E. Kellner, J. M. Waddington, and J. S. Price. Dynamics of biogenic gas bubbles in peat: Potential effects on water storage and peat deformation. *Water Resour. Res.*, 41:W08417, 2005. doi: 10.1029/2004WR003732.

E. Kellner, A. J. Baird, M. Oosterwoud, K. Harrison, and J. M. Waddington. Effect of temperature and atmospheric pressure on methane (CH_4) ebullition from near-surface peats. *Geophys. Res. Lett.*, 33:L18405, 2006. doi: 10.1029/2006GL027509.

F. Keppler, J. T. G. Hamilton, M. Braß, and T. Röckmann. Methane emissions from terrestrial plants under aerobic conditions. *Nature*, 439:187–191, 2006.

A. Kettunen. Connecting methane fluxes to vegetation cover and water table fluctuations at microsite level: A modeling study. *Global Biogeochem. Cycles*, 17, 2003. doi: 10.1029/2002GB001958.

A. Kettunen, V. Kaitala, J. Alm, J. Silvola, H. Nykänen, and P. J. Martikainen. Predicting variations in methane emissions from boreal peatlands through regression models. *Boreal Environ. Res.*, 5:115–131, 2000.

R. Kondo, K. Tsutsuki, and R. Mori. Indices for decomposition of peat as affected by change in vegetation and the drying tendency in peatland. *Jpn. J. Soil Sci. Plant Nutr.*, 68:527–535, 1997.

S. P. Mathur and M. Lévesque. Negative effect of depth on saturated hydraulic conductivity of histosols. *Soil Sci.*, 140:462–466, 1985.

E. Matthews. Wetlands. In M. A. K. Khalil, editor, *Atmospheric Methane: Its role in the Global Environment*, pages 202–233. Springer-Verlag, Berlin, 2000.

E. Matthews and I. Fung. Methane emissions from natural wetlands: Global distribution, area, and environmental characteristics of sources. *Global Biogeochem. Cycles*, 1:61–86, 1987.

M. D. Mattson and G. E. Likens. Air pressure and methane fluxes. *Nature*, 347:713–714, 1990.

R. A. Melloh and P. M. Crill. Winter methane dynamics in a temperate peatland. *Global Biogeochem. Cycles*, 10:247–254, 1996.

S. E. Mikaloff Fletcher, P. P. Tans, L. M. Bruhwiler, J. B.Miller, and M. Heimann. CH_4 sources estimated from atmospheric observations of CH_4 and its $^{13}C/^{12}C$ isotopic ratios: 1. Inverse modelling of source processes. *Global Biogeochem. Cycles*, 18, 2004. doi: 10.1029/2004GB002223.

N. Miyaji, K. Kohyama, H. Otsuka, and T. Kasubuchi. Surface subsidence of peatland in Bibai, central Hokkaido. *Jpn. J. Soil Sci. Plant Nutr.*, 66:465–473, 1995.

T. R. Moore and R. Knowles. Methane emissions from fen, bog and swamp peatlands in Quebec. *Biogeochemistry*, 11:45–61, 1990.

O. Nagata, F. Takakai, and R. Hatano. Effect of *Sasa* invasion on global warming potential in *Sphagnum* dominated poor fen in Bibai, Japan. *Phyton*, 45:299–307, 2005.

National-Astronomical-Observatory, editor. *Rikanenpyo (Chronological Scientific Table)*. Maruzen Co., Tokyo, 2002. in Japanese.

N. S. Panikov and S. N. Dedysh. Cold season CH_4 and CO_2 emission from boreal peat bogs (West Siberia): Winter fluxes and thaw activation dynamics. *Global Biogeochem. Cycles*, 14:1071–1080, 2000.

R. Puranen, M. Mäkilä, and H. Säävuori. Electric conductivity and temperature variations within a raised bog in Finland: implications for bog development. *Holocene*, 9:13–24, 1999.

W. D. Reynolds, D. A. Brown, S. P. Mathur, and R. P. Overend. Effect of in-situ gas accumulation on the hydraulic conductivity of peat. *Soil Sci.*, 153:397–408, 1992.

E. A. Romanowicz, D. I. Siegel, J. P. Chanton, and P. H. Glaser. Temporal variations in dissolved methane deep in the Lake Agassiz Peatlands, Minnesota. *Global Biogeochem. Cycles*, 9:197–212, 1995.

D. O. Rosenberry, P. H. Glaser, D. I. Siegel, and E. P. Weeks. Use of hydraulic head to estimate volumetric gas content and ebullition flux in northern peatlands. *Water Resour. Res.*, 39:1066, 2003. doi: 10.1029/2002WR001377.

D. O. Rosenberry, P. H. Glaser, and D. I. Siegel. The hydrology of northern peatlands as affected by biogenic gas: current developments and research needs. *Hydrol. Process.*, 20: 3601–3610, 2006. doi: 10.1002/hyp.6377.

N. T. Roulet, A. Jano, C. A. Kelly, L. F. Klinger, T. R. Moore, R. Protz, J. A. Ritter, and W. R. Rouse. Role of the Hudson Bay lowland as a source of atmospheric methane. *J. Geophys. Res.*, 99:1439–1454, 1994.

R. D. Shannon, J. R. White, J. E. Lawson, and B. S. Gilmour. Methane efflux from emergent vegetation in peatlands. *J. Ecol.*, 84:239–246, 1996.

D. T. Shindell, G. Faluvegi, N. Bell, and G. A. Schmidt. An emissions-based view of climate forcing by methane and tropospheric ozone. *Geophys. Res. Lett.*, 32:L04803, 2005. doi: 10.1029/2004GL021900.

S. Shiozawa, T. Kasubuchi, N. Miyaji, and K. Kohyama. Analysis of ground water level of Bibai wetland by using one dimensional steady groundwater flow models. *Trans. JSIDRE*, 63:11–22, 1995.

N. J. Shurpali and S. B. Verma. Micrometeorological measurements of methane flux in a Minnesota peatland during two growing seasons. *Biogeochemistry*, 40:1–15, 1998.

N. J. Shurpali, S. B. Verma, and R. J. Clement. Seasonal distribution of methane flux in a Minnesota peatland measured by eddy correlation. *J. Geophys. Res.*, 98:20649–20655, 1993.

R. Spahni, J. Chappellaz, T. F. Stocker, L. Loulergue, G. Hausammann, K. Kawamura, J. Flückiger, J. Schwander, D. Raynaud, V. Masson-Delmotte, and J. Jouzel. Atmospheric methane and nitrous oxide of the late pleistocene from antarctic ice cores. *Science*, 310: 1317–1321, 2005. doi: 10.1126/science.1120132.

M. Strack, E. Kellner, and J. M. Waddington. Dynamics of biogenic gas bubbles in peat and their effects on peatland biogeochemistry. *Global Biogeochem. Cycles*, 19:GB1003, 2005. doi: 10.1029/2004GB002330.

M. Strack, E. Kellner, and J. M. Waddington. Effect of entrapped gas on peatland surface level fluctuations. *Hydrol. Process.*, 20:3611–3622, 2006. doi: 10.1002/hyp.6518.

F. Takakai, O. Nagata, and R. Hatano. Effect of *Sasa* invasion on CO_2, CH_4 and N_2O fluxes in *Sphagnum* dominated poor fen in Bibai, Hokkaido, Japan. *Phyton*, 45:319–326, 2005.

T. Tokida, T. Miyazaki, M. Mizoguchi, and K. Seki. In situ accumulation of methane bubbles in a natural wetland soil. *Eur. J. Soil Sci.*, 56:389–395, 2005a. doi: 10.1111/j.1365-2389.2004.00674.x.

T. Tokida, T. Miyazaki, and M. Mizoguchi. Ebullition of methane from peat with falling atmospheric pressure. *Geophys. Res. Lett.*, 32:L13823, 2005b. doi: doi:10.1029/2005GL022949.

T. Tokida, T. Miyazaki, M. Mizoguchi, O. Nagata, F. Takakai, A. Kagemoto, and R. Hatano. Falling atmospheric pressure as a trigger for methane ebullition from peatland. *Global Biogeochem. Cycles*, 2007, in press.

A. Van den Pol-van Dasselaar and O. Oenema. Methane production and carbon mineralisation of size and density fractions of peat soils. *Soil Biol. Biochem.*, 31:877–886, 1999.

P. C. van der Molen and T. A. Wijmstra. The thermal regime of hummock-hollow complexes on Clara bog, Co. Offaly. *Proc. Royal Irish Academy*, 94B:209–221, 1994.

D. Wagner, C. Wille, S. Kobabe, and E.-M. Pfeiffer. Simulation of freezing-thawing cycles in a permafrost microcosm for assessing microbial methane production under extreme conditions. *Permafrost Periglac. Process.*, 14:367–374, 2003.

B. P. Walter and M. Heimann. A process-based, climate-sensitive model to derive methane emissions from natural wetlands: Application to five wetland sites, sensitivity to model parameters, and climate. *Global Biogeochem. Cycles*, 14:745–765, 2000.

G. J. Whiting and J. P. Chanton. Primary production control of methane emission from wetlands. *Nature*, 364:794–795, 1993.

E. Wilhelm, R. Battino, and R. J. Wilcock. Low-pressure solubility of gases in liquid water. *Chem. Rev.*, 52:219–262, 1977.

J. Windsor, T. R. Moore, and N. T. Roulet. Episodic fluxes of methane from subarctic fens. *Can. J. Soil Sci.*, 72:441–452, 1992.

Y. Zhang, C. Li, C. C. Trettin, H. Li, and G. A. Sun. An integrated model of soil, hydrology, and vegetation for carbon dynamics in wetland ecosystems. *Global Biogeochem. Cycles*, 16, 2002. doi: 10.1029/2001GB001838.

Acknowledgment

I would like to express my sincere gratitude to professors, colleagues, friends and my parents who have provided a lot of supports during my time as a PhD student. In particular I would like to thank:

- Professor Tsuyoshi Miyazaki for giving me the opportunity to carry our this thesis. I appreciate his encouragement, his confidence in my work and the freedom I was granted during my dissertation.
- Associate Professor Masaru Mizoguchi for his countless suggestions from the beginning of my study. I am grateful to him for taking me to stimulating environments, which always made me move one step forward.
- Mr. Hiromi Imoto for his excellent technical supports in laboratory and field experiments. Thanks are also due to his selfless support in daily life in the lab.
- Assistant Professor Katsutoshi Seki and all former and present members of Chisui lab for a lot of discussion and valuable suggestions throughout the six years of the study in the lab.
- Professor Kazuhiko Kobayashi, Professor Sho Shiozawa and Professor Tadatsugu Tanaka for their insightful and constructive comments which greatly improved the thesis.
- Dr. Osamu Nagata of National Agricultural Research Center for Hokkaido Region, Members of Soil Science Laboratory and Soil Amelioration Laboratory of Hokkaido University for their kind support in field surveys.

- Yosuke Yanai and other members of Soil Science Seminar for giving me wide spectrum of knowledge in related fields. Their own important works inspired me to greater efforts in scientific pursuits.
- Japan Society for the Promotion of Science for giving me finantial support for living and research expenses.

Finally, I want to say "thank you" to my friends for giving me moral support and remiding me that it's all about having fun even in difficult times. I would like to dedicate this thesis to my parents, Seizo and Shizuko Tokida and everything they did for me.