Emission of methane from northern lakes and ponds

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Abstract

Northern lakes and ponds are abundant and emit large amounts of the potent climate forcer methane to the atmosphere at rates prone to change with amplified Arctic warming. In spite of being important, fluxes from surface waters are not well understood. Long-term measurements are lacking and the dominant and irregular transport mode ebullition (bubbling) is rarely quantified, which complicate the inclusion of lakes and ponds in the global methane budget. This thesis focuses on variations in emissions on both local and regional scales. A synthesis of methane fluxes from almost all studied sites constrains uncertainties and demonstrates that northern lakes and ponds are a dominant source at high latitudes. Per unit area variations in flux magnitudes among different types of water bodies are mainly linked to water depth and type of sediment. When extrapolated, total area is key and thus post-glacial lakes dominate emissions over water bodies formed by peat degradation or thermokarst processes. Further, consistent multiyear measurements in three post-glacial lakes in Stordalen, northern Sweden, reveal that seasonal ebullition, primarily driven by fermentation of acetate, can be predicted by easily measured parameters such as temperature and heat energy input over the ice-free season. Assuming that most water bodies respond similarly to warming, this thesis also suggests that northern lakes and ponds will release substantially more methane before the end of the century, primarily as a result of longer ice-free seasons. Improved uncertainty reductions of both current and future estimates rely on increased knowledge of landscape-level processes related to changes in aquatic systems and organic loading with permafrost thaw, as well as more high-quality measurements, seldom seen in contemporary data. Sampling distributed over entire ice-free seasons and across different depth zones is crucial for accurately quantifying methane emissions from northern lakes and ponds.
List of papers

This thesis is based on five papers that are attached and referred to in the text using Roman numerals as listed below:


Paper I: M.W. compiled the database, made the analyses and wrote the manuscript. Paper II: M.W. designed the sampling strategy, made the measurements and analyses and wrote the manuscript. Paper III: M.W. made flux and temperature measurements and part of the analyses and wrote part of the manuscript. Papers IV-V: M.W. collected the data, made the analyses and wrote the manuscripts.
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1. Introduction

Climate-sensitive northern landscapes are likely to be most impacted by increasing temperatures from global warming (Collins et al., 2013) and have been partly blamed for the ongoing increase of methane (CH$_4$) in the atmosphere (Nisbet et al., 2014). Lakes and ponds are particularly common in the north and they are potent CH$_4$ emitters because of their often anoxic and carbon (C)-rich sediments (Cole et al., 2007; Bastviken et al., 2011). However, the importance of water bodies in terms of CH$_4$ has been overlooked in favor of more frequently measured wetland soils. The emission potentials of the many types of freshwater bodies are also uncertain, mostly due to irregular release mechanisms in combination with a lack of high-resolution measurements. Consequently, there is also little known about the response to a changing climate. Lakes are warming rapidly (O'Reilly et al., 2015) and their ice-free seasons are lengthening (Dibike et al., 2011). This warming, in combination with altered loading of organic C to aquatic systems (Kicklighter et al., 2013), may fuel higher CH$_4$ emissions from lakes and ponds (Cole et al., 2007).

This thesis first provides an overview on the role of CH$_4$ in the climate system and the role of northern lakes and ponds as a source. Thereafter it focuses on spatiotemporal controls on flux, challenges to reduce uncertainties, and future emission potentials. Within this context, the five listed research papers (Paper I–V) are summarized and put in perspective. Paper I is a review article that reports an unprecedented compilation of CH$_4$ fluxes from lakes and ponds north of 50°N, a revised large-scale regional estimate of total emissions and predictions how these will change with Arctic warming. Paper II investigates the complexity of ebullition (bubbling), an often dominant but seldom measured transport mode of CH$_4$ from anoxic sediments, using a unique multiyear dataset based on frequent measurements from three small lakes in Stordalen, northern Sweden. The temporal variability in ebullition is investigated further in Paper III using year round water temperature and shortwave (SW) radiation data. Paper IV analyzes the stable isotopes in the bubbles to identify CH$_4$ production pathways and how they link to the lakes’ underlying carbon sources, and compare to those of other northern natural systems. The large datasets from the Stordalen lakes, also including turbulence-driven diffusive flux, are further used in Paper V to investigate the minimum spatiotemporal measurement resolution required to estimate seasonal CH$_4$ fluxes with high accuracy, and to provide recommendations on sampling strategies.
2. Methane in the climate system

2.1 Methane is on the rise

The so-called ‘greenhouse effect’ is essential for life on Earth. It is dependent on the existence of radiatively active trace gases in the atmosphere that are capable of absorbing surface-emitted longwave radiation (heat), and reradiating that heat to the planet’s surface. Although water vapor and carbon dioxide (CO₂) dominate the greenhouse effect due to their abundance, CH₄ plays an important role. Methane is the most plentiful (yet the smallest) organic compound in the atmosphere (Reeburgh, 2003) and accounts for 18% of the total radiative forcing by trace gases; over a century, it is 33 times more effective at trapping heat than an equivalent amount of CO₂ (Myhre et al., 2013).

Methane in particular, but also other radiatively active trace gases, has increased dramatically to unprecedented levels, causing climate warming (Hartmann et al., 2013). The global average mixing ratio of CH₄ is today almost threefold higher (~1825 parts per billion; NOAA/ESRL global air sampling network) than what it was before the start of the industrial revolution (Figure 1; Nisbet et al., 2014). Atmospheric CH₄ is generally higher at high northern latitudes due to the skewed latitudinal distribution of landmass and sources as well as atmospheric mixing patterns (Bergamaschi et al., 2013).

The amount of CH₄ in the atmosphere and its growth rate are functions of emissions from both natural and human-related (anthropogenic) sources and losses to sinks, primarily

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**Figure 1.** Global average mixing ratios of CH₄ and other important radiatively active trace gases in the atmosphere over the last 2000 years (modified from Forster et al. [2007]).
oxidation by hydroxyl radicals in the troposphere (Wuebbles and Hayhoe, 2002; Ghosh et al., 2015). Although the distribution of CH₄ in the atmosphere is fairly well known, total annual emissions are not well constrained. Current estimates range from 526 to 852 teragrams (Tg) and reflect spatiotemporal uncertainties and inconsistencies among inverse (top-down) modeling approaches and methods combining ground-based (bottom-up) measurements, of which the latter account for the higher most likely overestimated number (Kirschke et al., 2013). Natural sources account for approximately half of the total amount but contribute to most of the uncertainty, and are dominated by CH₄ release from wetland soils (Melton et al., 2013). The contribution from freshwaters (lakes, streams and rivers) has been calculated as 8–73 teragrams (Tg) globally, making them one of the most uncertain sources and potentially the second largest after wetlands (Kirschke et al., 2013). Estimates of the contribution from northern lakes and ponds alone, the focus of this thesis, are described below (see ‘5. Large-scale estimates of lake and pond emissions’). Other natural CH₄ emitters include termites, wild ruminants, hydrates, and non-biogenic geological (including oceans) and wild fire sources. Anthropogenic emissions arise from domestic ruminants, rice agriculture, organic waste and landfills, and from non-biogenic processes such as deforestation, biomass burning and fossil fuel extraction (Wuebbles and Hayhoe, 2002; Ghosh et al., 2015).

2.2 Production pathways can be indicated by stable isotopes

In nature, CH₄ is primarily formed as the end-product of biological breakdown of biomass. This type of CH₄ production (methanogenesis) involves metabolic processes that are strictly anaerobic (free of oxygen [O₂]) and mainly controlled by the availability of labile organic material and by temperature (Zeikus and Winfrey, 1976; Kelly and Chynoweth, 1981; Yvon-Durocher et al., 2014). Roughly two-thirds of the biogenic CH₄ is formed by acetoclastic methanogenesis (equation 1), which is dissimilation of acetate (CH₃COOH) through fermentation, and about one-third by hydrogenotrophic methanogenesis (equation 2), which is the reduction of carbon dioxide (CO₂) to CH₄ with molecular hydrogen (H₂) (Cicerone and Oremland, 1988; Ferry, 1992). Methane-producing microorganisms (methanogens) are numerous in terms of species and represent the largest group in the biological kingdom of Archaea.

Ratios of the stable isotopes carbon-13 (¹³C) and deuterium (D) in the CH₄ indicate production pathway and whether or not residual CH₄ has been oxidized to CO₂ (equation 3) by CH₄-oxidizing bacteria (methanotrophs; Chanton et al., 2005). Acetoclastic
methanogenesis typically produces CH₄ that is enriched in ^13^C relative to ^12^C but depleted in D relative to protium, and hydrogenotrophic methanogenesis the opposite, depleted ^13^C and enriched D. Oxidation, on the other hand, enriches both ^13^C and D due to the methanotrophs’ preferred use of lighter isotopes (Whiticar et al., 1986; Chanton et al., 2005).

\[
CH_3COOH \rightarrow CH_4 + CO_2 \tag{1}
\]

\[
CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{2}
\]

\[
CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{3}
\]

The isotopic composition of CH₄ is useful when estimating the contribution of various sources to the global CH₄ budget using mass-balance approaches (Stevens and Engelkemeir, 1988; Ghosh et al., 2015). In terms of northern lakes and ponds, stable isotopes have also been used in efforts to partition emissions from different types of water bodies (Brosius et al., 2012) and their underlying sources (Walter et al., 2008). However, because of overlaps in isotopic signatures there are uncertainties in these types of approaches (see ‘7.5 Acetoclastic methanogenesis appears dominant’).

3. Lakes and ponds in the landscape

Earth is home to around 117 million freshwater bodies (rivers excluded) that are larger than 0.002 km². These cover altogether an area of 5 million km², equal to 3.7% of the planet’s nonglaciated land surface (Verpoorter et al., 2014). Many more water bodies exist that are smaller in size but are currently below the detection limit of remote sensing techniques (Downing et al., 2006; Verpoorter et al., 2014).

Approximately 40% of the total area of lakes and ponds (excluding the Caspian Sea) occurs north of 50°N (Verpoorter et al., 2014). At these latitudes, landscapes transition from continental boreal forests in the south to widespread tundra biomes in the north, dominated by permafrost peatlands (Peel et al., 2007; Chen and Chen, 2013). The distribution of permafrost is divided into zones based on regional abundance (Brown et al., 1998). In the southerly isolated and sporadic permafrost zones, scattered throughout subarctic boreal and tundra regions, permafrost occurs in patches throughout the landscape. These zones overlap
northward the discontinuous permafrost zone across which a much larger part of the landscape has permafrost. The northernmost continuous permafrost zone is dominated by arctic tundra and defined by ubiquitous, evenly distributed permanently frozen peatlands (Zhang et al., 1999; Heginbottom, 2002). Altogether, permafrost soils are estimated to store approximately 1700 Pg of C, which is twice the global atmospheric C pool (Tarnocai et al., 2009; Hugelius et al., 2013). This storage is highly climate sensitive and it is speculated that warming-induced permafrost thaw will liberate and mobilize a substantial amount of labile C, primarily as dissolved and particulate organic carbon (DOC and POC; Schuur et al., 2008; Tranvik et al., 2009; Tank et al., 2011), into aquatic systems, fueling CH₄ production (Cole et al., 2007; Walter et al., 2007).

The abundance of water bodies across northern landscapes increases with latitude and permafrost zone (Smith et al., 2007; Verpoorter et al., 2014). Lakes and ponds are most numerous in previously glaciated landscapes that now have continuous permafrost, indicating the importance of glacial processes and permafrost thaw dynamics in forming water bodies (Smith et al., 2007). Northern lakes and ponds, in spite of being predominantly small, fall under a broad range of various types that are determined by formation processes, topographic relief, location, and landscape history (Lehner and Döll, 2004; Branstrator, 2009). Four generalized categories that are commonly measured in terms of CH₄ emissions and used in Paper I include:

1) **Beaver ponds** formed by beaver activity in rivers and streams. Damming floods forest and wetland vegetation, generating anoxic conditions suitable for CH₄ production. Beaver ponds are common in boreal and subarctic regions (Woo and Waddington, 1990; Whitfield et al., 2014).

2) **Glacial/post-glacial lakes** of various sizes and depths formed by receding ice-sheets during the last deglaciation. These comprise most of the water bodies across continental and subarctic boreal regions and commonly include bedrock depressions, moraine dams, and kettle lakes (Branstrator, 2009). Lakes of presumably glacial/post-glacial origin account for a dominant part of the total area covered by water bodies at high northern latitudes (Smith et al., 2007; Branstrator, 2009).

3) **Peatland ponds** which are often very small and shallow water bodies formed by peat degradation unrelated to permafrost thaw and thermokarst. The process is slow (scale
of millennia); water accumulates and the features deepen while the surrounding peatland continues to accumulate C (Belyea and Clymo, 1998).

4) **Thermokarst water bodies** created as a result of rapid (scale of decades to centuries) thaw of ice-rich permafrost and ground subsidence (Kozlenko and Jeffries, 2000; Grosse et al., 2013). Horizontal expansion of these water-filled depressions may be rapid with further loss of permafrost and development of erosional margins (Pelletier, 2005). The lifetime of thermokarst water bodies is determined by the stability of their surrounding permafrost, which acts as an impermeable barrier preventing drainage and infiltration of water to the subsurface (Hinkel et al., 2005). Thermokarst water bodies are particularly numerous in regions with continuous permafrost where they can cover as much as 20–40% of local landscapes (Sellmann et al., 1975; Grosse et al., 2013).

4. **Turbulence-driven diffusive flux and ebullition**

Most of the CH$_4$ produced in lake and pond sediments is transported through the water column either in a dissolved state (commonly referred to as ‘diffusive flux’) or as a gas through ebullition (Figure 2; Martens and Val Klump, 1980; Bastviken et al., 2004). A third pathway involves transport mediated by emerged vascular plants (Ström et al., 2003). Because this type of vegetation occurs almost exclusively at the lake edge and is often covered by flux studies from wetlands, plant transport is not included in this thesis.

The mechanism of dissolved CH$_4$ transport is primarily turbulence-driven advection. It can be slow and allows for substantial oxidation by methanotrophs (Rudd et al., 1976; Bastviken et al., 2008). Only the very final step through the $\sim$100 $\mu$m thin boundary layer between the water and the atmosphere is diffusively controlled (Liss and Slater, 1974). Hence, ‘turbulence-driven diffusive flux’ is a more accurate formulation of this pathway and is hereafter used in the text of this thesis introduction. The amount of dissolved CH$_4$ that can potentially escape the water appears to be mainly controlled by wind mixing of the surface layer (epilimnion) and recharge from below. Because of this, emissions often vary spatially between wind sheltered and wind exposed parts of lakes (Schilder et al., 2013), and temporally depending on local weather and between day and night (Natchimuthu et al., 2015).

Lakes often stratify thermally during summer (MacIntyre et al., 2009; Wüest and Lorke, 2009). At this time, the transport via advection from the deep layer (hypolimnion) is
limited and the primary fates of CH$_4$ are oxidation or accumulation if the bottom water is anoxic (Bastviken et al., 2008). When the stratification breaks down, usually in the fall, the hypolimnion can rapidly release its stored dissolved CH$_4$ as a circulation-induced flux pulse (Bastviken et al., 2004; Laurion et al., 2010). Such events can also occur following ice-out in spring, releasing dissolved CH$_4$ that has accumulated over winter (Michmerhuizen et al., 1996; Phelps et al., 1998; Jammet et al., 2015).

Figure 2. Schematic illustration of CH$_4$ emission pathways, turbulence-driven diffusive flux, ebullition and plant transport, from a stratified lake (modified from Bastviken et al. [2004]). The large circular arrow indicates mixing of the epilimnion. During the ice-free season, a small amount of the CH$_4$ produced in the sediment (indicated by thick black arrows) reaches the epilimnion and atmosphere via turbulence-driven diffusive flux due to thermal stratification and microbial oxidation in the hypolimnion. Ebullition, on the other hand, is a more direct and rapid transport mode when the lake is ice-free. If the bottom water is anoxic, dissolved CH$_4$ can be stored until water column turnover in the fall or after ice-out (e.g., Michmerhuizen et al., 1996). Most of the DOC and POC entering lakes are terrestrially derived recalcitrant (resistant to biological degradation) humic substances in transit and only a small amount settles in the sediment, particularly in the deep zones (Tranvik et al., 2009). Shallow zone sedimentation is partly influenced by more labile debris from in situ aquatic plants (Vreča and Muri, 2010; Marinho et al., 2015).

Ebullition is considered to account for a dominant part of total CH$_4$ fluxes from surface waters, although its relative contribution is uncertain at most studied sites (Bastviken et al., 2011). Bubble formation occurs because CH$_4$ is relatively insoluble (Martens and Val Klump, 1980). The release mechanisms of bubbles are complex and involve differences in the partial pressure of sediment gas pockets and the overlying hydrostatic loading, and the
sediment structure (Fendinger et al., 1992; Algar and Boudreau, 2009). Bubbling events are highly heterogeneous both spatially and temporally, and commonly considered difficult to predict and model (Walter Anthony and Anthony, 2013; DelSontro et al., 2015). Large releases, primarily from shallow zones, are episodic and most often associated with decreases in hydrostatic pressure during frontal passages or water level changes (Mattson and Likens, 1990; Varadharajan and Hemond, 2012; Maeck et al., 2014).

Bubbles released into shallow water columns during the ice-free season are likely to bypass oxidation because of their rapid accent (McGinnis et al., 2006) and most of them have high percent range CH$_4$ concentrations when reaching the atmosphere (Chanton et al., 1989; Walter et al., 2008). During winter, bubbles are trapped in a thickening ice-cover (Walter Anthony et al., 2010; Wik et al., 2011) and before they are fully enclosed by the ice a substantial amount of the CH$_4$ has either been oxidized to CO$_2$ or dissolved, the latter leading to a build-up of dissolved CH$_4$ in the water (Boereboom et al., 2012; Greene et al., 2014). In high latitude water bodies almost the entire winter storage of CH$_4$ (both dissolved and that in trapped bubbles) is expected to be released to the atmosphere at ice-out (Sepulveda-Jauregui et al., 2015; Jammet et al., 2015).

Slumping of labile C and underlying taliks (thaw bulbs of permanently unfrozen ground) are associated with persistent ebullition from fixed points, seeps, in the sediment (Walter et al., 2007). Very high CH$_4$ fluxes from seeps have been observed near erosional margins of thermokarst water bodies, particularly those underlain by yedoma (Pleistocene-aged, ice-rich permafrost across regions of Beringa [Strauss et al., 2013]) or geologic sources in northern Siberia, Canada, and Alaska. Occasionally bubbling rates from these seeps are high enough to sustain open holes in the ice during winter (Anthony et al., 2012).

5. **Large-scale estimates of lake and pond emissions**

Although CH$_4$ emissions from northern lakes and ponds have been studied for decades (e.g., Rudd and Hamilton, 1978) and there are numerous publications on the topic, no syntheses have compiled the majority of reported fluxes. The three estimates that exist previously illustrate the uncertainties, ranging from 11.9 to 24.2 ± 10.5 Tg CH$_4$ y$^{-1}$ (Walter et al., 2007; Bastviken et al., 2011; Tan and Zhuang, 2015). These are all based on data from relatively few sites, low-resolution maps of lake areas, and do not bin and extrapolate fluxes by water body type and abundance.
Paper I is a synthesis of 41 studies that report CH$_4$ fluxes based on measurements from a total of 733 water body sites north of $\sim$50°N. The compiled data suggest that lakes and ponds in these regions emit 16.5 ± 9.2 Tg of CH$_4$ y$^{-1}$. This estimate can be considered an improvement; it accounts for different water body types, turbulence-driven diffusive flux and ebullition, findings on winter contributions (e.g., Phelps et al., 1998), and revised inventories of the areal extent of lakes and ponds (Verpoorter et al., 2014). However, the new scaling approach is conservative for a number of reasons explained in Paper I. For example, the myriad ponds smaller than 0.002 km$^2$ are excluded because these are not yet part of contemporary inland water inventories (Verpoorter et al., 2014). The estimate also highlights discrepancies among sources, being equal to 70% of inverse model calculations of total natural northern emissions, considered to be dominated by wetlands (Bruhwiler et al., 2014).

**Figure 3.** Boxplot from Paper I (Wik et al., 2016b) showing methane fluxes from the compiled data, binned by ecoclimatic regions, permafrost zones, water body types, and sediment types. Boxes show interquartile ranges (25th to 75th percentile) and error bars the 10th and 90th percentiles. Solid black circles are means and vertical lines denote medians. Small grey circles are outliers. Turbulence-driven diffusive flux (here labelled as ‘diffusion’) and ebullition are color-coded and listed numbers in the columns denote sample sizes of site-specific or local fluxes.
Further, statistical regressions and Analysis of Variance (ANOVA) show large variations in emission potential per unit area among water body types \( (P < 0.001) \); the turbulence-driven diffusive fluxes were on average highest per unit area from small and shallow water bodies, particularly beaver and peatland ponds whose formation is unrelated to permafrost thaw (Figure 3; Paper I). Water bodies with small water volumes heat rapidly after ice-out in spring or early summer because of high solar radiation at this time (Paper III; Deshpande et al., 2015), and they often have more labile organic material in their sediments compared to those of large and deep lakes which commonly store more decomposed and recalcitrant substrates (Torres et al., 2010). Previously, thermokarst water bodies were receiving most attention, primarily through observations of high ebullition rates and their potential to receive mobilized labile C from permafrost thaw (e.g., Walter et al., 2006). Although thermokarst water bodies are potent \( \text{CH}_4 \) emitters, the compiled data presented in Paper I emphasize that glacial/post-glacial lakes, despite their often larger area, deeper water columns and lower fluxes per unit area, dominate large-scale emissions due to their much greater total areal coverage. The compiled data also highlight the importance of releases following ice-out of \( \text{CH}_4 \) that has been stored in the hypolimnion and in the ice over winter, accounting for roughly 25% of total annual emissions.

The results in Paper I further show significantly higher \( \text{CH}_4 \) fluxes per \( \text{m}^2 \) from lakes and ponds in the subarctic boreal region underlain by sporadic/isolated permafrost \( (P < 0.001) \). Statistical analyses using general linear models (GLMs) imply that this geographical difference is driven by interaction effects of water depth and sediment type \( (P \leq 0.026) \), possibly due to a bias of many studied shallow ponds with peat-rich sediments in these regions. Because of few reported measurements of temperature and lack of detailed site descriptions it was not possible to determine whether or not variations in temperature or local setting affect the contemporary geographical differences in reported fluxes (Paper I).

It is also clear that site-specific ebullition data are overall scarce in comparison to that of turbulence-driven diffusive flux. This is particularly evident for beaver and peatland ponds, and water bodies south of the permafrost zone (Figure 3; Paper I). Many of the ebullition numbers that do exist are influenced by seep fluxes in thermokarst lakes, underlain by taliks or yedoma (e.g., Sepulveda-Jauregui et al., 2015), and are likely not representative for most water bodies on a panarctic scale.
6. Intensively studied lakes in Stordalen

As a result of the work leading to parts of this thesis, there are now three lakes, Inre Harrsjön, Mellersta Harrsjön and Villasjön, where measurements of CH$_4$ fluxes (primarily ebullition) have been made frequently and in a consistent manner over many years and are ongoing. The lakes are small and mostly shallow (0.01–0.17 km$^2$ and 1–7 m in maximum depth) post-glacial features located in a lake-rich landscape on the edge of the Stordalen Mire, a subarctic permafrost peatland with alternating fens and palsas east of Abisko in northern Sweden (68°21’ N, 19°02’ E; Figure 4). The overall shallow Villasjön and intermediately deep Inre Harrsjön have small inlets and are considered partly spring fed (Nilsson, 2006). The drainage from Villasjön flows across the fen and into the catchment’s main stream which carries water to the smallest but deepest Mellersta Harrsjön. The lakes are not underlain by permafrost and they have no erosional margins. The average DOC in their waters is ~10 mg L$^{-1}$ (Olefeldt et al., 2012; Lundin et al., 2013), which is similar to almost half of the reported values.

![Figure 4](image_url). Map showing the Stordalen Mire, east of Abisko in northernmost Sweden (modified from base map in Paper III [Wik et al., 2014]). The expanded views show the three study lakes, Inre Harrsjön, Mellersta Harrsjön and Villasjön and locations of the 40 bubble traps, temperature logger strings and the tower from which SW flux was measured.
from studied water bodies included in Paper I. The pH in the lakes and in the groundwater supply ranges from 6.5 to 7.5 (Nilsson, 2006; Olefeldt et al., 2012) and is partly buffered by underlying carbonate-rich Dolomite (Lindström et al., 1985). Because of the relatively high pH and low conductivity (20–60 µS cm⁻¹; Nilsson, 2006) little DOC will flocculate and contribute to sedimentation (Tranvik and Wachenfeldt, 2009), particularly in Mellersta Harrsjön where the residence time of the water is also very short (days–weeks; D. Olefeldt, personal communication, 2010).

Although trace gas studies have been made at Stordalen Mire since the early 1970s (Svensson et al., 1974), the local aquatic systems have received little attention in terms of flux studies. Thus, insights into the lakes’ CH₄ dynamics, presented in this thesis and elsewhere (Wik et al., 2011; Lundin et al., 2013), will add important information about the local C balance. The study site and the lakes are described further in Wik et al. (2011) and Paper II.

6.1 Bubbles are trapped using inverted funnels

A reliable measurement device for ebullition is the inverted funnel. It has been used for decades to trap bubbles released from aquatic sediments (e.g., Strayer and Tiedje, 1978; Huttunen et al., 2001). In this work, a cost efficient yet robust and reliable inverted funnel design was used (Figure 5). The spatial variability of ebullition, within and among the three study lakes in Stordalen, was investigated using a depth-stratified sampling scheme in which a total of 40 bubble traps were systematically distributed across different zones and depth intervals (Figure 4; Paper II). All traps were partly submerged when deployed and bubbles that entered them from below replaced the water and formed gaseous headspaces that were sampled using plastic propylene syringes. Frequent, most often daily, sampling was made from June to September of 2009–2014, allowing for detailed investigation of the temporal variability of ice-free season fluxes, both seasonal and interannual. So far, more than 10 000 manual bubble flux measurements have been made at the Stordalen lakes, a dataset unprecedented in studies of CH₄ fluxes from aquatic systems. These data have been primary focus in the analyses reported in Papers II, III, IV and V. Lumped as lake-specific averages, they were also included in the synthesis presented in Paper I.

All bubble samples collected at the Stordalen lakes were analyzed for CH₄ at the Abisko Scientific Research Station (ANS) using a gas chromatograph with a flame ionization detector. Mass fluxes were calculated in mg CH₄ m⁻² d⁻¹ based on the measured concentrations and the bubbles’ accumulated total volumes in the traps over time. Analysis
procedures and flux calculations are explained further in Paper II. Every other week during the summers of 2009–2011, bubble samples were stored on vials filled with saturated sodium chloride solution and capped with butyl rubber septas for later analysis of the stable isotopic compositions of $^{13}$C and D in the CH$_4$ (expressed in this thesis as standard delta ($\delta$)-notations [$\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$]; see Paper IV). These analyses were made using continuous-flow gas chromatograph isotope-ratio mass spectrometry at the Stable Isotope Laboratory (SIL) at Stockholm University (explained further in Paper IV). When used, statistical methods, including regressions, ANOVAs and GLMs, are described in the method sections of the listed papers.

Figure 5. Robust bubble trap design used for ebullition measurements in the Stordalen lakes. The funnel diameter is 50 cm including the transparent plastic extension. The right image shows the trap when deployed. It is not fixed in the water and drifts around a float connected to a mooring. The photos are from Paper II (Wik et al., 2013).

6.2 Floating chambers to quantify turbulence-driven diffusive flux

Measurements of turbulence-driven diffusive CH$_4$ flux were made in the same study lakes in Stordalen using floating chambers (Uhlbäck, 2011; Andersson et al., in prep.). Briefly, the chambers were deployed in pairs of which one had a sub-surface shield to prevent bubbles from entering. By filtering out ebullition it is possible to identify the contribution of
turbulence-driven diffusive fluxes to the total open water flux, and make strict comparisons to the ebullition captured by the traps. Chamber measurements were made over 24-hour time periods, either weekly or biweekly from June to September of 2010–2013. Although the focus of this thesis is on ebullition, turbulence-driven diffusive fluxes were part of the analyses presented in Paper V, which also describes the chamber measurements and flux calculations in more detail.

6.3 Year round temperature and shortwave measurements

Temperatures were measured throughout the water column and into the sediment in each of the three lakes using intercalibrated HOBO Water Temp Pro v2 loggers (Paper II). Data were logged every 5 and 15 min in summer and winter, respectively. Incoming shortwave (SW) radiative flux was measured using a 4-compoment Net Radiation sensor that was mounted on a tower over the surface of Inre Harrsjön (Figure 4), and at ANS using a pyranometer. Data from ANS were used for gap-filling; the SW flux differed by less than 2% between the two sites (Paper III).

7. Spatiotemporal variations in lake emissions

7.1 Ebullition dominates over turbulence-driven diffusive flux

There are very few sites where both CH$_4$ ebullition and turbulence-driven diffusive flux have been measured over several years and thus there are large unknowns in their relative contribution (Paper I). In the Stordalen lakes, ebullition is the dominant and most variable (see sections below) transport mode during the ice-free season, releasing on average 13.4 mg CH$_4$ m$^{-2}$ d$^{-1}$, $n = 6806$ (Paper II) which is roughly twice the turbulence-driven diffusive flux (7.1 mg CH$_4$ m$^{-2}$ d$^{-1}$, $n = 820$; Andersson et al., in prep.). Although these fluxes are low compared to those from some thermokarst water bodies and most peatland ponds, they are similar to almost half of the site-specific fluxes reported in the literature (Paper I), suggesting that the Stordalen lakes are representative on regional scales. Similarities with other lakes and ponds are discussed further in Paper V.

7.2 Heat energy is primary driver of ebullition

The frequent measurements at the Stordalen lakes, presented in Paper II, show large and often extreme daily variations in ebullition (Figure 6). The bubble CH$_4$ flux responds rapidly to the
warming and cooling of the water and sediment over the ice-free season, often peaking at the temperature maxima in July or early August (Paper II). There is also a strong exponential relationship with daily bubble flux and temperature ($r^2 = 0.94$; Figure 7a) which suggests that ebullition does not occur until the sediment reaches $\sim 7^{\circ}C$, presumably the point when the porewaters become saturated with dissolved CH$_4$ (Paper III). In shallow water columns, the saturation threshold is mainly controlled by temperature-driven changes in solubility and CH$_4$ production rates (Yamamoto et al., 1976; Martens et al., 1998). Once saturation occurs, any excess production directly fuels bubble formation with varying rates depending on temperature (Figure 7b). Thus, changes in the energy input and heat transfer to the sediment seem to control most of the daily and seasonal ebullition variation in the Stordalen lakes, and likely also in many other northern water bodies (Paper III).

Similar to results from previous studies (e.g., Maeck et al., 2014), the daily variation in ebullition from the Stordalen lakes is also partly related to changes in atmospheric pressure.
with generally higher bubble CH$_4$ fluxes during periods when the pressure is decreasing ($P < 0.001$; Paper II). Atmospheric pressure is, however, only effective as a trigger and not a control on ebullition; not all sudden pressure drops seem to generate large degassing events (Figure 6a; Paper II). Early in the season before the dissolved CH$_4$ exceeds its solubility there is likely too little gas in the sediment for bubbles to be released in response to pressure changes. Also, unless sediment temperatures are high enough to rapidly recharge a sufficient amount of gas after a large release, the effect of a consecutive drop in atmospheric pressure will be small (Papers II and III).

![Figure 7](image)

**Figure 7.** (a) Mean daily bubble CH$_4$ flux versus surface sediment temperature binned by 1°C intervals, and (b) an Arrhenius relationship with the natural logarithm of the flux data versus inverse sediment temperature in Kelvin. Red solid circles indicate data that correspond to surface sediment temperatures prior to and at the onset of ebullition. Error bars are 95% confidence intervals and lines denote polynomial fits. Note that this is an updated version of Figure 2 in Paper III (Wik et al., 2014), here based on six instead of four years of data from the Stordalen lakes (2009–2014; total of 10227 individual flux measurements).

### 7.3 Ice-free season length controls interannual variations

Consistent sampling over many years at the Stordalen lakes indicate that ice-free season ebullition can vary more than twofold from year to year (Figure 8; Papers II and III). This variation appears to be primarily controlled by differences in energy input as a function of ice-free season length; Paper III shows remarkably strong correlations ($r^2 = 0.997$) between seasonal bubble flux and incoming SW radiation from ice-out to end of September (Figure 8).
A two month longer ice-free season corresponds to a near doubling in the amount of CH$_4$ transported by bubbles. Earlier ice-out and the possibility of earlier heating of the lakes are likely to affect emissions all through the season. A larger total SW input provides more energy to the sediments and promotes high CH$_4$ production rates that can last longer in the fall and into the winter (Paper III).

**Figure 8.** Seasonal cumulative bubble CH$_4$ flux versus cumulative SW flux over the ice-free period for the Stordalen lakes. The color-coded lines are different degrees of polynomial fits with accompanying $r^2$-values. Note that this is an updated version of Supplementary Figure 2 in Paper III (Wik et al., 2014), here showing six instead of four years of data (each symbol is based on 1300–2300 individual flux measurements). Cumulative SW is calculated from ice-out to end of September.

The general understanding is that ebullition is difficult to model, but the strong relationships in Figures 7 and 8 and in Paper III show differently. Incoming SW, ice-free season length, and temperature are easily measured proxies that can used to predict seasonal bubble CH$_4$ flux in the Stordalen lakes. Most likely, these are also useful in other lakes and ponds with a stable organic source in their sediments, once the spatiotemporal variability of the bubbles has been determined (Paper III). The relationship of flux and ice-free season length has been used for back projections of CH$_4$ ebullition using documented ice-out dates in the Stordalen area over the last 100 years (Thornton et al., 2015) and in one of the first attempts to predict large-scale future emissions from northern lakes and ponds (Paper I).
7.4 Water depth drives the spatial heterogeneity

Paper II further shows that CH$_4$ ebullition can vary greatly among nearby lakes. In this case in Stordalen, bubble fluxes are fourfold higher in the overall shallow Villasjön (22.0 mg CH$_4$ m$^{-2}$ d$^{-1}$, n = 1404) than in the intermediately deep Inre Harrsjön where they are lowest (7.8 mg CH$_4$ m$^{-2}$ d$^{-1}$, n = 4515; $P < 0.001$). Further, the internal variability within each lake is much larger (up to 43-fold in Inre Harrsjön) which highlights the need for stratified sampling when measuring ebullition (see ‘7.6 High-accuracy flux estimates require extensive sampling’). These spatial variations, both within and among the lakes, are controlled by variations in temperature, sediment quality and organic loading, all ultimately determined by the lakes’ morphometry (depth in particular) and location in the landscape (Papers II, III and IV).

Similar to findings in other studies (e.g., Joyce and Jewell, 2003; Bastviken et al., 2004) bubbling events in the Stordalen lakes are generally larger and more frequently occurring from shallow zones (0–2 m). These areas have more labile organic material in their sediment, influenced by aquatic plants (see ‘7.5 Acetoclastic methanogenesis appears dominant’ and Paper V), and they warm faster and reach higher temperatures over summer (Paper II). However, when the shallow zones cool in the fall and the thermal stratification breaks down or weakens, there is heat transfer to the hypolimnion and warming of deep zone sediments, causing a shift in the distribution towards more equal flux magnitudes across depth intervals (Figure 6 and Paper II). Coupled with this is also a temporal shift in the bubbles’ CH$_4$ concentrations; by the end of the season, bubbles from depth show concentrations that have surpassed those of shallow zone ebullition (Paper II). All this suggests that low temperatures rather than lack of labile C are limiting deep zone ebullition in the Stordalen lakes. This further hints at possible higher fluxes from similarly deep lakes, and perhaps also those that are deeper, if water temperatures and ice-free season lengths are increasing as predicted (Dibike et al., 2011; O'Reilly et al., 2015).

7.5 Acetoclastic methanogenesis appears dominant

The isotopic analyses of the bubbles from the Stordalen lakes show a large range in both $\delta^{13}$C-CH$_4$ and $\delta$D-CH$_4$ (-78.4 to -53.1‰ and -369.8 to -218.8‰, n = 176) and suggest predominant acetoclastic methanogenesis with influence of hydrogenotrophic production with increasing depth, and little evidence of oxidation (Paper IV). Both Inre Harrsjön and Mellersta Harrsjön have abundant submerged aquatic plants in their shallow waters (Wik et al., 2011), which can provide labile C and acetate to the methanogens (Duddleston et al.,
Halloran et al. (2013) have found course plant debris in the sediment in the lakes’ shallow zones whereas (Kokfelt et al., 2009) report highly decomposed gyttja at depth, which is usually depleted in acetate (Whiticar et al., 1986). In comparison, the overall shallow Villasjön, which shows significantly higher δ^{13}C-CH\(_4\) (enriched in \(^{13}\)C; \(P < 0.001\)) has very little plant growth (Paper IV). Instead it is partly underlain by mixed peat (Sphagnum spp. and Carex spp.), possibly eroded from the mire around 2100 BP (Kokfelt et al., 2010), which appears sufficient to fuel ebullition through predominantly acetoclastic methanogenesis.

Acetoclastic methanogenesis is also considered the dominant pathway in most other studied northern lakes and ponds (e.g., Walter et al., 2008; Bouchard et al., 2015) and there are large overlaps in site-specific signatures on regional scales (Paper IV). For example, the δ^{13}C-CH\(_4\) in bubbles from the Stordalen lakes not only range across those of other post-glacial lakes, they also range across signatures reported from most studied thermokarst water bodies of which some are underlain by yedoma, and have persistent seep ebullition (Walter et al., 2008). It is possible that the potential influence of \(\textit{in situ}\) plants on bubble formation, hypothesized from the Stordalen data (Paper IV) and observed in tropical lakes (Marinho et al., 2015), also plays a role in most northern lakes and ponds, perhaps being more important than C loading from surrounding landscapes. Further, there are also overlaps in site-specific δD-CH\(_4\), possibly related to evaporation-driven fractionation of the water (\(\text{H}_2\) source for methanogens [Ferry, 1992]) during summer, which may affect shallow ponds more than deep lakes (Paper IV), and D-depleted water from melting ice-wedges entering some thermokarst lakes (Brosius et al., 2012). The overall consistencies across sites imply that it is currently difficult to label CH\(_4\) fluxes from different types of lakes and ponds using stable isotopes.

Further, the δ^{13}C-CH\(_4\) reported from northern lakes and ponds interestingly cover almost the whole range of that of high-latitude wetlands (e.g., Quay et al., 1988; Sriskantharajah et al., 2012; McCalley et al., 2014). This suggests that it is also difficult, if not impossible, to isotopically differentiate lake and wetland emissions, which has large implications regarding the accuracy of source strengths in global budgets (Bousquet et al., 2006; Ghosh et al., 2015). Possibly, top-down estimates using isotopic mass-balance calculations of CH\(_4\) release from wetlands may be influenced by input from lakes.

7.6 High-accuracy flux estimates require extensive sampling

Simulations of hypothetical sampling scenarios, using the substantial datasets from the Stordalen lakes, show that labor intensive efforts are required to achieve high-accuracy CH\(_4\)
flux measurements that cover most of the spatiotemporal variability (Figure 9; Paper V). The results imply that measurements on 39 sampling days, scattered throughout the ice-free season, are minimum for high confidence (95% probability) of accurately estimating ebullition on a temporal scale. In contrast, the less variable turbulence-driven diffusive flux requires 11 sampling days for a similar confidence of high accuracy. It is important to note that the spatial variability must be accounted for simultaneously. Paper V further suggests that turbulence-driven diffusive fluxes and ebullition require depth-stratified sampling on at least 3 and 11 locations, respectively.

**Figure 9.** Range in potential uncertainties of seasonal turbulence-driven diffusive CH$_4$ flux (red; here labelled ‘diffusive flux’) and ebullition (black) versus number of (a) sampling days and (b) locations. The uncertainties converge towards asymptotic values, which indicate the maximum accuracy achieved by the sampling schemes used in the Stordalen lakes. Dashed lines indicate the sampling needed to have high confidence (95% likelihood) of reaching within ± 20% of the asymptotic value. Vertical shaded areas denote variations in the sampling requirements among years. The figure is modified from Paper V (Wik et al., 2016a).

In the Stordalen lakes, low spatiotemporal resolutions in measurements would generate potential uncertainties up to several orders of magnitude and would more likely underestimate than overestimate seasonal CH$_4$ fluxes (Figure 9; Paper V). Assuming this is also the case elsewhere, most site-specific CH$_4$ emission estimates are highly temporally biased and possibly underestimated; as much as 83% of the studied northern lakes and ponds have been measured for turbulence-driven flux over surprisingly short time periods of three days or fewer (Paper I). Such few sampling days, often in combination with poorly distributed
sampling locations, are likely to miss rare yet large and important episodic ebullition events or late season fluxes from deep zones (Papers II and V), and days with high wind or water column turnover (e.g., fall mixing), important for high turbulence-driven diffusive flux (Laurion et al., 2010). In addition, ebullition is only measured at 7% of the sites, which contributes uncertainties when fluxes are scaled regionally.

8. Future emission potentials

Predicted increases of up to 9°C in Arctic mean annual air temperature within the next century (Collins et al., 2013) will cause warming of inland waters and longer ice-free seasons (Dibike et al., 2011; O'Reilly et al., 2015). This will also enhance energy input and microbial production and possibly plant growth (Prowse and Stephenson, 1986; Rouse et al., 1997), which ultimately feedbacks positively on CH₄ release (Natchimuthu et al., 2014; Wik et al., 2014; Yvon-Durocher et al., 2014). Further, warming induced permafrost thaw may cause an overall expansion of total water body area (Jorgenson and Osterkamp, 2005; Walter et al., 2006) or, perhaps more likely, drier environments by draining wetlands and water bodies. Recent findings indicate that the area of thermokarst water bodies has decreased with 2.5–30% on local scales over the last 50 years (Smith et al., 2005; Bouchard et al., 2014).

Using the ice-free season proxy in Paper III and modeled estimates that the ice-free season will lengthen by roughly 20 days on average until 2079 (Dibike et al., 2011), Paper I reports that total CH₄ emissions from lakes and ponds north of 50°N can potentially increase by 30% before the end of the century. Also assuming that the total area of thermokarst water bodies will either decrease or increase by around one-third over the same time period, the increase in emission varies from 20 to 54%. Other estimates by (Tan and Zhuang, 2015) predict even higher increases of 90–136% for lakes north of 60°N. These are however based on data from only five sites.

Although the results in Paper I suggest that changes in ice-free days will have the largest effect on future emission potentials, it is important to note that other processes that are currently difficult to model are likely to play important roles. Again, mobilization of labile C, either as DOC and POC or through slumping of vegetation into existing or newly formed lakes and ponds (Tank et al., 2011; Kicklighter et al., 2013) will favor anaerobic decomposition and release of radiatively active trace gases such as CH₄ (Cole et al., 2007).

For example, the compiled data in Paper I show higher fluxes from thermokarst lakes with higher concentrations of DOC in their waters. Changing precipitation patterns, including later
snowfall and increased rainfall in summer, might also alter organic loading to aquatic systems (McClelland et al., 2006; Kicklighter et al., 2013).

The fact that glacial/post-glacial lakes are more permanent in the landscape compared to most other water body types, also highlight their importance for future emission potential. If surface waters are warming as predicted, large and often deep lakes might also produce more CH₄, and because of their large hypolimnions there is potential for greater storage (Michmerhuizen et al., 1996), both during summer and winter, and larger releases of dissolved CH₄ at fall mixing and ice-out in spring. Also, ice-free seasons that stretch longer into winter will allow for prolonged direct bubbling to the atmosphere, from both shallow and deep zones. Thus, increased understanding of CH₄ dynamics during winter is a crucial part to add to the uncertainty reduction of both contemporary and future emission potentials of northern lakes and ponds.

9. Conclusions

This thesis revises large-scale emission estimates and emphasizes that lakes and ponds are a dominant but understudied source of CH₄ from northern landscapes. On local scales, sediment type and water depth appear to be the primary lake characteristics controlling the difference in flux magnitudes among different types of water bodies, whereas total area coverage is more important on regional scales. Hence, post-glacial lakes dominate large-scale emissions. The synthesis of data also highlights the importance of accounting for winter contributions when estimating the total amount of CH₄ released.

In the Stordalen lakes, and most likely many other water bodies, ebullition is primarily controlled by heat energy, both in shallow and deep zones. Consistent long-term measurements show remarkable correlations with energy input over the ice-free season and temperature, suggesting that ebullition becomes a predictable process with long-term measurements, assuming a stable organic source in the sediment.

The large spatiotemporal variability in CH₄ fluxes from lakes and ponds, particularly that of ebullition, require depth-stratified sampling over most of the ice-free season and over many years. Such sampling campaigns are, however, rare which jeopardizes the accuracy of large-scale estimates and limits further comparison of emission potential among water body types. Also, overlapping isotopic signatures and predominant acetoclastic methanogenesis, possibly fueled by aquatic plants, across sites and regions make it difficult to partition emissions from different lake and pond sites using stable isotopes.
It is likely that the CH$_4$ release from northern lakes and ponds will increase substantially with Arctic warming and longer ice-free seasons, but predictions are uncertain. This is in part due to unknowns in landscape-level processes and feedback mechanisms controlling C input, and, again, lack of long-term measurements, particularly of ebullition, from different types of water bodies. The depth-stratified sampling schemes used at the Stordalen lakes can be considered recommendations from which more site-specific methods can be developed. Measurements do not have to be complicated; manual sampling using simple and robust devices has been key in producing the results presented in this thesis.

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