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Quantifying Methane Emissions from Reservoirs: From Basin-scale to Discrete Analyses with a Focus on Ebullition Dynamics

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Summary

The role aquatic systems play in the global carbon cycle has become more relevant in recent years since it has been shown that they bury and transform more carbon than the whole of the oceans. Moreover, at least half of the natural sediment load to the oceans is now trapped by manmade impoundments, which are steadily increasing and thus retaining and remineralizing even more of the carbon that once reached the oceans. The efflux of carbon-based greenhouse gases from natural and artificial aquatic systems is an important negative climatic feedback. In particular, the dynamics of methane (CH₄), a much more potent greenhouse gas than carbon dioxide, has been studied in various systems and is of particular importance for reservoirs, which should be a more-or-less carbon-neutral energy source. Surface diffusion of CH₄ has been studied often and recently attention has turned to the release of CH₄-rich water through large tropical dams. A few studies have shown that CH₄ ebullition (bubbling) is likely the most efficient and dominant emission pathway in natural shallow systems, but less research has been done on its role in efflux from reservoirs. In general, ebullition dynamics is understudied relative to its stochastic and episodic nature complicating its accurate assessment.

The main hypothesis of this work is that ebullition can be a particularly effective transport mechanism for CH_4 in reservoirs. Two very different study sites were chosen in order to investigate this. Lake Wohlen is a very small run-of-river reservoir in the temperate zone of central Europe, while Lake Kariba is one of the world's largest reservoirs located in sub-Saharan Africa. The majority of work was carried out on Lake Wohlen, but a detailed campaign at Lake Kariba also drew some significant conclusions. Many other aspects of ebullition dynamics, some not previously considered, were identified during the course of these studies.

Throughout this work various old and new techniques were explored for direct and non-direct assessment of CH_4 emissions, with a particular focus on ebullition. Traditional equipment, such as floating chambers and gas traps, enabled direct capture of CH_4 emissions and showed that while they are successful in that sense they provide only limited spatial coverage. An innovative mass balance-based approach using only monthly dissolved CH_4 measurements and a temperature relationship with seasonal dissolved CH_4 accumulation was developed to estimate ebullition, and compared quite well with the direct measurement techniques. An eddy covariance CH_4 flux system was deployed in conjunction with another project and revealed its ability to capture the temporal variability of CH_4 ebullition, but was not as effective as it could be had the eddy covariance tower been placed in the center of the lake. Finally, an echosounder was used to collect hydroacoustic

measurements of ebullition in the water column, a procedure similar to that used in fish population studies. This non-invasive technique proved to be one of the most efficient methods for spatial coverage, as well as for identifying factors that help characterize ebullition dynamics.

The link between organic matter loading, as well as burial, and CH₄ ebullition was explored in a few chapters. It was discovered that the high sedimentation rate in Lake Wohlen results in the deep burial of labile organics with limited oxygen exposure. This efficient burial easily leads to CH₄ supersaturation in the sediments as diffusion rates cannot balance the methanogenesis. These processes thus explain the extreme bubble formation and release observed in Lake Wohlen during the warmer months when conditions are best for microbial activity. It was also shown that up to an order of magnitude more terrestrial surface area than that of small Lake Wohlen is required to balance the greenhouse gas emissions from the reservoir. Ultimately, these conclusions led to the hypothesis that the high organic loading from rivers into the large Lake Kariba basin should result in ebullition hot spots located in those river deltas. A comparison between river deltas and littoral zones without a river input revealed just that.

The role that ebullition plays in the overall CH₄ dynamics of the two very different systems – Lake Wohlen and Lake Kariba – was examined in detail. Ebullition was, in fact, the dominant emission pathway in both systems, but not in similar spatial or temporal patterns as one was large and tropical and the other small and temperate. Lake Wohlen's ebullition only occurs in significant magnitudes when temperatures are over 10° C, yet these warm emissions that occur along most of the reservoir dominate the rest of the potential pathways. Tropical Lake Kariba is more likely to produce year round emissions, but ebullition was found to occur as hot spots in littoral zones with a river inflow. The dendritic pattern of this reservoir along with the fact that there is limited release of CH₄-rich water through the dam led to the conclusion that these hot spots emit the most CH₄ compared to the rest of the system and other pathways.

Ebullition dynamics are complicated by the temporal and spatial variability of bubbling. In Lake Kariba, hot spots controlled the large-scale spatial variability of ebullition in that system. At the smaller-scale it was discovered that ebullition was not depth-dependent as had been suspected based on other studies, but instead was more dependent on distance from the river inflow, which brought in the organic substrate for methanogenesis. In Lake Wohlen, a year-long survey revealed that temperature played a significant role in the seasonal dynamics of ebullition, while the short-term temporal variations were shown to be a result mostly of hydrostatic changes due to lake level manipulation via dam operations.

Finally, hydroacoustic measurements helped to reveal new insights into ebullition dynamics. The ability to accurately locate and measure ebullition events in the water column is one of the main advantages to the hydroacoustic technique. It was shown that the differences in average flux from hot spots in Lake Kariba were controlled by differences in not only the frequency of ebullition locations, but also in the magnitude of the ebullition that occurred. Using Lake Wohlen hydroacoustic data the importance of bubble size to overall flux was revealed. Identifying the proper bubble size distribution is essential for understanding CH_4 flux in an aquatic system as the larger bubbles provide most of the gas volume and dissolve the least upon ascent. In addition, the density of bubbles in the water column can be an important factor in flux differences between various locations. Ultimately, these ebullition details are easily overlooked using techniques that integrate fluxes over large areas, such atmospheric eddy covariance measurements, or methods that have limited spatial coverage, such as floating chambers.

Zusammenfassung

In den letzten Jahren konnte gezeigt werden, dass aquatische Systeme für den globalen Kohlenstoffkreislauf relevant sind, da sie mehr Kohlenstoff ablagern und transformieren als die Ozeane. Zusätzlich wird zur Zeit mindestens die Hälfte der natürlichen Sedimentfracht in die Ozeane in künstlichen Stauseen zurückgehalten, und da deren Zahl kontinuierlich zunimmt, wird sogar mehr Kohlenstoff zurückgehalten und remineralisiert als früher die Ozeane erreicht hat. Der Ausstoss von kohlenstoffartigen Treibhausgasen aus natürlichen und künstlichen aquatischen Systemen ist eine wichtige negative Klimarückkopplung. Im Besonderen ist die Dynamik von Methan (CH₄), das ein viel wirksameres Treibhausgas als Kohlendioxid ist, in verschiedenen Systemen untersucht worden und ist von spezieller Wichtigkeit in Stauseen, die eine mehr oder weniger kohlenstoffneutrale Energieressource sein sollten. Die Oberflächendiffusion von CH4 ist oft untersucht worden, wobei sich in letzter Zeit die Aufmerksamkeit auf den Abfluss von CH₄reichem Wasser aus grossen tropischen Stauseen konzentriert hat. Einige Studien haben gezeigt, dass CH₄-Blasenströme wahrscheinlich der effizienteste und dominante Emissionsweg in natürlichen untiefen Systemen ist, es gibt jedoch weniger Untersuchungen zu deren Rolle für die Emissionen aus Stauseen. Generell ist die Blasenstromdynamik aufgrund ihrer stochastischen und episodischen Charakteristik, die eine genaue Beurteilung kompliziert macht, im Verhältnis zu ihrer potentiellen Signifikanz bezüglich des Kohlenstoffkreislaufs in natürlichen und künstlichen aquatischen Systemen nicht genügend untersucht.

Die Haupthypothese dieser Arbeit lautet, dass Blasenströme ein ausgesprochen effektiver Transportmechanismus für CH₄ aus Stauseen sein kann. Zwei sehr unterschiedliche Untersuchungsgebiete wurden ausgewählt, um dies zu untersuchen. Der Wohlensee ist ein sehr kleiner Stausee mit zugehörigem Laufwasserkraftwerk in der gemässigten Zone Zentraleuropas, währenddem der Karibasee einer der weltgrössten Stauseen ist, der sich im subsaharischen Afrika befindet. Diese Arbeit wurde mehrheitlich im Wohlensee durchgeführt, es konnten aber ebenfalls einige signifikante Schlussfolgerungen aus einer detaillierten Messkampagne im Karibasee gezogen werden. Viele weitere Aspekte der Blasenstromdynamik, die bisher nicht betrachtet wurden, sind im Verlauf dieser Studien identifiziert worden.

Während dieser Arbeit sind verschiedene alte und neue Techniken zur direkten und indirekten Beurteilung von CH₄-Emissionen getestet worden, wobei ein spezieller Fokus auf die Blasenströme gelegt wurde. Traditionelle Ausrüstung, zum Beispiel freischwimmende Flusskammern und Trichterfallen für Gasblasen, erlaubten CH₄-Emissionen direkt einzufangen und zeigten, dass zwar deren Einsatz in diesem Sinne erfolgreich war, ihre Aussagekraft zur räumlichen Abdeckung aber limitiert war. Ein innovativer Massenbilanz-Ansatz wurde entwickelt, basierend auf monatlichen Messungen des gelösten CH₄ und einer Temperaturabhängigkeit der saisonalen gelösten CH₄-Akumulation, um die Blasenströme abzuschätzen. Die Resultate stimmten mit den direkten Messungen recht gut überein. Ein Eddy-Kovarianz- CH₄-Fluss-Messsystem wurde in Zusammenarbeit mit einem anderen Projekt eingesetzt und zeigte dessen Fähigkeit, die zeitliche Variabilität von CH₄-Blasenströmen darzustellen, war aber nicht so effektiv, wie wenn das Eddy-Kovarianz-System im Zentrum des Sees platziert gewesen wäre. Schliesslich wurde ein Echolot benutzt, um hydroakustische Messungen der Blasenströme in der Wassersäule durchzuführen, eine Technik ähnlich derjenigen, die zur Untersuchung von Fischpopulationen eingesetzt wird. Diese nicht-invasive Technik erwies sich als eine der besten sowohl bezüglich der räumlichen Abdeckung, als auch für die Identifizierung von Faktoren, die helfen, die Blasenstrom-dynamik zu charakterisieren.

Der Zusammenhang zwischen dem Eintrag von organischem Material, dessen Ablagerung und den CH₄-Blasenströmen wurden in mehreren Kapiteln untersucht. Es konnte gezeigt werden, dass die hohe Sedimentationsrate im Wohlensee in einer permanenten Ablagerung von labilen organischen Substanzen unter limitiertem Kontakt mit Sauerstoff resultiert. Diese effiziente Ablagerung führt leicht zu einer CH₄-Übersättigung im Sediment, da die Diffusionsraten die Methanogenese nicht aufwiegen können. Diese Prozesse erklären demnach die im Wohlensee beobachtete extrem starke Bildung von Gasblasen und deren Ausstoss während der warmen Monate, wenn beste Bedingungen für mikrobielle Aktivität herrschen. Es konnte auch gezeigt werden, dass eine bis zu einer Grössenordnung grössere terrestrische Oberfläche als die des Wohlensees nötig wäre, um die Treibhausgasemissionen dieses Stausees auszugleichen. Diese Schlussfolgerungen führten schliesslich zu der Hypothese, dass der hohe Eintrag an organischem Material via die Zuflüsse des grossen Karibasees in Blasenstrom-Hotspots resultieren sollte, die in den entsprechenden Flussdeltas gelegen sind. Ein Vergleich zwischen Flussdeltas und Littoralzonen ohne einen Zufluss bestätigte genau dies.

Die Rolle von Blasenströmen für die gesamte CH4-Dynamik in den zwei sehr unterschiedlichen Systemen – Wohlensee und Karibasee – wurde detailliert untersucht. Blasenströme waren in der Tat der dominante Emissionsweg in beiden Systemen, aber unterschiedlich bezüglich räumlichem und zeitlichem Auftreten, der eine See gross und tropisch und der andere klein und in der gemässigten Klimazone war. Blasenströme im Wohlensee treten nur in signifikantem Ausmass auf, wenn Temperaturen über 10°C herrschen, und trotzdem dominieren diese warmen Emissionen, die in den meisten Bereichen des Stausees auftreten, die übrigen potentiellen Emissionswege. Der tropische Karibasee produziert mit einer höheren Wahrscheinlichkeit Emissionen während des ganzen Jahres, es konnte aber gezeigt werden, dass Blasenströme als Hotspots in den Littoralzonen mit einem Zufluss auftreten. Die dendritische Form dieses Stausees, zusammen mit der Tatsache, dass der Ausfluss von CH₄-reichem Wasser aus dem Damm relativ klein ist, führte zur Schlussfolgerung, dass diese Hotspots im Vergleich mit dem restlichen System und anderen Emissionswegen das meiste CH₄ emittieren.

Die Blasenstromdynamik ist aufgrund der zeitlichen und räumlichen Variabilität der Blasenbildung komplex. Hotspots kontrollierten die grossskalige räumliche Variabilität der Blasenströme im Karibasee. Für die kleinere räumliche Skala wurde herausgefunden, dass Blasenströme im Gegensatz zu Vermutungen in anderen Studien nicht tiefenabhängig waren, sondern stärker von der Distanz vom Zufluss abhängen, der das organische Substrat für die Methanogenese zuführte. Eine ganzjährige Studie im Wohlensee zeigte, dass die Temperatur eine signifikante Rolle in der saisonalen Dynamik der Blasenströme spielt, währenddem die kurzzeitlichen Variationen ein Resultat der hydrostatischen Veränderungen basierend auf den Seespiegelschwankungen waren, ausgelöst durch den Kraftwerksbetrieb.

Schliesslich haben hydroakustische Messungen zu neuen Einsichten in die Blasenstromdynamik geführt. Die Möglichkeit, Blasenstromereignisse in der Wassersäule genau zu lokalisieren und zu messen, ist einer der Hauptvorteile der hydroakustischen Technik. Es konnte gezeigt werden, dass die Unterschiede der durchschnittlichen Flüsse aus Hotspots im Karibasee nicht nur durch die Frequenz von Blasenströmen, sondern auch durch das Ausmass der auftretenden Blasenströme bestimmt waren. Unter Verwendung von hydroakustischen Daten vom Wohlensee wurde die Wichtigkeit der Blasengrösse für den Gesamtfluss offen gelegt. Die Identifizierung der genauen Verteilung der Blasengrössen ist essentiell, um den CH₄-Fluss in einem aquatischen System verstehen zu können, da grosse Blasen das grösste Gasvolumen beisteuern und sich während ihres Aufstiegs am wenigsten auflösen. Zusätzlich kann die Dichte der Blasen in der Wassersäule ein wichtiger Faktor für die Flussunterschiede an verschiedenen Stellen sein. Diese Details von Blasenströmen werden leicht übersehen, wenn Messtechniken eingesetzt werden, die Flüsse über grosse Flächen integrieren, die auf der atmosphärische Eddy-Kovarianz-Messung basieren oder die eine limitierte räumliche Abdeckung besitzen, zum Beispiel frei schwimmende Flusskammern. Hope, like faith, is nothing if it is not courageous; it is nothing if it is not ridiculous. Chapter 1

Introduction

1.1 Objective

The overarching hypothesis for this dissertation is that ebullition (bubbling) can be one of, if not the most, important methane (CH₄) emission pathway in many water bodies, particularly reservoirs. Despite increasing evidence that ebullition is an efficient and dominant pathway in shallow systems, it has been understudied compared to other pathways, especially diffusion. The main reason for this is the complexity involved in accurately measuring such a stochastic and episodic phenomenon (Bastviken et al., 2011). Therefore, the following chapters will:

- Explore traditional and new techniques for the direct and non-direct assessment of CH₄ emissions with a particular focus on ebullition.
- Define the links between organic matter loading and burial and subsequent CH₄ emissions in a reservoir with intense ebullition.
- Examine and quantify the role of ebullition in the overall CH₄ dynamics of two very different reservoir schemes.
- Identify the environmental factors influencing the temporal and spatial variability of ebullition on long and short timescales.
- Investigate the relationship between ebullition characteristics and CH₄ flux using hydroacoustic techniques.

1.2 Reservoirs in the global carbon cycle

The fact that CH_4 has a global warming potential up to 25 times stronger than carbon dioxide on a 100-yr scale has made the monitoring of this greenhouse gas of particular importance. Atmospheric CH_4 concentrations are currently at the highest levels observed in the last 650 kyr and have an ever-growing list of natural and anthropogenic sources (Forster et al., 2007). As CH_4 tends to prosper from the remineralization of organic matter in anaerobic environments, natural and anthropogenic sources of biogenic CH_4 (i.e., wetlands and landfills, respectively) contribute 70% to the global CH_4 budget (Reeburgh, 2007; Kiene, 1991). The dominant gaseous emissions from aquatic systems is in the form of carbon dioxide, however the potency of CH_4 makes its estimated emissions from inland waters roughly equal to carbon dioxide in terms of climatic impact (Tranvik et al., 2009). Despite this weighted contribution, aquatic systems have not yet been declared a significant CH_4 source or included in a terrestrial greenhouse gas budget (Bastviken et al., 2011).

Aquatic systems cover just over 3% of the world's landmass, only a minute fraction of the surface area of the ocean, but carbon burial in aquatic sediments exceeds that of the oceans (Tranvik

et al., 2009). Inland waters, including man-made impoundments, function as active conduits for terrestrial carbon transformation, remineralizing and emitting more than half the entering carbon (Cole et al., 2007; Tranvik et al., 2009). The sediments of inland waters provide ideal conditions for methanogenesis (Bastviken et al., 2004), which is the final organic matter degradation process occurring after all other oxidants are consumed (Martens and Berner, 1974). Greater than 50% of the natural sediment flux to the oceans has been retained behind man-made impoundments in the last 50 years (Vörösmarty et al., 2003) and with that more than 1 billion metric tons of carbon (Syvitski et al., 2005). Numerous unidentified small (< 1 km²) impoundments have made calculating the exact surface area of reservoirs difficult and the reservoir area is steadily increasing. As a consequence, the amount of carbon trapped in dams exceeds the burial in all existing natural waters and is still increasing (Cole et al., 2007; Syvitski et al., 2005).

There is more than 100 GW of hydropower potential remaining across the globe, of which could provide much needed economic and energy benefits to parts of Asia, South America, and Africa (Bartle, 2002). Despite the benefits societies are divided on hydropower implementation, mostly because large projects (dams) tend to have severe negative social, political, and/or environmental impacts on local and global scales (WCD, 2000). Making the environmental impact debate even more intense are growing concerns regarding human-induced climate change and climatic feedbacks (IPCC, 2007). Ultimately, understanding the carbon dynamics in inland waters is crucial to understanding the global carbon cycle and its role in the climate system.

1.3 Methane dynamics of aquatic systems

Methane emissions from sediments of any water body depend on the production by methanogens, which is a function of organic matter availability as well as sulfate and oxygen levels (Martens and Berner, 1974; Reeburgh, 2007). The oxygen- and sulfate-poor sediments of aquatic systems have thus been referred to as 'hot spots' of methanogenesis (Bastviken et al., 2004), and much attention has been drawn toward CH_4 emissions from wetlands, lakes, and reservoirs. Methane produced in sediments can migrate to or through the water column via three pathways (Figure 1.1): diffusion, advection through plant roots, or ebullition (bubbles).

If sediments are overlain by oxic water, a large portion of diffusing methane is quickly consumed when it reaches oxic sediment, even if the zone is only a few millimeters thick (Bastviken et al., 2008). However, in stratified waters (i.e., anoxic hypolimnion), CH_4 diffuses freely into the water column and accumulates to high levels, while at the oxycline and in the epilimnion dissolved levels are kept lower by rapid oxidation rates (Bastviken et al., 2008; Guérin et al., 2007). Dissolved CH_4 near the water surface can diffuse through the air-water interface,

which is a function of the gas exchange coefficient as well as CH₄ concentrations in the water and atmosphere (Crusius & Wanninkhof, 2003; Duchemin et al., 1999).

Emergent macrophytes can transport CH₄ directly from the sediment to the atmosphere, but this pathway tends to be only important in really shallow water (<1 m), such as in wetlands or the banks of lakes (Brix et al., 2001; Kankaala et al., 2005). This pathway is obviously seasonal in temperate and boreal regions as it is dependent on plant growth. In addition, the balance between acting as a greenhouse gas sink (i.e., carbon dioxide uptake) and source must be taken into consideration when estimating the role of macrophytes (Brix et al., 2001). This pathway will not be discussed further in this thesis.

Bubbles form in sediments when CH_4 production is sufficient enough to allow porewater concentrations to exceed solubility, thus forming an area of supersaturation for bubble nucleation. Also CH_4 production surrounding the bubble must remain at levels that maintain the CH_4 gradient near the bubble surface to allow the continuation of bubble growth (Algar and Boudreau, 2010). Thus, bubble formation in sediments is a function of organic carbon remineralization in sediments. Ebullition allows CH_4 to escape the sediment without being much affected by the oxygenated zone. However, as a bubble rises through the water column, gas exchange with the ambient water is constantly occurring (McGinnis et al., 2006). Thus, some CH_4 escapes into the water column where it can be oxidized in oxic water, stored in anoxic water, or eventually diffused at the air-water interface (McGinnis et al., 2006; Bastviken et al., 2008).

Methane is emitted to the atmosphere directly via ebullition, diffusion, and plants if they are present at the air-water interface. As bubble dissolution heavily depends on rising distance (or depth of bubble release), ebullition is most effective as an atmospheric emitter in shallow waters (< ~50 m). Diffusive atmospheric emission is assumed to dominate in deeper systems (McGinnis et al., 2006; Bastviken et al., 2004; Adams, 2005). Bastviken et al. (2004) showed that ~50% of all CH₄ emission from lakes is mediated by ebullition.



Figure 1.1. Methane dynamics in natural water bodies. Source: Bastviken et al. (2004).

System-specific atmospheric CH_4 emission pathways exist as well, such as mixing of a stratified water column. During overturn much of the CH_4 stored in the anoxic hypolimnion is oxidized at the (sometimes) rapidly eroding oxycline (Bastviken et al., 2002; Bastviken et al., 2008; Whiticar and Farber, 1986), but that which escapes oxidation has the potential to be released to the atmosphere (Michmerhuizen et al., 1996; Riera et al., 1999). In high latitudes or elevations where water bodies freeze, CH_4 emission during ice melt can be a substantial portion of the total emission (Walter et al., 2006; Walter-Anthony et al., 2010). Specific to reservoirs, degassing of CH_4 -rich waters at the turbines or diffusive loss from the downstream rivers can account for immense atmospheric emissions (Figure 1.2; Abril et al., 2005; Guerin et al., 2006; Kemenes et al., 2007).



Figure 1.2. Methane dynamics in a dammed reservoir. Source: UNESCO/IHA 2009.

1.4 Quantification of methane emissions

Quantification of CH_4 emissions from water bodies has markedly increased in the last decade or so with boreal lakes and tropical reservoirs receiving most of the attention. With recognition of a warming climate, there are concerns that boreal and arctic lakes, which are carbon-rich and numerous throughout the north of Europe, Canada, and Russia, will see an increase in CH_4 emissions with rising temperatures (Walter et al., 2006; Gudasz et al., 2010). As organic carbon mineralization is a function of temperature, tropical water bodies emit the highest amounts of total CH_4 (Bastviken et al., 2011). Reservoirs, in general, tend to become eutrophic, which ultimately leads to increased methanogenesis in warm and oxic-free conditions (Gunkel, 2009). In fact, tropical reservoirs in Brazil have been the center of an ongoing debate regarding whether hydropower reservoirs actually produce less greenhouse gases than an equivalent energy-producing coal-powered plant (Fearnside 1995; Rosa et al., 1996). Despite all of this, reservoirs in general remain understudied compared to natural systems.

Bastviken et al. (2011) has compiled the most comprehensive list of CH_4 emission estimates from lakes, reservoirs, and rivers globally to date. However, a comparison of estimates from natural lakes and reservoirs is not useful seeing as hundreds of more lakes have been surveyed than have reservoirs. Methane emission has been measured in just over 30 reservoirs from the tropical and boreal regions, while there is no data from the temperate zone. Although ebullition has been measured in less than a third of the amount of systems (mostly natural) than diffusion and the stored stock have been measured, ebullition emits more than twice the amount of CH_4 than those other pathways (Bastviken et al., 2011). In fact, between 40 and 60% of CH_4 emission from natural systems is most likely via ebullition, although its importance decreases with increasing depth of the water body (Bastviken et al., 2004).

The dominant emission pathway from the few surveyed tropical reservoirs, however, is the degassing of CH₄-rich anoxic waters at the turbine or downstream river (Abril et al., 2005; Kemenes et al., 2007), although the age of a reservoir seems to have an affect on the contribution of emission pathways. Abril et al. (2005) found after surveying a large reservoir in South America just after flooding that ebullition was emitting about half the emissions, but found that 10 years later ebullition rates dropped substantially and that degassing at the downstream weir was responsible for over 70% of the CH₄ emissions. It was thus hypothesized that the initial carbon input from the flooding of a vegetated area maintained high rates of methanogenesis and consequent surface emissions until the exhaustion of that flooded carbon pool. As reservoirs commonly become eutrophic, the creation of an anoxic hypolimnion is conducive to the storage of CH₄ emitted from anoxic sediments, which is then released through the dam if turbine intakes are located in the hypolimnion (Gunkel, 2009). However, from shallow regions of reservoirs, ebullition may remain the dominant pathway (Gunkel, 2009); although the general lack of ebullition data and inconsistency in the sampling methods used in those surveys that do exist prevent accurate assessments regarding ebullition emissions from reservoirs (Gunkel, 2009; Bastviken et al., 2011).

1.5 Ebullition dynamics

Bubble dynamics in fluid media have been well-studied, but bubble dynamics in and out of sediments are only partially understood (Boudreau et al., 2005). As stated earlier, the processes allowing the nucleation of a bubble are based on CH_4 production and thus biologically-driven. Bubble shape and its movement through and release from the sediment, however, are controlled mostly by physical mechanisms. Sediment type and its mechanical properties are perhaps the most

important factors controlling the size and shape of bubbles and their eventual pathway through the sediment. Meier et al. (2011) found via laboratory experiments that various particle sizes and densities of granular beds, such as lake sediments, produce two modes of emergence. In general, larger grains (> 1 mm diameter) allow bubbles to percolate out of the beds easier and thus the bubbles are smaller than those emerging from smaller grained beds, which prevent bubble emergence until the gas buoyancy can overcome the surficial tensions applied by the cohesiveness of the small grains. Bubble shape is also influenced by grain size with sandy (large grain) sediments allowing bubbles to grow more spherically. Muddy (small grain) sediments produce disc-shaped bubbles (also called oblate spheroids) that grow laterally within the medium until the internal pressure within the bubble exceeds the strength of the sediment, which then fractures allowing the bubble to grow upward forming a thin, elongated bubble (Gardiner et al., 2003; Boudreau et al., 2005). According to Boudreau et al. (2001a) and errata: Boudreau et al. (2001b), it would take between 20 and 150 days for a bubble to grow to 1 cm equivalent diameter in typical muddy sediments found in coastal bays and lakes. Bubbles can then follow fractures created by previous bubbles or they must continue to create their own fractures until they escape the sediment (Boudreau et al., 2005).

Once bubbles are present in the sediment, a variety of environmental factors can expedite their release if they have not yet overcome the sediment forces holding them back. The strongest factors are those that reduce the overlying hydrostatic pressure, such as tides in coastal regions (Martens and Val Klump, 1980) or water level drawdown in reservoirs (Ostrovsky, 2003). Algar and Boudreau (2010) proposed a mechanism by which the reduction in hydrostatic pressure in a region where bubble growth has been halted would allow the bubble pressure to overcome the sediment pressure preventing fractionation and upward movement. Increased ebullition was also observed in relation to decreased air pressure (Mattson and Likens, 1990) and as a response to strong winds (Keller and Stallard, 1994), both presumably due to a mechanism similar to what Algar and Boudreau (2010) described. Joyce and Jewel (2003) concluded that near-bottom current acceleration (shear stress at the sediment surface) often demonstrated a better correlation with ebullition events than with wind speed or current velocity alone. Ultimately, the spatial and temporal heterogeneity of ebullition particularly difficult.

1.6 Quantification of ebullition in aquatic systems

While large and fast bubble streams may induce strong upwelling flows (Chen et al., 1994) and subsequently enhance turbulent vertical mixing of methane, low flow ebullition from single bubble

streams typically do not induce an upwelling flow. Single bubbles ascend at their own rate, which is a result of initial bubble size, gas composition, and current velocities (Leifer and Patro, 2002). Methane transport via ebullition is thus limited to bubble dissolution into the water column or direct release to the atmosphere if the bubbles reach the air-sea interface. Traditionally, in situ ebullition studies in aquatic systems have involved some type of gas trap partially submerged or at the airwater interface (e.g., Bastviken et al., 2004; Keller and Stallard, 1994). For the most part traps are effective, but surveying a representative portion of the lake is nearly impossible because of time constraints and the number of traps needed. Therefore, gas trap results may actually be biased by their placement by the user, as well as by the large variations in lake ebullition. The temporal variability can at least be resolved by dynamic chambers (Ramos et al., 2006) or automated gas traps (Varadharajan et al., 2010) that record at a faster resolution, but the spatial limitations still remain. Innovative bubble-mapping techniques have been developed for quantification of ebullition in the Arctic based on bubbles caught in ice at the surface of frozen lakes (e.g., Walter-Anthony et al., 2010), but is obviously a technique specific to colder regions. Photo-optical methods are beginning to be used *in situ* (e.g., Thomanek et al., 2010), but various hydroacoustics techniques seem to be the most promising for efficient spatial coverage of a system as well as useful for temporal coverage (e.g., Ostrovsky et al., 2008; Greinert et al., 2010).

As fish, or rather their swim bladders, act as strong backscatters of acoustic signals, hydroacoustics is a common technique used to quantify and characterize fish abundance over a large area in an unobtrusive manner (Simmonds and MacLennan, 2005). Gas bubbles also act as ideal backscatters of acoustic signals and thus similar techniques have been adopted in the field of ebullition research. Ultimately, if a relationship between gas flow rate or bubble size and their acoustic signature can be established, then gas flux can be estimated using hydroacoustic data. Various bubble sources have been investigated using hydroacoustics, including micro-bubbles (Vagle and Farmer, 1992), biogenic lake ebullition (Ostrovsky et al., 2008), and thermogenic marine seepage (Hornafius et al., 1999). Extensive research on mud volcano (high flow) seeps in the Black Sea has shown the viability of hydroacoustic assessment of bubbling seeps (e.g., Greinert and Nützel, 2004; Schneider von Deimling et al., 2019). Greinert and Nützel (2004) showed that the volume backscattering strength of bubbles in a known volume of water measured by a single beam system can be used to estimate CH₄ flux at high flow seeps without prior knowledge of bubble size distribution. Using multiple single and multi-beam hydroacoustic systems, as well as observations of seeps via a submersible, accurate estimations of bubble size and flow rate of the Black Sea seeps have been made (Greinert et al., 2010). Furthermore, Greinert et al. (2010) has shown that hydroacoustic examination of ebullition in the water column combined with a bubble dissolution model introduced by McGinnis et al. (2006) can accurately estimate the dissolution of CH₄ bubbles into the water column upon ascent.

Low flow lake ebullition has also been observed hydroacoustically and methods have since been proposed for the calculation of bubble flux using hydroacoustic data (e.g., Ostrovsky et al., 2008). Using a 120 kHz dual-beam echosounder, two different techniques - echo counting (EC) and echo integration (EI) - were evaluated for estimation of bubble densities in Lake Kinneret, Israel (Ostrovsky, 2003). EI, which involves dividing the volume backscattering of the observed volume of water by the average backscattering cross-section (i.e., size) of observed targets, proved to be the more appropriate method when bubbles are released at the sediment bottom. EC simply requires the counting of individual acoustic targets in the water column, but tends to underestimate bubble density when bubbles are too close together near the lake bottom. Later, a relationship between known bubbles volumes and their acoustic strength was established in the lab in order to calculate the volumetric concentration of bubbles in the field (Ostrovsky et al., 2008). Then, from the CH_4 concentration in bubbles near the lakebed and the average bubble rise speed (also determined with hydroacoustics), a CH_4 flux rate from the sediment was established. Emission to the atmosphere was then calculated from the sediment flux rate using a bubble rise model estimating bubble dissolution upon ascent based on ambient conditions (Ostrovsky et al., 2008).

Although this atmospheric flux estimate was not corroborated by any other methods, it highlights the significance of CH_4 emission to the atmosphere from lakes and the usefulness of such hydroacoustic surveying of ebullition. The unobtrusive detection of bubbles and the ability to survey a significant area of a water body in a short amount of time is an obvious advantage to this method. However, since direct measurements of gas emission is not possible, complimenting hydroacoustics with direct measurement techniques such as gas traps would be useful and relatively easy. Disturbances from fish and other targets in the water column may cause difficulty in assessing ebullition hydroacoustically, but Ostrovsky (2009) has suggested a method around this. Finally, hydroacoustics is proving to be a useful tool in unraveling the complexities of ebullition dynamics, such as from water level drawdown (Ostrovsky, 2003) and tides and currents (Schneider von Deimling et al., 2010).

1.7 Study sites

The methane dynamics of two reservoirs was examined with particular focus on ebullition. A small temperate hydropower reservoir in central Europe was investigated in detail in four of the following chapters. A fifth chapter discusses ebullition in one of the world's largest hydropower reservoirs located in sub-Saharan Africa.

1.7.1 Lake Wohlen

Created in 1920 by the damming of the Aare River, Lake Wohlen is a run-of-river reservoir located a few kilometers downstream from Bern, the capitol of Switzerland. The Aare River originates in the Swiss Alps and passes through two large lakes, Brienz and Thun, as well as through several other hydropower schemes and past some waste-water treatment plants before entering Lake Wohlen, which lies at 481 m a.s.l. Hydropower operations result in no more than 0.5 m change in water level (Knusel, 1990). The lake receives relatively large organic matter and nutrient loads and is thus characterized as meso- to eutrophic. Carbon loading is also moderate with the majority of organic carbon entering in dissolved form. Several recent studies have shown that the waste-water treatment plants are not the primary cause for high nutrient loads (von Känel, 2008; AquaPlus, 2008; Mürle et al., 2009). The small (2.5 km²) reservoir lies in an east-west running valley surrounded almost entirely by agriculture and forested lands sitting on a plateau approximately 120 m above the lake surface. The lake maintains similar meandering patterns as the original river, which is visible by bathymetry contours clearly showing the old river channel until ~ 1 to 2 km from the dam where the basin is the deepest (~16 m in front of the dam; Knusel, 1990). This run-of-river reservoir remains oxic and well-mixed throughout the year thanks to an average river inflow of 121 m³ s⁻¹, thus resulting in an average residence time of 2.1 days for the whole reservoir (Albrecht, 1998). Water temperature also varies greatly (5°C to >20°C) depending on season or rain events. Overall, Lake Wohlen appears as a typical run-of-river reservoir found throughout central Europe.

1.7.2 Lake Kariba

On the border of Zambia and Zimbabwe along the Zambezi River in southern Africa lies Lake Kariba, the world's largest reservoir by volume and one of the largest by area in the world. After the completion of the dam in 1958 and consequent flooding that lasted four years, the 5,250 km² reservoir with 160 km³ of water was created. With multiple turbines on the north and south banks of the lake and a capacity of 1350 MW, the dam comprises ~60% of the total hydroelectricity output from Zambia and Zimbabwe (Magadza, 2006). Similar to other large reservoirs, Lake Kariba is elongated (280 km) and highly dendritic with approximately 2,100 km of shoreline (Coche, 1974). It is divided into four major basins with the largest being up to 100 m deep near the dam. The overall mean depth is ~30 m and hydropower operations along with the seasons allows for a ~4 m change in water level. The lake is primarily fed by the Zambezi River (~80%), but receives ~8% from the Sanyati River in the northernmost basin, while the remainder comes from dozens of

tributaries entering the lake from all sides (Marshall, 1988). The lake lies in a tropical zone at 16° S that experiences a dry and wet season annually with surface water temperatures remaining >20°C throughout the year. The residence time is ~3 years, but the lake is monomictic with mixing occurring typically in the middle of the dry season around July or August (Coche, 1974). The lake is oligotrophic with the development of an anoxic hypolimnion during stratification. The lake has experienced numerous environmental problems, including invasive weeds (Balon, 1978) and pesticide and heavy metal pollution from local agriculture and mining activities, respectively (Berg, 1995; Nakayama et al., 2010). Fish productivity was enhanced by the successful introduction of a sardine species native to Lake Tanganyika (Balon and Coche, 1974). The creation of this reservoir was considered one of the biggest tragedies in modern hydropower history with the inefficient relocation of over 80,000 people living along the former Zambezi River bank in that region (Magadza, 2006).

1.8 Overview

A brief summary of each manuscript chapter is given below. As of November 2011, three manuscripts have been published, one submitted, and the remaining will be submitted shortly.

1.8.1 Chapter 2: Extreme methane emissions from a Swiss hydropower reservoir: Contribution from bubbling sediments

This chapter was published in Environmental Science and Technology in 2010 and is the first in a series of manuscripts investigating the intense ebullition observed in Lake Wohlen. A yearlong survey of CH_4 dynamics in this system revealed a temperature-dependency of ebullition culminating in extreme emissions during the warm summer months. The temperature relationship also allowed the development of a unique mass balance-based system analysis in which atmospheric emissions were accurately estimated using only monthly dissolved CH_4 measurements.

1.8.2 Chapter 3. Extreme organic carbon burial fuels intense methane bubbling in a temperate reservoir

A sediment study conducted at Lake Wohlen is described in this chapter and was recently submitted to Geophysical Research Letters. Organic carbon burial efficiency was examined in several cores along the lake and was found to be extremely high for an aquatic system. The rapid and deep burial of labile organic matter not only created an efficient carbon sink, but also supplied ample substrate for deep methanogenesis in the anoxic sediments, which surpassed diffusion rates and led to CH_4 supersaturation. This is presented as one of the main reasons for the extreme CH_4 emissions observed in Lake Wohlen.

1.8.3 Chapter 4. Eddy covariance flux measurements confirm extreme CH_4 emissions from a Swiss hydropower reservoir and resolve their short-term variability

In this chapter, which has been published in Biogeosciences in 2011, we explore the usefulness of eddy covariance flux measurements of CH_4 over Lake Wohlen during a two month-long campaign in summer while ebullition was active. The peak fluxes measured by eddy covariance agreed with direct measurements using floating chambers, but the high resolution of the eddy covariance measurements allowed the identification of environmental variables causing short-term variations in flux. While increasing temperatures did enhance emissions, as was found in other studies, daily hydropower operations involving lake levels (i.e., hydrostatic pressure) had the highest impact on the short-term variability. In addition, we found that only a small fraction of the organic input to Lake Wohlen is needed to sustain the extreme CH_4 emissions observed there, but the carbon uptake of a terrestrial area up to four times larger than the reservoir is needed to balance the emissions.

1.8.4 Chapter 5. Hydroacoustic examination of reservoir ebullition: Variability explored in comparison with other methods

The value of hydroacoustics for measuring CH₄ ebullition in Lake Wohlen is explored in this chapter that will be submitted to Journal of Geophysical Research. A bubble calibration was performed with an echosounder in order to accurately estimate bubble size and CH₄ flux. The application of a method to measure ebullition in the presence of fish during a summer campaign in the most active ebullition region of Lake Wohlen revealed spatial patterns in flux and bubble size associated with the bathymetry of the reservoir and the old river channel. Bubble sizes were found to be quite variable, but tended to be larger when in higher density, such as in plumes. In addition, it was discovered that determining a proper bubble size distribution was crucial to understanding CH₄ flux from a system. A comparison between floating chambers and eddy covariance results suggests that hydroacoustic measurements provide the most representative average flux for this system and finally Lake Wohlen is placed in a global reservoir context.

1.8.5 Chapter 6. Spatial heterogeneity of methane ebullition in a large tropical reservoir

The manuscript from this chapter, which investigates methane dynamics of Lake Kariba in sub-Saharan Africa, was recently accepted for publication in Environmental Science and Technology. In this study we discovered that river deltas of this large reservoir act as ebullition hotspots and thus make ebullition the dominant emission pathway. Hydroacoustics and floating chambers were used to measure CH₄ ebullition and yielded similar average results, but hydroacoustics provided additional insight into ebullition variability. Differences between the littoral areas surveyed were either from differences in ebullition magnitude or frequency.

Chapter 2

Extreme methane emissions from a Swiss hydropower reservoir: Contribution from bubbling sediments

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Abstract

Methane emission pathways and their importance were quantified during a yearlong survey of a temperate hydropower reservoir. Measurements using gas traps indicated very high ebullition rates, but due to the stochastic nature of ebullition a mass balance approach was crucial to deduce system-wide methane sources and losses. Methane diffusion from the sediment was generally low and seasonally stable and did not account for the high concentration of dissolved methane measured in the reservoir discharge. A strong positive correlation between water temperature and the observed dissolved methane concentration enabled us to quantify the dissolved methane addition from bubble dissolution using a system-wide mass balance. Finally, knowing the contribution due to bubble dissolution, we used a bubble model to estimate bubble emission directly to the atmosphere. Our results indicated that the total methane emission from Lake Wohlen was on average >150 mg CH₄ m⁻² d⁻¹, which is the highest ever documented for a mid-latitude reservoir. The substantial temperature-dependent methane emissions discovered in this 90-year-old reservoir indicate that temperate water bodies can be an important but overlooked methane source.

2.1 Introduction

There is growing interest and concern regarding greenhouse gas emissions, mainly carbon dioxide (CO₂) and methane (CH₄), from lakes and reservoirs (St. Louis et al., 2000; Bastviken et al., 2004; Soumis et al., 2005; Tremblay et al., 2005). Organic-rich sediments in lakes and reservoirs are thought to be 'hot spots' of methanogenesis in particular, from which CH₄ can escape to the atmosphere via four major pathways - ebullition (bubbling), surface diffusion, advection through plants, and exposure of anoxic CH₄-rich deep waters to the atmosphere during convective mixing events (turnover; Bastviken et al., 2004). Additionally, gas is emitted from CH₄-saturated dam releases (Guèrin et al., 2006). Typically, surface diffusion is the dominant atmospheric emission pathway for CO₂, and for CH₄ from deep water bodies (>50 m; Abril et al., 2005; McGinnis et al., 2006). The low solubility of CH₄ relative to CO₂ means that CH₄ bubbles form more readily with typical diameters ranging from 2 to 8 mm (McGinnis et al., 2006; Ostrovsky et al., 2008; Greinert et al., 2010). While these bubbles typically dissolve in deep systems, in shallow waters (< 50 m) ebullition is the dominate CH₄ emission pathway because limited dissolution occurs during bubble ascent (Ostrovsky et al., 2008; Flury et al., 2010). Microbial oxidation depletes CH₄, mainly at the intersection of CH₄ and O₂ gradients near sediment-water interfaces and oxyclines (Frenzel et al., 1990; Bastviken et al., 2008)

 CH_4 bubble formation and transport to the atmosphere, combined with CH_4 's large global warming potential (~25 times more than that of CO_2 over a 100 year period; Forster et al., 2007), suggests that CH_4 emissions are important to understand and monitor. The methane fluxes from reservoirs reported in the literature, however, are very discordant and range over an order of magnitude (St. Louis et al., 2000; Soumis et al., 2005).

The aquatic methane fluxes are difficult to accurately estimate because measuring all the different flux pathways is complicated and time-consuming, particularly due to the high degree of spatial and temporal variability. Therefore, the goal of this study was to quantify the methane emission pathways within a relatively small run-of-river reservoir over a full year and then apply a system analytical mass balance approach to better calculate the methane diffusion and ebullition from sediments using basin-wide dissolved methane concentrations. Finally, all estimates were compared and validated based on actual observations and seasonal methane pathways and associated fluxes from the reservoir were calculated.

2.2 Materials and Methods

2.2.1 Study site

Lake Wohlen, a run-of-river hydropower reservoir located on the Aare River downstream of the city of Bern (Switzerland), was studied because of extensive ebullition observed during a previous campaign. Completed in 1920, the reservoir has a surface area of ~2.5 km² and holds 22 x 10^6 m³ of water with a maximum depth of 18 m near the dam (mean depth ~10 m). Located in a temperate region, the reservoir experiences seasonal water temperatures ranging from ~5°C in winter up to nearly 20°C in summer (Figure 2.1a; Hydrodaten, 2008). The turbine release is ~10 - 14 m below the lake surface. The yearly average discharge (Q) of ~122 m³ s⁻¹ (~40 - 400 m³ s⁻¹; Figure 2.1a) results in a mean water residence time of ~2 days (7.2 - 0.7 days) (Albrecht et al., 1998). Due to the short residence time and energetic mixing, the entire water column of Lake Wohlen is oxic year round.

Lake Wohlen receives a relatively large amount of organic and nutrient loading as it is located directly downstream of Bern, Switzerland and three wastewater treatment plants. Total organic carbon (TOC) concentration in the inflow is ~2.4 mg L⁻¹, while ~1.9 mg L⁻¹ is in the form of dissolved organic carbon (DOC). Total phosphorus and nitrogen are on average 30 μ g P L⁻¹ and 1 mg N L⁻¹, respectively (Naduf, 2009). Sediment dissolved oxygen uptake was determined to be around 35-40 mmol m⁻² d⁻¹ (McGinnis et al., 2008), which is typical for mesotrophic-eutrophic reservoirs. Macrophytes are largely absent. Sediments consist mainly of clay and fine silt and

contain about 2% organic carbon, except in the upstream region where they tend to be much coarser and enriched in mineral particles (Sobek, et al., in prep).

2.2.2 Sampling summary

Methane fluxes were assessed based on multiple sampling campaigns and are reported as areal fluxes in mg CH₄ m⁻² d⁻¹ \pm 1 standard deviation. Dissolved CH₄ concentrations ([CH₄]_d) were measured at the inflow (M_{IN}) and outflow (M_{OUT}) of the reservoir approximately monthly from June 2007 until June 2008 (total, 14 campaigns). The longitudinal and vertical distribution of [CH₄]_d were measured during three additional surveys in June, July, and December of 2007. Diffusion from the sediment to the water column (M_{SD}) was estimated from Fick's First Law of diffusion and CH₄ gradients in the porewater from 15 cores taken in September and November of 2006 and July, November, and December of 2007. Gas exchange of CH₄ at the water-air interface (M_{WD}) was calculated as described below based on $_{\rm [CH_4]_d}$ measurements taken on 20 sampling days between June 2007 and July 2008, as well as directly measured with anchored floating chambers (AC) in July 2008. Gas trap funnels were used to measure bubble flux from the sediment (M_{BF}) during surveys conducted in August and October 2007. The remaining pathways - bubble dissolution (M_{BD}) and bubble emission to the atmosphere (M_{BE}) - were estimated using a bubble dissolution model. Finally, drifting chambers (DC) were deployed in July 2008 to measure total atmospheric emissions via diffusion and ebullition over the lake surface.

2.2.3 Methane inflow, outflow, and distribution

 $[CH_4]_d$ inflow samples were collected monthly ~6 km upstream of the dam (Figure A.1a of Supporting Information, right star) at a shallow (< 5 m) area with relatively fast-flowing conditions. The $[CH_4]_d$ outflow samples were taken at 0, 4, 8, 12 and 16 m depths on the reservoir-side of the dam before turbine passage (Figure A.1a, left star). Average profile concentrations were used for the discharge. The three longitudinal surveys conducted for $[CH_4]_d$ distribution included profiles every kilometer through the center of the ~7 km long reservoir at a vertical resolution of 3 m (e.g., Figure 2.1b). From the inflow ($[CH_4]_{IN}$) and outflow ($[CH_4]_{OUT}$) concentration results of the monthly and longitudinal surveys (sampling method details can be found in Supporting Information), the mass of dissolved methane increase along the reservoir was calculated as

$$\frac{\Delta[\mathrm{CH}_{4}]}{\Delta t} \times V = Q \times [\mathrm{CH}_{4}]_{\mathrm{OUT}} - Q \times [\mathrm{CH}_{4}]_{\mathrm{IN}}$$
(1)

where V is the volume of the reservoir and Q is the discharge.



Figure 2.1. a) Temperature and discharge, Q, in Lake Wohlen during samplings. Q ranges from ~400 m³ s⁻¹ in summer (residence time, Rt, ~1 day) to 50 m³ s⁻¹ in winter (Rt ~7 days). **b**) Contour plot of dissolved methane distribution in Lake Wohlen on 21 June 2007. Black squares – actual samplings. Water flows in from right to the dam (left). Profiles were taken every kilometer at a vertical resolution of 3-4 m. Figure suggests that methane is vertically homogeneous, while concentrations can increase five times horizontally.

2.2.4 Sediment methane emissions

The methane gradient was measured in the porewater of the top 10 cm of 15 cores from different locations along the reservoir (Sobek et al., in prep; see Supporting Information for sampling details). Methane gas exchange at the sediment surface was calculated using Fick's First Law of diffusion and the molecular diffusivity given by Furrer and Wehrli (1996). Oxidation partially controls the dissolved CH₄ concentrations near the sediment-water interface (Frenzel et al., 1990; Huttunen et al., 2006); however, the 1 cm vertical sampling resolution did not allow us to resolve dissolved CH₄ within the top boundary layer. In most of the cores sediment methane concentrations declined linearly from ~10 cm sediment depth towards the sediment-water interface, likely due to methane oxidation (Sobek et al., in prep), and since the fine-scale details of the methane gradient at the surface were unknown, we used the CH₄ concentration difference between

the top sediment layer and the sediment layer at 1 cm depth to calculate a first estimate of the sediment diffusive CH₄ flux.

Sediment methane ebullition was measured with custom-made gas traps, which are inverted funnels with an opening of ~ 0.785 m^2 surface area (see Figure A.1b and the extended methods section in Supporting Information for design and sampling procedures). August gas trap surveys (Figure A.1a, filled triangles) covered almost the entire length of the reservoir in random locations. The October surveys (Figure A.1a, empty triangles) focused on the more active bubbling areas of the reservoir. In total, 38 measurements of ebullition were obtained from 26 different locations that varied from 2 to 16.5 m water depth.

2.2.5 Bubble dissolution and atmospheric emission

CH₄ bubbles exchange gases with the surrounding water (e.g., a pure CH₄ bubble will gain oxygen and nitrogen and lose CH₄) as they rise in the water column, thus a bubble gas exchange/dissolution model was used to predict the fractions of methane that dissolves in the water column and the fraction that reaches the atmosphere (see McGinnis et al. (2006) for details). The model was run for each funnel measurement. The water was assumed to be saturated with nitrogen and oxygen, while actual measured values of temperature and dissolved methane were used. Finally, for the purpose of this calculation, the initially released bubble was assumed to be pure methane and have a diameter of 6 mm, which is an average size often reported in literature (McGinnis et al., 2006; Ostrovsky et al., 2008; Greinert et al., 2010).

2.2.6 Surface methane emissions

Gas exchange at the air-water interface was measured using ACs, as well as by the boundary layer equation (e.g., Duchemin et al., 1999):

$$J_L = K_x * (C_w - C_{eq}), \qquad (2)$$

where K_x is the gas exchange coefficient, C_w is the average surface $[CH_4]_{d_1}$ which was directly measured, and C_{eq} is the atmospheric equilibrium concentration of CH_4 calculated according to Wiesenburg and Guinasso (1979) and the 2005 estimate for atmospheric CH_4 concentration (1774 ppb; Forster et al., 2007). K_x was calculated using equations (3) and (5) of Crusius and Wanninkhof (2003) and incorporates wind speed data that were measured ~2 km away (Meteoschweiz, 2009).

ACs were anchored at bubble-free locations in the dam basin and used to measure CH_4 diffusion to the atmosphere during two 2-day campaigns. For chamber design and gas sampling details, see Figure A.1c and extended methods section of the Supporting Information. Gas flux was calculated from the increase in methane concentration during the measuring period. Surface water samples for $[CH_4]_d$ were taken next to the AC at each gas sampling.

DCs were constructed nearly the same way as ACs (see Supporting Information), but were not anchored. DC surveys yielded total surface methane emissions due to both ebullition and diffusion and therefore account for the intermittency and spatial variability of ebullition. Two 2-day campaigns were conducted in which transects lasted up to an hour covering ~0.5 km. See Supporting Information for sampling and analysis details.

2.2.7 Methane oxidation

Two 2-day methane oxidation experiments were conducted in July 2008 according to the method of Bastviken et al. (2008), in which flexible air-tight containers were moored at 4.5 and 8.5 m depths in the reservoir. Water temperature was ~17°C during both campaigns. Enclosed waters were sampled every few hours for 2 days, corresponding to the average water residence time of the reservoir, and poisoned and analyzed using the same sampling procedure described in the Supporting Information for other water samples.

2.3 Results

2.3.1 Longitudinal and temporal changes of methane

Dissolved methane at the upstream sampling station ($[CH_4]_{IN}$) ranged throughout the year from 50 to 290 nM (average ~170 nM; Table A.1 in Supporting Information). At the dam, $[CH_4]_d$ before turbine passage ($[CH_4]_{OUT}$) ranged from 280 nM in winter to 2200 nM in summer (yearly average ~850 nM; Table A.1). Each longitudinal survey of $[CH_4]_d$ revealed immense increases of dissolved methane (up to 5x) along the reservoir and relatively well-mixed conditions vertically (e.g., Figure 2.1b). The average daily $[CH_4]_d$ discharge was estimated by integral averaging the product of the monthly $[CH_4]_d$ release and Q over the sampling year and dividing by reservoir surface area, thus yielding ~59 mg CH₄ m⁻² d⁻¹ (Table 2.1). The mass accumulation calculated for each survey was positively and exponentially correlated with water temperature (r^2 =0.92; Figure 2.2).

2.3.2 Sediment methane emissions

Sediment diffusion calculated from the 15 cores ranged from ~1 to 150 mg CH₄ m⁻² d⁻¹ (Table A.1) with an average of 41 ± 42 mg CH₄ m⁻² d⁻¹ (Table 2.1).

Gas traps that were deployed to capture sediment bubble flux (Figure A.1a) measured extremely variable ebullition rates (Table A.2, Supporting Information). The overall average was ~1000 \pm 1300 mg CH₄ m⁻² d⁻¹ (Table 2.1) and ~29% recovered no detectable ebullition. The standard deviation of the bubble flux measurements highlights the stochastic nature of ebullition over space and time. However, the mean fluxes and 95% confidence levels of the October 2007 survey measurements, in which locations were biased towards bubbling areas, were similar to those of the August 2007 survey when random locations were chosen (Figure A.2, Supporting Information). Gas samples contained on average 74% CH₄ and bubbles typically traveled <2 m through the water column before being collected in the funnel cylinder.

It was evident by the flux measurements and visual observations along the reservoir that there was considerable spatial heterogeneity in ebullition. Therefore, we used both the bathymetry and the similarity in flux measurements to divide the reservoir into 4 regions (Figure A.1a) with average rates of ebullition calculated for each region. Thus, a spatially-weighted ebullition flux from the sediment into the water column for the late summer/early fall season (~700 mg CH₄ m⁻² d⁻¹, Table 2.1) was found by summing the ebullition fluxes from the different regions.

2.3.3 Bubble dissolution and atmospheric emission

As it is impossible to accurately measure bubble dissolution and emission to the atmosphere, we performed a system mass balance described later in the System Analysis section. The first step, however, was to estimate which fraction of sediment-released bubbles dissolves in the water column and which fraction escapes to the atmosphere. These values were estimated using a bubble dissolution model (McGinnis et al., 2006) with boundary background $[CH_4]_d$ profiles, which ranged from 5 nM to 3500 nM, along with the parameters previously described. As bubbles typically contain mostly CH₄ and perhaps some nitrogen as they exit the sediment (Greinert et al., 2010), and as this calculation was to determine what fraction of the initial methane content of a bubble would reach the surface, we assumed 100% CH₄ concentration in the bubble model and found that ~70% of the initial methane in a bubble reaches the atmosphere with the remaining 30% dissolving in the water column upon ascent. In addition, selecting CH₄ compositions ranging from 70-100% did not significantly affect the results in terms of atmospheric CH₄ emissions (e.g., using 74% CH₄ composition in the model results in 65% of the initial CH₄ reaching the atmosphere).



Figure 2.2. Dissolved methane accumulation (net flux $[kg d^{-1}] = Q \times ([CH_4]_{OUT} - [CH_4]_{IN})$ or areal flux in mg CH₄ m⁻² d⁻¹ when divided by the lake area) in Lake Wohlen is very strongly and exponentially correlated with temperature. Methane sediment diffusion flux (grey points and dashed line) is treated as relatively constant through the year at ~20 mg m⁻² d⁻¹, while the exponential increase at temperatures >10°C (black points) is attributed to contributions from bubble dissolution.

As a first estimate using the gas trap volumetric measurements and the same regional subdivisions mentioned above, we calculated a spatially-weighted average for bubble dissolution as $\sim 220 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ and $\sim 480 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ as bubble emission to the atmosphere (Table 2.1).

2.3.4 Surface methane emissions

Based on the average surface $[CH_4]_d$, diffusion across the air-water interface was calculated with Equation (2) and ranged from ~0.1 to ~4 mg CH₄ m⁻² d⁻¹ (Table A.3 in Supporting Information) with an average of 1.5 ± 1.0 mg CH₄ m⁻² d⁻¹ (Table 2.1). The average directly-measured methane diffusion using all AC values was 12 ± 7 mg CH₄ m⁻² d⁻¹ (Table 2.1 and Table A.3) and was higher than the calculated fluxes, as also observed in other studies (Duchemin et al., 1999; Lambert and Frèchette, 2005). All DC samplings were used to estimate total CH₄ emissions from the reservoir surface (i.e., diffusion and ebullition) and the results varied greatly (Table A.3) with an average of 855 ± 824 mg CH₄ m⁻² d⁻¹ (Table 2.1).

2.3.5 Methane oxidation

The results from the methane oxidation experiments did not indicate significant, if any, methane oxidation over the residence time of water in the reservoir (data not shown). At no point during the course of the two oxidation experiments was a loss of methane observed.
Pathway (methods)	Notation	Point measurements ^a [mg CH ₄ m ⁻² d ⁻¹]	System-wide estimates ^a [mg CH ₄ m ⁻² d ⁻¹]	
Sediment Diffusion (porewater cores)	M_{SD}	41 ± 42	15 ± 9	
Surface Diffusion (anchored chambers - AC)	M_{WD}	12 ± 7		
Surface Diffusion ([CH ₄] _d , wind speed, BLE)	M_{WD}	1.5 ± 1.0		
Bubble Flux (average of all gas trap measurements)	M_{BF}	${\sim}1000\pm1300^{b}$		
Bubble Flux (gas traps spatially-weighted)	M_{BF}	~700 ^b	470 ^b	
Bubble Dissolution (bubble model & gas traps spatially- weighted)	M_{BD}	~220 ^b	140 ^b	
Surface Bubble Emission - (bubble model & gas traps spatially- weighted)	M_{BE}	~480 ^b	330 ^b	
Outflow ([CH ₄] _d)	M _{OUT}	~59 ^b	~58 ^{c,d}	
CH ₄ Oxidation	M _{OX}	negligible		
Total Atmospheric Emission (drifting chambers - DC)	M _{ATM}	855 ± 824^{b}	~156°	

Table 2.1.	Point measurements a	and system-wide	estimates from	n system	analysis	of Lake	Wohlen
		methane	fluxes.				

^a values are means \pm SD; ^bat 17°C; ^c annually-integrated daily average; ^d calculated as: $M_{SD} + M_{BD}$ + measured M_{IN} - measured M_{WD} ; [CH₄]_d, dissolved CH₄ concentration; BLE, Boundary Layer Equation

2.4 Discussion

2.4.1 System analysis

We used a system analytical mass balance approach to deduce the internal sources of methane to the water column and the CH₄ emission to the atmosphere based on the following considerations:

- The mass of CH_4 accumulating in the water as it passes through the reservoir is only from sediment diffusion (M_{SD}) and bubble dissolution (M_{BD}).
- Methane oxidation in the water column is negligible, as suggested by conducted experiments. Diffusion at the air-water interface represents the only sink for dissolved methane and is nearly negligible.

The only methane source to the water column during the winter was M_{SD}. Seasonal observations, measurements, and sonar surveys of Lake Wohlen (Del Sontro, unpublished data) indicate that ebullition is severely diminished during the colder winter months.

Thus, Lake Wohlen represents a relatively simple system for deducing the methane source fluxes - ebullition and sediment diffusion.

We began by calculating the M_{SD} values required to account for the observed [CH₄]_d during the 6 winter samplings (water temp < 10°C, November 2007 through April 2008) using Q for each day. This was performed by adjusting the sediment flux value until it most closely matched the observed concentration values ([CH₄]_d = M_{SD} /Q; see Figure 2.3b). The average of these calculated values (15 ± 9 mg CH₄ m⁻² d⁻¹, Table 2.1) was used as the baseline M_{SD} in the subsequent calculations (Figure 2.3a), meaning that M_{SD} represents a rather seasonally constant source of CH₄ to the water column, as demonstrated below.

Next, M_{BD} could be determined as the difference between the measured $[CH_4]_d$ accumulation and the amount contributed by the baseline M_{SD} for the Q at the time of sampling, i.e., any observed CH₄ accumulation in the water that cannot be attributed to M_{SD} must be due to the dissolution of CH₄ bubbles escaping the sediment. In fact, once the baseline M_{SD} was subtracted from the observations, the remaining CH₄ increases were exponentially correlated with temperature (Figure 2.2). M_{BD} can therefore be estimated as a function of temperature T (in °C) using

$$M_{BD} = 0.16e^{0.40T} \tag{3}$$

 $(r^2=0.92)$ for temperatures in the range 10-17°C. Estimated M_{BD} ranged from 12 mg m⁻² d⁻¹ at 11°C to ~130 mg m⁻² d⁻¹ at 17°C (the maximum temperature observed during sampling, Table 2.1). The estimated [CH₄]_d values fit the observed seasonal pattern of [CH₄]_d well, reproducing both seasonal patterns and the magnitude of net dissolved CH₄ in the reservoir (Figure 2.3a).

Finally, we used the estimated M_{BD} and the average fraction of CH_4 escaping rising bubbles (30%), as calculated from the bubble dissolution model, to determine the ebullition flux from the sediment (M_{BF} , 100%) and to the atmosphere (M_{BE} , 70%). Thus, we determined that M_{BF} ranges from ~40 mg CH_4 m⁻² d⁻¹ at 11°C up to ~470 mg CH_4 m⁻² d⁻¹ at 17°C resulting in a M_{BE} of ~30 to ~340 mg CH_4 m⁻² d⁻¹ to the atmosphere between 11°C and 17°C (Table 2.1).

2.4.2 Reservoir surface methane emissions

Ebullition emissions to the atmosphere at 17°C, as estimated by the system analysis (340 mg $CH_4 \text{ m}^{-2} \text{ d}^{-1}$), agrees remarkably well with the spatially-integrated M_{BE} from gas trap surveys (480 mg $CH_4 \text{ m}^{-2} \text{ d}^{-1}$), which were conducted throughout the reservoir also at ~17°C water temperature

(Table 2.1). DCs measured both diffusion and ebullition at the surface in ~17°C water, but resulted in much higher emissions (~855 mg CH₄ m⁻² d⁻¹) than the system analysis M_{BE} plus measured diffusion (340 mg CH₄ m⁻² d⁻¹ + 12 mg CH₄ m⁻² d⁻¹). The DC surveys, however, were not conducted throughout the reservoir, but rather only in a highly active ebullition region ~1-2 km from the dam. Ultimately, the system analysis provides a more reliable estimate as it averages emissions over space and time, while DC and gas trap measurements are spatially and/or temporally limited in resolution.

The daily CH_4 ebullition emission from Lake Wohlen at 17°C (340 mg CH_4 m⁻² d⁻¹) is comparable to most values reported for tropical reservoirs and much higher than the few values reported for temperate and boreal reservoirs (St. Louis et al., 2000; Soumis et al., 2005), except for a Finnish reservoir with comparable emissions (Huttunen et al., 2002). Lake Wohlen exhibits a large degree of seasonality in its emissions, therefore reporting a yearly-integrated average is more convenient for comparing methane emissions from other reservoirs.

On average throughout the year Lake Wohlen emits ~86 mg CH₄ m⁻² d⁻¹ via ebullition alone (M_{BE} , Figure 2.4), which still compares with or exceeds average estimates of ebullition from tropical, boreal and temperate reservoirs (St. Louis et al., 2000; Huttunen et al., 2002; Soumis et al., 2005; Abril et al., 2005). However, total surface emissions (diffusion plus ebullition) from some of the larger tropical reservoirs, such as Petit Saut in French Guiana (Abril et al., 2005) and Balbina in Brazil (Kemenes et al., 2007), far exceed Lake Wohlen's emissions, mostly due to the difference in surface area (~120 to 700 times larger).

2.4.3 System analysis constraints and limitations

One of the major assumptions needed for the system analysis is that methane oxidation in the water column is negligible, as our oxidation experiments confirmed. The lack of oxidation is most likely explained by the short residence time and well-mixed conditions in Lake Wohlen that (1) do not allow enough time for methane-oxidizing bacteria to colonize, and (2) contains relatively low levels of methane compared to the oxyclines of stratified waters where most oxidation occurs (Bastviken et al., 2002; Guèrin et al., 2007; Bastviken et al., 2008).

The average baseline M_{SD} calculated from the system analysis model ($15 \pm 9 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$) is well within the error of the average M_{SD} calculated from sediment cores ($41 \pm 42 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$). The variability between the results is likely because the baseline M_{SD} from the system analysis is a basin-wide estimate accounting for potential methane oxidation at the sediment surface because the observed [CH₄]_d in the water column was the basis of the estimation. The core-obtained values are point estimates that possibly underestimate oxidation near the sediment-water interface, which could lower the diffusive CH₄ flux by up to an order of magnitude (Frenzel et al., 1990).



Figure 2.3. Lake Wohlen system analysis results. **a**) Squares indicate measured dissolved methane in Lake Wohlen (outflow – inflow). Black squares indicate measurements at water temperatures, T, >10°C when ebullition is occurring, grey squares when T < 10°C (see Figure 2.2). Grey line – best fit of predicted concentration due to sediment diffusion (sed. diff.) only. Black line – model results for predicted CH₄ concentration using exponential fit for methane bubble dissolution (bub. diss.) as a function of temperature plus the constant sediment diffusion of 20 mg m⁻² day⁻¹ (Figure 2.2). **b**) CH₄ emission rates: Grey line – constant sediment diffusion input. Black thick line – predicted methane emission due to methane bubbles reaching the atmosphere (bub. escape). Black thin line – total predicted methane flux including discharge emissions.

The net methane increase estimated from the system analysis mostly agrees with the observed seasonal values, except for the December 2007 and January 2008 sampling that fall below the estimated $[CH_4]_d$ (Figure 2.3a). Some possible explanations are that (1) methane oxidation occurs in the water column, and/or (2) the outflow sample should have been matched with an inflow sample several days earlier in order to account for the residence time of up to one week during the winter season.

Because the temporal resolution of M_{SD} calculated from sediment cores was limited (July through December), M_{SD} throughout the temperature range of the reservoir (5°C - 20°C) was calculated using CH₄ diffusivity and solubility constants (details in McGinnis et al., 2006) to determine if there is any seasonality in diffusion. For this coarse calculation, we assumed that [CH₄]_d in the water column was negligible compared to porewater concentrations and that methane

saturation was reached by 10 cm depth, which is roughly consistent with Lake Wohlen cores (Sobek et al., in prep), and found that the diffusive CH₄ flux would be $31 \pm 2 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ and largely independent of temperature. Increasing the temperature from 5 to 20°C led to a ~30% decrease in CH₄ solubility (Figure A.3 in Supporting Information) and a concomitant ~30% increase in CH₄ diffusivity, resulting in seasonally stable diffusion. Hence, three independent estimates (cores, system analysis, and the saturation calculation) point towards a consistently low and seasonally stable sediment diffusion.

The sediment bubble flux approximation at $17^{\circ}C$ (470 mg m⁻² d⁻¹) is ~2/3 the gas trap-measured bubble flux (~700 mg m⁻² d⁻¹), but is well within the variability of the measurements. This small variability can be attributed to sampling bias towards active bubbling sites during some funnel surveys and the fact that funnel measurements only covered a very small fraction (10⁻⁵) of the reservoir area. Overall, the bubble flux approximation derived from the system analysis is more accurate because it is based on a spatially- and temporally-integrated dataset (i.e., the monthly [CH₄]_d samplings and Q).

Sediment ebullition was estimated via the bubble dissolution model and the relationship between temperature and $[CH_4]_d$ accumulation, implying that seasonal changes in $[CH_4]_d$ accumulations were best described by temperature (Figure A.3 in Supporting Information) (Nozhevnikov et al., 1997; Christensen et al., 2003). However, lake level changes have been shown to strongly influence ebullition rates (Smith et al., 2000; Ostrovsky 2003; Ostrovsky et al., 2008) and hence $[CH_4]_d$ values. Lake Wohlen does experience slight seasonal and moderate daily water level changes of less than 10 cm, which are due to hydropower operations. We performed a principal component analysis on water level fluctuation, temperature, and $[CH_4]_d$ accumulation, and found that temperature was much more strongly correlated with $[CH_4]_d$ than was any parameter describing the extent or rate of water level fluctuation (data not shown). While the <1% daily difference in hydrostatic pressure probably impacts the hourly variability in emission rates, longerterm average rates should be relatively unaffected.

2.4.4 Extreme methane emissions – maximum potential output

The $[CH_4]_d$ input from sediment diffusion and bubble dissolution within the water column is discharged through the turbines and what is not degassed there will eventually be released further downstream. Thus, total methane emission from the reservoir can be up to 500 mg CH₄ m⁻² d⁻¹ (>1 ton per day) on warm summer days (Figure 2.3b). On average throughout the year Lake Wohlen emits >150 mg CH₄ m⁻² d⁻¹ corresponding to > 40 g C m⁻² y⁻¹ (M_{ATM}, Figure 2.4). While this annual carbon emission is several orders of magnitude lower than that of the large tropical reservoirs (Abril

et al., 2005; Kemenes et al., 2007), it is the highest recorded for a temperate reservoir to date and, in contrast to the tropical reservoirs, the majority of the emission is due to ebullition (~80%, M_{BF} ; Figure 2.4). In addition, Saarnio et al. (2009) estimated CH₄ from European water bodies and the CH₄ emission rate of Lake Wohlen is well above that of the average small lake.



Figure 2.4. Average basin scale methane fluxes and pathways in L. Wohlen in mg CH₄ m⁻² d⁻¹ ($g \ C \ m^{-2} \ yr^{-1}$) derived from the system analysis or, if not available, from measurements. Pathways are: M_{ATM}, emission to atmosphere; M_{WD}, water surface diffusion; M_{BE}, bubble emission to atmosphere; M_{BD}, bubble dissolution; M_{SD}, sediment surface diffusion; M_{IN}, dissolved methane input; M_{OUT}, methane discharge passed dam; M_{BF}, sediment bubble flux driving the entire methane balance. Dashed lines outline bubble pathway. Main portion of methane is directly released to the atmosphere and the second part is dissolved to the water phase.

Finally, at the current yearly average water temperature of 11° C the reservoir emits ~0.2 tons of CH₄ per day via surface emissions and discharge. The projected temperature increase of 3° C in the coming century (Forster et al., 2007) could result in a doubling of CH₄ emission from Lake Wohlen, given the exponential dependence of CH₄ emission on temperature (Figure 2.2). Even if this statement is highly speculative, it clearly illustrates the need for further investigations on the temperature dependence of CH₄ emissions from lakes and reservoirs.

2.4.5 Implications

Our findings indicate that this 90-year-old, temperate reservoir is a very significant CH_4 source, almost entirely due to bubbling sediments. In addition, we found that $[CH_4]_d$ accumulation was highly temperature-dependent in Lake Wohlen and allowed us to estimate methane emissions using the $[CH_4]_d$ accumulation and flow rate of the reservoir. Even though the results of this study clearly point to a relationship between temperature and methane emission, many questions remain open

regarding what is causing such intense methane production and subsequent ebullition in this small oxic reservoir, especially since the 10-year high emission period following damming that has been observed in newly dammed reservoirs is long over (Abril et al., 2005).

A potential explanation is the combination of reservoir characteristics that made Lake Wohlen an easy system to analyze - a flow-through reservoir with a short residence time and minimal oxidation - as well as its high organic carbon load (~25 tons per day) and fast sedimentation rate (Sobek et al., in prep) all leading to an exceptional rate of methanogenesis, supersaturation, and subsequent ebullition. The high organic carbon load comes from several sources - (1) passage of the Aare River through the capital city, Bern (population >100,000), including input from several wastewater treatment plants; (2) drainage of the large Alpine and agricultural river basin (Zobrist et al., 2006) yielding terrigenous carbon; and (3) the input from two large Pre-alpine lakes, Brienz and Thun. Consequently, similar run-of-river reservoirs lying downstream of such organic carbon sources may also be large CH₄ producers. Therefore, the sampling and system analysis methods outlined in this paper are quite appropriate for studying other similar systems and could even be adapted for use in more complex ones. Depending on access to the reservoir, monthly inflow/outflow samplings are not too time-consuming and essential to this method. More detailed campaigns could include coring, funnel, and chamber surveys conducted seasonally when water temperature differences are obvious.

On a global scale of methane emissions from reservoirs, temperate ones are often overlooked because the largest reservoirs reside in tropical regions where warm temperatures support methanogenesis year round (St. Louis et al., 2000; Soumis et al., 2005; Lima et al., 2008). Our findings indicate that temperate reservoirs with high carbon inputs and burial rates (Sobek et al., 2009), as well as the sources of these carbon inputs, should be given some consideration in current greenhouse gas budgets, especially in a changing climate. A more detailed analysis of the biogeochemical and geographic setting of reservoirs in temperate areas is needed when assessing global methane emissions from water bodies.

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2.6 Appendix A

2.6.1 Extended methods section

Methane inflow, outflow, and distribution

Dissolved methane ($[CH_4]_d$) water samples were taken with a Niskin bottle and transferred to CuCl-poisoned 125 ml serum bottles, which were closed air-free according to a known method (Bastviken et al., 2002; Guèrin et al., 2007). $[CH_4]_d$ was measured via gas chromatography (Agilent 6890N Network Gas Chromatograph) with a flame ion detector (GC/FID) using the headspace method (McAllufie, 1971).

Sediment methane emissions

Porewater methane concentrations were measured in 15 cores from the reservoir (Sobek et al., 2009). Cores were taken using a custom-made gravity corer and a core tube with taped-over holes spaced every 1 cm. Two ml of sediment was extracted through the taped holes using a cut-off syringe and placed in 25 ml vials containing 4 ml of 2.5% NaOH. The vial was sealed immediately using a gas-tight butyl-rubber stopper and an aluminum crimp seal, shaken, and then stored upside down until analysis.

Custom-made gas traps with a collecting area of 0.785 m² were used to capture sediment ebullition. An air-tight cylinder of known volume with a septum-lined cap was screwed onto the top of the funnel for gas collection and sampling. The traps were deployed using a moored buoy system that allowed the funnel to hang upright ~1 m above the reservoir bottom (Figure A.1b). When deploying the funnels, care was taken to avoid catching gas bubbles that might be liberated from the sediments upon anchoring. Gas samples were taken from the cylinder top and transported to a N₂-filled serum bottle for measurement via GC/FID.

Surface methane emissions

Anchored chambers (ACs) consisted of a floating top bucket (22 L, 26 cm high) that collected gas diffused from ~855 cm² of the water surface and was connected to a much larger bucket ~0.3 m below the surface that caught rising bubbles, if any, and vented them to the atmosphere via a buoyed release hose before they could enter the upper diffusion bucket (Figure A.1c). Drifting chambers (DCs) were constructed the same way as ACs, but without the bottom bucket that directed bubbles directly to the atmosphere. Thus, DCs collected both diffusion and ebullition emissions. Gas collected in ACs and DCs were sampled in the same manner. Ten ml of gas was extracted and discarded before 20 ml was extracted and injected into 30 ml serum bottles. Serum bottles were

already capped with a butyl-rubber stopper and aluminum cap and filled with a saturated NaCl solution preventing CH_4 dissolution. An open needle allowed the NaCl solution to exit the bottle while the gas was injected and samples were stored upside down. Gas samples were measured via GC/FID as described above.

2.6.2 Supplementary result tables

$[CH_4]_d$		[CH	[4] _d	Sed. Diff. ^a			
Infl	0W 1	Outflow		Flux $(-2 - 2 - 1)$			
(<u>II</u>) Turna 2007	<u>(1)</u>	(n.vi)		(mg m u)			
June 2007 -	June 2008	June 2007 -	June 2008	2000-2007			
29	5	104	42	70			
49)	83	3	30			
27	6	79	8	19			
13	7	150	08	23			
14	3	79	4	19			
19	195		1	14			
13	4	2217		55			
23	9	1198		69			
22	6	811		18			
25	7	880		147			
10	0	282		4			
71	l	287		16			
11	5	766		114			
24	0	393		19			
12	1	457		1			
16	8	612					
173 +	- 76 ^b	851 + 486 ^b		$41 + 42^{b}$			

Table A.1. Inflow and outflow dissolved CH₄ concentrations ([CH₄]_d) and core-obtained sediment diffusion CH₄ fluxes

^aSed.Diff., sediment diffusion fluxes obtained from porewater core profiles ^baverage <u>+</u> standard devation;

Flux (duration)	Temperature (Region)	Flux (duration)	Temperature (Region)
mg m ⁻² d ⁻¹ (hh:mm)	°C (Figure A.1a)	mg m ⁻² d ⁻¹ (hh:mm)	°C (Figure A.1a)
8/2007	8/2007	10/2007	10/2007
145 (2:09)	18 (1)	0 (1:39)	16 (1)
1423 (2:11)	18 (1)	733 (3:56)	16 (1)
2356 (2:15)	18 (1)	472 (2:05)	16 (1)
2445 (2:25)	18 (2)	162 (1:15)	16 (1)
2526 (1:45)	18 (2)	552 (2:58)	16 (2)
5758 (1:17)	18 (2)	2126 (2:23)	16 (2)
935 (1:45)	16 (3)	5 (15:47)	16 (1)
577 (1:52)	16 (3)	1308 (1:58)	14.5 (2)
1068 (1:43)	16 (3)	2085 (2:46)	14.5 (2)
1823 (1:58)	16.5 (2)	1058 (1:24)	14.5 (2)
321 (2:23)	16.5 (2)	147 (3:43)	14.5 (2)
0 (1:56)	16.5 (1)	4158 (1:48)	14.5 (2)
0 (1:49)	16.5 (1)	3541 (2:24)	14.5 (2)
0 (16:11)	16.5 (1)	1916 (1:45)	14.5 (2)
0 (2:43)	16.5 (2)	825 (4:55)	14.5 (2)
0 (1:54)	16.5 (3)	176 (16:25)	14.5 (2)
0 (1:59)	16 (3)	567 (15:08)	14.5 (2)
0 (2:02)	16 (4)		
0 (1:30)	16 (4)		
0 (1:39)	16 (4)		
0 (14:26)	16.5 (4)		
922 ± 651^a		1166 ± 632^{a}	

 Table A.2. Gas trap (funnel) survey fluxes, duration, and location

^aAverage ± 1 standard deviation; also see Figure A2

BLE ^a	AC	BLE ^b	BLE ^b DC	
Flux	Flux (duration)	Flux	Flux (duration)	Flux (duration)
June 2007- June 2008	July 2008	July 2008	23-24 July 2008	29-30 July 2008
1.2	30 (2:41)	1.0	198 (00:39)	11 (00:28)
2.3	28 (1:46)	1.0	176 (00:41)	396 (00:36)
2.6	14 (2:47)	1.1	973 (00:34)	868 (00:24)
1.1	7 (15:30)	0.7	1940 (00:41)	2587 (1:46)
1.8	14 (2:04)	0.8	341 (00:35)	29 (00:41)
1.7	12 (2:57)	0.7	21 (00:33)	1413 (00:28)
2.8	21 (1:58)	1.2	1284 (00:28)	194 (00:31)
1.6	9 (2:42)	1.3	2442 (00:37)	1464 (00:38)
3.9	7 (15:17)	0.8	62 (00:33)	323 (00:33)
1.9	13 (2:08)	0.7	16 (1:00)	1275 (1:24)
2.6	10 (3:08)	0.7	778 (00:33)	413 (00:38)
1.7	12 (4:13)	0.5	28 (00:34)	1237 (00:30)
0.4	8 (2:19)	0.7		804 (00:29)
0.8	7 (18:00)	0.8		497 (00:56)
0.8	9 (2:48)	1.8		2886 (00:28)
0.1	15 (3:48)	1.1		1094 (1:46)
0.6	7 (2:42)	1.5		54 (00:35)
0.1	8 (18:06)	0.7		1139 (00:32)
0.7	10 (2:46)	1.5		
0.8				
$1.5 \pm 1.0^{\circ}$	12 <u>+</u> 7 ^c	1.0 ± 0.4^{c}	$735 \pm 850^{\circ}$	930 ± 824^{c}

Table A.3. Surface emission chamber fluxes (mg m⁻² d⁻¹) with deployment duration (hh:mm) and Boundary Layer Equation* (BLE) calculations for diffusion

AC is anchored chamber. DC is drifting chamber. *Using parameterization from Crusius and Wanninkhof (2003); ^a BLE used to calculate surface diffusion during the 20 different samplings throughout the year; ^bBLE used to calculate surface diffusion for the times of the anchored chambers; ^cAverage <u>+</u> standard deviation

2.6.3 Supplementary figures



Figure A.1. a) Gas trap sites during August (filled triangles) and October surveys (empty triangles) in 2007. Stars are inflow (east end) and outflow (west end) sampling stations. The regional subdivision of Lake Wohlen based on gas ebullition is also shown. **b)** Custom inhouse designed gas trap funnel in moored buoy system. **c)** In-house developed diffusion floating chamber with bubble catcher. Drifting chambers consisted of a similar set-up but without the bubble catcher bucket.



Figure A.2. The mean and 95% confidence level of the October funnel survey, when bubbling locations were specifically chosen, overlap with and are very similar to the mean and 95% confidence level of the August funnel survey, when all locations were randomly chosen (also see Table A.2).



Figure A.3. Saturation concentration of methane decreases with temperature, while methanogenesis increases with temperature (data adapted from Nozhevnikova et al., 1997) creating a potential threshold of ebullition at $\sim 10^{\circ}$ C.

Chapter 3

Extreme organic carbon burial fuels intense methane bubbling in a temperate reservoir

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Abstract

Organic carbon (OC) burial and greenhouse gas emission of inland waters plays a central role in the carbon balance of the continents, and particularly young reservoirs in the tropics emit methane (CH₄) at high rates. Here we show that an old, temperate reservoir acts simultaneously as a very strong OC sink and CH₄ source, because the high sedimentation rate supplies reactive organic matter to deep, anoxic sediment strata, fuelling methanogenesis and gas bubble emission (ebullition) of CH₄ from the sediment. Damming of the river has resulted in the build-up of highly methanogenic sediments under a shallow water column, facilitating the transformation of fixed CO₂ to atmospheric CH₄. Similar high OC burial and CH₄ ebullition is expected in other reservoirs and natural river deltas.

3.1 Introduction

In spite of their relatively small areal extent, inland waters play an important role in the carbon balance of the continents, both as carbon sinks due to the burial of organic carbon (OC) in the sediments, and as carbon sources due to the emission of the greenhouse gases carbon dioxide (CO_2) and methane (CH_4) to the atmosphere (Aufdenkampe et al., 2011; Battin et al., 2009; Tranvik et al., 2009; Dean and Gorham, 1998). Even though inland water CH4 emission is small in terms of carbon units compared to CO_2 emission, the 25 times higher global warming potential of CH_4 as compared to CO_2 implies that CH_4 emission from inland waters is relevant for the Earth's climate. Accordingly, it was recently estimated that inland water CH_4 emission offsets about 25% of the carbon sink on land (Bastviken et al., 2011). Particularly recently constructed hydroelectrical reservoirs in the tropics have been shown to emit CH_4 at high rates (Kemenes et al., 2007; Abril et al., 2005; Soumis et al., 2005; Tremblay et al., 2005; St. Louis et al., 2000).

In aquatic systems, OC burial and usually also CH_4 production are confined to the sediments. Of the OC being deposited onto the sediment surface, a certain part will be mineralized to either CO_2 or CH_4 , and the remainder will be buried in the sediment over geologic timescales. More detailed knowledge of factors regulating the OC fate in freshwater sediments is particularly relevant with respect to reservoirs, since they have been estimated to buy more OC in their sediments than the entire ocean (Dean and Gorham, 1998) and, at the same time, emit CH_4 equivalent to 18% of the total anthropogenic atmospheric emissions (St. Louis et al., 2000). Moreover, the global area of reservoirs is increasing (Downing et al., 2006), augmenting their role as OC sinks and CH_4 sources. Despite recent advances in our understanding of sediment OC fate (Gudasz et al., 2010; Sobek et al., 2009), large gaps remain. Importantly, the share of sediment OC that is converted to CH_4 and vented to the atmosphere can currently not be predicted from sediment properties. This is at least partially because CH_4 is emitted from sediments not only via diffusion, but also via ebullition, i.e., gas bubbles, which is frequently a major emission pathway to the atmosphere (Bastviken et al., 2004) and difficult to assess due to its stochastic nature. We report here results from studies of Lake Wohlen, a small hydroelectric reservoir in Switzerland, allowing us to relate sediment properties to both OC burial, and, for the first time, to CH_4 ebullition.

3.2 Materials and Methods

3.2.1 Site description

We conducted studies at Lake Wohlen, a small (2.5 km²) and shallow (mean depth 9 m) hydroelectric reservoir in Switzerland, constructed in 1920. Lake Wohlen is a mesotrophic to eutrophic run-of-river reservoir along the Aare river, and has an average water retention time of \sim 2 days (Albrecht et al., 1998). The water column is generally well-mixed and permanently oxygenated (DelSontro et al., 2010). A detailed study based on gas traps and mass balance calculations showed that CH₄ emission from Lake Wohlen to the atmosphere was the highest ever documented for a temperate reservoir, and mainly attributable to ebullition (DelSontro et al., 2010).

3.2.2 Sediment sampling and analyses

The sediments of Lake Wohlen were sampled with a gravity corer at 8 sites, from the dam upstream towards the inflow area (Figure B.1). At each sampling site, multiple sediment cores were sampled and analyzed for physicochemical properties, for oxygen penetration depth, and for dissolved methane in the sediment porewater. Details of methods are published in our recent study on lake sediments (Sobek et al., 2009). Additional information on methods can be found in the auxiliary material.

3.3 Results and Discussion

3.3.1 Sediment characteristics and burial efficiency

The sediments were relatively similar at all coring sites (Table B.1) with low OC content (range 0.27 - 2.8%), low water content (range 23 - 60%), low porosity (range 0.43 - 0.79). Mineral particles were mainly silt-sized (range of median grain size, $8-80 \mu$ m), apart from a sand layer in core H. The organic matter in Lake Wohlen sediments originates primarily from terrestrial sources, as suggested by independent indicators (see auxiliary material). Sedimentation rates were very high

and variable (range 5.2 - 11.5 cm yr⁻¹; Table 3.1), resulting in substantial but variable OC burial rates (range 569 - 1980 g C m⁻² yr⁻¹; Table 3.1). OC burial in Lake Wohlen was at the high end compared to other reservoirs (mean 500, range 14 - 3300 g C m⁻² yr⁻¹; Mulholland and Elwood, 1982), beyond the observed range for natural lakes (maximum OC burial in lakes 300 g C m⁻² yr⁻¹; Mulholland and Elwood, 1982; Sobek et al., 2009) and only surpassed by eutrophic farm ponds (mean 3200, range 148 - 17,392 g C m⁻² yr⁻¹; Downing et al., 2008). OC mineralization in Lake Wohlen sediment (range 86-229 g C m⁻² yr⁻¹) was within the range usually observed in freshwater sediments (16-740 g C m⁻² yr⁻¹) (Gudasz et al., 2010) and much lower than OC burial at all sites (Table 3.1), thus returning the highest OC burial efficiencies (buried OC : deposited OC; range 83 - 94%) in freshwater sediments so far reported in the literature (Sobek et al., 2009). Clearly, the sediments of Lake Wohlen constitute a strong and efficient OC sink.

Site	Sedimentation rate (cm yr ⁻¹)	O ₂ exposure time (d)	Mineralization (g C m ⁻² yr ⁻¹)	OC burial (g C m ⁻² yr ⁻¹)	OC burial efficiency (%)
А	5.2	22	95	536	85
В	5.3	50	86	656	88
С	7.4	7	173	1040	86
D	7.9	4	229	1110	83
Е	6.8	n.d.	n.d.	1120	n.d.
F	11.5	5	108	1660	94
G	11.3	n.d.	n.d.	1950	n.d.
Н	7.1	9	123	837	87
Mean+sd	78 + 24	16 + 18	136 + 55	1113 + 482	87 + 4

Table 1. Sedimentation rates, oxygen exposure times and carbon fluxes in Lake Wohlen sediments. n d = not determined

It is likely that the very high OC burial efficiencies in Lake Wohlen are linked to the extremely short oxygen exposure times. The rapid sedimentation rates of about 5-11 cm yr⁻¹ in conjunction with oxygen penetration depths of about 1 - 7 mm limits oxygen exposure time to a few days or weeks (Table 3.1). The fast transfer to anoxic sediments can be expected to limit the mineralization of the sediment OC as the OC burial efficiency of both marine and freshwater sediments has been shown to be negatively related to oxygen exposure time (Hartnett et al., 1998; Sobek et al., 2009).

3.3.2 Methane emission in relation to sediment characteristics

CH₄ emission surveys showed that ebullition from the sediments released about 33 g C m⁻² yr⁻¹ of CH₄ to the water column, of which 24 g C m⁻² yr⁻¹ directly reached the atmosphere (DelSontro et al., 2010). The proportion of gas bubbles that dissolved during ascent (9 g C m⁻² yr⁻¹) contributed greatly to CH₄ emission during turbine passage (16 g C m⁻² yr⁻¹). Adding CH₄ emission via

diffusion over the water-air interface, the estimated total CH₄ emission from Lake Wohlen to the atmosphere was 43 g C m⁻² yr⁻¹ (DelSontro et al., 2010). This is roughly one order of magnitude higher than the average CH₄ emission reported from temperate reservoirs (4.6 - 5.5 g C m⁻² yr⁻¹; Bastviken et al., 2011; Soumis et al., 2005; St. Louis et al., 2000) or lakes (3.2 g C m⁻² yr⁻¹; Bastviken et al., 2011), and within the range of the reported average CH₄ emission from tropical reservoirs (37 - 82 g C m⁻² yr⁻¹; Bastviken et al., 2011; Soumis et al., 2011; Soumis et al., 2011; Soumis et al., 2005).



Figure 3.1. Degradation indices (DI) of selected cores, calculated from the amino acid composition (Dauwe et al., 1999). (A) DI profiles at site B (filled circles) and site C (open circles). (B) DI profiles at site D (filled circles), site E (open circles) and site G (grey triangles). The lower the DI, the more degraded is the organic matter. For comparison, the DI of highly reactive plankton debris is in the range of 1 - 1.5, while highly degraded deep-sea sediments have DIs as low as -2.

We propose that the extreme CH₄ ebullition in Lake Wohlen is ultimately attributable to very high sedimentation rates that result in limited oxic degradation of organic matter and rapid transfer of OC to deeper sediment layers. Profiles of the amino acid-derived degradation index (DI) (Dauwe et al., 1999), which links the amino acid composition of organic matter to its reactivity, remained generally well above zero throughout the entire sediment column (Figure 3.1), indicating the presence of reactive organic matter in relatively deep sediment layers. This is unusual since the reactivity of organic matter rapidly declines with age (Middelburg et al., 1993), thus DI tends to decrease with depth in sediments (Meckler et al., 2004; Dauwe et al., 1993). Substantial OC reactivity was reflected in dissolved CH₄ concentration in sediment porewater being close to or above saturation below ~10 cm depth at most sites (Fig. 3.2, cores C, D, E, G). Contrarily, site B had a significantly lower DI than all other sites (Anova, Tukey post-hoc test, $F_{4,69}=7.27$, p=0.001) and porewater dissolved CH₄ was far below saturation throughout the core (Fig. 3.2). This strongly

suggests that high sedimentation rates rapidly shunt organic matter to deep sediment layers, where its reactive fraction fuels methanogenesis. As diffusion over tens of cm in low-porosity sediment (mean 0.68) is very limited, deeply formed CH₄ is bound to accumulate at depth, leading to supersaturation and consequent bubble formation and release. It is likely that this mechanism (Fig. 3.3a) is valid in freshwater sediments so long as sedimentation rate is high, and organic matter reactivity is high enough to sustain methanogenesis rates higher than CH₄ diffusion rates (see also auxiliary material). After release from the sediment, the fate of the CH₄ contained in a bubble depends on the depth of the water column. The majority of bubbles released in deep water (> ~40m) will substantially dissolve during rise, subjecting the dissolving CH₄ to oxidation by aquatic methanotrophs. If bubbles are released from shallow sediments (< ~10 m water depth), such as in Lake Wohlen, most of the bubble gas will reach the atmosphere, thus bypassing the aquatic methane oxidizers, and resulting in high atmospheric CH₄ emission (McGinnis et al., 2006).



Figure 3.2. Examples of profiles of dissolved CH_4 in the porewater of Lake Wohlen sediments. (A) CH_4 profiles at site B (filled cicles) and site C (open circles); water depth at these sites is 13 m. (B) CH_4 profiles at site D (filled cicles) and site E (open circles); water depth at these sites is 8 m. Dotted lines indicate the saturation concentration of CH_4 .

3.3.3 Effects of river damming on the carbon budget

In terms of carbon units, OC burial (1110 g C m⁻² yr⁻¹) outweighs the sum of CH₄ emission (43 g C m⁻² yr⁻¹) and CO₂ emission (24 g C m⁻² yr⁻¹; calculated from measured dissolved inorganic carbon concentration, temperature, pH, and wind speed). Accounting for the 25 times higher global warming potential of CH₄ compared to CO₂ returns a total greenhouse gas emission of 1520 g CO₂-equivalents m⁻² yr⁻¹, or roughly 40% of OC burial (4070 g CO₂-equivalents m⁻² yr⁻¹). However, such a budgeting would describe the effect of damming inappropriately; in the absence of Lake Wohlen dam, a large fraction of the suspended sediment load currently deposited in the reservoir would be

deposited in the natural downstream lake (Lake Biel) and thus replace Lake Wohlen as a strong OC sink. Reports of high OC burial efficiencies in the river mouths of natural lakes (60-80%; Sobek et al., 2009) support this assumption. On the other hand, assuming that methanogenesis was as intense in Lake Biel (in the absence of the dam) as it presently is in Lake Wohlen, only ~30% of the methane in a 6 mm bubble released from the mean depth of Lake Biel (31 m) would reach the atmosphere (McGinnis et al., 2006). The corresponding number for shallow Lake Wohlen is ~75%, suggesting the key effect of damming was the creation of highly methanogenic sediments overlain by only a shallow water column, resulting in a substantial increase in the transformation of fixed CO_2 to atmospheric CH_4 .



Figure 3. Conceptual graph of methane production and emission in freshwater sediments. (A) Lake Wohlen sediments have very high sedimentation rates (several cm yr⁻¹), resulting in minimal oxygen exposure times and reactive organic matter (as indicated by positive degradation indices) rapidly being transferred to deep sediment layers. This fuels substantial methanogenesis over the entire sediment profile (shaded area). Deeply formed methane accumulates at depth due to limited diffusion, until supersaturation leads to the formation and rise of gas bubbles. Values were taken from DelSontro et al., (2010). (B) Lake Zug in Switzerland, serving as an example of a typical lake sediment with moderate sediment (Meckler et al., 2004). Methane production is confined to surficial sediments, from where the methane can diffuse across the sediment-water interface (value is based on own data); hence accumulation of CH₄ in the sediment, followed by ebullition, is unlikely (see auxiliary material).

3.4 Implications

These results from Lake Wohlen suggest that in general, shallow inland waters with high sedimentation rates and significant organic matter reactivity ought to be considered potential CH_4 ebullition hot spots. Such conditions apply for river deltas in natural lakes but they are particularly prevalent in man-made impoundments, such as reservoirs and farm ponds (Sobek et al., 2009; Downing et al., 2008; Mulholland and Elwood, 1982). Therefore, we expect a significant and presently unaccounted CH_4 ebullition flux to the atmosphere from a variety of different freshwater systems. Consequently, inland water CH_4 emission to the atmosphere most likely offsets even more than the currently estimated 25% of the terrestrial carbon sink (Bastviken et al., 2011), especially since the globally impounded water surface area is predicted to double within the next 50 years if current growth rates are maintained (Tranvik et al., 2009; Downing et al., 2006).

3.5 Acknowledgements

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3.6 Appendix B

3.6.1 Extended methods

Grain size was determined by laser diffraction (Malvern Mastersizer). Oxygen penetration depths were measured in sediment cores using microsensors (Sobek et al., 2009), and were similar to published *in-situ* profiler measurements in Lake Wohlen (~2 mm; McGinnis et al., 2008). Site A was sampled in winter and summer, while the other sites were sampled once in summer. Oxygen penetration depths at site A in both winter and summer fell within 1.4 ± 0.2 mm (mean \pm standard deviation), indicating that the seasonal variation of oxygen penetration depth was low.

Determination of sedimentation rates

Due to the heterogeneous sedimentation regime in the reservoir, profiles of ¹³⁷Cs or ²¹⁰Pb could not be used to calculate sedimentation rates. Instead, sedimentation rates were derived from water depth surveys, conducted by the hydropower company (BKW, Switzerland) along 31 transects in 1990 and 2004. The difference in standardized water depth at a survey location was assumed to correspond to the average sedimentation rate during this 14-year period. Precision of the depth measurement was ± 1 cm, resulting in a sedimentation rate precision of $\pm 2\%$ on average. For each of the coring sites, the sedimentation rates of 2-4 nearby depth survey locations (mean distance form coring sites, 93 m) were averaged to represent the sedimentation rate of the coring site. The high sedimentation rates are corroborated by dividing the mean POC load in the Aare River upstream Lake Wohlen (139 g C s⁻¹; derived from biweekly monitoring data available for the years 1994-1996) with the lake area. Assuming that the entire POC load is deposited homogenously in Lake Wohlen returns a mean POC deposition of 1740 g C m⁻² yr⁻¹, i.e. the same order of magnitude as the sedimentation rate estimates derived from the water depth surveys.

Calculations

The burial efficiency of organic carbon (OC BE) was calculated as the ratio between OC burial (i.e., mean mass accumulation rate in the sediment, g C m⁻² yr⁻¹) and OC gross sedimentation (i.e., mean mass deposition rate onto the sediment surface, g C m⁻² yr⁻¹). Gross sedimentation was calculated as the sum of OC burial and OC mineralization. OC mineralization was calculated from porewater profiles of oxygen and methane using Fick's first law of diffusion. Oxygen fluxes were converted to carbon dioxide fluxes using a respiratory quotient of 0.9 (Granéli, 1979). Total OC mineralization was calculated as the sum of diffusive CO₂ and CH₄ flux from the sediment to the water column, plus the mean CH₄ ebullition flux from Lake Wohlen sediment (33 g C m⁻² yr⁻¹; DelSontro et al., 2010). Likewise, the mean CH₄ ebullition flux was subtracted from the calculated sediment OC accumulation rates in order to get OC burial, since CH₄ ebullition stems from non-buried portion of OC in deeper sediment layers. Oxygen exposure time was calculated by dividing the mean oxygen penetration depth by the sedimentation rate.

Amino acid analyses and degradation index

The degradation index (DI) was calculated from concentrations of hydrolysable amino acids in 5 selected cores, measured on a HPLC system (Dauwe et al., 1999). First, about 100 mg freezedried and homogenized sediment samples were hydrolyzed under N₂ atmosphere in 5 mL 6 M HCl at 100 °C for 24 h. Then the samples were centrifuged (5000 g, 10 min) and the supernatant was stored at -20 °C until analysis. An aliquot of 100 μ L was neutralized with 6 M NaOH. Fluorescent OPA (o-phtaldialdeyde) derivatives were formed prior to injection in a precolumn system. The amino acid derivatives were separated and detected on a HPLC system (Jasco) with a Nova-Pak C18 column (150 x 3.9 mm, Waters) and a fluorescence detector. Quantification was accomplished with a standard mixture of amino acids (AA-S-18, Sigma), with addition of the non-protein amino acids β-alanin (Merck) and γ -aminobutyric acid (Sigma). Analytical precision was ± 5%. With this method, the amino acids cysteine, tryptophan, proline, asparagine and glutamine could not be quantified. The DI was developed on marine sediments, but the high similarity in amino acid composition between aquatic and terrestrial organisms (Cowie and Hedges, 1992) makes the DI applicable to freshwater sediments as well (Meckler et al., 2004).

3.6.2 Extended discussion

Sources of organic matter

Several independent indicators suggest that the OC in Lake Wohlen sediments is primarily derived from terrestrial sources. First, the mean C:N ratio of sediment organic matter was 12.4, which is far from the C:N typically observed in phytoplankton (~7), and indicative of vascular plant-derived material. Second, amino acids contributed on average 9.7% (range 2.5 - 24%) to the total sediment OC, suggesting that the OC originates mainly from leaves and grasses, and that phytoplankton is a minor contributor (typical amino acid content >50% of OC; Cowie and Hedges, 1992). Third, the high content of lignin phenols (mean 2.4 % of OC, range 0.29 - 4.63) as well as their composition (ratio of cinnamyl to vanninyl phenols: mean 0.32, range 0.15 - 0.49; Schubert and Sobek, unpublished data) in sediment surface layers in 5 of the cores indicate a substantial share of leaf and grass-derived terrestrial OC in Lake Wohlen sediments. Hence, the two potential sources of aquatic organic matter, the upstream lakes Brienz and Thun, as well as primary production within Lake Wohlen, did not leave a discernable imprint in Lake Wohlen sediments. Possibly, effective OC sedimentation in the deep upstream lakes (maximum depth 261 and 136 m in lakes Brienz and Thun, respectively) prevents substantial export of aquatic organic matter, or particulate organic matter flushed out from the lakes may be effectively mineralized during deposition-resuspension cycles before reaching Lake Wohlen >40 km further downstream. Further, the water retention time of Lake Wohlen (~ 2 d) is similar to in-situ generation times of phytoplankton (Reynolds, 1984), precluding the establishment of viable phytoplankton populations in spite of meso- to eutrophic conditions (median total phosphorus 17 μ g L⁻¹, total nitrogen ~1.16 mg L^{-1} ; based on monthly monitoring by the Canton of Berne). Likewise, the terrestrial signature of the sediments indicates that benthic primary production probably largely is limited to shallow banks

of Lake Wohlen (McGinnis et al., 2008). Importantly, as only a small share (\sim 3%) of the OC deposited on the sediment is emitted as CH₄ via ebullition, the characteristics of the bulk sediment OC can not be used to constrain the source of the small reactive OC fraction driving methanogenesis in Lake Wohlen sediments.

Organic matter reactivity and sedimentation rate regulate ebullition

High organic matter reactivity is not enough to give rise to substantial ebullition, if not accompanied by high sedimentation rate, as exemplified by eutrophic Lake Zug in Switzerland (Figure 3.3b). As is typical for most natural lake sediments, the moderate sedimentation rate (~4 mm yr⁻¹) restricts the presence of reactive organic matter to the uppermost centimeters of Lake Zug sediment (Meckler et al., 2004), where CH_4 is readily lost by diffusion and oxidation and not likely to reach supersaturation. Accordingly, even though reactive organic matter is present and oxygen exposure times are short across the whole basin (Märki et al., 2009; Sobek et al., 2009; Meckler et al., 2004), hydroacoustic surveys in Lake Zug could only detect ebullition at the mouth of the inflowing Lorze River (I. Ostrovsky and D. McGinnis, unpublished data), where sediment laminations indicate high sedimentation rates. On the other hand, high sedimentation rates must be combined with a sufficient degree of organic matter reactivity in order to give rise to ebullition. This is exemplified by site B in Lake Wohlen, where organic matter reactivity was comparatively low (Figure 3.1), porewater CH₄ concentrations were far from supersaturation (Figure 3.2), and where ebullition was not observed (DelSontro et al., 2010).

3.6.3 Supplementary table

 Table B.1. Average characteristics of the studied sediments in Lake Wohlen. DI is the amino acid-derived degradation index (Dauwe et al., 1999). n.d. is not determined.

Site	Depth (m)	OC (%)	C:N	Median grain size (µm)	DI	O ₂ penetration depth (mm)
Α	17	1.79	n.d.	n.d.	n.d.	1.4
В	13	1.98	11.4	12.2	-0.05	7.3
С	13	2.00	10.7	13.8	0.37	1.4
D	8	1.84	10.9	20.2	0.27	0.9
Е	8	1.95	13.0	26.5	0.22	n.d.
F	8	1.77	n.d.	n.d.	n.d.	1.1
G	6	2.03	13.8	30.6	0.27	n.d.
Н	6	1.14	14.5	177	n.d.	1.7

3.6.4 Supplementary figure



Figure B.1. Map of sampling sites in Lake Wohlen.

Chapter 4

Eddy covariance flux measurements confirm extreme CH₄ emissions from a Swiss hydropower reservoir and resolve their short-term variability

Werner Eugster, Tonya DelSontro, Sebastian Sobek Biogeosciences, 2011, 8: 2815-2831. doi:10.5194/bg-8-2815-2011

Abstract

Greenhouse gas budgets quantified via land-surface eddy covariance (EC) flux sites differ significantly from those obtained via inverse modeling. A possible reason for the discrepancy between methods may be our gap in quantitative knowledge of methane (CH₄) fluxes. In this study we carried out EC flux measurements during two intensive campaigns in summer 2008 to quantify methane flux from a hydropower reservoir and link its temporal variability to environmental driving forces: water temperature and pressure changes (atmospheric and due to changes in lake level). Methane fluxes were extremely high and highly variable, but consistently showed gas efflux from the lake when the wind was approaching the EC sensors across the open water, as confirmed by floating chamber flux measurements. The average flux was $3.8 \pm 0.4 \ \mu g \ C \ m^{-2} \ s^{-1}$ (mean $\pm \ SE$) with a median of 1.4 μ g C m⁻² s⁻¹, which is guite high even compared to tropical reservoirs. Floating chamber fluxes from four selected days confirmed such high fluxes with 7.4 \pm 1.3 μg C m^{-2} $s^{-1}.$ Fluxes increased exponentially with increasing temperatures, but were decreasing exponentially with increasing atmospheric and/or lake level pressure. A multiple regression using lake surface temperatures (0.1 m depth), temperature at depth (10 m deep in front of the dam), atmospheric pressure, and lake level was able to explain 35.4% of the overall variance. This best fit included each variable averaged over a 9-hour moving window, plus the respective short-term residuals thereof. We estimate that an annual average of 3% of the particulate organic matter (POM) input via the river is sufficient to sustain these large CH₄ fluxes. To compensate the global warming potential associated with the CH₄ effluxes from this hydropower reservoir a 1.3 to 3.7 times larger terrestrial area with net carbon dioxide uptake is needed if a European-scale compilation of grasslands, croplands and forests is taken as reference. This indicates the potential relevance of temperate reservoirs and lakes in local and regional greenhouse gas budgets.

4.1 Introduction

The global network of eddy covariance (EC) flux sites (Fluxnet; Baldocchi et al., 2001; Baldocchi 2008) provides an excellent overview of the high diversity in terrestrial ecosystem functioning and how they influence the global greenhouse gas budget. Interestingly, the overall budget differs among estimates obtained via integration of land-surface EC flux sites and inverse modeling that use the atmospheric signal to deduce the carbon (C) uptake fluxes at the surface (Janssens et al., 2003; Schulze et al., 2009). Most of the focus on C fluxes in the Fluxnet community has been on carbon dioxide (CO_2), but a gap in knowledge of methane (CH_4) fluxes exists, which may be a reason for the discrepancy between methods in estimating global-scale greenhouse gas budgets. As ecosystem-scale CH₄ flux measurements are now becoming widely feasible with suitable fast-response sensors available on the market (e.g., Eugster & Plüss 2010; McDermitt et al., 2010), it becomes realistic to quantify CH₄ fluxes for a wide range of ecosystems that have not been considered in the larger-scale European greenhouse gas budgets presented by Schulze et al. (2009), who focused on dominant land-use types, such as forests, croplands, and grasslands. Not included were lakes and reservoirs (Cole *et al.* 2007; Tranvik et al., 2009), which only cover a small fraction of the land surface area in the temperate zone of Europe, but could potentially be substantial local sources of methane (DelSontro et al., 2010). In Schulze et al. (2010) the gross estimate for CH₄ and nitrous oxide (N₂O) emissions from all European surface waters was quantified at 147 Tg CO₂ equivalents per year, which is roughly 10% of all non-CO₂ gas sources considered by Schulze et al. (2010).

Freshwater sediments are landscape-scale hot spots of methanogenesis, since they typically are anoxic below a few mm or cm depth, exhibit low concentrations of other electron acceptors used for anaerobic respiration (e.g. sulfate), and receive a continuous supply of particulate organic matter (POM) from both internal primary production and terrestrial sources (Bastviken, 2009). The question of linkage between organic carbon leaching from upland sites (Kindler et al., 2011) and the C inputs to riverine systems have received increasing attention in recent years as it has been shown that rivers and inland waters are not merely passive C conduits between the terrestrial biosphere and the world's oceans (Siemens, 2003), but instead locations of active C transformation and storage (Cole et al., 2007). Ultimately, inland waters, which cover just over 3% of the continents, bury \approx 50% more C than the oceans and emit \approx 1.4 Pg of C in gaseous form to the atmosphere per year (Tranvik et al., 2009). Methane, a much more potent greenhouse gas than CO₂, is produced in the final stages of organic C degradation, and is particularly extensive in the anoxic sediments of lakes and reservoirs; thus, globally 0.1 Pg of CH₄ is released per year to the atmosphere, offsetting the terrestrial C sink by at least 25% (Bastviken et al., 2011).

Reservoirs are of particular concern regarding CH_4 emissions as they tend towards higher trophic statuses and even more anaerobic conditions (St Louis et al., 2000), especially the tropical ones, which emit most of their CH_4 via degassing of CH_4 -rich and oxygen-poor hypolimnetic waters at the turbines or further downstream after turbine passage (e.g., Guérin et al., 2006; Kemenes et al., 2007). Of the typical CH_4 emission pathways, most attention has focused on surface diffusion and much less on advection through plants or ebullition (bubbling), despite the latter emitting significantly more CH_4 (Bastviken et al., 2011). Ebullition remains underestimated, primarily due to its stochastic nature (Bastviken et al., 2011), which is a result of several environmental factors influencing its spatial and temporal variability. While physical factors such as bottom shear stress (e.g., Joyce & Jewell, 2003) or pressure changes (e.g., Mattson & Likens, 1990) may modify the timing of ebullition, it is factors like organic C input levels and temperature that most likely maintain the probability of ebullition occurring as they directly impact rates of methanogenesis (Bastviken et al., 2004). When CH_4 production rates exceed vertical diffusion through sediments, the consequent super saturation leads to bubble formation and growth, so long as the ambient CH_4 production maintains the gradient at the bubble perimeter (Algar & Boudreau, 2010). It has recently been shown that the highest ebullition rates in a small temperate reservoir occurred during the warm summer months (DelSontro et al., 2010), but in general not many small reservoirs, which far exceed the number of large ones (Downing et al., 2006), have been surveyed for ebullition. While global inland waters emit an order of magnitude less CH_4 than CO_2 , the greater global warming potential of CH_4 , along with the increasing number of manmade impoundments, make CH_4 emissions an important component of the global C cycle (Tranvik et al., 2009).

Hence, the aim of this article is to (1) critically validate earlier estimates of extreme CH₄ fluxes from a run-of-river hydropower reservoir on the Aare River in Switzerland with state-of-the-art EC flux measurements, (2) explore the importance of short-term variability of environmental conditions driving these CH₄ fluxes, and (3) relate the CH₄ fluxes from the reservoir to the net CO₂ uptake of the surrounding landscape to put this locally strong CH₄ source in the wider context of the regionalscale C budget. In addition to the fluxes from the hydropower reservoir we will also present contrasting CH₄ fluxes from the surrounding landscape for conditions when the wind was not blowing over the water surface.

We report the first direct EC flux measurements of CH_4 from a freshwater ecosystem, specifically a hydropower reservoir, from which the CH_4 fluxes were large enough to be a potentially non-negligible C source. The processes discussed here are also quantitatively relevant for other similar systems in the temperate zone of Europe, which also receive substantial POM inputs from upstream (and hence upland) areas.

4.2 Material and Methods

4.2.1 Site description

Lake Wohlen dam was completed in 1920, consequently creating the $\approx 2.5 \text{ km}^2$ reservoir that holds $\approx 22 \times 10^6 \text{ m}^3$ of water with a maximum depth of 18 m near the dam (mean depth $\approx 9 \text{ m}$). The Aare River, originating in the Central Alps and passing through several large lakes, directly feeds Lake Wohlen with an average flow of 122 m³ s⁻¹ (approximate range 4 to 400 m³ s⁻¹), which is equal to the discharge of this run-of-river reservoir, and amounts to a residence time no longer than a week and a fully oxic water column year round (Albrecht et al., 1998). It has been shown in Lake Wohlen that seasonal water temperature changes (from \approx 5°C in winter up to \approx 20°C in summer) best described and perhaps influenced the variability in CH4 emissions from the reservoir, of which ebullition was dominant and more variable, and diffusive fluxes were low and relatively constant (DelSontro et al., 2010). Total organic carbon concentrations are typically \approx 2.4 mg L⁻¹ at the inflow with \approx 1.9 mg L⁻¹ of that existing as DOC. Lake Wohlen is characterized as meso- to eutrophic and receives relatively large amounts of organic matter and moderately high phosphorus and nitrogen inputs (median concentrations of monthly measurements since 2001 were 17 µg P L⁻¹ and 1.16 mg N L⁻¹, respectively; unpublished data from Water Laboratory of the Canton of Bern, Switzerland). Monitoring data on POM concentrations in the Aare river in Bern, right upstream Lake Wohlen, are available from 1994–1996 (Naduf, 2000), but not for the year of our measurements (2008).

Measurements were carried out at the shore of Lake Wohlen at Jaggisbachau (46°57'52.17" N, 7°18'49.03" E, 481 m a.s.l.), roughly 10 km northwest of Bern, Switzerland. The instruments were placed directly on the lake shore (cf. Eugster et al., 2003) in such a way that the flux footprint area during the prevailing west winds was entirely on the lake. Towards the prevailing wind direction (west) the fetch was still 1.2 km. At the sampling site clear evidence of ebullition was seen at the lake surface in the form of clusters of bubbles rising in the water column and dissipating at the surface.

4.2.2 Eddy covariance flux measurements

The EC flux system was deployed on the shore of Lake Wohlen from June 4 to June 30 of 2008 and again from July 21 to August 12 of 2008. The system used in this study was described in full detail by Eugster & Plüss (2010). It consisted of a three-dimensional ultrasonic anemometer-thermometer (Gill, UK, model R2A; hereafter referred to as sonic anemometer) and an off-axis integrated-cavity output spectrometer (Los Gatos Research Inc., CA, USA, model 908-0001-0002; hereafter abbreviated as DLT-100) used for measuring CH₄ concentrations. An external vacuum pump (BOC Edwards XDS-35i, USA) was used for EC flux measurements, and main power (230 V AC) was drawn from the nearest building using a 130 m power cord with three leads of 4 mm² cross-section. Fully digital data acquisition at 20 Hz was achieved with an industry grade embedded box computer (Advantech ARK-3381, Taiwan). Both analyzers sent their data via RS-232 serial ports to the in-house data acquisition software running under the Linux operating system.

The sonic anemometer was installed at the lake border with a location that had undisturbed fetch over the lake towards the mean wind direction (west to north), and the terrestrial surface with least disturbance in the east (large sand box for horse riding). At the location of measurements, the lake is 300 m wide at its narrowest spot (towards the north), whereas the longest fetch for EC at this site was 1.9 km for winds approaching from the northwest. The sensor height was 2.14 m and 2.13 m above the lake level at time of installation for the first and the second field campaign, respectively. A 6.7 m long Synflex-1300 tubing (Eaton Performance Plastics, OH, USA) with 10 mm outer diameter (8 mm inner diameter) was attached to the sonic anemometer 0.15 m below the center of the EC sensor head to draw air at the lake edge and send it to the DLT-100. A standard plastic funnel was used to protect the inlet against rain, and 1-mm mesh cloth was used to prevent mosquitoes from entering the hose. In contrast to Eugster & Plüss (2010), only a 5 μ m filter was used in a combined water trap with a filter unit (SMC, Japan, model AF30-F03/0086095). This was sufficient during summer conditions to prevent mosquitoes from entering the instrument (note that the DLT-100 has an internal 2 μ m Swagelok filter to protect the sampling cell from dust particles). An in-depth assessment of the flux equipment used in this study has been carried out (Tuzson et al., 2010), in which the system performed very well when measuring a predefined methane flux.

4.2.3 Flux data processing

Data processing was done with the in-house *eth-flux* software version 13.19 (Eugster & Senn, 1995; Mauder et al., 2008) and R for statistical analysis (R Development Core Team, 2010). Since no standard processing exists for CH₄ fluxes, however, the approach chosen for this application is described here.

As noted by Eugster & Plüss (2010), CH₄ fluxes are expected to be more variable than CO₂ fluxes over vegetation canopies as CH₄ fluxes are produced by episodic and stochastic processes rather than continuous processes, such as plant CO₂ uptake. In the case of Lake Wohlen, the dominant CH₄ emission pathway during summer is ebullition (DelSontro et al., 2010). The gas bubbles are produced in the bottom sediments of the lake and, while their release is not well understood, it is known to be intermittent and vary in magnitude (e.g., Ramos et al., 2006). Hence, we tested various approaches to deal with the expected problem that bubbles may be released in intermittent plumes (i.e., extreme bursts of gas), and that perhaps the number of bubbles reaching the surface is not a random function of time. At the same time we tried to adhere to the accepted CarboEurope processing strategy for CO₂ as much as possible; that is, using block averages without detrending of the measured time series, and a two-step rotation to align the coordinates with the mean streamlines. The first rotation aligns the horizontal coordinates such that the mean wind speed *u* is aligned with axis *x* and with zero mean in the lateral axis *y*. The second rotation step then corrects for the inclination angle between the mean streamlines and the horizontal plane spanned by

the *x*- and *y*-axes of the sonic anemometer. Averages were computed for intervals of 5, 10, 30, and 60 minutes, but there was no clear indication that a specific averaging interval would necessarily lead to the highest accuracy in flux computations.

Moreover, the generally used tests of stationarity and integrated turbulence characteristics (Foken et al., 2004; Mauder et al., 2008) did not succeed in removing spurious data points (not shown). Since the EC instrumentation was mounted right at the lake border, our expectation was that whenever the wind blows along the lake shore with its shrubby vegetation, flux measurements should fail these tests. This was not the case, and hence we had to take a different approach that is detailed below to remove questionable flux data. It should be noted that a standard friction velocity (u_*) filtering approach (e.g., Gu et al., 2005) cannot be used over a lake surface. The higher heat capacity of water keeps the lake water warmer than its surroundings during the night, and hence near-neutral and unstable conditions were found over the lake 86% of the time at night (between 22:00 and 5:00 CET), but only 48% of the time during daytime (between 10:00 and 17:00).

Cases with unrealistic CH₄ fluxes could be distinguished by inspecting the time lag between vertical wind speed and CH₄ concentration. There is an expected time lag that can be computed based on the length and inner diameter of the tube sending air to the DLT-100 and the pump rate (in our configuration 0.24–1.44 s; see Eugster & Plüss 2010). Hence, if the automatic cross-correlation procedure to find the lag stopped at the inner or outer boundary of the search window that we specified, then this was a clear indication that either (a) the physically correct lag was not clearly represented by the measurements (this could however also be indicative of a zero flux, which is the most difficult value to measure with EC), or (b) episodic events in the time series dominated the mixing of CH₄ in the atmosphere, and hence neither stationarity nor representativity for the upwind footprint area can be assumed. It is important to note that the established stationarity test in CarboEurope compares the mean of six 5-minute averages with the 30-minute flux, and deviations less than $\pm 100\%$ are flagged as good quality ($\pm 30\%$ are flagged as highest quality; see Mauder & Foken, 2004). Hence, if one 5-minute period in a 30-minute interval shows a flux that is 600% higher (or lower) than during the other 5 intervals, then the stationarity test is still fulfilled and the data are considered good quality (a deviation of less than 180% would be highest quality). For the measurement of CH₄ fluxes over a lake where ebullition is the responsible process and fluxes can range over several orders of magnitude (DelSontro et al., 2010; Ramos et al., 2006), the CarboEurope quality flags for CO_2 and momentum flux were not used. They were instead used only to remove the cases without a clear peak in the cross-correlation function that was inside the specified time window. With this data selection criterion we could still use the standard 30-minute flux averages in our analyses.

Although we operated the CH₄ analyzer with a strong vacuum pump, the flushing of the sampling cell was not perfect (see Eugster & Plüss, 2010), and hence we applied a high-frequency damping loss correction according to Eugster & Senn (1995) to correct for the underestimation of EC fluxes. Using cases with well-developed cospectra (as in Figure 4.1) we determined a damping constant L \approx 0.14 s⁻¹, which was used for the Eugster & Senn (1995) correction.

The flux footprint area was computed with the Kljun et al. (2004) model. This simple parametric model estimates the cross-wind integrated flux footprint area in the upwind direction from the flux tower. The governing variables for flux footprint calculations are the upwind distance x (m), the measurement height above local ground zm (m), the height of the atmospheric boundary layer h (m), the friction velocity for mechanical turbulence $u * (ms^{-1})$, and the square-root of the variance of the vertical wind speed component $\sigma w (ms^{-1})$

4.2.4 Floating chamber flux measurements

Floating chamber campaigns for directly collecting surface CH4 emissions were conducted in 2008 on July 23, 24, 29, and 30 and were part of the DelSontro et al., (2010) whole-year sampling effort. Chambers consisted of a circular bucket (22 L, 26 cm high, 855 cm2 surface area) that collected gas diffused from the water surface and released from emerging bubbles (if present) while the chamber was kept afloat by buoys and upright by weights. An air-tight tube (\approx 40 cm long) was attached to the top of each chamber via a brass hose fitting (0.4 mm inner diameter) screwed into the chamber and made air-tight with an o-ring. Chambers were unanchored and allowed to drift on the lake adjacent to the EC tower location. Transects were approximately 0.5 km long and lasted anywhere from 20 minutes to an hour and 45 minutes depending on wind speed. Gas was collected using a 60 mL syringe and a 3-way stopcock at the end of the tubing. Ten mL of gas was extracted and discarded to mix the gas inside the tubing and to flush the syringe. Then 20 mL of gas was collected and injected into 30 mL serum bottles pre-capped with a butyl-rubber stopper and aluminum cap. Bottles were also pre-filled with a saturated NaCl solution to prevent CH4 dissolution and an open needle placed in the stopper allowed the displaced NaCl solution to exit the bottle while the collected gas was being injected. Samples were stored upside down until analysis on a gas chromatograph (Agilent 6890N) with a flame ionization detector.

4.2.5 Ancillary measurements

During the flux measurement campaigns, lake water temperatures (0.1 m depth) at the site of EC flux measurements were recorded as 5-minute averages with a self-contained temperature mini-

logger. Air temperature, relative humidity, cup anemometer wind speed and wind vane direction were recorded by an Aanderaa (Norway) weather station. Full-year measurements of Aare river discharge and temperature were obtained from the Schönau monitoring site upstream of our sampling area (daily resolution for discharge, hourly for temperature, obtained from the Swiss Federal Office for the Environment). The hydroelectric company BKW provided additional water temperatures at 10 m depth in front of the dam, together with lake level information (both at 15 minute intervals), and high-precision air pressure information was taken from the nearest MeteoSwiss station Mühleberg, which was 2.5 km west of our flux measurement site.

4.3 Results

4.3.1 Performance of the system

The performance of the methane analyzer used here was already described by Eugster & Plüss (2010). The field data that were shown in this previous study were collected on a landfill site in Switzerland in the time period between the two campaigns that were carried out for this study at Lake Wohlen. The overall technical performance of the equipment was very similar between the two Lake Wohlen campaigns, showing well-defined spectra of wind speed components and CH₄ concentration fluctuations, but more variable cospectra of CH₄ fluxes depending on flux strength and stationarity of conditions. Figure 4.1 shows an example for ideal conditions when the wind direction was from the lake. A minor damping at the highest frequencies was still seen in the CH₄ spectra (Figure 4.1b) with the configuration that we used, but the effect on CH₄ fluxes is rather small (Figure 4.1d). The two idealized curves in Figure 4.1d represent the damped (solid gray) and undamped (dashed gray) cospectrum as described by Eugster & Senn (1995). The damping constant was quantified at 0.14 s⁻¹, which requires a high-frequency damping loss correction that increases measured CH₄ effluxes by 16% on average (median is 9%). The CH₄ spectra clearly indicate a strong signal that is orders of magnitude larger than the white noise level of the DLT-100 instrument (Figure 4.1b). The cospectrum shown in Figure 4.1d shows an almost ideal period with continuous effluxes from the lake surface, whereas the vast majority of cases show a more variable and intermittent behavior of fluxes, even during periods where the vertical wind speed w and CH₄ spectra are rather smooth. As noted by Eugster & Plüss (2010), this was expected as we were measuring a phenomenon with episodic tendencies (i.e., bubble plumes released intermittently from the lake with less active or quiescent times of ebullition the rest of the time).



Figure 4.1: Example spectra of (a) vertical wind speed *w* and (b) CH₄ concentration *c*, (c) time lag between *w* and *c*, and (d) cospectrum of CH₄ flux over Lake Wohlensee. The data used were collected during 1.75 hours (2^{17} records) between 18:00 and 19:45 on 21 July 2008 with a mean horizontal wind speed of 1.5 m s⁻¹ and wind direction 284°. Spectra and cospectrum were bandwidth averaged using 100 bands of equal spacing on the log frequency axis. Idealized curves are shown in gray. Dashed gray lines in (b) and (d) are idealized curves for an ideal system without high-frequency damping losses, and black dashed line in (b) shows white noise level of CH₄ analyzer.

4.3.2 Turbulent conditions at the measurement site

After having removed the conditions with instationary fluxes, the accepted fluxes primarily were measured at moderate ($< 4 \text{ m s}^{-1}$) wind speeds when wind was coming from the lake, and during rather calm conditions ($< 1 \text{ m s}^{-1}$) when winds were from the land surface (Figure 4.2). The observed horizontal wind speed dependence on wind direction was expected as Lake Wohlen is located in an east–west running valley of the Aare River with the surrounding plateau \approx 120 m above lake level. The prevailing synoptic westerly winds could therefore approach our measurement station with minimal obstruction, whereas winds from other directions were always associated with very local thermo-topographical wind systems driven by differential heating between the cold lake surface and the warmer (day) or even colder (night) land surface during this time of year (see e.g., Whiteman, 2000 or Pielke & Avissar, 1990 for a general overview of such local secondary circulations).



Figure 4.2: Horizontal wind speed as a function of wind direction. For reference, a panorama image taken at the position of the sonic anemometer sensor head is shown in the top section. Data were aggregated for overlapping wind direction sectors of 10° with 50% overlap. Median (bold line), interquartile range (shaded area; 50% of all values), and maximum and minimum values (dashed lines) are shown. The predominent wind direction from the west is also reflected by highest wind speeds. The inset below the panorama image shows the number of records available for each wind direction sector.

Clear effects of obstructions to both sides of the flux tower system are apparent in the aerodynamic roughness seen by the sonic anemometer. The roughness length z_0 (m) can be computed from momentum flux u'w' (m² s⁻²) measured at height *z* above ground (m), horizontal wind speed *u* (m s⁻¹), and Monin-Obukhov stability *z/L* (Monin & Obukhov, 1954) that are directly measured by the sonic anemometer,

$$z_0 = \frac{z}{\exp\left[\frac{\overline{u} \cdot k}{u_*} + \Psi(z/L)\right]}$$
(1)

where u_* is the friction velocity derived from momentum flux measurements $(u_* = (-u'w')^{1/2}$ for conditions where u'w' < 0 m² s⁻²), and $\Psi(z/L)$ is the stability correction function parameterized by Paulson (1970) based on the concept of the universally valid diabatic wind profile (Monin & Obukhov, 1954). Overlines denote averaging over time (30 minutes in our study), and primes indicate the short-term deviation from such a mean. Since momentum flux measured with EC tends to require longer averaging times than scalar fluxes (Wyngaard, 1990), we expect to see any effects of obstructions and inhomogeneous fetch most clearly in u'w' or in an entity such as z_0 that is
derived from *u'w'*. For the sector with wind speeds exceeding 1 m s⁻¹ (around 220°–310° in Figure 4.2) where there is a fetch of several hundreds of meters over the water surface, median z_0 computed with Eq. (1) was 0.005 m. This is an appropriate order of magnitude as it is higher than that expected over large water bodies (< 0.001 m; Panofsky & Dutton, 1984), but lower than that tabulated for short-cut grass over flat ground (≈ 0.007 m, Panofsky & Dutton, 1984).

4.3.3 Lake methane effluxes

To analyze lake methane effluxes measured by EC we extracted the data where the 30-minute vector-averaged wind direction was from the lake (between 200° and 10°, see also Figure 4.2). During both deployments, CH₄ concentrations in ambient air at EC height were a minimum of 1.853 ppm, which is slightly above the background concentration (1.774 ppm; Forster et al., 2007). Methane concentrations and fluxes did not differ significantly between the two periods (p = 0.7701 and p = 0.4651, respectively; two-sample t-test).

Figure 4.3 clearly shows very high concentrations in > 50% of all cases when winds were from the NW, which was the direction towards the lake where ebullition was easily seen at the surface and chambers caught some of the highest effluxes. Methane emissions from the lake (and from other potential sources in the valley) are strongly contained in the atmospheric boundary layer above the lake surface due to the relatively cold surface water (Figure 4.4a; summer maximum $\approx 20^{\circ}$ C), which limits convection during daytime, but enhances turbulent mixing during nighttime. Using wind from the lake direction always resulted in positive CH₄ fluxes indicating an efflux from the lake to the atmosphere (Figure 4.5). With the exception of a few measurements exceeding 80 µg $m^{-2} s^{-1}$ found in the near-shore sector of the lake (220°–260°) during higher wind speeds, median fluxes were highest when winds were low (< 1 m s⁻¹, Figure 4.2) and from the NW ($310^{\circ}-340^{\circ}$; Figure 4.5). A detailed inspection of the flux footprint area contributing to the CH₄ fluxes observed during our two field campaigns shows that the shallow near-shore areas were best covered (Figure 4.6). The flux footprint area as computed with the Kljun et al., (2004) model was much smaller than we expected when we designed the field experiment. Figure 4.6 shows a composite of relative footprints for each 30-minute period weighted by the respective CH_4 efflux. These calculations show that the most relevant surface areas that led to the strong effluxes were in the southwest where the high frequency of wind from this direction (west is the prevailing wind direction at the site) is combined with large effluxes, and an area in the northwest where infrequent winds were associated with the highest median fluxes that we measured (see Figure 4.5).



Figure 4.3. Ambient CH_4 concentrations as a function of wind direction. The effect of ebullition from the water is clearly seen when winds are from the NW (315°), and these high concentrations also influence the maximum values observed when wind arrives from other directions. Data were aggregated for overlapping wind direction sectors of 10° with 50% overlap. Median (bold line), interquartile range (shaded area; 50% of all values), and maximum and minimum values (dashed lines) are shown.



Figure 4.4. Driving variables of CH_4 efflux from lake Wohlensee at daily resolution, (a) temperature of the river waters (-0.1 m; bold line with gray band showing daily range of values) and the dam (-10 m, dashed line); (b) lake level measured at the dam (bold line with gray band showing daily range of values); and (c) atmospheric pressure (bold line with gray band showing daily range of values). Data courtesy of Swiss Federal Office for the Environment (a, river temperature), Bernische Kraftwerke BKW (a, dam temperature, and b), and MeteoSwiss (c). P1 and P2 indicate the period when eddy covariance flux measurements were carried out.



Figure 4.5. Methane fluxes as a function of wind direction. Data were aggregated for overlapping wind direction sectors of 10° with 50% overlap. Median (bold line), interquartile range (shaded area; 50% of all values), and maximum and minimum values (dashed lines) are shown. The top inset shows the number of records available for each wind direction sector, and the box and whisker plot at right shows the range of CH₄ fluxes obtained by floating chambers. Note that CH₄ fluxes were always positive when wind was approaching over the lake surface (200° to 10°).

4.3.4 Comparison with chamber fluxes

Since we expected a larger footprint area with the EC system than the posteriori computations actually showed for the subset of data with wind from the lake (Figure 4.6), the drifting chambers were deployed just outside the footprint of the EC flux measurements. Still, if we assume that our EC flux measurements should be representative for the lake, then a general agreement with the chamber flux measurements should be found. In fact, the flux data obtained from 29 chamber deployments show the same order of magnitude and variability of fluxes (Figure 4.6 and boxplot in Figure 4.5) as measured by the EC flux system. The median CH₄ efflux from the lake measured by EC (which includes the necessary high-frequency damping loss corrections) was $1.42 \ \mu g \ C \ m^{-2} \ s^{-1}$; mean $\pm SE \ 3.76 \pm 0.39 \ \mu g \ C \ m^{-2} \ s^{-1}$; N=513 half-hour averages), whereas the chamber flux measurements obtained a median flux of 7.43 $\mu g \ C \ m^{-2} \ s^{-1}$; (interquartile range $1.53-11.11 \ \mu g \ C \ m^{-2} \ s^{-1}$; mean $\pm SE \ 7.43 \ \pm \ 1.33 \ \mu g \ CH_4 \ m^{-2} \ s^{-1}$; N=29 chamber deployments). This flux is extremely high for a temperate hydropower reservoir, but agrees well with the values expected for summer conditions based on data obtained by DelSontro et al. (2010) using a multi-temporal discrete water sampling and mass balance approach from June 2007 to June 2008.



Figure 4.6. Flux footprint for CH₄ efflux from Lake Wohlen and tracks (arrows) and mean efflux measurements (color) of floating chambers deployed on four days in 2008: 23 July (top left), 24 July (top right), 29 July (bottome left), and 30 July (bottom right). Isolines of eddy covariance flux footprints show percentage of contribution to flux measurements of both periods. Isolines are drawn for 10, 30, 50, 70, and 90 % flux of the footprint area. The inset in upper right panel shows the lake sector and the sandbox (S) in greater detail. The white circle shows the position of the flux tower on the lake shore (background image © 2010 swisstopo, reproduced with the authorization of swisstopo JD100042/JA100020).

4.3.5 Methane fluxes from contrasting surfaces

Eddy covariance flux measurements may be very accurate point measurements, but may not be representative (Wyngaard, 1990) for a larger upwind surface area (the flux footprint area) if a handful of simplifying assumptions cannot be made. To be able to relate a high-quality EC flux to the larger surface area, the common assumptions to be made are (1) that turbulent conditions are stationary such that the time-for-space substitution (Taylor's frozen turbulence field hypothesis; Taylor, 1938) is valid; (2) that CH₄ sources and sinks are randomly distributed in space (homogeneity of surface); and (3) that source or sink strengths must be spatially representative (see Schmid, 2002 for an overview of footprint concepts and assumptions). With our placement of instruments these conditions are met in the undisturbed sector facing the prevailing wind (the lake sector, which allows us to measure fluxes from the water body), and possibly in the SE wind sector, where the sand box is found. Other directions are heavily disturbed and are hence only shown for reference. Figure 4.5 shows the fluxes measured from all directions without eliminating conditions where the above assumptions are not met. This is of particular interest to test a common but largely untested hypothesis that EC flux measurements are useless if the above assumptions are not perfectly met. And as a second objective, it allows us to test whether the CH₄ flux to or from the sand box in the SW is small. In such well-aerated sandy soils either a small CH₄ sink (e.g., Hütsch

et al., 1994; Castaldi et al., 2007) or a small source should be expected (e.g., Radl et al., 2007). Using Radl et al.'s fluxes from moderately impacted pastures in spring a flux in the range 0.03 to 0.14 μ g C m⁻² s⁻¹ would be expected from the sand box.

Our results show similarly small fluxes for the wind sectors between 135 and 160° (from the sandbox, $0.07 \pm 0.11 \ \mu g \ C \ m^{-2} \ s^{-1}$, mean $\pm SE$), which agrees well with our expectation. This indicates a rather good performance of the system, although it should be noted that the alignment between these relatively small minimum fluxes and the center of the sand box is not perfect. Still, from this comparison we expect our EC system to be suitable also for efflux measurements from the lake sector. In strong contrast to the sand box fluxes, there were no cases with CH₄ uptake over the lake (220°–10°), whereas the obstructed lake border and terrestrial hinterland surfaces did show downward CH₄ fluxes, namely in the sector 160° to 200°.

4.3.6 Environmental drivers

The hydropower generation of the lake follows a typical diurnal pattern with highest lake level in the morning and lowest in the evening (before 22:00), which most likely caused the diurnal variability observed in CH₄ effluxes (Figure 4.7). The regression against lake level measurements is able to explain 23.1% of the variation in CH₄ efflux from the lake (Table 4.1, adj. R²=0.231, p < 0.000001, based on log-transformed 30-minute flux averages), despite the relative change of lake level with respect to a 2-day retrospective moving average only being \pm 0.1 m (or 10 hPa and not much stronger than atmospheric pressure variability due to changing weather patterns). Also every 3 to 4 weeks in summer, the hydropower company lowers the lake level artificially by an extra 0.15 m (Figure 4.4b), which superimposes a longer-term variability that we were not able to resolve with two field campaigns of a few weeks each, but most likely affects the seasonal efflux as shown by Ostrovsky et al. (2008).

Table 4.1: Linear regression between the log-transformed CH₄ effluxes from Lake Wohlen and lake level changes as a potential driving variable for fluxes.

Variable	Estimate	Std. Error	t value	Pr(> t)
Residual lake level (m)	-17.42	1.40	-12.42	< 0.000001
Intercept	0.769	0.050	15.50	< 0.000001

Residual standard error: 1.1 on 511 degrees of freedom Multiple R-squared: 0.232, Adjusted R-squared: 0.2305

F-statistic: 154.4 on 1 and 511 DF, p-value: < 0.000001



Figure 4.7. CH_4 effluxes as a function of hour of day which reflects the hydropower generation. The typical diurnal pattern sees highest lake level in the morning and lowest in the evening (before 22:00 CET), which most likely causes the diurnal variability observed in CH4 effluxes. Shaded areas denote hours of day with less than 10 observations. Chamber flux measurements are added to the right as in Fig. 4.5.

A strong diurnal cycle is also found in the near-surface water temperatures that we measured at the field site (mean diurnal range was 2.91, 3.04, 3.05, and 2.04 K in Jun, Jul, Aug, and Sep, respectively), but synchronous measurements of temperatures and CH₄ fluxes only showed a weak correlation (at smoothing time 0 in Figure 4.8, $R^2 = 0.13$). Hence we wanted to know whether (1) time lag effects or (2) time integration effects might be essential for the explanation of CH₄ fluxes from this dynamic aquatic system. To address these two components we used (1) lagged crosscorrelation analysis and (2) smoothing of the variables under consideration. Figure 4.8 shows the final result after the following steps: (1) each of the potential driving variables was smoothed over 0-5 days using a boxcar moving average to yield two modified time series, (a) a mean and (b) a residual component as modified driving variables; (2) with each of these modified smoothed time series a cross-correlation analysis with measured CH₄ flux (when the flux footprint was over the lake surface) was carried out; (3) the modified driver variable was then shifted according to the most appropriate time lag found using the cross-correlation procedure (highest R^2); (4) the R^2 was assigned with the respective length of the smoothing interval and plotted in Figure 4.8; (5) in the same way we proceeded with the multiple regression model (Table 2); (6) finally, an arrow was added to the three lines in Figure 4.8 that yielded the highest R^2 .

The time lag analysis directly showed the time delay between the temperature measurements taken at the hydropower dam at 10 m depth and lake surface temperature measured at the flux site, which was 4.5 hours. Since no other relevant time lag effects could be found we shifted this time

series by -4.5 hours. This allowed us to conclude that time lag effects in our system are associated purely with the time it takes the water in the flux footprint of our measurements to reach the dam. In contrast, the second component (i.e., time integration) revealed more significant results. Since CH₄ fluxes are not normally distributed (see e.g., Ramos et al., 2006; Eugster & Plüss, 2010), for these analyses we used the log-transformed CH₄ fluxes.



Figure 4.8. Correlation analysis of CH₄ efflux with driving variables smoothed with a moving average of lengths up to 5 days (lines with symbols), and the residual variables (lines without symbols) resulting from the smoothing process for: lake surface water temperature (T_{lake}), dam 10-m temperature (T_{dam}), water level height, and atmospheric pressure); and the multiple regression shown in Table 4.2. For each smoothing time a cross-correlation analysis was carried out to obtain the highest time-lag corrected R^2 (adj, R^2 for the multiple regression) which is then displayed as a line for each variable. The arrows show the optimum smoothing time for the three variables with the highest overall R^2 . Although lake surface water temperature shows the greatest explanatory power for short averaging times, none of the single drivers reach the level that the linear combination used in the multiple regression approach achieved.

The smoothing was done under the theoretical consideration that CH₄ production and transport in the lake may not respond to the environmental variables at the 30-minute timescale of our averaging intervals, but to longer integration periods of up to 5 days, well beyond the peak of best multivariate correlations (Figure 4.8). Hence we generated new averaged (smoothed) time series of atmospheric pressure (*P*), lake surface temperature measured in the footprint of the flux site (T_{lake}), and 10-m deep water temperature measured at the dam (T_{dam}). We used a retrospective moving average filter with equal filter weights to produce these new time series. The computations were carried out for integration periods (i.e., filter lengths) of 0 to 5 days in 1-hour time steps. For each time step (except for lag 0) both the smoothed values and the residuals were used in the regression analysis. This was considered meaningful because, for example, a change in pressure might increase or decrease the bubble flux in the water column, but only during a certain time period until a new equilibrium is established. In this setting, a good correlation with a smoothed variable would indicate a buffered system with slow adaptation to changing conditions. Contrastingly, a better correlation with the residuals than with the smoothed variable implies a rapid adaptation of the relevant mechanisms influencing CH_4 efflux in response to environmental conditions changing on relatively short timescales.

Figure 4.8 shows the result of this analysis as a function of retrospective time integration (smoothing). The highest explained variance – which indicates an optimum integration time over 9 hours – reached a modest adj. $R^2 = 0.3542$ (p < 0.000001; Table 4.2 and arrow in Figure 4.8). While (smoothed) T_{lake} increases methane efflux (Table 4.2; Figure 4.9c), the short-term deviation (residuals) of the lake water level tends to decrease the flux (Figure 4.8a), similar to the short-term atmospheric pressure variations (Figure 4.9b). Each of the temperature variables (Figure 4.9c,d,e) suggests an increasing flux with increasing temperature. In combination, however, T_{lake} has the strongest explanatory power in the analysis (Table 4.2), whereas T_{dam} corrects for the exaggerated diurnal temperature range of T_{lake} (negative regression slope in Table 4.2). This means that the best place for the temperature measurements to explain CH₄ fluxes would have been at a depth between the T_{lake} (surface) and T_{dam} (-10 m). Overall, our linear model explained $\approx 35\%$ of the variation seen in CH₄ emissions from Lake Wohlen (adj. $R^2 = 0.3542$, p < 0.000001, Table 4.2). This suggests that although short-term variability responds to temperature and pressure effects other unmeasured components are also essential. We suspect that this may be the substrate supply for methanogenesis in the sediments (i.e., POM inputs from the river). We were however unable to find a strong relationship between POM import and CH₄ emission on the short timescales studied here, since it takes some time (one year or longer) for deposited POM to reach the deep sediment layers responsible for ebullition (data not shown).

4.4 Discussion

Eddy covariance flux measurements showed extremely high CH₄ emissions from Lake Wohlen, which confirms a previous study's results using a system analysis mass balance approach, as well as floating chambers, to assess the fluxes (DelSontro et al., 2010). These extreme fluxes were mainly driven by water temperature, but are strongly reduced whenever pressure exerted by lake level and

air pressure increased. All temperature variables show increasing CH₄ flux with increasing temperature, as would be expected from a biologically-sourced CH₄ flux that depends on the metabolic activity of methanogens decomposing organic matter under anoxic conditions (Figure 4.9c,d) (Takita & Sakamoto, 1993; Conrad 1989). However, on an annual timescale, emission estimates based on dissolved methane concentrations (DelSontro et al., 2010) show a much clearer water temperature dependency of fluxes was found for temperatures exceeding 10°C. Even if CH₄ emission fluxes measured by eddy covariance generally agreed with chamber-derived fluxes, it was not possible to relate individual chamber flux values to EC fluxes from the same periods. In a few cases the agreement was quite good, but in general the lack of overlap between the chamber transects and the EC flux footprint, as well as the difference in temporal resolution of the sampling methods, makes for a difficult direct comparison.

In parallel with high EC fluxes, the CH₄ concentration in the air above the lake was often surprisingly high. It is highly unlikely that some atmospheric CH₄ might stem from the Teuftal landfill roughly 1 km to the west. However, the ratio between CH₄ efflux from the lake and CH₄ concentration in the air above is suggesting a rather consistent emission velocity v_e around 5 mm s⁻¹ (median value) during the hours of day with highest concentrations and effluxes (18–20 hours CET), compared to $v_e < 3 \text{ mms}^{-1}$ during morning hours with moderate fluxes and concentrations. Since footprint areas of turbulent fluxes are typically almost one order of magnitude smaller than footprint areas of concentrations (Schmid, 1994; see also Vesala et al., 2008), we would have expected lowest - not highest – v_e during periods with highest CH4 concentrations if these high concentrations had been caused by off-site effluxes from a landfill outside our flux footprint area shown in Figure 4.6.

With the high temporal resolution of EC flux measurements, the short-term process of pressure changes due to changes in reservoir level and/or changes in atmospheric pressure became an important confounding factor of CH_4 emission. In the following, we first address the question of whether biological (temperature-driven) or physical (pressure-driven) processes – or both together – are crucial for understanding CH_4 fluxes from this hydropower reservoir. Next we discuss what the C sources are and whether they are sufficient to sustain the extreme CH_4 emissions measured. Finally, the CH_4 fluxes will be put in relation to net C uptake of the surrounding terrestrial ecosystems to estimate the potential relevance of aquatic ecosystem fluxes to the local and regional greenhouse gas budgets.

Table 4.2. Multiple linear regression between the log-transformed CH₄ effluxes from Lake Wohlen and potential driving variables with 9-hour retrospective boxcar smoothing that led to highest overall explanation of variance (adj. $R^2=0.35$). Lines in italics are not significant (p > 0.05). T_{lake} and T_{dow} denote lake surface (-0.1 m) and dam water (-10 m) temperatures respectively

and T _{dam} denote take surface (-0.1 m) and (uani water (-	10 m) tempera	iures, resp	Jethvery.
Variable	Estimate	Std. Error	t value	Pr(> t)
Residual lake level (m)	-19.07	1.98	-9.654	< 0.000001
T_{lake} (9 h mean lake surface temperature, °C)	0.4828	0.0671	7.200	< 0.00001
Residual pressure (hPa)	-0.3695	0.05924	-6.237	< 0.00001
$T_{\rm dam}$ (9 h mean dam water temperature, °C)	-0.3088	0.0697	-4.431	0.000012
T_{lake} residual (°C)	-0.2572	0.0715	-3.597	0.00035
Intercept	1205.9	719.0	1.677	0.094
9 h mean lake level (m)	-2.487	1.497	-1.661	0.097
9 h mean pressure (hPa)	-0.0143	0.0145	-0.983	0.33
T_{dam} residual (°C)	-0.1124	0.1313	-0.856	0.39

Residual standard error: 1.017 on 504 degrees of freedom

Multiple R-squared: 0.3643, Adjusted R-squared: 0.3542

F-statistic: 36.1 on 8 and 504 DF, p-value: < 0.000001

4.4.1 Temperature versus lake level response

In an earlier study by DelSontro et al. (2010) a strong dependence between temperature and CH₄ ebullition in Lake Wohlen was observed at an annual scale. Along with the reactivity of the organic matter, temperature is an important regulator of organic matter degradation in sediments (Gudasz et al., 2010; Kelly and Chynoweth, 1981; Nozhevnikova et al., 1997), and consequently also of CH₄ production (Bastviken, 2009). However, at the shorter timescales of the present study, variations in temperature are small and hence the effect on methanogenesis is most likely also smaller. Moreover, short-term variations in water temperature do not directly result in corresponding temperature changes in the deeper methanogenic sediment layers. At short timescales, bubble release from the sediment may well be related to the mechanical properties of the sediment (not addressed in this study), such as elasticity, compaction, and fractures (Boudreau et al., 2005).

Earlier surveys (DelSontro et al., 2010) did not use the temperature measured at the locality of flux measurements, but the upstream river temperature from the routine long-term measurements by the local authorities at Schönau, Bern (Naduf, 2000). To rule out the possibility that such a methodical difference could be responsible for the important differences in correlation between CH_4 flux and temperature, we also carried out our analysis with these temperature readings (Figure 9.8e) instead of those measured on site (Figure 9.8c). There is however no indication that this is an issue as our EC-measured CH_4 fluxes show a similar response to both temperatures and in both cases the order of magnitude corresponds with that reported by DelSontro et al. (2010) (DS2010 lines in Figure 9.8c,e).

In addition, the high resolution flux sampling provided by EC allowed the introduction of shortterm 'noise' from processes acting on shorter timescales. The physical processes related to the short-term deviations from the smoothed lake water level (Figure 4.9a) and atmospheric pressure (Figure 4.9b) tend to decrease fluxes when pressure increases, or enhance the efflux when pressure decreases, but only until a new equilibrium is reached. This, however, does not change the fact that biological activity (i.e., decomposition of organic matter in the sediments) is responsible for the CH₄ fluxes observed over longer time periods. As well, our flux footprint (Figure 4.6) only covers the shallowest areas of the lake (depth < 3 m) and it is known from other studies that episodic bursts of CH₄ are characteristic of the shallow littoral zone (e.g., Hofmann et al., 2010).

Also, we found order of magnitude larger fluxes during the few cases where wind was approaching from the Northwest (Figure 4.5), which corresponds to the only cases where our flux footprint reaches beyond the shallow littoral zone (Figure 4.6). These larger fluxes from the direction of the old river channel also agree best with the floating chambers, which actually bypassed the shallow littoral zone and drifted along the old river channel only. Regardless, it may be that in Lake Wohlen the methane production in the sediments of the deeper parts of the lake dominates the overall CH_4 emissions. Due to the lack of stratification of the lake, mean temperatures at depth are not expected to dramatically differ from the temperatures that we measured for the surface waters when averaged over days or longer.

4.4.2 What are the C sources and are they sufficient to sustain CH_4 emissions?

Since Lake Wohlen is oxic in summer without a clear stratification (see Figure 4.4a), it is unlikely that substantial CH₄ production occurs in the water column itself; hence production must be constrained mostly to the anoxic sediments underlying this oxic and well-mixed lake (Kiene 1991; McGinnis et al., 2008).

Three studies in 2008 investigated the water quality of the Aare river, including Lake Wohlen, using three different indicators: (1) bioindication of algae (von Känel, 2008), (2) silicious algae (AquaPlus, 2008), and (3) macroinvertebrates (Mürle et al., 2009). All three assessments found very high water quality (highest mark) for most biological and chemical aspects investigated. Good quality (second highest mark) was found for DOC, nitrite and total phosphorous. However, these are only qualitative measurements, whereas quantitative estimates only were made more than a decade ago. If we consider these monitoring data from 1994–1996 to be representative for 2008, an average POM import by the Aare river of 139 g C s⁻¹ to Lake Wohlen can be expected. When put in relation to the 2.5 km² lake surface, and assuming that all imported POM settles to the sediments, this corresponds to a POM sedimentation of roughly 56 μ g C m⁻² s⁻¹. These calculations indicate that only a small fraction of the river POM import, on the order of 3%, is needed to account for the observed extreme CH₄ emission (3.76 μ g C m⁻² s⁻¹) from Lake Wohlen.



Figure 4.9: Dependence of lake CH_4 effluxes from (a) lake level changes, (b) air pressure changes, (c) near-surface lake temperature, (d) 10-m water temperatures, and (e) upstream near-surface water temperatures. Individual 30-minute flux averages (open circles) are ploted on top of bin-averaged median (bold line), interquartile range (gray band), and 95% confidence interval (broken lines). Bin sizes are: 0.02 m for lake level changes, 0.5 hPa for air pressure changes, and 1.0 K for temperatures. As a reference for published pressure response the Mattson and Lichens (1990) curve is shown in panel (b), and the temperature responses reported by Takita and Sakamoto (1993) and DelSontro *et al.* (2010) are shown in panels (c)– (e) with thick broken lines.

4.4.3 How important are CO₂ effluxes?

In this study we only measured CH_4 flux, and did not consider CO_2 flux. This is justified by the fact that in contrast to natural lakes with acidic waters, this run-of-river reservoir has slightly alcaline waters with a pH around 8.1 on average. During the period of our measurements, pH ranged between 8.14 and 8.25 in the waters entering Lake Wohlen (data taken from the hydrological data book 2008 of the Canton of Bern, site AC52 "Eymatt, neuer Steg": http://www.wea.bve.be.ch/geoportal/qog/pdf/hydrografisches_jahrbuch2008.pdf).

Similar pH values are found throughout the year and also in other years (minimum pH around 7.7 is typically found in November, and maximum pH of 8.38.4 in late spring). At such relatively high pH values, most of the inorganic carbon pool is present as bicarbonate and carbonate, not in the form of gaseous CO₂. Based on annual courses of alkalinity, pH, temperature, air pressure and wind speed, potential CO₂ effluxes from Lake Wohlen are estimated at 24 g C m⁻² yr⁻¹, i.e. much less than annual CH4 emissions.

4.4.4 Link between upland ecosystems and inland waters

The terrestrial ecosystem flux community has largely ignored CH₄ effluxes from inland waters in terrestrial C budgets; therefore, it is of interest to make a rough estimate of how the CH₄ fluxes from Lake Wohlen relate to typical C uptake rates of the surrounding landscape. The compilation of multi-year net ecosystem exchange (NEE) of grasslands, croplands and forest by Kindler et al. (2011) resulted in an average NEE of the European sites under investigation to be 296 ± 61 g C m⁻² y⁻¹ (in CO₂ equivalents this is $34 \pm 7 \ \mu\text{g}$ CO₂-eq m⁻² s⁻¹). Our measured summer CH₄ effluxes from Lake Wohlen (average, $3.76 \pm 0.39 \ \mu\text{g}$ C m⁻² s⁻¹) expressed as CO₂ equivalents (factor 25 for a 100yr time horizon, Solomon *et al.* 2007) to quantify their global warming potential yields $125 \pm 13 \ \mu\text{g}$ CO₂-eq m⁻² s⁻¹, whereas DelSontro et al. (2010) found ≈45 μg CO₂-eq m⁻² s⁻¹ for the annual average. Hence, for each square meter of Lake Wohlen, at least 3.7 m² terrestrial surface area with the sufficiently large net C uptake estimated by Kindler *et al.* (2011) is required to neutralize the greenhouse forcing exerted by the summer CH₄ effluxes from the reservoir, but less (≈1.3 m²) on the annual average. Therefore, temperate reservoirs can be a relevant component in local and regional greenhouse gas budgets, even if the total lake surface appears small at larger scales.

4.5 Conclusions

We carried out the first direct EC flux measurements of CH₄ from a freshwater ecosystem, a run-of-river reservoir in the temperate climate zone. The average flux was $3.8 \pm 0.4 \ \mu g \ C \ m^{-2} \ s^{-1}$ (mean \pm SE) with a median of 1.4 $\mu g \ C \ m^{-2} \ s^{-1}$, which is quite high even compared to tropical reservoirs. These flux measurements confirmed the extreme CH₄ emissions reported based on the conventional sampling in DelSontro et al. (2010). Using the same technique with floating chambers on four selected days during the period covered by EC flux measurements were of the same order of magnitude with an average of $7.4 \pm 1.3 \ \mu g \ C \ m^{-2} \ s^{-1}$.

The direct comparison between EC and floating chamber fluxes was however limited due to two factors: (1) with our set-up of the eddy covariance flux equipment on the shore, our flux footprint was closer to the shore than what would be necessary to cover the same area as the floating chambers, and (2) even during chamber deployments, the local variability of wind direction did not allow for a 1:1 comparison of fluxes.

Future studies should therefore carefully aim at matching EC flux footprints with chamber deployments. Mounting EC equipment on a floating platform may be an improvement over our experimental set-up. This would also have the advantage that the EC footprint would cover a larger fraction of the deeper water areas as compared to the mostly shallow water depth near the shore in our flux footprint.

The methane effluxes, converted to CO_2 equivalents and put in relation to net CO_2 uptake of the surrounding vegetated landscape, were shown to be a relevant component in the C budget that cannot be neglected. The short-term variability of CH_4 effluxes from the reservoir were however only partially explained by lake level changes, atmospheric pressure changes and temperatures. Hence, future studies should put additional emphasis on substrate input via particulate organic matter and explore small-scale spatial heterogeneities of methane production in the lake bottom sediments.

4.6 Acknowledgements

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Chapter 5

Hydroacoustic examination of reservoir ebullition: Sources of variability explored in comparison with other methods

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Abstract

A small temperate hydropower reservoir known for intense summer ebullition was surveyed for methane ebullition emissions following the calibration of the 120 kHz split-beam echosounder for bubble size. Our bubble size calibration agreed very well with a similar calibration and the hydroacoustic technique presented to estimate methane bubble flux in the presence of non-bubble targets was the best post-processing method for this reservoir. The average methane ebullition flux from the sediments to the water column from seven campaigns was $580 \pm 1150 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$. Bubble size distribution, which included 1 to 20 mm diameter bubbles, was strongly related to sediment ebullition flux and important to the dissolution rates used for surface efflux estimates. Using the Sauter mean diameter to represent the volume to surface area ratio of the bubble size distribution in a bubble dissolution model resulted in a surface methane efflux of 490 ± 1000 mg CH₄ m⁻² d⁻¹. Hydroacoustic results were more conservative than simultaneous drifting chamber survey results as the chamber method integrates over low methane fluxes. Hydroacoustic fluxes and concomitant eddy covariance methane flux measurements revealed a flux dependence on hour of day related to water level changes. Ebullition fluxes and bubble size were related to each other and the reservoir bathymetry. Hydroacoustic flux surveys were fast and efficient and produced results corroborated by a previous study in this reservoir that show it emits above global average levels of methane via ebullition.

5.1 Introduction

Production of methane (CH₄) is the terminal process of organic carbon degradation in anoxic sediments, be it in wetlands, peatlands, lakes, reservoirs, or the ocean (Chanton and Whiting, 1995). The high global warming potential of CH₄ (25 times more than carbon dioxide on a 100-yr time scale) has made it an important greenhouse gas to monitor from all systems where it is produced, yet aquatic systems remain overlooked in global budgets (Forster et al., 2007). As knowledge about the role of natural and manmade aquatic systems in the global carbon cycle is gained, the significance of CH₄ ebullition, one of the more efficient transport pathways, has come to light but remained understudied due to its complexity. While sufficient methods do exist for monitoring the surface efflux of CH₄ from water bodies, not many aid in the understanding of or provide detailed information about the variability of ebullition dynamics.

Recent work has shown that the aquatic system as a whole may be offsetting the terrestrial greenhouse gas sink by at least 25 % via their significant emissions of CH₄ (Bastviken et al., 2011). Despite the fact that the current inland water system globally buries more carbon than the ocean and

emits as much in the form of carbon dioxide as the ocean uptakes in carbon, manmade impoundments continue to be constructed (Tranvik et al., 2009). Moreover, the role that small water bodies (\sim 1 km²) play in the carbon cycle has often been overlooked in regional studies, although their cumulative area dominates the continental freshwater system (Downing et al., 2006). Methane emissions from all sizes of lakes have been studied (Bastviken et al., 2004), but as for reservoirs the attention has been focused on the larger ones (Soumis et al., 2005). Atmospheric CH₄ emission pathways include diffusion, ebullition, and advection through plants (Bastviken et al., 2004), with the additional degassing pathway at or downstream of a dam occurring in hydropower reservoirs (Guérin et al., 2006). Due to the release of CH₄-rich anoxic hypolimnetic water, dam and downstream river degassing is typically the most sizeable emitter in many large tropical reservoirs (e.g., Kemenes et al., 2007), while ebullition is typically the dominant emission pathway in natural lakes and temperate and boreal reservoirs (Bastviken et al., 2011; Flury et al., 2010; Walter et al., 2007; Soumis et al., 2005). Unfortunately, the spatiotemporal variability of ebullition has stifled progress in truly assessing its emission importance globally.

Adding to the difficulties associated with making accurate or representative estimates of ebullition emission is the fact that the mechanisms causing its variability are not fully understood. Bubble formation within sediments is not well constrained, let alone the processes which allow or exasperate their release. The reduction in hydrostatic pressure, whether due to tides (Varadharajan et al., 2010; Martens and Val Klump, 1980) or water level drawdown in a reservoir (Ostrovsky, 2003), typically increases ebullition rates. Models attempting to explain this process (Scandella et al., 2011; Algar and Boudreau, 2010) are relatively similar in that they center on the idea of the bubble being able to overcome the resistance induced by the sediment because total hydrostatic pressure has been reduced. Other environmental phenomena have been observed that affect the timing of ebullition, such as air pressure (Mattson and Likens, 1990), wind stress (Keller and Stallard, 1994), and shear stress at the sediment-water interface (Joyce and Jewell, 2003). Large seasonal variations, presumably due to temperature affects on methanogenesis, have recently been shown in a temperate reservoir (DelSontro et al., 2010). As for the spatial variability of ebullition, there is compounding evidence that sediment type (grain size, porosity) along with gas flow rate controls the shape and size of bubbles (Meier et al., 2011; Leifer and Culling, 2010; Boudreau et al., 2005), which could influence the presence and magnitude of ebullition. A few studies have observed a depth-dependence of ebullition (Bastviken et al., 2004; Keller and Stallard, 1994) with respect to surface emissions, which is not surprising since bubble dissolution upon ascent is strongly related to the water depth at which the bubble was released (McGinnis et al., 2006). This fact has also most likely contributed to the lack of knowledge regarding ebullition as these studies

showed a significant decrease in ebullition emission from already quite shallow depths (< 10 m), thus prompting others to neglect ebullition in deeper systems.

Directly measuring atmospheric CH₄ emissions has typically been done with the use of floating chambers (e.g., Ojala et al., 2011; Vachon et al., 2010; Abril et al., 2005) and, along with some additional data post-processing, the contribution from ebullition can also be assessed from static (Bastviken et al., 2004) or dynamic (Ramos et al., 2006) floating chambers. Submerged gas traps have been the easiest choice for measuring only ebullition (e.g., Abril et al., 2005; Keller and Stallard, 1994) and have recently been advanced with long-term automated measurement for higher temporal resolution (Varadharajan et al., 2010). In general, however, these types of instruments cannot supply substantial spatial coverage of a water body since they are usually quite small and must remain in a single location for a certain amount of time in order to get decent measurements. As surface diffusion depends upon surface water CH₄ concentrations that tend to be homogeneous over relatively large spatial scales, the lack of spatial resolution provided by floating chambers may not be a big disadvantage for estimating diffusion. Ebullition, on the other hand, has been shown to be quite spatially variable (e.g., DelSontro et al., 2011; DelSontro et al., 2010; Ostrovsky et al., 2008), and would require either many more traps/chambers or a lot more time to resolve. In addition, primitive, non-automated gas traps and floating chambers are not able to resolve the temporal variability of ebullition that their automated counterparts have shown can be quite substantial (e.g., Ramos et al., 2006; Varadharajan et al., 2010).

Recent development of hydroacoustic techniques for the study of ebullition dynamics seems to be the most promising method to overcome the limitations traditional methods have in resolving the spatiotemporal variability of ebullition. Greinert et al. (2010) used a combination of multibeam and single-beam systems to extrapolate CH₄ emissions from an active Black Sea seepage area to the rest of the seep field. With a bubble dissolution model they were able to estimate CH₄ emission to the atmosphere from seeps deeper than 70 m, but met some challenges when trying to discern the temporal resolution. The multibeam system presented by Schneider von Diemling et al. (2010), however, successfully resolved tidal-controlled variability of ebullition in the North Sea. Limnological hydroacoustic techniques using echosounders have also been developed to not only estimate bubble gas flux into the water column and the atmosphere, but also to determine the bubble size distribution (Vagle et al., 2010; Ostrovsky et al., 2008). Until now, however, their use to delineate potential mechanisms controlling the spatial and temporal variability of ebullition in aquatic systems has not been exploited.

Here, we present results from a bubble calibration of our split-beam 120 kHz echosounder, which allowed us to accurately estimate CH₄ ebullition flux from a dense ebullition area in a

reservoir known for intense CH₄ bubbling (Lake Wohlen, Switzerland; DelSontro et al., 2010). The application of a hydroacoustic post-processing technique used for estimating sediment ebullition flux in the presence of fish (Ostrovsky, 2009) is also presented and evaluated compared to other hydroacoustic methods. Using a bubble dissolution model (McGinnis et al., 2006), we then approximate surface CH₄ efflux from sediment CH₄ ebullition and critically assess the results spatially and temporally, as well as against other surface emission measuring techniques deployed simultaneously. The importance of bubble density and bubble size distribution on gas flux, as well as how to represent bubble volume to surface area ratios accurately, is discussed in response to the unique dataset provided by the hydroacoustic technique. Finally, the estimates from this study area are put in a global context to show the remaining lack of knowledge regarding CH₄ ebullition

5.2 Material and Methods

5.2.1 Sampling site

The high rates of CH_4 ebullition that has been observed in Lake Wohlen (DelSontro et al., 2010) was examined in detail using various methods during an intensive summer campaign. The reservoir was described in more detail elsewhere (Eugster et al., 2011; DelSontro et al., 2010), but in short, Lake Wohlen is a run-of-river hydropower reservoir built in 1920 along the Aare River downstream from Bern, Switzerland. With a discharge ranging from ~40 to 400 m³ s⁻¹ that translates into a residence time of typically less than a week (average, 2 days), this 2.5 km² riverine reservoir remains vertically well-mixed and oxic all year. Dissolved CH_4 concentrations increase along the reservoir toward the dam as a result of ebullition (DelSontro et al., 2010). In addition, seasonal water temperatures ranging from 5°C to 20°C have been correlated with ebullition, which is most prominent in late summer and early fall when temperatures are the highest (DelSontro et al., 2010). For this study, we surveyed only a small section of the reservoir where intense and consistent ebullition has been observed (Figure 5.1).



Figure 5.1. Bathymetry of study site in Lake Wohlen, Switzerland. Coordinates are in CH1903 (Swiss coordinates), in which 1 = 1 m. Depth contours are in 1 meter resolution. (background image © 2010 swisstopo, reproduced with the authorization of swisstopo JD100042/JA100020)

5.2.2 Sampling strategy

Ebullition was quantified via three independent methods during summer 2008. Surface methane emissions from Lake Wohlen were measured via floating chambers and atmospheric eddy covariance, while ebullition in the bottom 3 m of the water column was measured hydroacoustically with an echosounder. The eddy covariance set-up used an off-axis integrated-cavity output spectrometer (Los Gatos Research In., CA, USA) for CH₄ measurements and is described in detail in Eugster and Plüss (2010). The data processing and analysis of all eddy covariance results from Lake Wohlen were described in Euster et al. (2011). The eddy covariance tower was in place from June 4 to 30 and July 21 to August 12 of 2008, while hydroacoustic and chamber surveys took place on June 10, 11, and 24 of 2008 and on July 23, 24, 29, and 30 of 2008. Gas traps (inverted funnels) were also deployed during hydroacoustic surveys to capture bubbles for CH₄ analysis via gas chromatography (Agilent 6890N) and a flame ion detector. The gas trap and floating chamber designs, as well as the sampling of them, are fully described in DelSontro et al. (2010).

5.2.3 Echosounder calibration

Ebullition was surveyed using a downward-looking Simrad (Kongsberg Maritime AS, Norway) split-beam echosounder (EK60, 7° beam angle) with a 120 kHz transducer operating at a rate of 5 pings s⁻¹ and recording with a lower threshold of -120 dB. A previous study with a 120 kHz dualbeam echosounder (BioSonics, DE5000) has shown that the acoustic signature or target strength (TS) of bubbles typically lies between -30 and -70 dB (Ostrovsky et al., 2008). TS is actually the log representation of the backscattering cross-section of a target, σ_{bs} (m²), in which TS = 10 × $log_{10}(\sigma_{bs})$. The echosounder was calibrated for TS detection using a 23 mm diameter standard copper target (Foote et al., 1987).

To use the hydroacoustic results to calculate bubble flux, the relationship between σ_{bs} (or TS) and bubble volume must be found. Therefore, we also performed a bubble calibration with our echosounder following the methods of Ostrovsky et al. (2008). The field calibration was carried out at a boat dock in a small harbor on the northern edge of Lake Lucerne in Switzerland during May and August 2009 and August 2010. A bubble system was used to produce and video record bubbles between 10 and 11 m release depth, while the echosounder was mounted to the boat dock and recorded from the surface. Conductivity-temperature-depth casts were made for ambient water conditions and samples were taken for dissolved CH₄ concentrations, which are both important for calculating bubble size and composition changes with rise.

The bubble system frame was triangular and made from 1 m long L-shaped steel beams. The frame held a CH₄ tank (Pangas, >99.99%) along one of the edges with a regulator (Tescom, Germany) that was custom-made to be submersible and pressure-proof (WSM-Armaturen, Germany). Air-tight tubing extended from the regulator to a hose fitting (Swagelok) and an intermediate regulator that allowed for more precise gas flow adjustment. A metal pipe adaptor (Swagelok) connected this regulator to the final air-tight tubing that contained a three-way stopcock at the end which held the needles used for making bubbles. Small and large bubbles were created differently (discussed below), but regardless the location of the bubble release was aligned with the underwater video camera (SuperSeaCam D6000, DeepSea Power & Light, California, USA) recording at 30 frames per second. The camera and an underwater light (DeepSea Power & Light) could be controlled (power, zoom, and focus) from the surface via connection by an underwater cable to the SuperSeaCam rackmount controller (S/N 104, Deepsea Power & Light, California, USA). The video was recorded using Dazzle Video Creator Platinum (DVC107, Pinnacle Systems, Avid Technology), which was connected via an S-video cable to the rackmount controller.

There were two different set-ups for creating small bubbles ($\sim 1 - 4$ mm equivalent diameter) and a single large size (~ 12 mm equivalent diameter). Small bubbles were produced using

disposable medical needles (e.g., Terumo, Microlance) with various orifice diameters up to 1.2 mm diameter and two larger 2R2 stainless steel medical needles (see Table 5.1). The needles extended from the three-way stopcock and then attached to the frame so to be kept in the camera's field of view. A gray board was placed behind the needle so as to better illuminate the bubble during video-recording. The board was on a hinge with a line to the surface so it could be lowered during acoustic data collection. Gas flow rate was adjusted at the surface to produce approximately one bubble per second before lowering the bubble system to the bottom. The large bubble set-up also used a needle to produce bubbles, but the bubbles were then collected within an upside down syringe until the gas had reached the 1 ml mark on the receptor as seen via live video streaming. The syringe was held in place by two aluminum pieces that were connected to a cylindrical steel rod attached to the bubble system. Via a line attached to one of the aluminum arms we were able from the surface to rotate the syringe around the cylindrical steel rod to point upward. Thus the bubble could be released once the 1 ml mark was reached.

The volume of the large bubble was known as a volume-calibrated syringe was used to create that bubble. However, the volumes of the bubbles released from needles were not known and were estimated from the video. Video images of the bubble just before the point of release were analyzed in ImageJ (National Institutes of Health, USA) with the known width of the needle providing the pixel scale in the images. To find the volume of the bubble, a line was drawn down the center of the bubble and the length from each pixel in the middle to the outer edge was measured on both sides of the bubble. The volume of each pixel segment was calculated using the formula of a cylinder, $V = \pi r^2 h$, where r (radius) was the distance of half a pixel and h (height) was the distance from the middle line to the outer edge of the bubble. The volumes of each segment were summed to find the volume of the bubble. For each bubble size 15 bubbles were analyzed in this manner and the standard deviations of the calculated volumes were used to estimate the errors.

The hydroacoustic data were processed with Sonar 5 Pro (Lindem Acquisition, Norway) after conversion with a time-varied gain of $40 \times \log_{10}$ (R), where R is range or depth of target, which compensates for beam spreading and absorption due to distance of a target from the transducer. A single bubble will contain several echoes and thus several values for TS as it rises and is continuously recorded by the echosounder. An accurate TS distribution of single echoes of many bubbles of the same size is needed for bubble calibration and so only echoes holding to the following criteria were accepted during conversion for the single echo detection echogram: (1) pulse lengths within 0.8 and 1.20 relative to the transmission pulse, (2) maximum angle standard deviation of 0.30 degrees, and (3) maximum gain compensation of ± 3 dB. In addition, only bubbles released and remaining in the center of the beam (± 1 degree in both the along and athwart ship directions) were used for analysis. Useful TS values could not be recorded for bubbles at the point of release due to interference in the signal from the bubble system itself; therefore, the TS values used were from bubbles that had already risen approximately 1 m and 0.5 m for the 2009 and 2010 calibrations, respectively, and were thus a slightly different volume than the originally released bubble. To correct for this a discreet bubble model (McGinnis et al., 2006) was used to calculate the change in volume of the ~100 % CH₄ bubbles during rise to the acoustically-measured depth. Actual local temperature and dissolved CH₄ and oxygen concentrations were used in the model. Between 37 and 87 bubbles were analyzed for each small bubble and 15 for the 1 ml bubble resulting in anywhere from 100 to over 800 individual echoes used for determining the TS distribution for each bubble size.

5.2.4 Hydroacoustic analysis

With the known acoustic signature of different size bubbles, bubble gas volume in the water column and flux to the atmosphere can be calculated. Ultimately, bubble target density in the observed water volume, N (# m⁻³), must be found and scaled by the TS distribution of bubbles in that water volume. The bubble calibration was then used to convert TS to CH₄ bubble volume. N can be found via two different methods: echo-counting, which is used when targets are well separated with clearly identifiable single echoes; or echo-integration, which was used in this study for densely packed targets where individual single echoes are not easily distinguished, such as within fish schools or bubble plumes (Simmonds and MacLennan, 2005). Sonar 5Pro (Lindem Acquisition, Norway) was used for post-processing after the same time-varied gain conversion that was used for the bubble calibration. A cross-filter detector (Balk and Lindem, 2000) was used to find a sufficient amount of single echo detections for a representative TS distribution. Thus, the Sonar 5Pro echo-integration method we used determined N [# m⁻³] by scaling the total acoustic energy (called the volume backscattering coefficient), s_v [m⁻¹], of the observed volume of water by the TS (or σ_{bs} [m²]) distribution of all targets in that volume of water.

There were, however, single echoes from bubbles as well as non-bubbles (i.e., fish or plankton) present throughout the water column. To determine N for only bubbles, we used the fish-bubble separation method proposed by Ostrovsky (2009) and from here on called bubble/non-bubble separation (BNS) method. The BNS method states that the proportion of desired targets - in our case, bubbles (A_b) - can be found within a given volume of water by relating the TS distribution for identifiable bubbles (F_b) and for identifiable non-bubbles (F_{nb}) to the TS distribution of all single detections (F_a), so that:

$$F_a = F_b \times A_b + F_{nb} \times (1 - A_b).$$
(1)

Therefore, N of all targets can be scaled by A_b to find bubble density only. This method will only work, however, within water layers or transect segments where the bubble to non-bubble density ratio remains similar. For flux estimation, only the 3 m water layer above the bottom was analyzed, and each transect was divided into segments of approximately the same distance (40 – 70 m) via visual inspection of the echograms for changing bubble/non-bubble densities. The segment distance must have also been large enough to provide a sufficient number of single echo detections for representative TS distributions of the various targets. Any abnormally large fish, fish schools, or other unidentifiable strong backscattering targets seen in the water column were manually removed prior to segment analysis as they would cause obvious overestimations in gas volume.

Each segment was then treated in the same manner with the identifiable bubbles and nonbubbles being tracked based on rise velocity. Bubbles appear as diagonal tracks in echograms with a rise velocity between 15 and 50 cm s⁻¹, while non-bubble tracks remained horizontal with almost no vertical velocity. The three TS distributions (F_a , F_b , F_{nb}) were all divided into 2 db bins between -70 and -30 dB and A_b was found for each bin. The frequency of bubbles present in each bin was then multiplied by N (density of all targets) to find bubble density (N_{bub}) per bin. Next, the gas volume represented by each bin was found using the bubble calibration and then multiplied by N_{bub} to find gas volume per bin (ml m⁻³). Total gas volume per segment equalled the sum of the bin volumes and bubble flux per segment was then the product of the total gas volume and average bubble rise speed, which was provided by the hydroacoustic data. Finally, CH₄ flux was calculated by multiplying the bubble volumetric flux by the actual CH₄ composition measured in bubbles caught with gas traps. This flux, however, is merely the flux escaping the sediment and thus flux to the atmosphere was found by estimating bubble dissolution during ascent using a discrete bubble model based on McGinnis et al., (2006).

5.3 Results

5.3.1 Echosounder bubble calibration

We calibrated seven bubble sizes ranging from .001 to 1 ml (~1 to 12 mm equivalent diameter) with our split-beam echosounder (Table 5.1). The TS distributions for each bubble size across multiple replicates were narrow for the smallest bubbles and became wider for bubbles over 0.01 ml (Figure 5.2a). This is most likely a result of larger bubbles varying more in shape upon release and during ascent, as has previously been observed (Ostrovsky et al., 2008).

Similar to the results from Ostrovsky et al. (2008), we found that σ_{bs} and bubble volume, V_b , were strongly correlated ($R^2 \sim 0.92$, p<0.001; Figure 5.2b):

$$\log_{10} (\sigma_{\rm bs}) = 0.7443 \times \log_{10} (\rm V_b) - 4.413.$$
 (2)

Therefore, V_b can accurately be estimated from hydroacoustic results for σ_{bs} using the following transformed equation:

$$V_{\rm b} = 849825 \times \sigma_{\rm bs}^{1.3435} \tag{3}$$

Our calibration corresponds closely to that from Ostrovsky et al. (2008) (see Figure 5.2b), despite the fact that they used a greater range in bubble sizes, including much larger ones, with a dual-beam 120 kHz echosounder. The agreement is especially noteworthy considering that Ostrovsky et al. (2008) performed their calibration under laboratory conditions, while our calibration was carried out under field conditions that were less easily controlled. Our calibration included some of the most commonly observed bubble sizes in nature. Leifer and Culling (2010) found bubbles from natural marine seeps off of the California coast produced bubbles ranging from 1.5 to 12 mm in equivalent diameter. Ostrovsky et al. (2008) found that 90% of bubbles in a natural freshwater, Lake Kinneret (Israel), were between 2.6 and 9 mm in diameter and that 50% of them had diameters between 4 and 6.4 mm.

The 4 mm diameter range for bubbles is well represented in our calibration, but producing bubbles of larger sizes (i.e., not with needles) was found to be quite difficult. One by-product of calibrating under field conditions was a gap in calibration for bubbles with diameters between 5 and 12 mm because maintaining bubble release rates was not readily controlled in the field and using objects with orifices larger than needles. In addition, bubbles in that size range were much more difficult to analyze using video images as a portion of the bubble remains inside the orifice even at the time just before release. However, our calibration agrees closely with the lab calibration of Ostrovsky et al. (2008) that had better coverage in this size range (Figure 5.2b). In addition, the relationship between our calibration bubble volumes and rise speed agree well with previous detailed experiments with air bubbles (Haberman and Morton, 1954; see our Table 5.1 and also Figure 6 of Ostrovsky et al. (2008)). Ultimately, our calibration compares quite well with Ostrovsky et al. (2008) and we feel confident using our calibration for the hydroacoustic analysis of bubble sizes and CH₄ fluxes in Lake Wohlen.



Figure 5.2. a) TS frequency distributions for each bubble size used for calibration. Number of single echo detections used for analysis listed as n for each size. **b)** Our bubble calibration results (with error bars) showing relationship between bubble volume (V_b) and backscattering cross-section (σ_{bs}) of said bubble: $\log_{10} (\sigma_{bs}) = 0.7443 \times \log_{10} (V_b) - 4.413$ (R² ~0.92). Circles are the calibration results from Ostrovsky et al. (2008).

	Bubble volume analysis				Bubble TS analysis			
Needle size	Bubbles analyzed	Volume, V _b	Standard deviation	Bubble equivalent diameter	Bubbles analyzed	TS	Standard deviation	Rise speed
[mm]	[#]	[× 10 ⁻³ ml]	[× 10 ⁻³ ml]	[mm]	[#]	[d B]	[dB]	[m s ⁻¹]
0.4	30	1.2	0.20	1.3	70	-66.10	0.56	0.31
0.6	15	4.4	0.22	2.0	38	-63.33	0.29	0.32
0.9	15	9.5	0.49	2.6	42	-60.37	0.47	0.28
1.2	15	12	0.64	2.9	52	-56.47	1.27	0.25
2	16	35	0.74	4.0	54	-55.64	1.00	0.24
3	16	40	1.4	4.3	87	-51.32	1.63	0.22
1 ml	40	1005	33	12.4	15	-45.42	1.64	0.23

Table 5.1. Echosounder bubble calibration results

5.3.2 Sediment ebullition flux

Hydroacoustic surveys for ebullition were conducted on seven different days covering between 400 and 1600 m² of the study area and a total surveyed area of 7670 m² (Table 5.2). Each transect was subdivided into segments based on target (bubble and non-bubble) densities resulting in a total of 556 segments with an average distance of 46 m. The mean depth for all segments was 5.9 m but the total depth range surveyed was from 1.5 to 11.1 m (Figure 5.1), thus with a 7° beam angle echosounder coverage ranged from 0.03 to 1.5 m².

Using the BNS method with our echosounder calibration and after correcting for the $70 \pm 5\%$ CH₄ measured in bubbles collected with funnels ~1 m above the sediment bottom, the average sediment ebullition flux (i.e., flux from bottom to overlying water) from all 556 segments was 580 ± 1150 mg CH₄ m⁻² d⁻¹ (Table 5.2). Maximum fluxes were in the 10³ mg CH₄ m⁻² d⁻¹ range on all days, except July 23 which had a few segments in the 10⁴ mg CH₄ m⁻² d⁻¹ flux range. The high variability across segments, which ranged over four orders of magnitude, was expected as transects were subdivided based on bubble and non-bubble densities that was also variable. Zero flux segments were observed on each survey day (Table 5.2). Of the 556 total segments analyzed over several campaigns, only 11% of them contained absolutely no ebullition; however it should be noted that surveys were purposely conducted in a region known for active ebullition. In terms of total areal coverage, of the 7660 m² surveyed over seven days, 1330 m² (~17%) was not bubbling at the time of surveying (Table 5.2).

Date	Segments	Total distance	Acoustic coverage ^b	Area of no ebullition	Average sediment CH ₄ ebullition	Maximum sediment CH ₄ ebullition
	[#]	[m]	[m ²]	[m ²]	$[mg m^{-2} d^{-1}]$	$[mg m^{-2} d^{-1}]$
10 June	24	1714	420	80	130	1040
11 June	61	4218	1130	90	440	3430
24 June	82	4351	1260	200	360	4550
23 July	98	4504	1640	240	1450	15500
24 July	135	5226	1570	470	380	2980
29 July	74	2869	840	60	430	3260
30 July	82	2835	810	190	460	3460
Sum/Avg ^a	556	25717	7670	1330	580 ± 1150	

 Table 5.2. Hydroacoustic analysis results according to survey day

^a Sum for all columns, except for flux where it's the average ± 1 SD.

^b Coverage equals distance of segment multiplied by diameter of echosounder beam at average depth of segment

There were some general spatial trends in ebullition observed in our sampling area, which are illustrated in Figure 5.3 by the contours of four campaigns. During the four July campaigns, there was typically a low flux (blue area, Figure 5.3) zone in the deepest part of the old river channel along the north side of the lake (see Figure 5.1 for associated bathymetry). Also, when surveys did extend further to the south, a low flux zone was found on the shallow shelf parallel and adjacent to the south bank. In general, there was a high flux (yellow, orange, red, Figure 5.3) zone located in between the two low flux zones running parallel with the bathymetry of the area (Figure 5.1).



Figure 5.3. Sediment ebullition contours for four July campaigns. Fluxes are of sediment CH_4 ebullition. Crosses are mid-segment locations. Red star was eddy covariance tower location. Coordinates in CH1903 (Swiss coordinates). Highest fluxes observed were on July 23 with the consistently low and zero fluxes observed the following day (July 24). On most days a high flux zone (orange-red) was observed in the middle of the study area with a low flux zone (blue) on either side corresponding to the deepest part of the old river channel (northern zone) and the shallow shelf adjacent to the south bank. (background image \mathbb{C} 2010 swisstopo, reproduced with the authorization of swisstopo JD100042/JA100020)

Differences in ebullition frequency and magnitude were observed between the seven campaigns with the most apparent between the consecutive survey days of July 23 and 24 (Table 5.2 and Figure 5.3). The highest fluxes of the entire study were observed on July 23, while the most zero and low fluxes were observed on July 24. Total hydroacoustic coverage on those days was similar (Table 5.2), but spatially slightly different with the July 23 survey covering a longer and more narrow region than the July 24 survey (Figure 5.3). The low flux zone in the old river channel is observed in both, but the high flux zone is much more pronounced on July 23 and extends further

to the west as well. The consecutive July 29 and 30 surveys, on the other hand, showed remarkably similar results (Table 5.2). The June surveys showed similar trends as the July surveys (Figure C.1). June 11 and 24 were quite similar to the other days (Table 5.2), while the very limited coverage in a mostly low flux area on June 10 resulted in overall lower fluxes than observed in the other campaigns.

5.3.3 BNS method performance

The performance of the BNS method was evaluated using other hydroacoustic post-processing techniques to assess its applicability in Lake Wohlen and whether it is the best process to use to estimate bubble flux in the presence of fish. The BNS method used in this study was essentially an echo-integration technique in which the mean volumetric backscattering coefficient, s_v, was used to determine target (i.e., bubble) density instead of only using single echoes, which is done in an echocounting procedure. The difference between the full energy amplitude of a segment (which s_v is based on; see examples on left in Figure 5.4) and only the single echoes (examples in middle in Figure 5.4) can be quite substantial, for example, when fish are in schools or bubbles are emitted closely together or in plumes. Thus, using echo-counting in such cases typically results in a loss of data and accuracy. Ostrovsky (2003) has shown that echo-counting and echo-integration provided similar densities in the epilimnion of Lake Kinneret where bubbles were well separated, but echocounting underestimated bubble density in the hypolimnion because more multiple echoes (echoes of 2 or more targets closely together combining into one echo observed by the echosounder) were present near the bottom and at increased distance from the echosounder. Echo-integration typically corrects for this by using the full acoustic energy of the sample volume, but scaling it to the TS distribution of only the accepted single echoes.

We found that echo-counting densities were, as expected, typically less than the BNS results, which in turn resulted in lower bubble fluxes. Figure 5.5a shows the ratio of segment fluxes from both methods for a transect with many segments on July 23. The ratio consistently falls below the 1:1 line (black line) meaning that echo-counting underestimated flux compared to echo-integration, implying that bubbles are frequently emitted quite close together or in plumes from the bottom of Lake Wohlen. As we did not analyze more than the 3 m above the lake bottom, we cannot say for sure that echo-counting results would be closer to echo-integration results higher in the water column. Visual inspection of echograms from deeper regions of the lake suggests that the results may be more similar as bubbles tend to separate further away from each other as they rise. However, the mean depth of our survey area was ~ 6 m and this is most likely too shallow for the use of echo-counting as the bubbles do not have much time to gain substantial distance from each

other. Ultimately, echo-integration is the better choice of density analysis methods when calculating flux from bubble plumes or in shallow regions.



Figure 5.4. Example segments from 23 July showing sediment ebullition fluxes of (**a**) 6200 mg CH₄ m⁻² d⁻¹ and (**b**) 2700 mg CH₄ m⁻² d⁻¹. The full energy amplitude of the segment is shown left, and only single echo detections are shown in the middle. Bottom axis is ping number. Color bar is of TS in dB. Right axis (R) is depth in m. Red lines are the 3 m above bottom boundary where measurements were made. On right are the TS frequency distributions for identifiable bubbles echoes and the contributions of each TS bin to the total volume from all bubbles. Both segments have similar bubble densities, so the factor of two difference in flux is mostly because of the few bubbles larger than -40 dB present in segment (**a**).

Ostrovsky et al. (2008) suggested an additional procedure for an estimation of flux that could be used in the absence of exact bubble size data, but with approximate information about the average bubble size in a water body. Volumetric bubble density, $V_{\Sigma B}$ (ml m⁻³), is the product of the bubble target density, N (# m⁻³), and the average volume of observed bubbles, V (ml). N is defined as s_v divided by mean σ_{bs} , while the bubble volume is based on the echosounder calibration. Thus, $V_{\Sigma B}$ can be related to σ_{bs} and s_v in the following manner:

$$V_{\Sigma B} = NV = (s_v \sigma_{bs}^{-1}) (849825 \times \sigma_{bs}^{-1.3435})$$
(4)

where our echosounder calibration is used to find V. More details regarding this proof are given in Ostrovsky et al. (2008), but after combining the two σ_{bs} and substituting the weighted mean σ_{bs} of bubbles found in Lake Wohlen (TS = -51.3 dB, Figure 5.6a and discussed later), $V_{\Sigma B}$ can be estimated merely by the s_v of the sampled water volume in question:

$$V_{\Sigma B} \approx 14700 \times s_{v}.$$
 (5)

Since the s_v estimation uses the entire acoustic energy of the segment, bubble flux results can only be trusted in segments where bubbles were the only targets. The s_v was already zero in 8 of the 66 segments identified as having zero ebullition by the BNS method, meaning no targets at all existed in those segments. The other 58 segments, however, did still contain fish, and were not zero, as seen in Figure 5.5b. These fluxes were thus artificially set equal to a zero flux and left out of the correlation with the BNS results, which correlated fairly well (y = 0.7701x + 0.5517; $R^2 = 0.9086$; red line, Figure 5.5b). This surprising match is mostly due to the fact that in general there were not many fish present in the lake and we erased the few largest ones that were observed. The nonbubble targets that remained were so small (Figure 5.6a and discussed later) that they contributed very little to s_v relative to the bubbles. The majority of fluxes, which fall between 10^2 and 10^4 mg $CH_4 \text{ m}^{-2} \text{ d}^{-1}$ for both methods, agree the best, while the s_v estimation method overestimates the lower fluxes and underestimates the higher fluxes compared to the BNS method. The overestimation of lower fluxes by s_v estimation was most likely because when fewer or smaller bubbles exist in a segment (thus producing low fluxes) the presence of fish, even small ones, contributes more to the overall s_v. The slight underestimation of higher fluxes by s_v estimation is likely due to the fact that it is based only on the (weighted) average bubble size of the system.



Figure 5.5. Comparing the flux results (always in mg CH₄ m⁻² d⁻¹) of the BNS method to the (a) flux results of the echo-counting method on all segments of the July 23 transect from which Figure 5.4 was based, and to the (b) flux results of the s_v estimation method (used when bubble size distributions are not known) for all 556 segments. In both panels the black line is the 1:1 ratio. Echo-counting always results in lower fluxes as it only uses the detected single echoes. The s_v estimation shows a reasonable correlation (red line, $R^2 = 0.91$) with the BNS method. At lower fluxes, the s_v estimation overestimates flux while at higher fluxes it slightly underestimates flux, but for the majority of fluxes (in 10² to 10⁴ mg CH₄ m⁻² d⁻¹ range) the two methods agree nicely.

Since the BNS method used the s_v and the actual bubble size distribution of each segment to calculate flux, it is most likely that the highest fluxes calculated with that method were likely a result of larger bubbles, which were potentially larger than the average bubble size found for the whole system (TS = -51.3 dB; ~0.1 ml bubble with an equivalent diameter of 5.9 mm). Ostrovsky et al. (2008) points out that the s_v estimation will only work in systems with consistent bubble sizes. As can be seen in Figure 5.6a, the bubble size distribution in Lake Wohlen is fairly wide covering bubbles between -40 and -70 dB. In addition, even though there are fewer of the larger bubbles (> - 50 dB) they contribute much more heavily to the total volume of bubbles, as can be seen by the volume distribution (thin black line) associated with the bubble size distribution in Figure 5.6a. Therefore, we should use a more representative mean for the bubble size distribution that better relates the size distribution to its total volume.

The Sauter mean diameter (SMD) is often used in fluid dynamics and other fields where the volume-to-surface area ratio is of importance (e.g., Orsat et al., 1993), which is true for our case since bubbles larger than -51.3 dB contain much more gas than smaller bubbles and thus contribute more to the total bubble volume of Lake Wohlen (volume, Figure 5.6a). The SMD calculates the diameter of a sphere that would have the same volume-to-surface area ratio as the distribution of bubbles by giving more weight to the larger bubbles in the following equation:

$$SMD = \frac{\sum_{n=1}^{n} d_i^{3}}{\sum_{n=1}^{n} d_i^{2}}$$
(6)

where d_i is equivalent diameter for each bubble present in the population, *i*. Thus the average bubble size in Lake Wohlen was raised from the weighted mean of 5.9 mm diameter to the SMD of 10.1 mm diameter. Using the SMD for the s_v estimation method yields a new equation ($V_{\Sigma B} \approx$ 21696 × s_v) that improves the fit only slightly ($R^2 = 0.91$) as the original equation was already quite a good approximation for the majority of the fluxes. The biggest difference is observed in the larger fluxes, which the new s_v estimation based on the SMD underestimates less. Overall, after erasing the larger fish and using the SMD instead of the weighted mean bubble size, the s_v estimation reproduced the flux values well in Lake Wohlen. Ultimately, the BNS method provided the most reliable results for this system. The method comparisons however revealed the importance of bubble size to flux estimates. Larger bubbles contribute heavily to the gas flux from a water body and it is thus necessary to either accurately determine the proportion of larger bubbles, or use a representative mean, such as the SMD, instead of the arithmetic or weighted mean when estimating ebullition flux from a system.

5.3.4 Bubble size

From the 556 segments, 6773 bubbles and 3618 non-bubble targets were identified. As stated earlier, the largest fish, which were already quite rare in Lake Wohlen, were removed during post-processing; therefore, there was very little overlap between bubble and non-bubble TS distributions (Figure 5.6a). Non-bubbles were typically less than -60 dB with over 50% of them near -70 dB and presumably even smaller. These extremely small detections were most likely plankton (Simmonds and MacLennan, 2005) and appeared mostly in depths shallower than 5 m.

The observed bubbles had a much wider TS distribution with similar amounts present between - 65 and -51 dB, but slightly more between -51 and -54 dB (Figure 5.6a). As stated earlier, the weighted mean TS for all observed bubbles was -51.3, which according to our calibration regression is equivalent to a 0.108 ml bubble having an equivalent diameter of 5.9 mm. Ostrovsky et al. (2008) similarly found that the average bubble in Lake Kinneret was 0.097 ml (5.7 mm equivalent diameter). Greinert et al. (2010) also found that 6 to 7 mm diameter bubbles were most common from seeps in the Black Sea.



Figure 5.6. (a) Target strength (TS) distribution for all bubbles and non-bubbles detected in all 556 segments of hydroacoustic data from 7 campaigns on Lake Wohlen. Majority of nonbubbles were small and mostly likely plankton. Bubbles spanned many sizes. Solid line is volume frequency of observed bubbles per TS bin. Higher TS bubbles contribute the most volume despite existing much less in number. Thus, using an arithmetic mean TS for bubble calculations does not accurately represent the bubble size distribution and its contribution to CH_4 flux. (b) The weighted mean bubble size may be more representative for a segment, but the most appropriate in terms of mass transport is (c) the Sauter mean diameter, which accounts for the volume to surface area ratio for a sphere and gives more weight to the bigger bubbles, which contribute the most to the surface flux.

When looking at the weighted mean bubble size per segment, we find that over 15% of the segments had a mean bubble volume less than 0.1 ml with diameters mostly between 4 and 6 mm (Figure 5.6b). Ostrovsky et al. (2008) found that over 50% of Lake Kinneret bubbles had diameters between 4 and 6.4 mm; therefore, Lake Wohlen bubbles vary much more in size than those of Lake Kinneret, which has important implications for gas flux as larger bubbles contribute much more to the total CH_4 efflux. For example, Figure 5.4 includes two segments from July 23 that, despite appearing similar in bubble density (which they are), have sediment ebullition flux rates that differ by a factor of two (segment (a) is 6200 mg CH₄ m⁻² d⁻¹ and segment (b) is 2700 mg CH₄ m⁻² d⁻¹). Since the densities are similar, the cause for this flux difference must be due to difference in bubble size. The frequency of bubble size and each TS bin's contribution to the total gas flux of that segment are shown on the right of Figure 5.4. Segment (b) does not contain any echoes larger than -40 dB, while segment (a) has a few bubbles larger than -40 that are contributing heavily to the total gas volume in that segment. The weighted mean bubble diameters for these segments are 9.5 and 7.2 mm, while their SMDs are 18 and 10.6 mm, respectively. The difference in weighted means for these segments, however, does not truly represent the difference in fluxes observed. The SMD of each segment, on the other hand, would as it is equivalent to a sphere having the same volume-tosurface area ratio as the observed bubble distribution.

However, to examine the spatial distribution of bubble sizes, it is best to use the weighted mean of the population as it represents the actual size of bubbles released. Again, the majority of bubbles are below ~6 mm diameter (green-blue circles, Figure 5.7) and they seem to be scattered throughout the study area. However, there are areas where bubbles of similar size distributions were clustering together, such as on the shallow shelf adjacent to the south bank of the lake where mostly quite small bubbles (< 4 mm) were present. Small bubbles were also quite common in the deepest parts of the old river channel adjacent to the north bank. These locations correlate with the regions that we observed as having low sediment ebullition fluxes (Figure 5.3). Larger bubbles (> 6 mm diameter; yellow, orange and red circles, Figure 5.7) were observed mostly along the 6 to 8 m depth range between the shallow shelf and old river channel, where the highest ebullition fluxes were observed (Figure 5.3). Similar bubble size trends were observed in the June campaign data as well (Figure C.2) and closely resemble the sediment ebullition flux trends on those days as well (Figure C.1). It appears that the spatial variability observed in sediment ebullition fluxes may be partially due to the spatial differences in bubble size.



Figure 5.7. Bathymetry of study site overlain by color-coded scatter plots of the weighted mean bubble diameters (circles in mm) for each segment for the four July campaigns. X's are of segments with zero flux and thus no bubbles (black and white mean the same). Red star was eddy covariance tower location. Coordinates are in CH1903 (Swiss coordinates). Color bar scale in equivalent bubble volume is 7, 1, 0.1, 1×10^{-2} , and 1×10^{-3} ml for 24 to 1 mm, respectively. Smallest bubbles and zero fluxes consistently occur on the shallow shelf adjacent the south bank, as well as in the deeper parts of the old river channel to the north. Large bubbles observed in middle region where depths are 6 to 8 m and coincide with the high flux zone observed in Figure 5.3. (background image © 2010 swisstopo, reproduced with the authorization of swisstopo JD100042/JA100020)

5.3.5 Surface ebullition comparison

As CH₄ bubbles rise, they experience pressure changes and exchange gas with the ambient water (McGinnis et al., 2006); thus an estimation for bubble dissolution is needed to approximate flux to the atmosphere from sediment ebullition flux. Here is a situation in which neither the arithmetic mean nor the weighted mean would be an appropriate representation for bubble size distribution in a segment. The dissolution rate of a bubble relies heavily upon the size of a bubble, in which smaller bubbles dissolve much faster than larger bubbles (McGinnis et al., 2006). Thus larger bubbles have a much higher chance to reach the atmosphere and inevitably contribute greatly to the surface efflux of CH₄. Therefore, the model was run for each segment with average conditions in Lake Wohlen during surveys (17.5°C, 750 nmol 1^{-1} dissolved CH₄, 70% CH₄ in bubbles), along with the average depth and the SMD as the bubble release depth and initial bubble diameter parameters, respectively. The SMD slightly skewed the bubble size distribution of the segments towards larger bubbles, but more so widened the distribution (Figure 5.6b and 5.6c).

The overall mean dissolution rate was 22%, meaning on average 78% of the CH₄ from rising bubbles makes it to the atmosphere, which is consistent with the overall mean release depth of 5.9 m and mean SMD of 8.8 mm for all segments. Had we used the weighted means for average bubble size of each segment, the average CH₄ escape rate to the atmosphere would have been reduced to 68% for the reservoir. Thus, following the corrections for CH₄ composition and dissolution during ascent, surface ebullition from all 556 segments was estimated (Figure 5.8a). Surface fluxes spanned several orders of magnitude, as expected, and had an overall average of 490 ± 1000 mg CH₄ m⁻² d⁻¹. This average CH₄ emission rate agrees very well with previous CH₄ ebullition estimates from this reservoir using two other methods also conducted in summer – gas traps (480 mg CH₄ m⁻² d⁻¹; DelSontro et al., 2010) and a mass balance-based system analysis (330 mg CH₄ m⁻² d⁻¹; DelSontro et al., 2010) – despite the current study only surveying one active ebullition area (~0.5 km long) while the other methods included the other 5+ km of the elongated reservoir. The agreement with gas traps is not surprising considering they were also conducted in an active ebullition time (i.e., summer and fall), while the mass balance approach produced lower results because it included seasonal changes throughout the year (DelSontro et al., 2010).

Average (asterisks in Figure 5.8) and median (lines in boxplots, Figure 5.8) surface fluxes between campaigns compare well, but there are some obvious differences similar to those found for sediment ebullition fluxes. The most CH_4 by far was emitted on July 23, while the least was observed on June 10, but this is most likely due to the limited coverage on the latter day. The remaining days all exhibit more or less similar trends with 50% of the segments falling within the same range (boxes in Figure 5.8a). While more low fluxes were observed on July 24, the average fell in line with observations on other days. July 23 and 24 may be special cases that will be discussed later.

Interestingly, the drifting chambers (red boxplots, Figure 5.8b) that were deployed in the same study area during four survey days (23, 24, 29 and 30 of July) measured higher average CH₄ fluxes on each day, except July 23. In general, chamber measurements from different days agree with each other, while hydroacoustic measurements also agree with each other. However, there was not a great agreement between the methods on most survey days, except for July 23 when the quartile ranges from both methods corresponded remarkably well. Despite the minor differences, the order of magnitude for fluxes was similar between chamber measurements and hydroacoustic results with the majority between 10^2 and 10^3 mg CH₄ m⁻² d⁻¹. The full range (boxplots whiskers) of hydroacoustic results on each day did include the chamber results, but also much lower fluxes that were not measured by the chambers. All chambers collected gas during all surveys, and only a few measurements were in the range of surface diffusion only levels (~12 mg CH₄ m⁻² d⁻¹, see
DelSontro et al., 2010), while quite low (< 10 mg $CH_4 m^{-2} d^{-1}$) and zero fluxes were measured with the echosounder.



Figure 5.8. Box represents the 25th and 75th percentile. Middle line is the median. Asterisk, *, is the average. Whiskers are the maximum and minimum values. Crosses are outliers. (a) Surface CH₄ fluxes on each campaign day. Shown for each day is total number of segments analyzed for flux (n) and number of segments that had zero ebullition (z), which are not included in the log representation of fluxes. (b) Comparison of surface CH₄ ebullition results from hydroacoustics (H) and drifting chambers (C) for the four days that chamber surveys were conducted. Number of chamber measurements given (n). On July 23 results were similar, and although the range in hydroacoustic results covers that of the chamber results, chambers on average measured higher surface emissions than estimated by hydroacoustics (along with the bubble dissolution model) on the other survey days.

Eddy covariance measurements for CH_4 flux were also made during the hydroacoustic and chamber campaigns. A detailed discussion of those results appeared in Chapter 4 (Eugster et al., 2011). Just as a direct comparison between the eddy covariance fluxes and chamber emissions could not be made because of differences in temporal and spatial resolutions, we were unable to

directly compare our hydroacoustic and eddy covariance results. The eddy covariance footprint (Eugster et al. (2011) and white lines in Figure C.3) did not extend far enough from the eddy tower location on the south bank to overlap with the hydroacoustic transects. Mostly fluxes from the shallow southern shelf were recorded by eddy covariance. There was a northwest stretch of the footprint that measured fluxes close to the high flux region observed at 6 m depth with hydroacoustics, but these eddy covariance measurements were only made when winds were fairly strong (Eugster et al. 2011). Regardless, the average CH₄ efflux measured by eddy covariance was 430 mg CH₄ m⁻² d⁻¹ (Eugster et al., 2011), which agrees remarkably with the average surface ebullition flux estimated by hydroacoustics (490 mg CH₄ m⁻² d⁻¹).



Figure 5.9. Surface fluxes of CH₄ measured by eddy covariance (green shading), hydroacoustics (blue shading), and chambers (red boxplot). Data were aggregated for each hour +/-1 hour (50% overlap). Median (bold line), interquartile range (shaded area; 50% of all values), and maximum and minimum values (dashed lines) are shown. Minimum value for hydroacoustics is zero during most hours and is not visible. Gray shaded area were times when wind was from land and thus eddy covariance measurements were not of the lake. Eddy covariance and hydroacoustic flux measurements agree reasonably well and both show an increase in flux later in the day (after 15:00). Chamber measurements cover the entire range of fluxes, but tend to be higher than results from the other methods.

Despite the lack of ability to directly compare fluxes, we did discover that the methods exhibited similar temporal trends. Both eddy covariance and hydroacoustic measurements showed a correlation between flux and hour of the day (Figure 5.9), in which flux increases after 16:00. The increase was more pronounced in the median (black lines) and quartile ranges of the acoustic data (blue shading) than in eddy covariance data (green shading), but the maximum values (upper dashed lines) measured correspond surprisingly well between the two methods. A possible explanation for the late day increase is that the hydropower company artificially lowers the reservoir level around that time each day during summer (Eugster et al., 2011). Although the level is lowered by no more than 10 cm (Figure 4.3b in Chapter 4), it may be enough to increase ebullition from this fairly shallow reservoir, as has been observed in other systems albeit with larger water level differences (Ostrovsky et al., 2008).



Figure 5.10. Average surface CH₄ emission from all 7 hydroacoustic campaigns is shown (top panel) along with the standard deviations (bottom panel). Lower fluxes (top panel, red-pink) occur on the shallow shelf adjacent to the southern edge of the lake as well as in the old river channel near the north shore. High surface fluxes (top panel, green-blue) were consistently along the center slope between the southern shelf and the old river channel and near the point extending from the northwest. Background image \mathbb{C} 2010 swisstopo, reproduced with the authorization of swisstopo JD100042/JA100020.

5.3.6 Average surface CH₄ ebullition flux

Ultimately, the surface CH_4 ebullition fluxes estimated for the 7 campaign days using the hydroacoustic data can be averaged to produce a composite contour showing the average daily CH_4 emission from Lake Wohlen during summer (Figure 5.10). We see that ebullition fluxes are

typically highest (> $10^3 \text{ mg CH}_4 \text{ m}^2 \text{ d}^{-1}$) along the middle 6 to 8 m deep slope, while often the lowest fluxes (< $10^{1.5} \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$) are observed on the shallow south bank and deepest portion of the old river channel along the north bank, which is consistent with our observations from the sediment ebullition flux contours (Figure 5.3). In addition, fairly high fluxes were present along the north-western edge of our study site adjacent to the deforested field and towards the east along the north bank, which is also part of the old river channel. Although we did not initially interpret this from the sediment ebullition flux contours (Figures 5.3 and C.1), upon closer inspection it is apparent that often there were higher fluxes in that region. In fact, fluxes measured there were consistently over $10^2 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ with quite little variation across campaigns, as is seen in the flux standard deviation composite in Figure 5.10. Fluxes varied the most in regions where we had limited measurements, such as the very southern edge of the study site. There was also considerable variability in fluxes measured along the central slope and in the old river channel. Overall, the most consistent results and best coverage were found in the middle and north western portion of the study area.

5.4 Discussion

5.4.1 Differences between chamber and hydroacoustic data

The hydroacoustic estimates of surface CH₄ ebullition were conservative compared to the simultaneous drifting chamber measurements made in Lake Wohlen, which is in contrast to a similar study in another system where drifting chamber surveys produced lower estimates than hydroacoustic surveys (DelSontro et al., 2011). Several possibilities exist for this, beginning with the obvious fact that chambers integrate over zero or low flux measurements when they are deployed in active ebullition areas. Since the BNS method required the subdivision of transects based on varying target densities, zero and low flux regions were actively found along each transect. Such regions would never be identified with a drifting chamber. Anchored floating chambers could integrate over fluxes as well, but more in a temporal manner. If only one large plume was emitted during the entire deployment period, then that gas flux would be associated with that location, although it may have been a very infrequent event.

The extent of spatial coverage could be another reason for the divergence between the method results. This was the case described in the next chapter (DelSontro et al., 2011), where chambers most likely underestimated fluxes because of an order of magnitude less coverage and a lack of overlap between hydroacoustic surveys and chamber transects. During the Lake Wohlen campaign, however, chamber coverage was only about $40 \pm 24\%$ less than that of the hydroacoustic surveys on

the same day. In addition, the study area was so small that chamber transects easily overlapped with hydroacoustic survey lines (Figure C.3). Also, many of the chambers drifted through the most active ebullition regions of the study area (i.e., the 6 to 8 m slope; Figure C.3) and consequently measured high CH_4 fluxes. We therefore do not believe that this is the major cause for the observed difference between chamber and hydroacoustic measurements. It is most likely a result of the integration over low fluxes by the chambers, while our hydroacoustic technique allowed (and required) the identification of low flux zones.

Above all, hydroacoustic surveys are a more efficient way to estimate CH_4 ebullition than chamber surveys. At a boat speed of 0.5 m s⁻¹, one can survey ~18 km in of transects in a day with an echosounder. At slow wind speeds, an average chamber would cover ~ 2 km in a day; therefore, one would need to deploy ~10 chambers simultaneously all day to equal the distance covered by an echosounder. Post-processing of acoustic data takes roughly one hour for each hour of survey, thus one full day of surveying requires a day of processing. This is significantly less time than it would take to analyze a day's worth of samples from 1-hour long deployments of 9 floating chambers (i.e., 90 samples for 10 hours).

5.4.2 Flux variability

We observed similar trends in the general locations of high and low fluxes that corresponded with the bathymetry of the study area. Lake Wohlen is a run-of-river reservoir with the inflowing river water carrying a moderate organic load (DelSontro et al., 2010) down the old channel that is flanked by slopes on either side. Ostrovsky et al. (2008) showed that in areas with shallow sloping bathymetry ebullition was highest along the slope, but when the slope was steeper ebullition tended to concentrate at the bottom of slope rather than on it. They attributed this to regions with higher accumulations of organic-rich sediment. We found that some of the highest ebullition fluxes in Lake Wohlen occurred along the gentle slope between the shallow shelf and the old river channel in the eastern section of the study area and at the bottom of the steep slope in the southwestern section. The deep center of the old river channel in Lake Wohlen, however, was a location of low flux on most survey days although it is flanked by two slopes. The low fluxes could perhaps be explained by the inflow of colder and relatively rapid river water during summer rains. Velocities in the littoral zone of Lake Wohlen can be 25 cm s⁻¹ (McGinnis et al., 2008) and most likely much faster in the old channel, potentially scouring the bottom and preventing efficient burial of labile organics. This is, however, speculation, but warrants further study.

Consistently low fluxes were found in the shallow reaches of the study area (along the southern bank), which was not expected as ebullition is thought to be prevalent in the shallow

littoral of water bodies (Bastviken et al., 2004). This region is adjacent to farmland and thus must receive some organic and nutrient load, but it is also quite shallow and gently-sloping with substantial submerged vegetation. To the northwest we consistently found high fluxes concentrating around a small point of land covered by a vineyard and forest. The land drops steeply into the old river channel but only to a depth of ~9 m. These two regions (low flux on south bank and high flux near point) have differing bathymetry and are adjacent to two different types of land use schemes. Exploring the causes between the variability in flux estimates from these two regions would provide interesting insight into conditions needed for active ebullition.

As for temporal changes, the ranges of fluxes, as well as the average from the study area, were similar on four of the seven campaign days (Figure 5.8a). Deviating from this trend were June 10, which was most likely from limited spatial coverage compared to the other surveys (Figure C.1), and July 23 and July 24, which is more difficult to explain. The wind was faster than usual (avg, 2 m s⁻¹ and up to 4 m s⁻¹; typical average, 1 m s⁻¹) and abnormally persistent (~10 hours; typically only ~4 hours) on July 23. Keller and Stallard (1994) found a correlation between wind speed and ebullition in Lake Gatun, Panama, so perhaps the fast persistent winds helped drive ebullition on July 23 by accelerating the surface water, which consequently transferred turbulent energy down towards the sediments to increase shear stress that has been shown to enhance increase ebullition (Joyce and Jewell, 2003). Since the lake is quite shallow, perhaps the generation of surface waves induced ebullition (Leifer and Boles, 2005). Algar and Boudreau (2010) have proposed a mechanism by which waves could enhance ebullition by reducing hydrostatic pressure, thus pushing bubbles within the sediment that are halted in growth due to reduced CH₄ production near their perimeter into the regime in which they can escape. If this is the case, then potentially the low ebullition we observed on July 24 was a result of much of the gas reserves in the upper sediment column being exhausted the day before on July 23. That could possibly explain why these consecutive campaigns had such different results, while the July 29 and July 30 campaigns had such similar results (i.e., magnitude and frequency of ebullition were nearly the same). This idea of gas supply exhaustion and recharge within sediments is an interesting aspect of ebullition dynamics that has not been well-studied and deserves more attention.

There is, however, another possible explanation for the flux differences between July 23 and 24. Fluxes on July 23 appeared to be highly related to the hour of the day with the highest fluxes occurring at the latest sampling times, which we have already shown was potentially caused by the lowering of the lake level during summer afternoons (Figure 5.9). Upon further inspection of lake level changes in relation to CH_4 flux (Figure C.4), we see that fluxes tend to be highest during the initial lowering stages (e.g., June 11). This is quite prominent on July 23 when the first fluxes

Measurements on July 24, on the other hand, were made at least 3 hours after the onset of lake level decrease. Interestingly though, measurements on July 29 and July 30 were made at approximately the same period in the daily water level adjustment cycle (Figure C.4) and these consecutive campaigns again had similar flux results (Figure 5.8). Water level variation most definitely has an impact on the ebullition dynamics in this system and it may be in the same manner as described above regarding the wind-induced fluxes. The increase in ebullition observed at the immediate stages of water level lowering may be the result of an ebullition pulse caused by the rapid release of all the bubbles on the border between the no growth and release regime (Algar and Boudreau, 2010). During the remainder of lowering more bubbles would be released, but perhaps the initial lowering temporarily exhausted the surface sediments of gas resulting in lower overall fluxes. To resolve these temporal changes, ideally, the same transects should be surveyed several times per day and for consecutive day campaigns to cover a large range of conditions affecting ebullition rates.

5.4.3 Bubble density and size

In order to calculate bubble flux using the BNS method, the bubble proportion of the total target density is scaled by the bubble size distribution in that segment. Therefore, bubble flux is a function of density as well as the size of bubbles. Bubble density and volume typically portray the same pattern, as shown in Figure C.5., where when bubble density is high, bubble volumes tend to be higher. This implies that bubbles tend to be larger when released together or, in other words, bubble plumes contain larger bubbles than singly released bubbles. However, when density and volume are contrasting (i.e., one increased and the other decreased), the flux is more influenced by bubble volume, unless density is extremely low (e.g., June 24 in Figure C.5). It appears though that the divergence of density and volume does not occur often. Further work is needed to truly understand the causes for density and bubble size distributions, but it is most likely interplay between CH_4 production and sediment type (Meier et al., 2011; Algar and Boudreau, 2010).

As we have already shown in Figure 5.4, bubble size is of great importance, especially in shallow systems, since just one or two large bubbles are able to increase gas flux so drastically. Greinert and Nützel (2004) have also reported this when they found that the larger bubbles (> 7 mm) in their study transported the majority of gas even though they also represented only a small portion of the total bubble size distribution. The difference in bubble distribution can make quite the difference in the variability of fluxes between segments. For example, the SMD of segment (a) in Figure 5.4 is 18 mm (3.05 ml volume), while the SMD of segment (b) is 10.6 mm (0.62 ml

volume). Thus, approximately 5 times as many bubbles from segment (b) are needed to create the flux observed in segment (a). Moreover, this substantial additional amount of bubbles needed is merely to balance the sediment ebullition flux of the segments. The surface ebullition flux is further affected by the bubble size distribution as bubble dissolution rate upon ascent strongly depends upon size. On average, we found that the SMD was 1.5 times larger than the weighted mean bubble diameter in each segment and that the SMD correlated better with sediment flux ($R^2 = 0.51$) than did the weighted mean diameter ($R^2 = 0.44$). In addition, using the SMD instead of the weighted mean for dissolution estimations with the discrete bubble model (McGinnis et al., 2006) decreased the average bubble dissolution rate for all segments by $\sim 10\%$. Using the SMD did not drastically change the final flux results in our study because we surveyed in a relatively shallow area (average, 6 m deep) where dissolution rates were already minimal. The importance of using the SMD instead of the weighted mean for calculating dissolution rates occurs when estimating surface ebullition flux from deeper waters with a wide range of bubble sizes. Since the volume of a bubble increases with the cube of its radius, the influence large bubbles have on gas flux is not surprising. This, however, also means that one must take care not to overestimate bubble size when estimating gas flux with hydroacoustic data, which is why large fish, fish schools, and any unidentifiable (nonbubble) strong echoes were removed prior to flux analysis.

We also observed that bubble size variability correlated well with the spatial flux variability observed in Lake Wohlen (Figure 5.7), which would be expected to some extent considering flux is strongly tied to bubble volume. However, it is interesting to see that similar bubble size distributions tend to cluster together in certain areas, such as the high frequency of small bubbles (blue circles, Figure 5.7) observed on the shallow shelf adjacent the south bank. As has been shown in a few studies (Meier et al., 2011; Leifer and Culling, 2010; Bourdreau et al., 2005; Gardiner et al., 2003), different sediment types influence bubble shape and size. Sandy sediments with high porosity tend to allow spherical bubbles to grow and release quickly, which typically produces smaller bubbles. Cores taken along the edges of the lake often recovered sandy sediments (DelSontro et al., 2010; Sobek et al., submitted), which could potentially explain the small bubbles found on that shallow shelf in the current study. It is more difficult to speculate as to why small bubbles were observed in the center of the river channel. Sediments there are often muddy or clayey (small grain sizes), which tend to act more elastically causing irregularly-shaped (oblate spheroid) bubbles to form that are only released when their buoyancy can overtake the sediment forces (Boudreau et al., 2005). This process, which is related to grain size and sediment cohesiveness, most likely produces larger bubbles than those from sandier sediments (Meier et al., 2011). The largest bubbles occurred where the high fluxes were observed along the center 6-8 m slope, which

makes sense. However, mostly average-sized bubbles (4 – 6 mm diameter) were observed near the point in the northwest where high fluxes were also consistently found (Figure 5.7). Therefore, this must be a case where the density of bubbles released controlled the total gas flux rather than the size of the bubbles. In fact, on the day with the highest fluxes observed (July 23), the segments in this region do have a very high density of bubbles. Again, both factors – density and size – are responsible for CH_4 ebullition flux magnitude, and additionally they can help identify other environmental features influencing ebullition variability.

5.4.4 Lake Wohlen in a global context

If an average of 580 mg CH₄ m⁻² d⁻¹ is released from the sediment to the water column in the form of bubbles from this study area and only 490 mg CH₄ m⁻² d⁻¹ reaches the atmosphere, then 90 mg CH₄ m⁻² d⁻¹ must remain in the water column, which on a daily basis equates to 844 mol CH₄ dissolved in the study area. We measured an average CH₄ concentration of 750 nmol l⁻¹ in the study area during the seven campaign days, which after scaling by the volume of the study area (150,000 m3) equates to 675 mol CH₄. This agreement between actual measured CH₄ and that which was estimated via hydroacoustics and a bubble dissolution model further promotes our methods for estimating flux.

In addition, DelSontro et al. (2010) reported that there is negligible oxidation in this oxic reservoir with an average 2-day residence time; thus all CH₄ escaping the bubbles into the water column will be sent to and through the dam and likely degas during its path in the downstream river. Ultimately, all 580 mg CH₄ m⁻² d⁻¹ is released to the atmosphere during summer from this ~0.15 km² study area of Lake Wohlen. DelSontro et al. (2010) found that diffusion was between 1 and 12 mg CH₄ m⁻² d⁻¹, which can be considered negligible during summer when ebullition emissions are an order of magnitude higher. When seasonal emission estimates calculated for the entire reservoir by the mass balance approach reported DelSontro et al. (2010) are summed and scaled to create a daily average, Lake Wohlen emits ~150 mg CH₄ m⁻² d⁻¹ throughout the year (DelSontro et al., 2010). Therefore, this study area that is only 6% of the total reservoir area emits about four times more CH₄ then the typical daily average. Is it possible then that this sampling area is producing all of the CH₄ emitted from the 2.5 km² reservoir? If the emission average from the study area (580 mg CH₄ m⁻² d⁻¹) is scaled to the full area of the reservoir, we find that only ~35 mg CH₄ m⁻² d⁻¹ would be emitted. Thus, the sampling area in the present study is not the only bubbling region of the reservoir.

Finally, placing this miniscule sampling area in context with ebullition emissions from other water bodies, we find that it is definitely above average. Bastviken et al. (2011) found that 15.8 Tg

CH₄ is emitted every year via ebullition from freshwater in the temperate zone globally, which when scaled back by the area of temperate freshwater bodies equals an average emission rate of 32 mg CH₄ m⁻² d⁻¹. We thus surveyed an ebullition hot spot that emitted ~20 times more CH₄ than the global temperate average, but only contributed 0.0002% to yearly global emissions. Ultimately, several independent methods (this study, DelSontro et al. (2010), and Eugster et al., (2011)) found CH₄ ebullition rates in Lake Wohlen that are far higher than the current known global averages, and thus highlights the fact that knowledge regarding CH₄ ebullition emission is still severely lacking.

The hydroacoustic techniques described in this study provide a fast, non-invasive, and representative CH₄ flux estimate for a system. The spatiotemporal variability of ebullition can be quite extreme and chamber surveys cannot resolve the equivalent area in the time that hydroacoustic surveys can. The mass balance approach reported in DelSontro et al. (2010) is a convenient method for quick ebullition estimates, but it is specific to run-of-river reservoirs or other flow-through water bodies. It also does not allow one to delve into the complexities of ebullition characteristics, such as bubble size and density distributions, as hydroacoustic methods do. As well, hydroacoustic methods can be done in any water body, even large ones, with depth coverage up to the limit of the transducer frequency (e.g., up to 150 to 200 m with our 120 kHz transducer). However, hydroacoustic measurements are not reliable within ~1 m of the transducer due to near-field disturbance (Simmonds and MacLennan, 2005), and data from less than 1.5 m deep are hard to analyze as the targets in the water column are not easily identifiable due to bottom interference and benthic flora and fauna. Thus, hydroacoustic surveys could be complimented by shallow chamber measurements for surface efflux and funnels for bubble capture and compositional analysis. Finally, adding an eddy covariance CH₄ flux tower atop a floating platform in the center of the lake would be ideal, particularly for the high temporal and spatial coverage resolution afforded by that technique.

5.5 Acknowledgements

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5.6 Appendix C

5.6.1 Supplementary figures



Figure C.1. Sediment CH₄ ebullition contours for the three June campaigns. Fluxes are of sediment CH₄ ebullition. Crosses are mid-segment locations. Red star was eddy covariance tower location. Coordinates in CH1903 (Swiss coordinates). June 10 had limited coverage and thus not a very representative survey for the whole system. On the other two days the low flux zone (blue) in the shallow shelf adjacent to the south bank was visible. The high flux zone (orange-red) on the slope toward the old river channel was observed on June 11, but not on June 24. In fact, the slope looks like it has a lower flux than the old river channel on June 24. Background image © 2010 swisstopo, reproduced with the authorization of swisstopo JD100042/JA100020.



Figure C.2. Bathymetry of study site overlain by color-coded scatter plots of weighted mean bubble diameters (circles in mm) for each segment for the three June campaigns. X's are of segments with zero flux and thus no bubbles (black and white mean the same). Coordinates are in CH1903 (Swiss coordinates). Color bar scale in equivalent bubble volume is 7, 1, 0.1, 1×10^{-2} , and 1×10^{-3} ml for 24 to 1 mm, respectively. Small bubbles were seen on the shallow southern shelf on all days, except there were some very large bubbles on the shelf on June 11. Large bubbles were observed along the 6 to 8 m slope and coincide with the high flux zone observed in Figure C.1. for June 11. Background image © 2010 swisstopo, reproduced with the authorization of swisstopo JD100042/JA100020.



Figure C.3. Surface CH₄ ebullition contours based on hydroacoustic measurements from the four July campaigns. Thick lines represent transects of the drifting chamber surveys also conducted on those days. Circles on both ends of the line illustrate the surface CH₄ flux measured using the same color bar as for the contours. Circle with black line border is start of transect. Chamber fluxes generally agree with the hydroacoustic contours with high and low fluxes being measured in roughly the same places. Chamber transects were mostly conducted through the center of the area, which coincides with the high flux zone. White contour lines are of the overall footprint from the eddy covariance CH₄ flux measurements conducted simultaneously. Hydroacoustics and chamber transects only occasionally overlap with the eddy covariance footprint. Background image © 2010 swisstopo, reproduced with the authorization of swisstopo JD100042/JA100020.



Figure C.4. Methane fluxes (black dots, right axes) according to date and time measured along with the water level (blue line, left axes) at that time. Water level is in meters minus 480, which is the typical lake surface altitude above sea level (a.s.l.).



Figure C.5. Both target density in the water column (black line) and bubble volume (dashed line; based on Sauter mean diameter) contribute to the sediment ebullition flux (red line) of a segment, but their influence may vary from place to place. In general, density and volume exhibit the same trend indicating that often bubbles tend to be larger when in higher density, perhaps while in plumes. There are times (e.g., June 11) when density and volume differ, thereby flux will be affected more by one than the other. Note that each time series was smoothed by a moving average with a 20-sample window.

Chapter 6

Spatial heterogeneity of methane ebullition in a large tropical reservoir

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Abstract

Tropical reservoirs have been identified as important methane (CH₄) sources to the atmosphere, primarily through turbine and downstream degassing. However, the importance of ebullition (gas bubbling) remains unclear. We hypothesized that ebullition is a disproportionately large CH₄ source from reservoirs with dendritic littoral zones because of ebullition hot spots occurring where rivers supply allochthonous organic material. We explored this hypothesis in Lake Kariba (Zambia/Zimbabwe; surface area > 5000 km²) by surveying ebullition in bays with and without river inputs using an echosounder and traditional surface chambers. The two techniques yielded similar results, and revealed substantially higher fluxes in river deltas (~10³ mg CH₄ m⁻² d⁻¹) compared to non-river bays (< 100 mg CH₄ m⁻² d⁻¹). Hydroacoustic measurements resolved at 5 m intervals showed that flux events varied over several orders of magnitude (up to 10⁵ mg CH₄ m⁻² d⁻¹), and also identified strong differences in ebullition frequency. Both factors contributed to emission differences between all sites. A CH₄ mass balance for the deepest basin of Lake Kariba indicated that hot spot ebullition was the largest atmospheric emission pathway, suggesting that future greenhouse gas budgets for tropical reservoirs should include a spatially well-resolved analysis of ebullition hot spots.

6.1 Introduction

Inland waters are quantitatively important biogeochemical reactors that store, transform, and emit carbon as it travels from terrestrial ecosystems to the ocean (Cole et al., 2007). The construction of > 800,000 dams over the past century has reduced sediment loads to the oceans by ~50% (Vörösmarty et al., 2003), and consequently retained and transformed substantial amounts of organic carbon that would have previously reached the ocean (Tranvik et al., 2009; Syvitski et al., 2005). In the anoxic, organic-rich, and sulfate-poor sediments of both lakes and reservoirs, 10-50% of organic carbon mineralization occurs via production of the potent greenhouse gas, methane (CH4; Bastviken et al., 2008). Recent estimates suggest that lakes, a previously underappreciated source of CH4, account for 10–15% of natural CH4 emissions to the atmosphere (Bastviken et al., 2004). Reservoirs have been suggested to be a substantial anthropogenic emission source (St. Louis et al., 2000), although more attention is needed to establish pre-dam emissions and assess the net increases in CH4 emissions (dos Santos et al., 2006). Improving our understanding of CH4 emissions from tropical reservoirs is particularly important since estimates based on limited data indicate that their contribution may dominate global reservoir emissions (St. Louis et al., 2000).

Methane produced in anoxic layers of lake and reservoir sediments can experience multiple potential fates, beginning with oxidation of a portion of the upward diffusing CH₄ at the sediment oxic-anoxic interface (Frenzel et al., 1990). When sediments are overlain by anoxic bottom waters in stratified basins, CH₄ diffuses freely from the sediments into the water column, typically accumulating to concentrations in the µM range (Guérin and Abril, 2007). During seasonal deep mixing of stratified lakes, CH₄ stored in the anoxic hypolimnion may undergo oxidation during the gradual deepening of the thermocline (Schubert et al., 2010). Alternatively, CH₄ may mix into the epilimnion, where it can undergo oxidation or diffusive exchange to the atmosphere across the airwater interface (Schubert et al., 2010; Bastviken et al., 2008; Guérin and Abril, 2007). Ebullition, the efflux of CH₄-rich bubbles from sediment porewaters supersaturated with CH₄, results in the rapid release of CH₄ from sediments. As these bubbles rise, some CH₄ dissolves into the water column, the fraction of which is determined by the depth of bubble release, initial bubble size, temperature, and gaseous concentrations in ambient water (McGinnis et al., 2006). If the bubble reaches the surface, the remaining gaseous CH₄ will cross the air-water interface. Under certain conditions (e.g., strongly reducing sediments, shallow water column), ebullition can be an efficient and potentially dominant CH₄ source to the atmosphere.

CH₄ ebullition in lakes and reservoirs has recently received much attention (Ostrovsky, 2003); however, the episodic and stochastic nature of CH₄ ebullition complicates the analysis of fluxes (Soumis et al., 2005). Measuring ebullition in lakes has traditionally been a matter of capturing bubbles by deploying relatively small ($< 1 \text{ m}^2$) surface floating chambers or funnels (DelSontro et al., 2010; Bastviken et al., 2004). This approach provides a coarse estimate of ebullition flux derived from a small measured area, and typically provides only limited depth-related information regarding the spatial variability of ebullition. As a result, the spatial distribution of ebullition has not been systematically studied, but has been generalized as a mostly depth-dependent phenomenon (Gunkel, 2009; Bastviken et al., 2004). Recent studies have demonstrated the use of hydroacoustic (sonar) techniques for the precise identification of ebullition zones in water bodies (Vagle et al., 2010). After calibration against bubbles of known size, and combined with data on CH₄ concentration in bubbles, hydroacoustic measurements can also be used to quantify real-time ebullition volume and flux (Ostrovsky et al., 2008).

The high loadings and rapid burial of organic matter that occur in river deltas may foster high rates of CH₄ production (DelSontro et al., 2010; Kelly and Chynoweth, 1981). The relatively shallow depth and lower hydrostatic pressure in these areas facilitate the formation and release of bubbles from sediments, and the shorter travel path to the atmosphere limits bubble dissolution. Therefore, we hypothesized that deltaic zones in reservoirs or lakes could act as important hot spots

for CH_4 ebullition. Exploring this issue in tropical reservoirs is of particular importance given the lack of knowledge regarding this emission pathway and the fact that they are considered the major CH_4 emitter among global impoundments (Soumis et al., 2005). The continued push for more hydropower development in areas such as Sub-Saharan Africa (Bartle, 2002), as well as growing recognition that environmental impacts of new reservoirs should be better mitigated (WCD, 2000), further support the need for more information regarding CH_4 dynamics in existing reservoirs.

We explored the 'deltaic-zone' hypothesis by performing hydroacoustic and floating chamber surveys in shallow embayments with and without river inlets in one of Africa's largest reservoirs, Lake Kariba (Figure D.1). We quantified various CH_4 emission pathways with a particular focus on ebullition and its spatial distribution, and compared results from the traditional chamber technique and hydroacoustic surveys. We also used the high spatial resolution afforded by hydroacoustic measurements to examine the characteristics of ebullition that contribute to the average differences seen between study sites. Additionally, we compared the relative importance of bubble emissions to the atmosphere with other pathways and, finally, placed Lake Kariba emissions in context with other large tropical reservoirs.

6.2 Experimental

6.2.1 Study site

Lake Kariba, located along the border of Zambia and Zimbabwe (Figure D.1), is one of the largest reservoirs worldwide (Coche, 1974) with a surface area of 5,400 km2, volume of 160 km3, and maximum depth of 97 m. The highly dendritic shoreline consists of 66% unexposed bays, some with river inflows (Coche, 1974). While the Zambezi River is the main inflow of Lake Kariba, dozens of smaller rivers contribute ~20% of the total inflow and the Sanyati River alone represents ~8% (Marshall, 1988). Despite their low share on total inflow, secondary rivers contribute substantially to the overall input of organic matter and nutrients to Lake Kariba and are therefore an important factor in determining its productivity (Coche, 1974). Although a high initial productivity was reported in Lake Kariba (Coche, 1974), it is now considered quite oligotrophic (Marshall, 1988), and stratifies for at least 10 months per year with turnover occurring in late July or August each year (Coche, 1974).

Fieldwork focused on Lake Kariba's subbasin IV, the reservoir's largest subbasin by area and volume, located adjacent to the Kariba Dam (Figure D.1; Kunz et al., 2011). Five littoral embayments in subbasin IV were examined. The sites named "Lufua River" (LR), "Gache Gache River" (GR), and "Charara River" (CR) had significant river inflows and will be referred to as

'river deltas'. The sites called "Gache Gache Bay" (GB) and "Charara Bay" (CB) were relatively unaffected by inflows and called 'non-river bays'.

6.2.2 Sampling methods

Sample collection, processing, and analysis are described briefly here with additional details in the extended methods section in Appendix D and DelSontro et al. (2010). Detailed surveys for dissolved CH₄, as well as sediment and surface CH₄ emissions, were conducted in the five bays in June 2009, while open water CH₄ profiles were taken during campaigns in July 2007, May 2008, February and June 2009 (Figures D.1, D.2). Depth profiles of conductivity, temperature, and dissolved oxygen were taken at most open water stations and at least once in each bay (Figure D.7). Dissolved CH₄ was sampled with a Niskin bottle, transferred to and poisoned in gas-tight serum bottles, and subsequently analyzed by gas chromatography (Agilent 6890N) and a flame-ion detector (GC/FID). Sediment cores were collected in each bay and diffusion was calculated using the CH₄ gradient measured in the porewaters via GC/FID. Gross surface CH₄ emissions (ebullition plus diffusion) were measured in each bay (except CB) using drifting chambers and analyzed via GC/FID (Table 6.1). Surface diffusion was estimated using measured surface water CH₄ concentrations and wind speed.

6.2.3 Hydroacoustic surveys

The methodology of analyzing ebullition hydroacoustically with an echosounder is similar to the process of measuring fish biomass (Ostrovsky et al., 2008; Simmonds and MacLennan, 2005). Hydroacoustic surveys of ebullition were conducted with a down-looking Simrad split-beam echosounder (EK60, 7° beam angle) with a 120 kHz transducer pinging at 5 s⁻¹ and a lower threshold of -120 dB. Bubbles could be readily distinguished from fish based on their travel path as rising bubbles appear as inclined tracks whereas fish appear as nearly horizontal tracks (Figure D.3a; Ostrovsky, 2003). After filtering out fish and noise, bubble density, N (# m⁻³), can be calculated for the water volume covered by the sonar beam. This was calculated by dividing the total acoustic backscatter of the analyzed water volume, s_v (m⁻¹), by the mean acoustic signature, called the backscattering cross-section, σ_{bs} (m²), of all identified bubbles. For a calibrated relationship between σ_{bs} and bubble volume, bubble density can be converted to gas volume density, $V_{\Sigma b}$ (ml m⁻³). For this study we used the bubble volume calibration conducted by Ostrovsky et al.(2008). The volumetric density was converted to bubble gas flux (mg m⁻² d⁻¹) by adjusting for the pressure at the analyzed depth and multiplication by the bubble rise velocity (m s⁻¹), as measured by the echosounder. Lastly, CH₄ flux was scaled by the average bubble CH₄ concentration, as measured in submerged gas traps (see Appendix D methods). Data was postprocessed using Sonar 5 Pro (Lindem Acquisition, Norway). For more details, see Appendix D methods and Ostrovsky et al.(2008).

6.3 Results and Discussion

6.3.1 Methane concentrations and emissions in the littoral zone

Dissolved CH₄ concentrations in the five sampled bays varied considerably, but always exceeded saturation levels (Table D.1, Figure D.2). LR and CR had CH₄ concentrations up to 5 and 2 μ M, respectively, while the dissolved concentrations in GR and the two non-river bays were less than 1 μ M (Figure D.2). Surface water CH₄ concentrations were highly variable within individual bays and tended to decrease in the offshore direction. The surface concentrations in the river deltas were up to an order of magnitude higher than those from the open water stations (Figure D.1), illustrating the local importance of littoral sources. The concentration variability between bays most likely reflects the variability of CH₄ sources in the littoral zone, which can be diffusion from sediments or dissolution of rising bubbles (DelSontro et al., 2010). Sediment diffusion estimates, calculated using porewater CH₄ profiles from various regions of Lake Kariba (Figure D.2), fell within one order of magnitude of each other (Figure 6.1d, Table D.1) and were comparable with estimates from other systems (Adams, 2005). Dissolution from rising bubbles will be discussed later.

Surface chamber emissions, which included ebullitive and diffusive emissions, varied greatly between bays (range 3 to 2100 mg CH₄ m⁻² d⁻¹). The differences in chamber emission magnitudes demonstrated that the three river deltas emitted substantially more CH₄ than the non-river bays (Figure 6.1a, Table 6.1). Surface diffusion fluxes (Figure 6.1c) calculated from surface water CH₄ concentrations were much lower than the chamber-captured emissions and only slightly higher than open water surface gas exchange; thus the measured surface emissions could not be dominated by diffusion. Ultimately, since surface and sediment diffusion were low compared to chamber emissions and relatively constant across various regions of Lake Kariba, the variability in chamber emissions and dissolved CH₄ profiles within and between bays must be due to another CH₄ release pathway. Differences in ebullition fluxes between bays, and subsequent partial dissolution of CH₄ bubbles during their ascent, was therefore a potential mechanism regulating both water-air fluxes and the dissolved CH₄ concentrations in the littoral zone.

study sites		drifting cha en	mbers nission	: surface	hydroacoustics: surface ebullition			
bay name (abbr.)ª	mean depth [m]	flux [mg m ⁻² d ⁻¹] ^b	time [h]	area (N) ^c [m²]	transect average flux [mg m ⁻² d ⁻¹] ^d	time [h]	area (N) [m²]	
Lufua River (LR)	18	2100 ± 1200	8.7	1500 (8)	1450 ± 1200	4.7	18000 (13)	
Gache Gache River (GR)	9	400 ± 300	11.5	1800 (14)	770 ± 810	5.7	17000 (10)	
Charara River (CR)	7	70 ± 90	11.3	1500 (9)	400 ± 190	3.7	7000 (4)	
Gache Gache Bay (GB)	8	3 ± 2	4.3	900 (6)	60 ± 100	3.0	15000 (6)	
Charara Bay (CB)	4	na ^e	na	na	0.6 ± 0.8	1.0	1800 (3)	

Table 6.1. Drifting chamber and hydroacoustic results from subbasin IV bays of Lake Kariba

^{*a*} LR, GR, and CR are river deltas; GB and CB are nonriver bays. ^{*b*} Average flux from all chamber transects \pm one standard deviation. ^{*c*} N is number of transects. ^{*d*} This is the average (\pm one standard deviation) of the transect sediment ebullition fluxes corrected for average CH₄ bubble content, for pressure/volume change at the surface, and for bubble dissolution. ^{*e*} No chambers were deployed in CB.

6.3.2 Hydroacoustic estimates of ebullition

Hydroacoustic data were used to further explore ebullition in the five study sites. The hydroacoustic method provided a very rich dataset, resulting in > 70,000 individual observations at some sites. To evaluate the data, observations were pooled into 5 m distance bins along each transect. The sediment gas flux for each bin was calculated in the bottom 3 m layer of the water column, and corrected for CH₄ composition of bubbles captured at each site (59-66% CH₄ by volume; see Appendix D methods for details). Binning yielded up to 3000 distance- and bubble plume-integrated flux measurements (from here on called 'bin flux') per site, with each bin flux having a well-defined depth (\pm 2 m). A bin flux could consist of a few single bubbles, one or more distinct bubble plumes, or no bubbles at all (Figure D.3b), and thus incorporated all active ebullition areas and non-bubbling areas within that 5 m distance.

The observed bin fluxes spanned 5 orders of magnitude, and fluxes having substantial magnitude were detected at a high frequency even down to 40 m depth (Figure 6.2). At LR and GR, the magnitude of non-zero bin fluxes were log-normally distributed with means of $\sim 10^3$ mg CH₄ m⁻² d⁻¹, while at other sites the mean fluxes were clearly lower (Figure 6.2b). Extreme fluxes of $>10^4$ mg m⁻² d⁻¹ were observed at LR and GR, and although these values seem quite large, they resulted from episodic releases of gas that were clearly visible in echograms (Figure D.3b). Ramos et al. (2006) also observed intermittent extreme fluxes up to 2×10^4 mg CH₄ m⁻² d⁻¹ while measuring CH₄ flux at 5 minutes resolution on a reservoir surface with stationary dynamic chambers.



Figure 6.1. Whisker boxplots of CH₄ fluxes (mg m⁻² d⁻¹) during June 2009 sampling of CH₄ pathways from Lufua River (LR), Gache Gache River (GR), Charara River (CR), Gache Gache Bay (GB), Charara Bay (CB), and open water stations of subbasin IV (BIV). Box represents the 25th and 75th percentile. Middle line is the median. Whiskers are the maximum and minimum values. Crosses are outliers. Number of samples used for (a) and (b) are the number of transects in Table 1. Number of samples for (c) and (d) are number of stations in Table S1. (a) Surface chamber emission estimates include gas directly captured at the surface from diffusion and, if present, ebullition using drifting chambers. (b) Surface ebullition is CH₄ bubble escape to the atmosphere based on the transect averages of hydroacoustic sediment ebullition flux near the lake bottom and corrected for bubble dissolution upon ascent. (c) Surface diffusion is calculated from measured dissolved CH₄ concentrations in surface water and average daily wind speed. (d) Sediment diffusion is calculated using the CH₄ gradient measured in porewater cores.

To compare hydroacoustic estimates with drifting chamber measurements for each bay, average surface ebullition fluxes of the hydroacoustic transects were calculated (Figure 6.1b). These hydroacoustic flux averages were found by first calculating the mean of the bin fluxes (including zero fluxes) along the multiple transects within each bay, then by correcting for actual bubble CH₄ content and for bubble dissolution during ascent using a discreet bubble model (see Appendix D methods; McGinnis et al., 2006). The mean surface fluxes from hydroacoustic surveys and drifting chambers agreed reasonably well (same order of magnitude; Figure 6.1a-b, Table 6.1) at LR and GR. The agreement with chamber measurements at CR and GB were not as strong as at the other sites, and some of the difference between hydroacoustic and chamber estimates at any site likely arises from differences in transect locations and coverage (Figure D.2, Table 6.1).

The hydroacoustic measurements corroborate the findings from chamber measurements that CH₄ fluxes across the air-water interface in river deltas were 1 to 3 orders of magnitude higher than in non-river bays. While both methods identified river deltas as ebullition hot spots, the distinction was even more apparent in the hydroacoustic data (Figure 6.1), where flux estimates from GR and CR were more similar to LR. Although the mean hydroacoustic fluxes of GR and CR were 2- to 4-fold lower than LR (Table 6.1), all river delta ebullition fluxes were at least an order of magnitude greater than that of the non-river bays.



Figure 6.2. a) Frequency of sediment ebullition found in bins according to depth for Lufua River delta (LR), Gache Gache River delta (GR), Charara River delta (CR), Gache Gache Bay (GB), and Charara Bay (CB). Axis labels are same in all panels. **b)** Magnitude of sediment ebullition bin fluxes according to depth (left) and overall distribution of measured fluxes (right) in each surveyed bay. Note different x-axis scales between panels. Non-zero fluxes shown on log scale. Red line is 1-m average including zero flux values.

In contrast to their considerable qualitative agreement, the two methods differed dramatically in their effectiveness. The hydroacoustic transects covered an order of magnitude more area than the chambers and were acquired in less than half the time (Table 6.1). Moreover, while both techniques yielded mean flux estimates, only the hydroacoustic method provides more precise information about how ebullition varies over finer spatial scales. For example, the 5 m hydroacoustic bin fluxes document the heterogeneity of ebullition along a single transect (Figure 6.3), which would be averaged out in a drifting chamber measurement. This heterogeneity, specifically differences in ebullition frequency and ebullition magnitudes, also contribute to the variability in average fluxes observed between the surveyed sites (Figure 6.2). For example, the magnitudes of the non-zero bin fluxes (Figure 6.2b) were substantially higher in LR and GR (mean, 4600 and 4200 mg CH₄ m⁻² d⁻¹, respectively) than in the non-river bays (mean, 1800 and 30 mg CH₄ m⁻² d⁻¹ for GB and CB, respectively). However, the mean sediment ebullition magnitude in the CR delta (1900 mg $CH_4 m^{-2}$ d^{-1}) and the non-river GB were almost the same (Figure 6.2b); thus the factor of 7 difference in transect averages between these two sites was due to the frequency of ebullition (i.e., 37% of the surveyed area of CR was bubbling, while only 5% in GB; Figure 6.2a). Overall, ebullition frequency was higher in the river deltas than the non-river bays (Figure 6.2a).

The differences in ebullition magnitude and frequency amongst the river delta sites are also noteworthy as they indicate the extreme variability of ebullition within an ebullition hot spot. While LR had an average transect flux that was 2-fold higher than that of GR (Table 6.1), they had similar non-zero flux distributions (Figure 6.2b). Therefore, the higher transect flux from LR was primarily due to the higher frequency of ebullition (67% versus 37%) rather than the magnitude of the non-zero fluxes. On the other hand, the difference between the transect averages for LR and CR appears to have been a function of both the magnitude of the non-zero fluxes (mean, 4600 versus 1900 mg CH₄ m⁻² d⁻¹) as well as ebullition frequency (67% versus 37%; Figure 6.2).

The hydroacoustic data was also used to explore the extent to which water column depth influences sediment ebullition flux. CH₄ surface emissions from ebullition have been shown elsewhere to be negatively correlated with depth (Gunkel (2009) and references therein). Those studies, which relied on surface chambers, attributed the depth dependency of emissions to increased bubble dissolution with height of bubble rise. It has also been suggested that the sediment ebullition flux could decrease with depth due to increasing hydrostatic pressure (Ostrovsky et al., 2008; Bastviken et al., 2004). Although there was considerable variability, over a depth range of 5 to 40 m in LR we observed an order of magnitude decrease in the average bin flux (including zero

fluxes) as a function of depth (red line, Figure 6.2b), and a similar decrease in the mean of the nonzero bin fluxes.



Figure 6.3. Hydroacoustic sediment ebullition bin fluxes in Lufua River delta. A constant of 0.1 was added to all fluxes to allow plotting of the zero fluxes on a log scale. Bathymetry contours (labelled by numbers 4 to 20) are at 2 m resolution. River inflow is indicated with an arrow. A low ebullition flux zone is apparent along the shallow northern shelf (blue circle) and a high ebullition zone in the deep part of the former river channel (red circle).

These variations of ebullition magnitude and frequency with depth at LR were likely more related to the geomorphology and sedimentation dynamics of this site rather than with depth itself. For example, depth may serve as a proxy for distance from the river mouth (Figure D.2), and the decrease in average ebullition flux with depth may reflect decreased organic matter input to sediments further (up to 40 m depth) from the river mouth, and a resulting decrease in CH₄ production. The lower frequency of ebullition in shallow regions of LR (< 10 m), which was not necessarily expected, may also be an artifact of the bay's geomorphology. The bay into which the Lufua River empties has a deep (~20 m) submerged channel. The shallower sides of the bay may receive less sediment loading than the submerged river channel, potentially resulting in less CH₄ production and less ebullition. This appears to indeed be a plausible explanation based on the spatial variability of bin fluxes in LR (Figure 6.3). Ebullition was quite low along the shallow northern part of the bay (blue circle, Figure 6.3), while higher fluxes were found in the deep channel (red circle,

Figure 6.3). The higher ebullition fluxes at depth could also be a result of increased bubble release due to higher velocities at the sediment-water interface due to currents (Keller and Stallard, 1994). Whatever the cause, the 10-fold decrease in sediment ebullition flux with depth observed in LR is greater than the 5-fold decrease in surface flux that would result from additional bubble dissolution (assuming average LR conditions: 9 mm diameter bubble with 59% CH₄ by volume at 24°C). Thus, systematic spatial variations in sediment ebullition flux can be quantitatively more important than dissolution-related decreases in surface ebullition.

A depth-flux relationship was not observed in GR or CR (Figure 6.2b); however, the surveys did not extend as deeply into those bays as in LR. Interestingly, the majority of observations made in the shallow region of GR were found to have no ebullition (Figure 6.2a). This may also be partly due to the geomorphology of the bay for the same reason as in LR (i.e., shallow sides disconnected from main channel), and also because observations essentially began in the river itself (Figure D.2). It is also important to note that at most sites flux estimates were not made for the shallowest regions (< 2-3 m) due to interference from submerged vegetation or the near-field limitation of echosounding (Simmonds and MacLennan, 2005). Ebullition dynamics in these shallow regions could potentially alter the overall average ebullition estimates for each site and any observed depth relationships, but the results discussed here for the depth ranges that were well-covered by hydroacoustic surveying remain valid.

6.3.3 Subbasin IV methane sources and fate

A basic box model approach was used to assess the relative importance of the main processes governing CH₄ dynamics in subbasin IV over a full year (Figure 6.4), which typically includes 10 months of stratification (Figures D.5, D.6).

Methane loading to the epilimnion was calculated by considering both diffusion and dissolution from bubbles. For the diffusion loading estimate, an average diffusive flux from sediment core data of the bays ($40 \pm 20 \text{ mg m}^{-2} \text{ d}^{-1}$; Table D.1) was applied to the epilimnetic sediment area (depth < 30 m; Figure D.7) and resulted in ~17,000 t CH₄ y⁻¹ entering the epilimnion. However, the actual amount of diffusing CH₄ that reached the water column may have been substantially less due to CH₄ oxidation at the sediment-water interface and the fact that the diffusion rate estimate was calculated from CH₄-rich cores taken in the bubbling bays.

Ebullition was assumed to occur only in the subbasin IV bays with river inputs since negligible amounts of ebullition emission were found from bays with no river input. Therefore, total ebullition was estimated in the three surveyed river deltas plus three river deltas that were not surveyed but have substantial catchment areas and flows (Figure D.1a, Table D.2). The average hydroacoustic

ebullition flux for each surveyed delta (Table 6.1) was applied to that bay's area. The areas of the three deltas not surveyed were scaled by the average flux of LR, GR, and CR (870 mg m⁻² d⁻¹). Recognizing that methane production rate may vary seasonally due to differences in organic matter loading (e.g., wet versus dry seasons, which are dynamic in this system), we conservatively estimated that ebullition occurs in the subbasin IV deltas for only half of the year (Karenge and Kolding, 1995). Water level changes also can significantly influence ebullition rates (Ostrovsky et al., 2008). This dataset did not allow for such an effect to be quantified; however, water levels before and during fieldwork were high and constant, so our flux estimate may be considered a minimum. The overall estimate for ebullition emission to the atmosphere from the six deltas in subbasin IV was 16,000 t CH₄ y⁻¹ (Figure 6.4). To calculate this estimate, average bubble parameters from the hydroacoustic data of the three surveyed deltas (bubble diameter of 9 mm containing 62% CH₄) were assumed, and an average depth of 15 m was used to determine that ~35% of the CH₄ from rising bubbles dissolved into the water column, equating to 9,000 t CH₄ y⁻¹.

If the total CH₄ mass that entered the epilimnion from bubble dissolution and diffusion (26,000 t) had been mixed over the entire epilimnetic volume via horizontal mixing it would have yielded a concentration of ~32 μ M, which is 2 orders of magnitude greater than the measured concentration in the surface waters of the lacustrine part of the lake (< 0.1 μ M; Figure D.1b). Thus, CH₄ released from littoral sediments did not accumulate in the water column, but must have been oxidized (either in the oxic surface layer of the sediments or the water column), as has previously been suggested (Guérin and Abril, 2007; Kankaala et al., 2007). The required oxidation rate in the water column to offset this accumulation (90 nmol L⁻¹ d⁻¹) is consistent with aerobic oxidation rates observed elsewhere (Bastviken et al., 2002).

The atmospheric releases considered in this analysis included diffusive flux across the air-water interface, export of CH₄ via turbines, and ebullition. Gas exchange at the air-water interface, calculated using the average surface water CH₄ concentrations of open water and bays as well as monthly mean wind speeds (Mungwena, 2002), amounted to ~180 t CH₄ y⁻¹. Methane export through the turbines over a year was approximated by estimating the zone of influence of the turbine intakes and seasonal variations in CH₄ profiles (Figures D.1b, D.5, D.6, and Appendix D methods). This approach resulted in ~170 t CH₄ y⁻¹ released via the turbines. Ebullition, however, was the dominant atmospheric release pathway of CH₄ with 16,000 t escaping directly to the atmosphere (Figure 6.4).

Accumulation of CH₄ in the basin's hypolimnion was quantified using dissolved CH₄ concentration profiles at several stations sampled during different stages of stratification across multiple years (Figures D.1, D.4 and Appendix D methods). Methane accumulation set in after the

onset of anoxia, and on the order of ~11,000 t CH₄ accumulated in the hypolimnion over ten months of stratification. The total flux from the hypolimnetic sediment area required to support this accumulation (23 mg m⁻² d⁻¹) was comparable to the estimated sediment diffusion flux from hypolimnetic sediments (30 mg m⁻² d⁻¹, calculated from a lacustrine subbasin IV core). Other potential sources to the hypolimnion, such as deep ebullition, are therefore not needed to explain the CH₄ accumulation.

The fate of the 11,000 t of CH₄ stored in the basin's anoxic hypolimnion during stratification must be assessed indirectly. In the completely mixed water column sampled in July 2007 only 30 t of CH₄ was present (Figure D.4). Temperature data from subbasin IV during our years of observation (data not shown) indicate that the thermocline deepened and was gradually eroded over the course of May to July until the water column was fully mixed, which was consistent with past observations (Coche, 1974). During this period, export of CH₄ via diffusion across the air-water interface plus export through the turbines can explain < 1% of the decrease in CH₄ storage. Thus, almost all of the stored CH₄ must have been oxidized by methanotrophic microbes during the gradual deepening of the thermocline and oxycline, as has been observed elsewhere (Schubert et al., 2010).

Overall, the dominant fates of CH_4 in Lake Kariba were oxidation (total = 37,000 t) and export of CH_4 -rich bubbles across the air-water interface (16,000 t). Ebullition export, which we conservatively assumed to occur only in river deltas with reasonable spatial and temporal considerations, exceeded the estimates for surface diffusion and CH_4 export through the turbines by two orders of magnitude (Figure 6.4), thus making ebullition the dominant CH_4 emission pathway in Lake Kariba's largest basin.



Figure 6.4. Subbasin IV CH₄ mass balance just before seasonal mixing (end of stratification period) when accumulation is at its maximum in the hypolimnion. Arrows show annual CH₄ emissions in t y^{-1} for sediment diffusion to the hypolimnion and epilimnion, diffusion at the lake surface, discharge through the dam, ebullition dissolution into the epilimnion, and atmospheric methane release from bubbles. Locations of CH₄ oxidation are labelled.

6.3.4 Implications for tropical reservoir emissions

Estimating CH_4 emission from the entire reservoir is of interest given the size of Lake Kariba and that the subbasin IV results suggest that ebullition is quite important to the lake's overall CH_4 budget. Recognizing the considerable uncertainty in extrapolating the ebullition emission rates from three river deltas to the entire lake, such as other studies have done with much less spatial coverage, a conservative approach for upscaling the estimates from this study was taken. Our goal with such a rough estimate of total ebullition emission was to allow an order of magnitude comparison between the different CH_4 fates and pathways within the lake, and in comparison to other tropical reservoirs.

The CH₄ flux via turbine/downstream degassing remains unchanged. Using surface concentrations from open water stations of subbasin IV (Figure D.1) and the other basins (data not shown), a diffusion estimate of ~540 t CH₄ y⁻¹ was calculated for the surface of Lake Kariba. The ebullition flux can be extrapolated in various ways; for example, with the method employed by other published studies where a limited number of chamber or gas trap measurements were used to extrapolate ebullition to the rest of the unmeasured littoral area (e.g., see dos Santos et al., 2006). Along these lines (albeit without the depth-integration used in other studies because our drifting chamber measurements already average flux over depth) a surface ebullition estimate could be calculated by multiplying the average chamber measurement of 640 mg CH₄ m⁻² d⁻¹ to the 2,000 km² littoral zone of the lake (depth < 20 m) to obtain an estimated annual flux of > 4 × 10⁵ t y⁻¹.

However, our observations of the spatial heterogeneity of ebullition in Lake Kariba indicate that this approach is not adequate and, with no ebullition data for the other subbasins, the following estimate is the closest approximation that can be made with the available data. We employed the same spatially and temporally conservative method as described above for subbasin IV, assuming ebullition only occurs in the deltas of substantial rivers (roughly 4% of total lake area) during half of the year (Table D.2). This approach resulted in an order of magnitude lower estimate of $3.9 \times$ 10⁴ t CH₄ y⁻¹ (Table D.2) that remains two orders of magnitude greater than the other atmospheric emission pathways combined. Thus, ebullition flux from river deltas, a previously undocumented CH_4 source from large reservoirs, has the potential to be the dominant atmospheric CH_4 source from Lake Kariba despite being a minimal fraction of the total lake area. When all our potential sediment CH₄ release estimates (diffusion and ebullition) are summed and converted to carbon release units, the value (88,000 t CH₄-C y⁻¹) is generally consistent with a recent study that estimated OC loading and burial efficiency in Lake Kariba sediments (see Appendix D methods; Kunz et al., 2011). We are therefore confident in the order of magnitude of our estimates for all CH₄ emission pathways in this system, which indicate that ebullition is most likely the dominant emission pathway in Lake Kariba.

The substantial contribution of ebullition to total CH₄ emissions in Lake Kariba contrasts strongly with observations in other large tropical reservoirs where dominant CH₄ emissions were at the turbines (Table D.3 and references therein). This disparity results in part from the vertical placement of water intake levels in Lake Kariba, which lead mostly surface waters rich in oxygen and poor in CH₄ to the turbines (Figures D.5, D.6; Anderson et al., 1960). Other well-studied tropical reservoirs have turbine inlets that withdraw anoxic hypolimnetic water or a mixture of hypolimnetic and epilimnetic water (Table D.3). Therefore, an important design strategy for reducing greenhouse gas emissions from reservoirs is the placement of turbine intakes in order to avoid the release of anoxic deepwater.

Although we used a conservative approach to estimate CH₄ ebullition in the dendritic littoral zone of Lake Kariba, ebullition export of CH₄ from this 60-year-old hydropower scheme turned out to be the highest among the well-studied tropical reservoirs (Table D.3). Total areal emission from Lake Kariba, however, was the lowest, potentially due to the advanced age of the Kariba Dam (Abril et al., 2005; Soumis et al., 2005). It could then be inferred that the high ebullition emission measured in river deltas reflects the most recent carbon input from the catchment and thus the deltas have no relation to the reservoir age. Ultimately, a direct quantitative comparison of the CH₄ emission pathways in Lake Kariba with those from other tropical reservoirs is difficult because the idea of potential ebullition hot spots or littoral heterogeneity were not considered in most of those studies. Such hot spots could easily be missed in large systems, and therefore more detailed (re)analysis of CH₄ fluxes at terrestrial-aquatic linkages with better integrating technologies, such as eddy covariance (Eugster and Plüss, 2010), or spatially explicit methods like hydroacoustics is warranted.

6.4 Acknowledgements

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6.5 Appendix D

6.5.1 Extended methods section

Dissolved CH₄ concentrations

Water samples for dissolved CH₄ were taken using a Niskin bottle and flushed through 125 ml serum bottles before being poisoned with CuCl and closed air free with a stopper and aluminum cap. For analysis, the headspace method was used (McAllufie, 1971). Thus, a N_2 headspace was added through the stopper with a second, open needle expelling the displaced water. Samples were then shaken vigorously and placed in a sonic bath for 30 minutes to allow for equilibration before the headspace was analyzed with gas chromatography and flame ionization detection (GC/FID).

Sediment emissions

Methane diffusion from the sediment was calculated from the porewater concentration gradient assuming a Fickian diffusive process with diffusivities derived by Furrer and Wehrli (1996) and as described in DelSontro et al. (2010). The CH₄ gradient was measured using a sediment corer and tubes with pre-drilled holes at 1-cm resolution for porewater sampling with a small syringe. The wet sediment was transferred to a serum bottle and conserved with a CuCl solution to prevent CH₄ oxidation before closing it with a stopper and aluminum cap. As air was acting as the headspace gas, control samples were also taken to know the atmospheric CH₄ content at the time. Samples were stored upside down and then shaken thoroughly before analysis to allow equilibration of the dissolved CH₄ within the headspace (McAllufie, 1971). Methane concentrations were measured via GC/FID and the control concentration was subtracted from all porewater results.

Surface emissions

Surface gas exchange was calculated using the boundary layer equation along with measured surface water CH_4 concentrations and wind speed (see Duchemin et al. (1999) for example). Drifting chambers were unanchored floating diffusion chambers that consisted of a buoyed bucket (surface area 0.086 m², volume 22 L) to collect gas diffused at the air-water interface and surfacing bubbles (see DelSontro et al. (2010) for more details). Chambers were released upwind in the area of interest and allowed to drift. Airtight tubing was secured to a hole at the top of the chamber with a three-way stopcock for sampling the collected gas. The gas volume of the tubing was flushed before sampling, then the actual gas sample was preserved by injecting it into a serum bottle pre-filled with a saturated NaCl solution and pre-closed airtight with a stopper and aluminum cap. The solution replaced by the gas was discarded via an open needle and samples were stored upside down

until analysis. Methane flux over the deployment period was calculated from the concentration increase, which was measured via GC/FID.

As the drifting chambers collected both diffusion and ebullition, we also calculated diffusion at the lake surface using the boundary layer equation (e.g., DelSontro et al., 2010). The piston velocity was calculated according to equations 3 and 5 of Crusius and Wanninkhof (2003), although actual wind speed data was scarce. Wind speeds were constructed from the few readings available at the Kariba airport during sampling (NOAA, USA) and long-term daily means and diurnal differences compiled by Mungwena (2002) and Balon and Coche (1974). Specifically, for the calculation of surface diffusion in the bays, all measured surface methane concentrations were used along with the piston velocity based on either the available daytime wind speed for July (Mungwena 2002) or the actual wind speed.

Hydroacoustic surveys

Surveys of ebullition were conducted with a vertically-down oriented Simrad split-beam echosounder (EK60, 7° beam angle) with a 120 kHz transducer operating at a ping rate of 5 s⁻¹ and a lower threshold of -120 dB. The echosounder was mounted ~30 cm below the water surface and calibrated with a 23 mm diameter standard copper target (Foote et al., 1987). The surveys consisted of either grid or zigzag transects depending on the shape of the bay (red lines, Figure D.2). Data was processed with the Sonar 5 Pro software (Lindem Acquisition, Norway) after conversion with a time-varied gain (TVG) of 40*log₁₀(R), where R is range or depth of target, for a more accurate measurement of acoustic strength of a target called the backscatter cross-section, σ_{bs} (m²). Target strength (TS) is the common log representation of σ_{bs} , calculated as $10*log_{10}(\sigma_{bs})$ in units of dB (Simmonds and MacLennan, 2005). For a more accurate TS measurement, only single echoes holding to the following single echo criteria were accepted during conversion: (1) pulse lengths within 0.8 and 1.20 relative to the transmission pulse, (2) maximum angle standard deviation of 0.30 degrees, and (3) maximum gain compensation of ± 3 dB.

In order to determine bubble density, N (# m-3), the echo-integration method of Sonar 5 Pro called TS-sv scaling was used. The acoustic energy in the desired volume of water, s_v (m⁻¹), is divided by the average TS of the targets in question (in this case, bubbles), thus yielding N. Bubble density was calculated for the bottom 3 m water strata starting from a 0.5 m buffer line above the lake bottom reflection as to avoid disturbance from sediments, plants, or fish lying on or near the bottom. Another buffer line was placed 1 m from the echosounder depth to avoid shallow locations where the bottom approached the near field zone (Simmonds and MacLennan, 2005). A cross-filter detector (Balk and Lindem, 2000) was applied to the file for more reliable bubble tracking, which is

needed to determine the TS distribution of bubbles. Bubbles were tracked in the bottom 3 m water layer of each transect. Bubbles and non-bubbles (i.e., fish or plankton) were distinguished based on their rise velocity. Rising bubbles have angled tracks when recorded from a moving boat (0.15 m s⁻¹ > Vz < 0.5 m s⁻¹), while non-bubbles tend to have horizontal tracks in echograms with almost no vertical velocity (Vz < 0.1 m s⁻¹; Ostrovsky 2003). Finally, N was calculated after cleaning all non-bubbles from the echograms with a working threshold of -70 dB.

In order to convert N to gas volume density, the bubble volume associated with the mean TS of the tracked bubbles was used. Bubble volume was calculated using the TS-bubble volume relationship in equation (4) from the echosounder calibration of Ostrovsky et al. (2008). Gas volume density found for each bin was converted to mass density using the Ideal Gas Law for the depth at which the bin was located. Finally, hydroacoustic sediment CH₄ flux was calculated from gas volume density using the average rise velocity of all tracked bubbles and the bubble gas composition, which was found via GC/FID analysis of gas bubbles collected with traditional gas traps. As CH₄ bubbles dissolve partially during their ascent in the water column, a discreet bubble model (McGinnis et al., 2006) was used to estimate surface emission flux from the hydroacoustic sediment flux. Bubble dissolution heavily depends on initial bubble size and release depth as well as composition of the bubble and the ambient water.

Gas traps

The custom-made gas traps, which are inverted funnels with an opening of ~0.280 m² surface area, were placed at ~1 m height above the lake bed (see DelSontro et al. (2010) for more details). Collected gas volume was measured at the lake surface in an attached cylinder and flux was calculated in ml m⁻² s⁻¹. In addition, collected gas was sampled via an air-tight glass syringe through a septum at the top of the cylinder and delivered to a sterile serum bottle pre-filled with N₂ and closed airtight with a stopper and an aluminum cap. Samples were analyzed for CH₄ by GC/FID.

Subbasin IV hypolimnion CH₄ accumulation

The monthly CH₄ stock in subbasin IV was extrapolated from all subbasin IV CH₄ profiles measured (Figure D.1), thus only values for February, May, June, and July were calculated. The average concentration of sampled depths from all profiles measured was applied to their corresponding depths. Concentrations between two sampling points of a profile were assumed to change linearly. The concentration profile was then multiplied by the volume of each depth strata to find CH₄ mass per strata, which were then summed to find total CH₄ stock for the basin. The CH₄ stock for the four sampled months nicely represented the major transitions in the annual

hydrological cycle of subbasin IV and revealed that an exponential increase in CH₄ accumulation was likely over the course of one year (Figure D.4). Therefore, the CH₄ stock likely during the remaining 8 months of the year that were not sampled were calculated using the exponential regression best representing the hydrologic conditions illustrated by the four measured stocks (CH₄ stock = $15.851e^{0.5707x}$, where x is month, R² > 0.99, n = 4; Figure D.4).

Dam discharge estimation

The degassing flux (J_{deg}) was approximated using an approach similar to that used by Soumis et al. (2005) and Galy-Lacaux et al. (1997):

$$J_{deg} = (C_{w,u} - C_{w,d}) * Q, \qquad (D.1)$$

where $C_{w,u}$ is the CH₄ concentration in water upstream of the dam, $C_{w,d}$ is the methane concentration in water leaving the dam, and Q is dam discharge.

Concentrations at B99, station closest to the dam (Figure D.1), were used for determining the CH₄ concentration of waters passing through the dam. The four samplings at B99 and an exponential regression were used to extrapolate concentrations to the eight months not sampled. The oxycline level progression throughout one year was determined using temperature and dissolved oxygen data from 2007 until 2009 (data not shown) and was corrected for changing water levels.

Kariba dam has two turbine intakes on the south bank and one on the north bank; therefore, a mixture of water from different heights passes through to the downstream river. Based on the capacities of the turbines, it was estimated that 47% of total discharge passes through the one intake to the north bank turbines, 36% enters the higher intake, and 17% leaves through the lower intake on the south bank. In 2009, no water passed through the spillgates.

Finally, to determine the stratified flow through the turbine intakes and the withdrawal layer thickness, D (m), a slot orifice equation adapted from Fan (2008) was used:

$$D = 2.0 (Q w^{-1} N^{-1})^{1/2}$$
(D.2)

Where Q is discharge, w is the width of the basin arm next to the intakes, and N is the buoyancy frequency (strength of density stratification) that was determined based on conductivity, temperature and depth profiles. Figure D.5 and D.6 shows bi-monthly results of stratified flow through Kariba Dam, including the migrating boundary between the CH₄-poor epilimnion and CH₄-rich hypolimnion.

Whole lake emission upscaling and carbon loading comparison.

For the comparison with the carbon loading to the system, diffusion from sediments in the other subbasins must be calculated along with the total ebullition emissions. Subbasin IV diffusion plus the diffusion from the other subbasins (assuming 30 mg CH₄ m⁻² d⁻¹ calculated in a subbasin IV core) is equivalent to 43,900 t C y⁻¹ (58,500 t CH₄ y⁻¹). Ebullition emissions from the entire lake were extrapolated assuming only river deltas were active emitting regions for half of the year. The active ebullition area of the river deltas was assumed to be directly in front of the river and only up to where the bay met the open water or 20 m, whichever came first. Thus, surface ebullition from Lake Kariba deltas resulted in 38,600 t CH_4 y⁻¹ in atmospheric emissions. Assuming a bubble dissolution rate of 35% allows us to calculate that a total of 44,500 t C y⁻¹ (59,400 t CH₄ y⁻¹) is released from the sediments via ebullition. Therefore, via diffusion and ebullition a total of 88,400 t C y⁻¹ is possibly released from Lake Kariba sediments in the form of CH₄. Kunz et al. (2011) calculated a net carbon accumulation of 120,000 t C y⁻¹ based on profundal core data as well as that from the deltas of the two major inflows (Kunz et al., 2011). A burial efficiency of 41% was also found (Kunz et al., 2011). If we assume that 50% of the carbon remineralization results in CH_4 (Bastviken et al., 2008), then an emission of ~86,000 t C y^{-1} is possible based on the Kunz et al. (2011) estimate. Any differences between the carbon release estimates would arise from the fact that Kunz et al. (2011) did not account for all deltaic zones in Lake Kariba, and while the burial efficiency in deltas tends to be higher than in the lacustrine, the organic loading and sedimentation rates tend to also be higher in these areas (Sobek et al., 2009).

Study Sites	Dissolved CH ₄ Profiles	Porewater Cores		
Bay Name	Bay Type ^a	[CH ₄] ^b (µM)	Flux ^c (mg m ⁻² d ⁻¹)	
(Abbreviation)	(Mean depth, m)	(Number of stations)	(Number of stations)	
Lufua River (LR)	RD (18)	2 ± 2 (10)	50 ± 20 (3)	
Gache Gache River (GR)	RD (9)	0.4 ± 0.4 (9)	70 ± 40 (3)	
Charara River (CR)	RD (7)	0.9 ± 0.7 (7)	30 ± 20 (2)	
Gache Gache Bay (GB)	NB (8)	0.1 ± 0.4 (3)	$40 \pm 40 (1)$	
Charara Bay (CB)	NB (3.5)	0.4 ± 0.01 (1)	$4 \pm 3(1)$	

6.5.2 Supplementary tables

 Table D.1. Dissolved CH4 profiles and porewater cores measured in bays of subbasin IV

^{*a*} RD = river delta; NB = non-river bay; ^{*b*} Average of surface water CH₄ concentrations at each station (usually two measurements within every 5 m) \pm one standard deviation; ^{*c*} Average flux \pm one standard deviation (duplicate core taken at each station)

River	Subbasin	Area ^a	Q ^b	Surface Ebullition ^c	Total Emission ^d	
Delta	Number	[km ²]	$[m^3 s^{-1}]$	$[mg CH_4 m^{-2} d^{-1}]$	[t CH ₄ y ⁻¹]	
Lufua	IV	17.9	8	1450	4665	
Gache-Gache	IV	13.5	1.7	770	1865	
Charara	IV	3.9	2.2	400	281	
Ume	IV	30.3	35.1	873	4765	
Sanyati	IV	2.8	153.4	873	434	
Nyaodza	IV	27.6	6.2	873	4335	
Chipepo	III	16.2	1.2	873	2541	
Chezya	III	56.5	2.2	873	2358	
No name	III	21.5	1.1	873	3388	
No name	III	3.0	0.7	873	479	
Zongwe	III	11.7	3.9	873	1839	
Maze	III	10.1	4.4	873	1588	
Masumu	III	9.0	1.1	873	1417	
Sengwa	III	21.2	6.1	873	3335	
Nagandu	II	1.2	1	873	190	
No name	II	1.3	0.7	873	204	
No name	II	1.6	0.8	873	248	
Lokola	II	15.5	5.2	873	2435	
Zambezi	Ι	9.5	1100	873	1498	
Namazanda	Ι	4.7	5.7	873	734	
Total		237			38600	

Table D.2. All potential ebullition hot spots (river deltas) in Lake Kariba (see Figure D.1a)

^aBoundary of delta area extended to either the 30 m depth contour or the visual extent of the bay, whichever came first. ^bFlow rates modeled using a physical-based model (SWAT) and catchment area (see Landert, J. 2009). ^cSurface ebullition is the mean flux from each measured delta or the average of the measured deltas (Lufua, Gache-Gache, and Charara) for all unmeasured bays. ^dTotal emission based on 6 months of active ebullition due to the wet and dry season variability.

Reservoir	Z (m)	Surface Area	Diff	Ebull (kt v ⁻¹)	De- gas	Total Emission (kt v ⁻¹)	Total Emission per area (t km ⁻² v ⁻¹)	Source*
Petit Saut, French Guiana	35	300	1	0.4	5	6.4	20	Abril et al., 2005
Balbina, Brazil	35	1,770	3	0	40	70	40	Kemenes et al., 2007
Serra da Mesa, Brazil	146	1,784	60	20	200	280	160	Bambace et al., 2007; dos Santos et al., 2006
Tucurui, Brazil	90	2,430	90	7	2000	2097	860	Bambace et al., 2007; dos Santos et al., 2006
Kariba, Zambia/Zimbabwe	97	5,364	0.5	38.6	0.2	40	7	this study

Table D.3. Tropical reservoir surface CH₄ emissions

Z = maximum depth; Diff = diffusion; Ebull = ebullition; Degas = dissolved CH₄ degassing through turbines and/or downstream *Reservoirs with two sources: diffusion and ebullition from first source; degassing from second source
6.5.3 Supplementary figures



Figure D.1 – **a)** Lake Kariba with open water stations and five study bays labeled. Arrows point to river inflows with discharge in $m^3 s^{-1}$ (Landert, 2009). **b**) Methane profiles for open water stations in subbasin IV. Each panel is a different sampling campaign labeled with the month and year. Note that the upper left panel is only up to 1 μ M scale, while the others are up to 80 μ M.



Figure D.2 – Top: Sampling in bays. Legend refers to all maps. CB1 is only station in Charara Bay. Images from Google Earth. **Bottom:** Methane profiles in bays. Legend refers to all four panels (i.e., station 1 is red in every panel). Station numbers refer to above map. Charara Bay had only the single red profile in the lower right panel and the other three are from Gache Gache Bay.



Figure D.3. a) Example of a Lufua River delta echogram showing the sediment bottom, bubbles, and fish. b) Example of 5 m distance bins in 3 m layer above bottom in Lufua River delta. Bin fluxes calculated for each bin vary from zero (#) to > 10,000 mg CH₄ m⁻² d⁻¹ (*). In both panels, Z is depth in meters. Colors are target strength (TS) of echoes in dB and x-axis is time in hh:mm:ss.



Figure D.4. Standing CH_4 stocks per month in subbasin IV. Months based on measured data shown in red. The remaining months were calculated using the exponential regression shown that represents the accumulation based on measured data. **data**



Figure D.5. Methane dynamics and dam outflow typical of January, March, and May in Lake Kariba. Dashed line is location of oxycline separating CH_4 -rich hypolimnion (concentrations in pink) from the CH_4 -poor epilimnion (concentrations in blue). The complicated flow regime through the two turbines on the south bank and the one on the north bank (heights of turbines shown in m.a.s.l) was estimated using an adapted slot orifice equation (see SI methods section and Fan (2008)). Stratified flow results are illustrated by the black lines labeled with an elevation (in m.a.s.l) showing the water layer thickness that flowed through each turbine. The percentage of epi- and hypolimnion percentage of the water flowing through each turbine is shown and was used to calculate CH_4 discharge through the dam.



Figure D.6. Methane dynamics and dam outflow typical of July, September, and November in Lake Kariba.



Figure D.7. Temperature and oxygen profiles at each surveyed bay and subbasin IV station B99. River deltas are LR (Lufua River), GR (Gache-gache River), and CR (Charara River). Non-river bays are GB (Gache-gache Bay) and CB (Charara Bay). Station numbers as shown in the legend title correspond with Figure D.2.

Chapter 7

Conclusion and Outlook

7.1 Techniques for assessing methane emissions

Throughout the previous chapters multiple techniques for assessing CH₄ emissions from aquatic systems were investigated. These techniques included traditional ones, such as floating chambers and gas traps, as well as new and less invasive methods, such as eddy covariance, hydroacoustics, and mass balance approaches. In Chapter 2, a relationship between water temperature and dissolved CH₄ accumulation along Lake Wohlen led to the development of a mass balance-based system analysis that estimated surface CH₄ emissions corroborated by traditional and direct gas trap methods. The value of this simple and precise analysis lies in the fact that it was easily performed and can be applied to other run-of-river reservoirs, although this has not yet been done. In addition, in Chapter 4 it was discovered that eddy covariance CH₄ flux measurements over a lake can accurately and efficiently estimate emissions. While this may not be the least expensive option for measuring CH₄ fluxes, it does allow for long-term and high temporal resolution monitoring – two factors not easily acquired with other techniques. It was, however, learned that the most effective placement of an eddy covariance tower is in the center of the lake, instead of on the shore, as the flux footprint of the measurements should cover as much of the bubbling regions as possible.

Chapters 4 and 5 explored the usefulness of hydroacoustic methods with an echosounder for bubble flux measurements in two very different reservoirs. The non-invasive technique proved to be a fast and efficient way to survey large areas or make multiple surveys over small areas. In both reservoirs, simultaneous floating chamber surveys were conducted in an attempt to compare the methods. While in neither case the measurements matched exactly, they fell within the same order of magnitude, which is quite good for such a stochastic phenomenon as ebullition. Chambers measure CH₄ efflux directly while hydroacoustic methods estimate it based on bubble size and density in the water column, but one is able to survey much more area in the same time period with an echosounder than with chambers. It may be that some precision is lost with hydroacoustic measurements and the modeling required to estimate surface efflux, but this is well-balanced by the spatial coverage gained from such a technique. While the post-processing of hydroacoustic data is not trivial, the wealth of data provided from this method allows one to really investigate ebullition dynamics by giving them a full view of the water column and sediment-water interface. Although this is also not the least expensive option, the value awarded from the ability to measure and examine the spatiotemporal variability of ebullition is worth it. Ultimately, hydroacoustics may be able to provide the most comprehensive average ebullition flux from a region than any other method.

7.2 Linking organic matter loads and burial with methane ebullition

A few chapters and particularly Chapter 3 attempted to define the link between organic matter loading, as well as burial, and CH₄ ebullition. The extreme CH4 emissions along with the high sedimentation rate observed in Lake Wohlen prompted the theory proposed in Chapter 3 regarding this linkage. The rapid sedimentation in this run-of-river reservoir efficiently buries the moderate influx of labile terrestrial organics deep in the sediments and quickly out of the oxygenated zone. It was proposed that the rate of diffusion through the tens of centimeters of sediment under which methanogenesis is occurring is not fast enough to balance the production occurring as a result of the substrate abundance. Thus CH₄ supersaturation and subsequent bubble formation can occur, ultimately leading to intense bubble release observed in Lake Wohlen during the warmer months when conditions are best for microbial activity. Also, it was found that the sedimentation rate is probably the primary driver of high methanogenesis in this system as limited production and ebullition was found in another Swiss lake with similar amounts of organic matter loading.

In fact, only a fraction (< 3%) of the organic matter flowing into the system is actually required for the CH₄ emission observed, as was shown in Chapters 3 and 4. In addition, as stated in Chapter 4, carbon uptake from a terrestrial area up to fourfold larger than the surface area of Lake Wohlen is needed to balance the global warming potential of this reservoir. However, Lake Wohlen does remain 40-fold 'cleaner' than its coal-powered counterpart. Although, since it is the river-like conditions that make this reservoir such an extreme CH₄ emitter, it is safe to assume that other runof-river reservoirs with similar organic loads, of which there are plenty in Switzerland, may also produce sizeable amounts of CH₄. Ultimately, these conclusions from the Lake Wohlen studies led to the hypothesis that the high organic loading from the rivers entering Lake Kariba should result in ebullition hot spots located in those river deltas. A comparison between river deltas and littoral zones without a river input in Lake Kariba revealed that indeed ebullition was order of magnitudes higher in river deltas. However, this would not be expected to be the case in Lake Biel, downstream of Lake Wohlen, if the Wohlen dam did not exist along the Aare River. The Aare delta in Lake Biel is on average ~20 m deeper than Lake Wohlen, thus about twice as much bubble dissolution will occur from the release of bubbles in Lake Biel.

7.3 Role of ebullition in the methane dynamics of two systems

Two chapters (2 and 6) focused on the CH_4 dynamics of two very different reservoir schemes. In both cases it was discovered that ebullition was the dominant pathway for CH_4 emission to the atmosphere, despite the considerable size difference between Lake Wohlen and Lake Kariba. Even though both lakes are reservoirs, they are substantially different systems. Lake Wohlen is a very small (2.5 km²) and shallow (< 18 m) run-of-river reservoir that remains fully oxic and mixed all year and experiences temperature ranges from 5° to 20°C. Lake Kariba is one of the largest reservoirs on earth (5,250 km²) with a deep (~100 m) dam basin that stratifies and forms an anoxic hypolimnion each year, but water temperatures never drop below 20°C. The fact that ebullition dominated the CH₄ emissions from Lake Wohlen was not surprising as the ebullition observed there was quite intense in the warm summer months. Ebullition efficiently transports CH₄ to the atmosphere, bypassing oxidative losses, with minimal dissolution in such a shallow reservoir as Lake Wohlen. Also, even though ebullition only occurs during the warmer times of the year, the reservoir is small enough that surface diffusion, which is minimal but presumably occurs all yearlong, does not surpass the ebullition emissions.

Lake Kariba, on the other hand, is quite a large system with much more surface area to allow for diffusion. However, oxidation at the top of the hypolimnion during the stratified period, which can last up to 10+ months, effectively regulates CH₄ accumulation at the oxycline and thereby maintain low dissolved CH₄ levels in the epilimnion. In contrast to other large tropical reservoirs, Lake Kariba's main CH₄ emission pathway is not degassing at the turbines or further downstream. All the turbine intakes at the dam remain in or just at the bottom of the epilimnion throughout the year, thus no CH₄-rich hypolimnetic waters are discharged through the dam. That ultimately leaves ebullition from the littoral zone, which Lake Kariba has plenty, as the dominant CH₄ emitter. Even with very conservative temporal and spatial estimates, it was discovered that ebullition from river deltas around the perimeter of the lake release orders of magnitude more CH₄ than the other atmospheric pathways. It is very clear from both of these very different examples that ebullition deserves a lot more attention when assessing greenhouse gas emissions from water bodies.

7.4 Environmental drivers of ebullition variability

The stochastic and episodic nature of ebullition is one of the primary causes for how complicated it is to measure ebullition accurately. The temporal and spatial variability of ebullition is not unknown, but the factors governing it are not well constrained. Furthermore, both biogeochemical and physical environmental drivers exist. In Lake Wohlen, it was discovered that seasonal temperature changes played a crucial role in the temporal variability of CH_4 emission (Chapter 2), which is not surprising since microbial activity is so closely linked with temperature. However, temperature did not affect emissions as strongly on a short-term basis as did hydrostatic pressures changes due to the hydropower dam regulation of water level, as was identified in Chapter

4 via eddy covariance CH_4 flux measurements. Water level drawdown is probably the most effective driver for altering ebullition emissions on short time scales and was also observed via hydroacoustics in Chapter 5. While neither of these drivers was unknown per se, they both have now been corroborated by independent methods in the same system throughout Chapters 2, 4 and 5.

The spatial variability of ebullition can also be expressed in terms of large and small scales. The causes for the emissions in Lake Wohlen have already been stated and its characteristics define a rough model of which to look for when determining potential reservoir (or lake) hot spots. Likewise, in Lake Kariba, the presence of inflowing rivers (and organic substrate) controlled the large-scale spatial variability of ebullition in that system. However, at the small-scale (within ebullition hot spots of Lake Kariba) it became evident that ebullition was not depth-dependent as has been suspected in other studies, but potentially more related to distance from the river inflow. In the small-scale survey of an active ebullition area of Lake Wohlen (Chapter 5) it was shown that ebullition was correlated with the bathymetry of the reservoir. The highest CH_4 fluxes observed in the study area occurred along a gently-dipping slope parallel to the old river channel and concentrated around a point causing a meander in the elongated reservoir. It is suspected that these locations thus provide more substrate and better conditions for deep organic matter burial than the shallow bank and deepest part of the old river channel where ebullition fluxes were much lower.

7.5 Identifying ebullition characteristics with hydroacoustics

Chapters 5 and 6 particularly focused on the advantages of the hydroacoustic technique and the interesting new information about ebullition that was gained from it. The ability to precisely locate and subsequently measure CH_4 ebullition in the water column is one of the most alluring features of a calibrated echosounder. Hydroacoustic surveys in five different littoral regions of Lake Kariba revealed substantial variability in average CH_4 flux with the largest difference between areas with a river input and those without. Not only was the frequency of ebullition higher in a study site with a river input, but also the relative magnitudes of the 5-m segment fluxes were higher. In fact, the three river deltas that were identified as ebullition hot spots displayed a pattern in which the frequency and magnitude of ebullition increased with increasing average flux from the three sites. These particular ebullition characteristics were not revealed via the accompanying drifting chamber surveys.

The hydroacoustic data from Lake Wohlen provided additional insight into the intricacies of ebullition, namely the importance of bubble size distribution. The fact that bubble volume is related to the cube of the equivalent bubble radius means that larger bubbles tend to supply the majority of gas to the total efflux. Thus, identifying the proper bubble size distribution is essential for

calculating CH₄ flux from an aquatic system. It was also shown that bubble density plays a role in gas flux, but to a lesser degree. Bubble size tends to be the more important factor also because bubble dissolution is heavily dependent upon size with larger bubbles dissolving slower and emitting more CH₄ to the atmosphere. Bubble size variability seemed to show some spatial trends that deserve more study, for which hydroacoustic techniques would be particularly useful. Ultimately, these ebullition details are easily overlooked using techniques that integrate fluxes over large areas, such atmospheric eddy covariance measurements, or methods that have limited spatial coverage, such as floating chambers.

7.6 Implications and outlook for future CH₄ emission research

Our research has shown that run-of-river reservoirs in temperate regions can be quite significant CH_4 emitters. These types of reservoirs have been generally overlooked as they tend to be small and regarded as unimportant on regional and global scales. We developed a simple mass balance model using only monthly water sampling campaigns and temperature to approximate CH_4 emission from a small flow-through reservoir. It would be beneficial to use our model again in Lake Wohlen or other run-of-river reservoirs in Switzerland and Europe to further test its application, particularly as the temperature dependence of ebullition will become more critical in a warming climate.

As well, the high sedimentation rate in this run-of-river reservoir was shown to be one of the major factors influencing its intense ebullition, despite the organic and nutrient loading to be moderate. Perhaps this feature could contribute to a conceptual model (high sedimentation and moderate carbon/nutrient loading) as to how to locate bubbling water bodies and the ebullition hot spots within them. In fact, we already showed that this concept can be applied to large reservoirs. We were able to locate ebullition hot spots in one of the world's largest reservoirs by surveying in areas we expected higher sedimentation rates and organic loads - river deltas along the littoral zone. Considering that most large reservoirs tend to have highly dendritic patterns similar to Lake Kariba along with old tributaries still entering the former river channel, this concept can be applied in other reservoirs to locate hot spots or used to predict ebullition locations in future hydropower schemes. Furthermore, we have shown that when turbine intake levels are not located in the CH_4 -rich hypolimnetic water of a large reservoir that CH_4 ebullition can be the dominant emission pathway. Thus, ebullition should be better monitored in such large systems as their littoral zone could be a disproportionately large CH_4 source as it was in Lake Kariba.

It is known that the spatiotemporal variability of ebullition has hindered progress in not only estimating global CH₄ emissions, but also in understanding the dynamics of ebullition so that it can be better predicted. We have identified long- and short-term causes for temporal changes in

ebullition that should be considered when attempting to predict or estimate ebullition emissions from a system. While water level changes modify ebullition on short timescales, temperature (as a proxy for CH_4 production) alters emissions on a seasonal or yearly timescale. Normally such small changes as the 10 cm differences seen in Lake Wohlen would not be expected to cause large variations, but it appears that they should be taken into consideration when estimating emissions from a reservoir. However, water level changes only modify emissions, while the production of CH_4 is most likely the true determinant of flux magnitude and frequency. As such, temperature may be a very good factor to use when predicting seasonal changes in CH_4 emissions, particularly in climatic zones that experience large temperature fluctuations. Further studies designed specifically for identifying the true variability caused by these factors should include a method that can record at a high temporal resolution, such as an echosounder or eddy covariance, located in one place for multiple days along with a pressure sensor to resolve the water level fluctuation response. This should be done in the same location several times a year so that one could also determine the variability caused by changing methanogenesis rates.

As ebullition does ultimately depend on CH_4 production in the sediments, determining the production and the free gas reservoir in the sediments would be quite beneficial. Unfortunately there are no efficient methods for measuring dissolved CH_4 in the sediments, let alone the production rates. An in situ method for dissolved CH_4 concentrations such as aquatic eddy covariance that has been developed for dissolved oxygen would be ideal, but there are no appropriate CH_4 sensors yet on the market. However, since echosounding works because of the impedance between water and gas, then perhaps hydroacoustic methods could be developed to estimate the size of the free gas reservoir in the sediments.

Finally, as we have shown with hydroacoustics, bubble size distributions can be very different across systems and within a system, and is essential to understanding gas emission from a water body as bubble size determines bubble dissolution. Others have shown that bubble size is dependent upon both the CH_4 production rate in and characteristics of the sediment and thus a detailed study of these factors could lead to a fairly comprehensive gas flux model. Laboratory studies to improve the use of hydroacoustics to determine bubble size could include bubbling CH_4 through sediments with varying characteristics and from various systems to better understand the affect of sediments on the hydroacoustic return of bubbles. Until now calibrations of echosounders have only been performed on 'clean' bubbles. Perhaps the target strength calibration would be slightly altered by the use of 'dirty' bubbles, which potentially exist more in nature. Ideally, one could attempt to completely simulate lake ebullition from start to finish by incubating sediments from various systems to allow for CH_4 production and subsequent bubble formation and release. The use of an echosounder and a

video camera would allow one to truly visualize and begin to understand the ebullition process in an almost natural environment. Ultimately, the application of hydroacoustic methods for the study of ebullition has just begun, but will likely contribute much to the understanding of ebullition dynamics and its role in the global carbon cycle.

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Tonya S. Del Sontro Curriculum vitae

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Education

- 2007 2011 Ph.D., ETH Zürich, Switzerland Department of Environmental Science & Eawag, Swiss Federal Institute of Aquatic Science and Technology Title: *Importance of ebullition for methane emissions from reservoirs* Advisor: Prof. Dr. Bernhard Wehrli
- 2003 2006 M.S., University of California Santa Barbara, CA, USA Marine Science Program & Earth Sciences Department Title: *Determining the distribution, sources, and processes of beach asphalt accumulation at Coal Oil Point, CA* Advisor: Prof. Dr. Bruce Luyendyk
- 1999 2003 B.S., Richard Stockton College of New Jersey, USA Marine Science Program: Oceanography and Geology Graduated with program distinction and Class of 2003 Valedictorian

Professional Experience

- 2006 2007 Staff Research Associate, University of California, Santa Barbara, USA
- 2006 Independent Contractor California State Lands Commission, USA
- 2003 2005 Teaching Assistant, University of California, Santa Barbara, USA Intro to Oceanography, Methods in Oceanography, Antarctica, Engineering Geology

Research Experience

- 2007 2011 Eawag, Swizerland Aquatic fieldwork; Sediment coring; Echosounder data collection and processing; Gas chromatography labwork. Field areas: Switzerland, Sweden, Zambia/Zimbabwe, Greenland
- 2003 2006 UC Santa Barbara, USA Design, development, calibration, and deployment of turbine gas and oil seep traps; Organization and assistant scientist of multiple research cruises in Santa Barbara Channel, CA
- 2006 Science party member, Four week geophysical cruise along the Galapagos spreading center, Galapagos Islands, Pacific Ocean
- 2004 Science party member, Twelve-day geophysical cruise, Ross Sea, Antarctica
- 2003 Richard Stockton College GIS modelling of dune susceptibility on New Jersey barrier islands