Freshwater methane and carbon dioxide fluxes

Spatio-temporal variability and an integrated assessment
of lake and stream emissions in a catchment

Sivakiruthika Natchimuthu

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Abstract

Freshwater bodies such as lakes and streams release the greenhouse gases methane (CH_4) and carbon dioxide (CO_2) into the atmosphere. Global freshwater CH_4 and CO_2 emissions have been estimated to be of a similar magnitude to the global land or ocean carbon sink, and are thus significant components of global carbon budgets. However, the data supporting global estimates frequently lacks information regarding spatial and temporal variability and are thus highly inaccurate. In this thesis, detailed studies of the spatio-temporal variability of CH_4 and CO_2 fluxes were conducted in the open water areas of lakes and streams within a whole catchment in Sweden. One aim was also to evaluate the importance of spatio-temporal variability in lake and stream fluxes when making whole catchment aquatic or large scale assessments. Apart from the expected large spatio-temporal variability in lake fluxes, interactions between spatial and temporal variability in CH_4 fluxes were found. Shallow lakes and shallow areas of lakes were observed to emit more CH_4 as compared to their deeper counterparts. This spatial variability interacted with the temporal variability driven by an exponential temperature response of the fluxes, which meant that shallow waters were more sensitive to warming than deeper ones. Such interactions may be important for climate feedbacks. Surface water CO_2 in lakes showed significant spatio-temporal variability and, when considering variability in both space and time, CO_2 fluxes were largely controlled by concentrations, rather than gas transfer velocities. Stream fluxes were also highly variable in space and time and in particular, stream CH_4 fluxes were surprisingly large and more variable than CO_2 fluxes. Fluxes were large from stream areas with steep slopes and periods of high discharge which occupied a small fraction of the total stream area and the total measurement period, respectively, and a failure to account for these spatially distinct or episodic high fluxes could lead to underestimates. The total aquatic fluxes from the whole catchment were estimated by combining the measurements in open waters of lakes and streams. Using our data, recommendations on improved study designs for representative measurements in lakes and streams were provided for future studies. Thus, this thesis presents findings relating to flux regulation in lakes and streams, and urges forthcoming studies to better consider spatio-temporal variability so as to achieve unbiased large-scale estimates.

Keywords: Lakes, streams, spatio-temporal variability, CH_4 flux, CO_2 flux, gas transfer velocity

Sammanfattning

Sötvatten som sjöar och vattendrag är källor till växthusgaserna metan (CH_4) och koldioxid (CO_2) i atmosfären. De globala utsläppen av CH_4 och CO_2 från sötvatten har uppskattats vara av samma storleksordning som den globala land- eller havskolsänkan och är därmed viktiga delar av jordens växthusgasbudget. De globala uppskattningarna saknar ofta information om variation i tid och rum och är därmed mycket osäkra. Denna avhandling behandlar hur CH_4 - och CO_2 -flöden från öppet vatten i sjöar och vattendrag i ett avrinningsområde varierar rumsligt och tidsmässigt. Ett syfte var också att utvärdera betydelsen av dessa variationer när data extrapoleras för att göra storskaliga uppskattningar av växthusgasflöden från vattenmiljöer. Förutom de förväntade stora rumsliga och tidsmässiga variationerna i sjöars gasflöden identifierades interaktioner mellan rumsliga och tidsmässiga variation för CH_4 -flöden. Den rumsliga variabiliteten med högre CH_4 -flöden från grunda vatten interagerade med tidsvariationen, som i sin tur drevs av en exponentiell temperaturrespons av gasflödena. Det betyder att grunda vattenområden var mer känsliga för uppvärmning än djupare vatten och därmed att vattendjupet har betydelse för hur sjöars CH_4 -utsläpp påverkas av klimatet. Koncentrationer av CO_2 i sjöars ytvatten uppvisade också en betydande rumslig och tidsmässig variation som tillsammans visar att CO_2 -flöden över längre perioder till stor del styrs av koncentrationer snarare än av gasutbyteshastigheter. Vattendragens gasflöden varierade också mycket i tid och rum. Detta gällde i synnerhet CH_4 -flödena vilka var förvånansvärt stora och mer varierande än CO_2 -flödena. Gasflödena var höga från områden i vattendrag med högre lutning och då det var höga vattenflöden, trots att dessa områden och tidsperioder utgjorde en bråkdel av den totala arean och mätperioden. Att inte räkna med dessa gasflöden från bäcksektioner med höga vattenhastigheter eller korta perioder med höga flöden, leder till underskattningar. De totala CH_4 - och CO_2 -flödena från öppet vatten i hela avrinningsområdet uppskattades genom att kombinera mätningar i sjöar och vattendrag. Denna avhandling visar att rumslig och tidsmässig variabilitet har stor betydelse, och den ger information om hur denna variation kan beaktas för bättre framtida mätningar och storskaliga uppskattningar av växthusgasflöden från sjöar och vattendrag.

Nyckelord: Sjöar, vattendrag, rumsliga och tidsmässiga variationer, CH_4 -flöden, CO_2 -flöden, gasutbyteshastighet

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List of Publications

The thesis is based on the following papers, which will be referred to in the text by the corresponding Roman numerals:

- I. Natchimuthu S, Sundgren I, Gålfalk M, Klemedtsson L, Crill P, Danielsson Å, Bastviken D (2015) Spatio-temporal variability of lake CH₄ fluxes and its influence on annual whole lake emission estimates. Published online in *Limnology and Oceanography*.
- II. Natchimuthu S, Sundgren I, Gålfalk M, Klemedtsson L, Bastviken D. Spatio-temporal variability of lake pCO₂ and CO₂ fluxes in a catchment. *In review*.
- III. Natchimuthu S, Wallin MB, Klemedtsson L, Bastviken D. Spatio-temporal patterns of stream methane and carbon dioxide emissions in a catchment. *In review*.
- IV. Natchimuthu S, Wallin MB, Klemedtsson L, Bastviken D. Disproportionate contribution of hotspots to whole-catchment aquatic carbon gas emissions. *Manuscript*.

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Author's contributions to the list of publications

- I. The author was involved in planning the study. The author organised and conducted the field work, laboratory analysis, and analysis of the results, and wrote the first draft of the manuscript and coordinated the writing process.
- II. The author was involved in planning the study. Field work and laboratory analysis were organised and conducted by the author. The author analysed the results and wrote the first draft of the manuscript.
- III. The author contributed to the planning of the study. Field work and lab work were organised and conducted by the author. The author analysed the results, wrote the first draft of the manuscript, and coordinated the writing process.
- IV. The author was involved in designing the study. The author performed the data analysis and wrote the first draft of the manuscript.

Additional Publications

In addition to the above, the author has contributed to the following publications, which are not included in this thesis:

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Panneer Selvam B, Natchimuthu S, Arunachalam L, Bastviken D (2014) Methane and carbon dioxide emissions from inland waters in India - implications for large scale greenhouse gas balances. *Global Change Biology*, **20**, 3397-3407.

Bastviken D, Sundgren I, Natchimuthu S, Reyier H, Gålfalk M (2015) Technical Note: Cost-efficient approaches to measure carbon dioxide (CO₂) fluxes and concentrations in terrestrial and aquatic environments using mini loggers. *Biogeosciences*, **12**, 3849-3859.

Podgrajsek E, Sahlée E, Bastviken D, Natchimuthu S, Kljun N, Chmiel HE, Klemetsson L, Rutgersson A (2015) Methane fluxes from a small boreal lake measured with the eddy covariance method. Published online in *Limnology and Oceanography*.

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Abbreviations

C	Carbon
CH ₄	Methane
CO ₂	Carbon dioxide
DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
GHG	Greenhouse gases
k	Gas transfer velocity or piston velocity (expressed in m d ⁻¹)
k_{600}	k normalised to a Schmidt number of 600
Mg	Mega gram (10 ⁶ g)
pCO _{2aq}	Partial pressure of CO ₂ in equilibrium with surface water concentration
Pg	Peta gram (10 ¹⁵ g)
SRC	Skogaryd Research Catchment

1 Introduction

Methane (CH_4) and carbon dioxide (CO_2) are important greenhouse gases (GHGs) in the Earth's atmosphere, and play a major role in shaping the planet's climate. The concentration of CH_4 and CO_2 in the atmosphere has been increasing since the Industrial Revolution, and current levels of CH_4 and CO_2 are 150 and 40% higher than in 1750, respectively (Hartmann *et al.*, 2013). One of the uncertainties in the global greenhouse budget is the limited knowledge of sources and sinks, along with an incomplete understanding of their climate feedbacks. Freshwater systems such as lakes and streams have been identified as active and important components of the global carbon cycle, although they occupy only a small portion of the Earth's surface (Cole *et al.*, 2007; Raymond *et al.*, 2013; Tranvik *et al.*, 2009). Yet, the strength of these sources, and the mechanisms regulating CH_4 and CO_2 fluxes within them, are still poorly understood.

Global lakes and streams/ivers are estimated to occupy 3.7 and 0.5%, respectively, of Earth's non-glaciated land surface (Raymond *et al.*, 2013; Verpoorter *et al.*, 2014). Thus, only a fraction of the Earth's land surface is covered with lakes and streams, and yet they contribute disproportionately to the global carbon budget (Bastviken *et al.*, 2011; Raymond *et al.*, 2013). Notably, small inland waters such as ponds have been shown to release large amounts of CH_4 and CO_2 (Holgerson & Raymond, 2016). It has been estimated that roughly 0.65 Pg of C (CO_2 equivalents) yr^{-1} in the form of CH_4 (Bastviken *et al.*, 2011) and 2.1 Pg C yr^{-1} of CO_2 (Raymond *et al.*, 2013) are emitted from inland waters globally. To put this into perspective, approximately 2.3 Pg C yr^{-1} is thought to be sequestered by the oceans and 2.6 Pg C yr^{-1} by terrestrial soils (when land-use change is not accounted for) (Ciais *et al.*, 2013), emphasising the importance of global inland waters as a source of GHGs. Despite the growing body of literature highlighting the importance of lake and stream GHG emissions, there is a general lack of detailed studies of spatial and temporal variability in gas fluxes. Such studies are critical to ensure that extrapolations are representative, and to reveal the controlling factors of CH_4 and CO_2 fluxes.

1.1 Sources of CH₄ and CO₂ in freshwater bodies

Anoxic conditions in the sediments of lakes lead to the anaerobic decomposition of organic matter by the process of methanogenesis, resulting in the production of CH₄ (Zeikus & Winfrey, 1976). Under anoxic conditions, utilising alternative electron acceptors such as SO₄²⁻, Fe³⁺, Mn⁴⁺, and NO₃ yields more energy than methanogenesis. Thus, the presence of these alternative electron acceptors often inhibits methanogenic archaea (Borrel *et al.*, 2011; Segers, 1998). Recently, however, some studies have reported significant CH₄ production in oxic water columns by oxygen-tolerant methanogens, supported by the substrates provided by phytoplanktons in the water column (Bogard *et al.*, 2014; Grossart *et al.*, 2011; Tang *et al.*, 2014). In lakes, a large proportion of the CH₄ produced is oxidised into CO₂ by methanotrophic bacteria under primarily oxic conditions, especially where oxic and anoxic waters meet (Guerin & Abril, 2007; Oswald *et al.*, 2015; Rudd *et al.*, 1976), although there also exists some evidence for the occurrence of freshwater anaerobic CH₄ oxidation (Eller *et al.*, 2005; Segarra *et al.*, 2015). Between 50 and 95% of the CH₄ produced in lake sediments can be oxidised in the oxic sediment surface, and another 45 to near-100% in the water column after escaping the sediment surface, greatly reducing emissions (Bastviken, 2009). CH₄ that escapes the oxidation process can reach the atmosphere by simple diffusion (diffusive flux), in the form of bubbles (ebullition), or during lake mixing periods (Figure 1; Bastviken *et al.*, 2004). Among these pathways, ebullition is one of the most important (comprising between 40 and >80% of total CH₄ fluxes) (see e.g. Deshmukh *et al.*, 2014; Keller & Stallard, 1994; Walter-Anthony *et al.*, 2010; Wik *et al.*, 2013), and this is crucial due to the fact that CH₄ bubbles travel faster, allowing less time for CH₄ oxidation to occur (Bastviken *et al.*, 2004).

Lakes are important sources of CO₂ in the atmosphere, and most global freshwater bodies are supersaturated with CO₂ (Cole *et al.*, 1994; Marotta *et al.*, 2009; Richey *et al.*, 2002; Sobek *et al.*, 2005). CO₂ in freshwater bodies can be the result of the respiration of both internally produced and externally derived organic matter, as well as the CO₂ received directly from the surrounding soil (Figure 1). Until recently, it was widely believed that the aquatic degradation of terrestrially produced organic matter in lakes was responsible for CO₂ supersaturation (Duarte & Prairie, 2005; Sobek *et al.*, 2003); however, some studies have reported that the direct introduction of CO₂ from soil respiration in the catchment could be a dominant source (Maberly *et*

al., 2013; McDonald *et al.*, 2013; Weyhenmeyer *et al.*, 2015). Most of the CO₂ emission occurs as diffusive flux, as CO₂ is highly soluble in water.

Figure 1. Several of the major sources of CH₄ and CO₂ in lakes and streams.

Unlike lakes, streams are fast-moving, turbulent, and often lack vertical gradients, and so the dynamics of carbon gas fluxes differ. CH₄ supersaturation in streams has been largely attributed to the inputs of externally-produced CH₄ from the catchment (Figure 1; Crawford *et al.*, 2013; Dawson *et al.*, 2004; Jones & Mulholland, 1998). Ebullitive fluxes of CH₄ have also been found to be important in some studies of streams (Baulch *et al.*, 2011; Crawford *et al.*, 2014). CO₂ is mostly transported to streams through groundwater rich in CO₂ (Dinsmore & Billett, 2008; Hope *et al.*, 2004). Although internal production of CO₂ by respiration also occurs in streams, external CO₂ inputs from terrestrial ecosystems could be a dominant source in small streams (Hotchkiss *et al.*, 2015).

1.2 Why is spatio-temporal variability a concern?

Large spatio-temporal variability in lake and stream fluxes has been observed and related to many different factors. In many studies, concentrations and fluxes of CH₄ have frequently been found to be higher near the shores of lakes than in their centre; this has been attributed to

many factors, including an increased likelihood of ebullition in shallow waters, greater turbulence, the presence of macrophytes, and more effective transfer of heat to sediments (Bastviken *et al.*, 2010; Hofmann, 2013; Juutinen *et al.*, 2003; Wang *et al.*, 2006). Ebullition, which forms a major part of total CH₄ flux, is well known to be episodic and spatially variable (Varadharajan & Hemond, 2012; Walter *et al.*, 2006; Wik *et al.*, 2013). Stream or river water inflows into lakes could also lead to spatial variability in CH₄ (DelSontro *et al.*, 2011; Murase *et al.*, 2003; Yamada *et al.*, 2001). Higher CO₂ fluxes were observed in littoral zones and close to macrophytes in some studies (Pacheco *et al.*, 2015; Rudorff *et al.*, 2011; Soja *et al.*, 2014), but the opposite, with higher central CO₂ fluxes, has also been reported (Schilder *et al.*, 2013). Gas exchange velocity (k ; a physical parameter which governs gas exchange rates) can be spatially heterogeneous within the lakes, resulting in spatially variable diffusive CH₄ and CO₂ fluxes (Hofmann, 2013; Schilder *et al.*, 2013; Vachon & Prairie, 2013). Wind events resulting in thermocline tilt could bring dissolved substances from the hypolimnion to the surface (Mortimer, 1952; Shintani *et al.*, 2010), and may also cause spatial heterogeneities in lake CO₂ concentrations (Heiskanen *et al.*, 2014).

Furthermore, CH₄ and CO₂ fluxes in lakes vary in response to several short-term and seasonal changes. Large amounts of CH₄ and CO₂ are emitted during lake mixing events in the spring and fall (Ducharme-Riel *et al.*, 2015; Karlsson *et al.*, 2013; López Bellido *et al.*, 2009; Michmerhuizen *et al.*, 1996). Weather events such as drops in air pressure have been shown to affect CH₄ fluxes (Casper *et al.*, 2000; Mattson & Likens, 1990; Wik *et al.*, 2013) and, in some studies, precipitation events have resulted in an increase in CH₄ and CO₂ in lakes (López Bellido *et al.*, 2012; Ojala *et al.*, 2011; Rantakari & Kortelainen, 2005). Increased CH₄ production in response to increased temperature has been shown in many laboratory studies (Duc *et al.*, 2010; Segers, 1998; Zeikus & Winfrey, 1976) and some field studies (Natchimuthu *et al.*, 2014; Wik *et al.*, 2014; Yvon-Durocher *et al.*, 2014). The production of CO₂ in sediments has also been shown to increase with temperature (Gudasz *et al.*, 2010; Marotta *et al.*, 2014). More than two-fold differences in diel CH₄ and CO₂ have been demonstrated, highlighting the importance of including diel variability in flux measurements (Bastviken *et al.*, 2010; Natchimuthu *et al.*, 2014; Podgrajsek *et al.*, 2014).

Streams often have higher emissions per m^2 owing to high k (Humborg *et al.*, 2010; Lundin *et al.*, 2013; Raymond *et al.*, 2013). High spatial variability in fluxes has been noted in streams even on small spatial scales due to the heterogeneous characteristics of stream networks. Using modelled data, studies have shown that head water and lower order streams have the highest CH_4 and CO_2 fluxes, and that this gradually decreases downstream (Butman & Raymond, 2011; Wallin *et al.*, 2013). Spatial variability in fluxes within the streams has been linked to variabilities in both sources of gas supply and k , which dictates the loss of gas due to turbulence (Wallin *et al.*, 2014). Gas concentrations have been observed to change based on changes in, for example, groundwater inputs and soil type (Crawford *et al.*, 2013; Hope *et al.*, 2004; Jones & Mulholland, 1998). In streams, k is highly variable, can have local hot spots, and is dependent on slope, depth, flow velocity, etc. (Long *et al.*, 2015; Raymond *et al.*, 2012; Wallin *et al.*, 2011).

Temporally, stream flux rates have been related to variabilities in discharge (Roberts *et al.*, 2007), although this can be very site-specific (Wallin *et al.*, 2011). Stream velocity has been demonstrated to be an important controlling factor of k , thus affecting fluxes (Raymond *et al.*, 2012), and it has been suggested in some studies that k could be more important in governing fluxes than concentrations (Wallin *et al.*, 2011). Spring floods after the melting of snow (Campeau *et al.*, 2014; Dyson *et al.*, 2011) and storm events (Billett & Harvey, 2013; Dinsmore & Billett, 2008) can affect gas fluxes in streams due to the dilution of gas concentrations or an increased supply of dissolved gases from the catchment. Diel variabilities in CO_2 have also been recorded in streams (Peter *et al.*, 2014). Changes in the terrestrial supply of gases from catchments as a result of changes in soil-water linkages can, moreover, affect the degree of supersaturation in streams (Dinsmore & Billett, 2008).

Thus, previous studies have underscored the spatio-temporally complex nature of lake and stream carbon fluxes, and stressed the need for more intensive measurements. Large numbers of studies are being published that consider one or more of these aspects, and are increasingly adding to our current knowledge of variabilities. Yet, studies that take into account both spatial and temporal variability with enough resolution are rare. Spatial variability in fluxes may change temporally, and linking both types of variability is crucial to improving our understanding of aquatic fluxes. Furthermore, there is a necessity to quantify the amount of system-

atic bias introduced by limited sampling designs so as to recognise the effect of such approaches in large-scale measurements.

1.3 Integrated analysis of lakes and streams is crucial

In a global estimate by Bastviken *et al.* (2011), lakes were shown to emit more CH₄ than rivers. On the other hand, streams could be more important than lakes with regard to the release of CO₂, according to some studies (Kokic *et al.*, 2015; Lundin *et al.*, 2013), and the marked dominance of streams and rivers for global CO₂ emissions has been estimated by Raymond *et al.* (2013). There are also great differences with regard to the amount of turbulence generated in lakes and rivers/streams due to morphological variation. In global studies, k in streams was generally found to be very high as compared to lakes, making them hot spots for gas emission (Aufdenkampe *et al.*, 2011). Despite the large differences between these two types of aquatic ecosystem, separate studies of lakes, streams, and rivers are common, making it difficult to assess the total catchment scale of aquatic emissions and the regulating factors. Thus, integrated studies, merging fluxes from both lakes and streams in the catchment and including both CH₄ and CO₂, are essential in order to evaluate their role in landscape GHG balances. Some published studies have attempted this, with limited spatial and temporal resolution and unclear consideration of hot spots (Buffam *et al.*, 2011; Campeau *et al.*, 2014; Lundin *et al.*, 2013), and there is a need for more comprehensive integrated catchment-scale studies.

2 Research objectives

Comprehensive studies that aim to describe and evaluate the spatio-temporal variability of CH₄ and CO₂ fluxes in lakes and streams, and to study the effect of these variabilities on integrated catchment-scale aquatic emissions, are very rare, and yet are critical for upscaling, particularly in areas rich in inland waters. In this thesis, lakes and streams in a small hemiboreal catchment in the southwest of Sweden were chosen, and sampling of open water (fluxes through plants were not considered) CH₄ and CO₂ fluxes was conducted during 2012-2013 in lakes and 2013-2014 in streams. Specifically, spatial variability in lakes and streams over time were covered to an extent rarely considered in previous studies. The study design allowed for the investigation of the spatio-temporal variability of the total aquatic CH₄ and CO₂ fluxes from all of the open waters in the catchment.

The specific research objectives were:

- 1) To determine the spatio-temporal variability of CH₄ and CO₂ fluxes in the lakes of the catchment (I & II).
- 2) To explore the spatio-temporal variability of CH₄ and CO₂ fluxes in the streams of the catchment (III).
- 3) To analyse the factors affecting the variability of CH₄ and CO₂ fluxes, and to investigate how this variability affects annual- and whole-system estimates (I, II, & III).
- 4) To estimate the total aquatic fluxes from the catchment, and to analyse the relative importance of lakes, streams, and specific flux hot spots to the aquatic C budget (IV).

3 Methods

3.1 Study site

The studies were conducted in the Skogaryd Research Catchment (SRC; www.fieldsites.se), situated in the southwest of Sweden (58°22' N, 12°9' E). The SRC had a total catchment area of 7 km² and was dominated by forest, mostly covered with *Picea abies* (L.) H. Karst., *Pinus sylvestris* L., and, to a lesser degree, agricultural land. The annual mean temperature and precipitation for the years 1983-2013 in the SRC were 7.0 °C and 910 mm, respectively (Swedish Meteorological and Hydrological Institute; <http://luftwebb.smhi.se/>). This catchment was a suitable choice for this study as it had three lakes, each with different characteristics, and a 9 km stream network, including multiple stream slope categories, from slow-flowing ditches to waterfalls. The SRC also had the infrastructure necessary for various aquatic measurements, including four monitoring stations in the streams which continuously logged discharge; one of these also recorded water temperature, electrical conductivity, and pH (Figure 2). The area thereby combined easy access to additional data and measurement locations in highly variable types of waters, typical of the inland, water-rich boreal biome.

The SRC included three lakes, as shown in Figure 2. Erssjön (58°22'23" N, 12°9'55" E) is a largely macrophyte-free lake with an area of ~62,000 m² and a maximum depth of ~4.5 m. Low densities of *Nuphar lutea* (L.) Sm. and *Equisetum fluviatile* L. were found along the shores, and *Phragmites australis* (Cav.) Trin. ex Steud. and *Carex spp.* were also present along the Northern and Southern shores (Figure 2). Följesjön (58°22'32" N, 12°9'14" E) is smaller (37,500 m²) and represents a late stage in the lake succession. It is a shallow lake with a depth of between 0.3 and 0.6 m in the studied parts, and is covered by macrophytes such as *Phragmites australis*, *Nuphar lutea*, and *Carex spp.*, except for some areas of open water in which the studies of this thesis were conducted. Boats could not be used, and a boardwalk was constructed in the summer of 2011 to facilitate access to the lake. Skottenesjön (58°21'16" N, 12°7'53" E) is a larger lake (~721,800 m²) situated in the downstream of the catchment, and receives the outflow of the streams of the SRC. Measurements were made in this delta area as its CH₄ and CO₂ flux were assumed to be largely derived from various forms of C from the catchment. The lake bottom was relatively flat, with a maximum depth of 1.2 m in the delta and the occurrence of

macrophytes such as *Nuphar lutea* and *Nymphaea alba* L. in low densities. The lake measurements were performed only in open water areas (emissions through macrophytes were not studied). The open water areas of the lakes considered were 56,700, 10,540, and 5,400 m² for Erssjön, Följesjön, and the delta region of Skottenesjön, respectively.

Figure 2. A map of the SRC showing the extent of the catchment, with lakes and streams along with aerial photos of the lakes studied. The black circles on the map (red circles in the aerial photos) denote some of the sampling points in the lakes and streams (see individual papers for detailed sampling locations and the parameters sampled). The red circles on the map denote the four monitoring stations in the streams. Propane injections for k measurements (see Paper III) were performed at the locations marked by red arrows.

Man-made ditching conducted 100-150 years ago to improve forest and agricultural productivity has affected most parts of the stream network of the SRC. The main stream originates in a mire upstream of Erssjön and flows through Följesjön before draining into Skottenesjön (Figure 2). The majority of the upper part of the stream between Följesjön and Skottenesjön is wide, flat, and slow-moving, whereas other parts of the stream network include both flat and steep sections and some turbulent waterfalls.

3.2 Surface water CH₄ concentrations (I, III, IV)

Surface water CH₄ concentrations were determined using a headspace extraction method (McAuliffe, 1971), described in detail in Paper I. In lakes, the CH₄ concentrations were used along with the flux measurements to estimate k and the diffusive flux, and thereby the share of ebullition and diffusive flux from each chamber, in accordance with the methodology of Bastviken *et al.* (2004). To capture spatial variability in lakes, water samples were collected close to 8-13 chambers in Erssjön, 4-5 chambers in Följesjön, and 5-6 chambers in Skottenesjön, which were chosen to cover depth-dependent variability (see Paper I). Water samples were collected from the streams at four monitoring stations at biweekly intervals (2013 and 2014). In addition, 20 locations along the stream network were sampled on five occasions during different discharge regimes in 2014 (Figure 1 in Paper III).

3.3 Surface water CO₂ concentrations (II, III, IV)

Surface water CO₂ concentrations were measured so as to analyse spatio-temporal variability in lakes and streams, as well as to derive fluxes in streams. CO₂ concentrations were measured by deploying floating chambers and allowing them to equilibrate with the CO₂ in the water, and the headspace gas was analysed either manually or using mini CO₂ loggers (Papers II and III). Most previous large-scale studies have estimated CO₂ indirectly using pH, total alkalinity, and water temperature measurements (e.g. Lauerwald *et al.*, 2015; Raymond *et al.*, 2013; Weyhenmeyer *et al.*, 2012), but this indirect method has been criticised recently for two primary reasons: 1) This method cannot be used in waters with no alkalinity, a condition which occurs frequently in boreal regions; these waters have been found to contain higher CO₂ concentrations than waters with alkalinity (Wallin *et al.*, 2014). 2) This method could overestimate CO₂ concentrations, with high bias in organic-rich and acidic waters (Abril *et al.*, 2015). Thus, a direct method was used to measure CO₂ in this thesis. In the lakes, the chambers used for sampling CH₄ flux were also sampled for CO₂ concentrations as they were deployed, with a sufficiently long time to reach equilibrium with the water concentrations. Additionally, many chambers fitted with mini loggers were deployed in the lakes (see Paper II) so as to continuously monitor CO₂ concentrations. In the streams, they were placed in 8-20 selected locations to monitor CO₂ concentrations (Paper III).

3.4 Floating chambers to measure lake CH₄ and CO₂ fluxes (I, II, IV)

Fluxes of CH₄ and CO₂ in the lakes were measured using plastic floating chambers on the surface of the water. This method has been shown to provide unbiased flux estimates provided the chambers are constructed and deployed properly (Cole *et al.*, 2010; Gålfalk *et al.*, 2013). Another recently adopted method for gas flux measurements in lakes is the eddy covariance (EC) method (e.g. Eugster *et al.*, 2011; Heiskanen *et al.*, 2014; Jonsson *et al.*, 2008; Schubert *et al.*, 2012). Although this method can provide high-resolution temporal data, spatial coverage is an issue (particularly in small lakes such as the ones studied here) as the footprint of the EC towers depends on the direction and speed of wind (Podgrajsek *et al.*, 2015). If the EC method is used in small lakes, a systematic bias can arise if only some parts of the lake are accounted for (e.g. central parts, while high CH₄ fluxes from lake shores may not be captured in representative ways), and there could also be a temporal bias due to the constantly-changing footprint, which can lead to measurements outside of the lake area, hampering representative estimates (Podgrajsek *et al.*, 2015). In addition, EC measurements do not easily resolve within-lake spatial variability. Therefore, floating chambers were used in this study in order to better address the spatio-temporal variability of lake fluxes.

For CH₄, chambers were deployed for approximately 24 hours so as to incorporate diel variability (Bastviken *et al.*, 2004; Keller & Stallard, 1994), and samples were collected manually from the chamber headspace after the deployment period to be analysed for CH₄. Both diffusive and ebullitive fluxes were estimated (see Paper I), and were added together to obtain total CH₄ fluxes. Mini CO₂ loggers driven by 9 V batteries (CO₂ Engine® ELG, SenseAir AB, Sweden) were fitted inside the floating chambers to log CO₂ concentrations every 5 minutes for 30 minutes, and were also used to derive CO₂ fluxes (Bastviken *et al.*, 2015). Due to the fact that CO₂ in the water phase attains equilibrium with the chamber headspace within a few hours, 24-hour measurements are not appropriate for CO₂ fluxes, and so short-term measurements were performed during the day (diel variability analysed separately; see below). Details on the construction of the chambers are given in Papers I and II.

Chambers for CH₄ fluxes were distributed in different depth zones in Erssjön (18-22 chambers), Skottenesjön (9 chambers), and along the boardwalk in Följesjön (8-10 chambers), where

depth separation could not be made due to the lake's shallow nature (see Paper I). For CO₂ fluxes, three chambers were placed, with one near the shore, one in the centre/deepest part, and one between these two (0.5, 2.5, and 4 m in Erssjön, and 0.5, 1, and 1.2 m in Skottenesjön). In Följesjön, three chambers were placed along the boardwalk (see Paper II). In Erssjön, CO₂ fluxes with higher spatial resolution were additionally estimated from concentrations and k , as described in Paper II. All of the measurements in the lakes were repeated at biweekly intervals during the ice-free period in 2012 and 2013 so as to factor in temporal variability. Ice-out fluxes were estimated from late winter water column gas concentrations. Some diel variability campaigns were also carried out.

3.5 Estimation of CH₄ and CO₂ fluxes in streams (III, IV)

The floating chamber method of measuring flux is not appropriate for streams due to their high turbulence. Hence, k had to be measured separately by injecting a trace gas (propane; see Marzolf *et al.*, 1994; Wallin *et al.*, 2011) which was combined with the water concentrations to estimate fluxes. This method did not allow the detection of ebullition in streams, as has been shown to occur by several studies (Baulch *et al.*, 2011; Crawford *et al.*, 2014), and so the CH₄ estimates in this study are conservative. Propane injections were made in six locations on five occasions, representing varying water discharge regimes, and a regression model to predict k from stream velocity and slope was constructed (Paper III). By using slope and daily velocity estimates for the stream network, daily k was estimated for the entire stream network for 2013 and 2014. Concentration measurements of CH₄ and CO₂ were interpolated to obtain water concentrations for the whole stream network, and combined with k to estimate daily fluxes (see Papers III and IV).

3.6 Effect of increased sampling on flux uncertainties (I, II, III, IV)

The ability of various sampling efforts to generate representative whole-lake/stream or annual mean fluxes was studied by creating subsets of our measured data with an incremental number of chambers/reaches and sampling days, using a method similar to that of Wik *et al.* (2016). For the lakes, the total CH₄ fluxes and the estimated CO₂ fluxes from k and pCO_{2aq} (see Paper II) for Erssjön for 2013 were used for this analysis. In the streams, estimated CH₄ and CO₂ fluxes for the whole stream network (131 reaches; see Paper IV) for 2013 and 2014 were used.

The data in spatial and temporal analyses were normalised to remove temporal variability (dividing each value by the sampling day average; spatial dataset) and spatial variability (dividing each value by the annual mean from each specific measurement location; temporal dataset) from the analysis. For spatial variability, the spatial dataset was organised into several bins, each representing different scenarios based on an increasing number of chambers/reaches, and average flux was plotted against the number of chambers/reaches (see Wik *et al.*, 2016). The first bin consisted of annual mean flux from each separate chamber/reach, representing all possible single chamber/reach means. Bins 2, 3, 4, up to n consisted of means of each 100 random combinations of 2, 3, 4 chambers/reaches up to n (where $n = 21$ for lake chambers and 130 for stream reaches), in order to analyse the change in variability with the increase in the number of chambers/reaches. A similar analysis as above was done for temporal variability with the temporal dataset so as to check the effect of including samples from many days against the uncertainty of the annual mean (n was 14 for the lake, and 283/338 for streams in 2013/2014 respectively). Increasing the number of random samples to more than 100 produced similar results in all cases.

3.7 Integration of fluxes from lakes and streams (IV)

In order to investigate the relative importance of lakes and streams and the emission hot spots in the SRC, the fluxes from them, obtained over the course of two years, were combined. Fluxes from lakes during ice-free periods (totalling 547 days) were extrapolated to a whole year, based on relationships between fluxes and environmental variables. Gradients of CH₄ and CO₂ concentrations under ice were measured in March 2013 to also estimate potential ice-out emissions. The total yearly flux from entire streams was calculated using the modelled daily k (using slope and stream velocity; see Paper III) and interpolated concentrations for ice-free periods (623 days). The combined estimates were analysed so as to ascertain the relative contributions of CH₄ and CO₂ from open water areas of lakes and streams to the total aquatic emission of the SRC. By using the information on the depth-based variability of CH₄ flux in the lakes and the spatial variability in stream fluxes based on slope, the contribution of hot spots to total aquatic C fluxes was analysed (see Paper IV for details).

4 Results and discussion

4.1 Spatio-temporal variability in lake water concentrations (I, II)

Among the three lakes, concentrations of CH₄ and CO₂ were the highest in Följesjön (mean concentrations: CH₄ - 8 µM and pCO_{2aq} - 5690 µatm; Papers I and II). This was likely due to a combination of factors, including shallow water, macrophyte cover, abundant organic material supply, wind shelter by the surrounding forests, and low oxygen concentrations in the water column (Paper I). The concentrations of CH₄ and CO₂ were much lower in Erssjön and Skottenesjön (mean concentrations: CH₄ - 0.4 and 0.8 µM and pCO_{2aq} - 1630 and 1420 µatm, respectively) as they were deeper and had less macrophyte cover. Upstream Erssjön had higher CO₂ and while the downstream and more nutrient-rich Skottenesjön had higher CH₄. Within the lakes, shallow depths had 1.4 and 1.3-fold higher CH₄ concentrations than the whole-lake averages for Erssjön and Skottenesjön respectively (no spatial analysis was done in Följesjön as it was shallow and covered a small area), which is consistent with similar depth-related patterns identified in other studies (e.g. Hofmann, 2013; Schilder *et al.*, 2013). Higher CO₂ concentrations were found in shallow depths in Erssjön and Skottenesjön; however, the effects of depth could not be separated from those relating to proximity to stream inlets (Paper II). Similar patterns of elevated concentrations near stream inlets were also observed for CH₄ (Paper I).

In Erssjön, where surface water CO₂ concentrations were intensively measured, oscillations of the thermocline due to wind (see e.g. Mortimer, 1952; Shintani *et al.*, 2010) likely caused large spatial variabilities in CO₂. Up to three-fold differences in spatial variability were observed, with larger differences during the growing season (Figure 3).

Temporal variabilities in CH₄ concentrations were less clear with regard to the lakes. Barring a limited correlation between CH₄ concentrations and precipitation in Erssjön, no other significant correlations were found (Figure A8 in Paper I). CO₂ concentrations were correlated with DOC, total nitrogen, oxygen concentrations, temperature, and wind speed in the different lakes (Table 2 in Paper II), and seemed to be somewhat more predictable than CH₄ concentrations. Significant diel changes in pCO_{2aq} were also found in the study lakes (Figure 6 in Paper

Figure 3. $p\text{CO}_{2aq}$ from manual measurements in Erssjön during 2013, interpolated by the inverse distance weighted method. The coloured scale denotes the date-specific $p\text{CO}_{2aq}$, and the inset map denotes scale in relation to $p\text{CO}_{2aq}$ for the whole year for the purposes of comparison. The arrows at the top of the panels and the numbers above them

show the average wind direction and speed (m s^{-1}) during the 24-hour deployment period, and the cross arrows denote changing winds. The curved arrows at the bottom of panels A, L, and M denote mixing periods. See Figure 2 for the locations in which these measurements were made.

II), with clear patterns indicating less $\text{pCO}_{2\text{aq}}$ during the middle of the day than at night, particularly during the summer months; this was presumably due to the balance between photosynthesis and respiration.

4.2 Spatio-temporal variability in lake fluxes (I, II)

Between-lake differences in total CH_4 and CO_2 fluxes were similar to the concentration patterns, and the highest CH_4 (both diffusive flux and ebullition) and CO_2 fluxes were observed in Följesjön, followed by the other two lakes (Figure 4; see also Figure 3 in Paper II).

Figure 4. Total fluxes of CH_4 in the lakes in 2012 and 2013, separated by measurement occasion. A low-pressure event on 18 September 2013 seemed to affect fluxes, and is marked with an arrow. Note the $\log_{10}$ scale on the y-axis. The boxes show quartiles and the median, the whiskers denote data within 1.5 times the interquartile range, and the closed circles denote outliers.

Higher fluxes of total CH₄ (diffusive flux and ebullition) and lower fluxes of CO₂ were recorded in the shallow depths of Erssjön and Skottenesjön. For CH₄, higher total fluxes near the lake shore were likely due to higher ebullition (Figures A3 and A4 in Paper I). However, for CO₂, observations of lower k in the near-shore areas than the centre (Figure A3 in Paper I) likely contributed to low CO₂ fluxes near the shores (Figure 5 in Paper II). Elevated levels of total CH₄ flux were also noted in the stream inlets and, in some isolated hot spots, near to emergent macrophytes in Erssjön. Ebullition was a significant pathway for CH₄ fluxes, and contributed between 56 and 79% of the total CH₄ emissions in the three lakes.

CH₄ fluxes (ebullition, diffusive flux, and total fluxes) in all three lakes increased exponentially with temperature (explaining 16 to 78% of the temporal variability in fluxes; Figure A6 and Table A3 in Paper I), in line with the known positive effect of temperature on methanogenesis (Marotta *et al.*, 2014; Zeikus & Winfrey, 1976); it should be noted, however, that this has not been clearly shown for air-water lake fluxes in previous studies. Additionally, previous studies have been unable to separate direct temperature and seasonal substrate effects on fluxes due to seasonal sampling (Yvon-Durocher *et al.*, 2014). Using frequent samplings in our study, the similarity between spring and fall fluxes could be shown (Figure 5 in Paper I), indicating that the direct temperature effect is stronger than that of a hypothetical substrate effect. Furthermore, using data from lakes encompassing between- and within-lake variability allowed it to be demonstrated that the temperature dependence in the comparatively shallow Följesjön was stronger than in the other lakes (Figure 5), which was likely due to the more efficient warming of shallow depths. This demonstrated an interaction between depth and temperature, and indicated that small shallow lakes could be more sensitive to warming than larger, deeper lakes. Thus, the size and depth of lakes could, along with temperature, be important factors when predicting CH₄ fluxes for lakes.

The CO₂ fluxes in the three lakes were not correlated with temperature, but increased with wind speeds (R^2 , ranging from 0.30 to 0.35; see Table 2 in Paper II). However, the relationships between CO₂ fluxes and water CO₂ concentrations were stronger, and the concentrations in turn were correlated with DOC, dissolved oxygen, and total nitrogen in the three lakes (Table 2 in Paper II). This indicated that the renewal of CO₂ to surface waters was more important for fluxes in the lakes than the turbulence caused by wind.

Figure 5. Natural log of total CH_4 flux plotted against the inverse of water temperature in the three lakes. Open circles, closed circles, and crosses denote Erssjön, Följesjön, and Skottenesjön, respectively. Panel (a) shows data from all depths in the lakes, and panel (b) only shows data from depths of below 0.5 m. The apparent activation energies (E_a) obtained from the slopes are given in brackets.

In general, spatial and temporal variability in CH_4 fluxes changed in a predictable way, and the changes were caused by similar factors in the lakes studied. On the other hand, CO_2 fluxes had a more complex spatio-temporal variability and the three lakes showed differing patterns, each of which warrants further investigation using frequent CO_2 measurements so as to better understand the regulating factors.

4.3 Large variability in stream fluxes (III)

The ranges of k and water concentrations of CH_4 and CO_2 measured in the streams were within those reported by other studies, both in Sweden and elsewhere (Billett & Harvey, 2013; Humborg *et al.*, 2010; Jones & Mulholland, 1998; Wallin *et al.*, 2011), although high k values were measured in steep parts of the stream, including the waterfalls. Analysis of k_{600} , water concentrations of CH_4 and CO_2 and fluxes from the stream network of the SRC revealed large variabilities in terms of both space and time (Figures 6 and 7). Estimated k for the stream network showed that the mean k was five times higher in the steepest and most turbulent reaches, which formed only 0.9% of the total stream area, than the overall mean k (Table 3 in Paper III). Mean CH_4 and CO_2 fluxes were almost three and four times higher, respectively, in the steepest

reaches than the overall mean from all reaches (Table 3 in Paper III), making these small areas with steep slopes important for whole-stream estimates.

Figure 6. Mean modelled CH₄ (a) and CO₂ (b) emissions from the streams of the SRC. Note the large emissions from short, steep reaches in various parts of the stream network.

Temporal variability in CH₄ and CO₂ concentrations were complex, and no significant correlations with variables such as water temperature and discharge were found. Concentrations of CH₄ and CO₂ were negatively correlated with k , indicating that increased turbulence led to greater gas loss from the streams. In previous studies, concentrations and fluxes of CH₄ and CO₂ were found to depend on the net balance between inputs from soil and aquatic sources along the network, and the rate of loss of gas was determined by k (Hope *et al.*, 2001; Wallin *et al.*, 2014). Similarly, higher gas concentrations in streams surrounded by organic-rich soils were found, and the variability in k affected concentrations, irrespective of gas input. Temporal variability in CO₂ fluxes could be best explained by variability in k (83%), whereas only 50% of variability in CH₄ fluxes were explained by k . This suggests that the variability in CH₄ concentrations were larger than those of CO₂ concentrations, and had more control over CH₄ fluxes than k . Furthermore, the degree of supersaturation of CH₄ in water was two to 11,000 times greater relative to atmospheric concentrations, and hence more pronounced than CO₂,

which corresponded to 1.3 to 54 times. The highest discharge periods resulted in greater-than-tripled mean fluxes as compared to the overall mean (Table 3 in Paper III). Large inter-annual differences in k , and thus the fluxes, were noted, and the mean k_{600} , CH_4 , and CO_2 fluxes were 1.4, 1.6, and two times higher in 2014 than in 2013, respectively, likely due to the higher discharge in 2014. This emphasises the fact that inter-annual variability is important, and that studies of different annual discharge regimes are required in order to constrain the fluxes.

Figure 7. Daily emissions of CH_4 (a) CO_2 (b) from the studied streams over the course of two years. The inset panels in (a) and (b) show the cumulative emissions of the two gases for the corresponding period. The shaded region

represents emissions, assuming an uncertainty of ± 60 and 25% around the mean for CH₄ and CO₂, respectively (see Paper III for details).

4.4 Limited information on variabilities resulted in uncertainties (I, II, III, IV)

Many large-scale studies of lakes and streams (Bastviken *et al.*, 2011; Kortelainen *et al.*, 2006; Panneer Selvam *et al.*, 2014; Teodoru *et al.*, 2009; Weyhenmeyer *et al.*, 2012; Yang *et al.*, 2015) have been based on single- or few-point measurements of concentrations over the course of one or a few seasons. Given the considerable variability measured in the lakes and streams in this study, it is reasonable to state that large-scale estimates that do not account for such uncertainties may lead to biases. This thesis demonstrates that sampling for CH₄ fluxes at either the shore or the centre of a lake leads to overestimation or underestimation, respectively, of whole-lake emissions, and that a balanced sampling design based on depth is desirable (Table 2 in Paper I). As CH₄ flux was found to be strongly dependent on temperature, samples from any one season could also significantly bias the annual flux estimates, and sampling should ideally be representative of the temperature range of multiple seasons (Table 3 in Paper I).

For CO₂ fluxes, temporal variability was greater than spatial variability (Figure 8). However, when comparing spatial variability from different sampling periods, higher variability during the productive months was found when compared to others (compare panels F, H, I, and J with B, C, M, and N in Figure 3, for example). The temporal variabilities in CO₂ fluxes, driven by pCO_{2aq}, which changed based on different factors in different lakes, suggest a need for continuous monitoring where possible, rather than isolated sampling in different seasons. The combined data from Papers I and II indicate that k varies more than pCO_{2aq} in space at any given point in time, but that pCO_{2aq} varies more than k over time – the latter making pCO_{2aq} very important for overall long-term integrated CO₂ fluxes.

An analysis of subsets of our measured data to simulate the results of different sampling approaches shows that the variability in CH₄ fluxes was, in general, more pronounced than the variability in CO₂ fluxes (Figure 8). Confidence in the flux measurements is highly dependent on the number of chambers/reaches and sampling days. For instance, to achieve an uncertainty (expressed as standard deviation) of within $\pm 20\%$ of our mean total for CH₄ flux from all of

the measurements in Erssjön, the number of chambers and the sampling days should be at least 14 and 9, respectively (Figure 8), and these measurements should be distributed both throughout the lake and in time.

Figure 8. Uncertainties in the whole-lake (a, b; normalised to time so as to analyse the importance of spatial variability and number of measurement points) or annual (c, d; normalised to flux measurement location in order to analyse the influence of the number of measurement times) CH₄ (a, c) and CO₂ (b, d) flux estimates, relative to the number of chambers and sampling days in Erssjön. See section 3.6 for a detailed description of normalisation procedures. The red area denotes the standard deviation. All panels are plotted to the same scale so as to facilitate comparison.

The spatial variability in CO₂ flux was small; however, frequent monitoring of few measurement points that include river/stream inlets, shores, and the lake centre is more desirable than continuous monitoring in the lake centre or sampling in many points less frequently. CO₂ fluxes must be measured over the course of at least five days, distributed over a year, so as to

reach an annual mean of within $\pm 20\%$ of the measured mean based on all sampling days (Figure 8). A similar analysis by Wik *et al.* (2016) concluded that CH_4 ebullition needs to be measured over at least 39 days in 11 locations, and diffusive flux on 11 days in three locations, so as to obtain representative estimates. Both studies point out the benefits of a stratified sampling approach based on depth, with measurements from many days spread throughout the year to generate representative annual flux values. This optimised sampling effort is practically feasible, making floating chambers useful in long-term lake GHG monitoring.

Fluxes during spring ice melt have been found to be important in many studies (Ducharme-Riel *et al.*, 2015; Karlsson *et al.*, 2013; Michmerhuizen *et al.*, 1996); however, such ice-out fluxes were not observed to play a major role in annual flux estimates in the lakes studied (Papers I and IV).

Figure 9. Uncertainties in the whole stream network (a, b; normalised to time so as to analyse the importance of spatial variability and number of measurement reaches) or annual (c, d; normalised to flux measurement reaches in order to analyse the influence of the number of measurement times) CH_4 (a, c) and CO_2 (b, d) flux estimates,

relative to the number of reaches and sampling days in the streams of the SRC. See Section 3.6 for a detailed description of normalisation procedures. The red area denotes the standard deviation. All panels are plotted to the same scale so as to facilitate comparison.

For streams, this thesis demonstrates that fluxes increase as the slope of the reach and discharge increase (Table 3 in Paper III). The percentage of area that was occupied by steep sections and the frequency of high discharges were small overall, but their mean fluxes were very high, and ignoring them would lead to underestimations for annual whole-stream estimates. To reach an annual mean within $\pm 20\%$ of our estimated mean based on all 131 reaches and modelled daily fluxes for the whole year, at least 44 and 49 reaches, covering the various slope categories, had to be measured on 11 and 12 days, distributed over the course of a year in this catchment, for CH₄ and CO₂, respectively (Figure 9). Taken as a whole, this detailed spatio-temporal analysis has demonstrated the importance of variability that has been discussed previously, but had hitherto rarely been quantified for the open waters of a whole catchment.

4.5 Contribution of hot spots to the aquatic C budget (IV)

Integrated assessments of lakes and streams on a catchment scale are fundamental so as to gauge their relative importance and understand their climate feedbacks. Thus, the emissions from the open water areas of lakes and streams reported in Papers I, II, and III were used to perform a combined analysis of aquatic fluxes from the catchment. Areal fluxes of CH₄ and CO₂ (i.e. flux per m²) were higher in the streams than in the lakes (Figure 10). Thus, even though streams occupied just 11% of the total aquatic area (the rest being covered by lakes), they contributed 51% of the total aquatic CO₂ equivalent emissions (Paper IV). Lakes contributed more to the total aquatic CH₄ emissions (66%) than streams, and lakes and streams contributed almost equally to total CO₂ emissions. Furthermore, most of the aquatic emissions were released as CO₂ (89%). Subsets of data from different depths in lakes and slope categories in streams were analysed to assess the importance of adequate spatial coverage. In lakes, 65% of CH₄ emissions were emitted from 33% of the total lake area, which was comprised of shallow and near-shore areas (< 0.5 m; Table 2 in Paper IV), making the shallow depths the largest contributor to the total lake CH₄ emissions in the catchment. Steep reaches of streams with slopes ranging from 6 to 21% covered just 0.6% of the total stream area, but contributed 17% of total stream C emissions.

Figure 10. Spatial variability in CO₂-equivalent emissions in lakes and streams of the SRC. Panel (a) denotes the emissions per m² of the aquatic area, showing higher rates of emissions from some parts of the streams which had steep slopes. Panel (b) shows the total emissions per year from different reaches of the streams and lakes, highlighting the parts which had high annual emissions. White areas in lakes and streams denote areas not studied (in one of the lakes, the majority was covered by macrophytes).

This illustrates that small hot spot areas are important for correctly estimating large-scale fluxes, and that catchment-scale aquatic emissions can be significantly biased if measurements from a few points are extrapolated to a whole catchment without considering the emission hot spots. Therefore, future measurements need to carefully consider these hot spots, as well as temporal variabilities when making large-scale assessments.

5 Outcomes and recommendations

Some of the major outcomes and recommendations of this thesis are:

- Large spatial variabilities in CH₄ fluxes in lakes were measured, and higher fluxes can be expected in shallow near-shore areas or close to stream inlets. About 65% of the total lake CH₄ emissions were emitted from depths of < 0.5 m, which constituted 33% of the total lake area in the catchment.
- CH₄ fluxes in lakes increased exponentially with increased temperature, and shallow areas responded faster to temperature than deeper ones due to the more efficient warming of shallow sediments. Thus, CH₄ fluxes from small or shallow lakes may be more sensitive to a warming climate than fluxes from deeper lakes.
- The spatial and temporal variability of lake CH₄ fluxes were, in general, higher than those of CO₂ fluxes.
- The temporal variability in lake CO₂ fluxes was twice as large as the spatial variability. The data analysed in this study indicates that k varies more than pCO_{2aq} in space at any given time point, but pCO_{2aq} varies more than k over time; thus, multi-day monitoring of pCO_{2aq} with a consideration of spatial variability is important.
- Stream CH₄ fluxes were dependent on CH₄ concentrations, whereas stream CO₂ fluxes were primarily regulated by variabilities in k . This emphasises the large variabilities in stream CH₄ concentrations, and suggests that more stream CH₄ studies are needed.
- Limited sampling efforts covering few locations or occasions could significantly bias the annual estimates of fluxes in lakes and streams. To estimate yearly whole-lake CH₄ fluxes with an uncertainty of lower than $\pm 20\%$, measurements from at least 14 chambers covering nine full days distributed over the course of a year were needed in the studied lake. For CO₂ fluxes, the spatial variability was small, but measurements over at least five days in a year were required in the studied lake. In the streams, the inclusion of a minimum of 44 to 49 reaches (out of 131) in various slope categories in the SRC on 11 to 12 days was required to estimate yearly emissions for the whole stream network with an uncertainty of lower than $\pm 20\%$.

- The aquatic systems of the SRC (~ 81,550 m²) were estimated to emit 23 Mg of C per year (as CO₂ equivalents).
- Lakes and streams contributed roughly equally to the aquatic carbon budget of the SRC, and stream emissions per area were particularly significant as they occupied only a small part of the aquatic area (11% of total aquatic area).
- Shallow and near-shore areas in lakes and steep turbulent reaches in streams contributed disproportionately to total aquatic C emissions, thus requiring adequate attention in future measurements.

In summary, this thesis highlights the importance of adequately accounting for spatial and temporal variability in lakes and streams in order to provide representative estimates of open water CH₄ and CO₂ fluxes. Measurements in different depth zones in lakes and slope categories in streams over multiple days scattered over the course of a year are recommended so as to reduce the risk of underestimations. Enhanced CH₄ fluxes from shallow lakes and increased gas fluxes during high discharge periods could be expected in a warmer, wetter climate, and could provide important climate feedbacks.

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