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Greenhouse gas emissions and carbon burial in a small pond

Växthusgasutsläpp och kolbindning i en liten damm

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Civilingenjörsprogrammet i miljö- och vattenteknik

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ABSTRACT

There are a lot of uncertainties when it comes to global greenhouse gas (GHG) emissions which affects society's ability to effectively respond to climate change. Small ponds have been found to potentially play a large role in global warming. More research is needed, however, to determine to what extent they act as sources or sinks for GHGs, and what factors may contribute. The aim of this thesis was to study carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) emissions, and carbon burial in a small pond in Uppsala, Sweden. The pond was a source for both CO_2 and CH_4, but a sink for N_2O. About 50% of CH_4 emissions came from ebullition (bubbles). CO_2 flux was higher in the vegetated area than in the open water area, no difference was found for CH_4 flux. Both CO_2 and CH_4 flux were higher on colder days, while CH_4 ebullition was higher on warmer days. Limited accumulation of CO_2 and CH_4 occurred under the winter ice coverage. For water chemistry, CO_2 flux had the strongest negative relationship with electrical conductivity (EC), nitrate (NO_3^-) and nitrite (NO_2^-), and positive with total phosphorous (TP). CH_4 flux showed the strongest negative correlation with chlorophyll-a (chl-a) and total nitrogen (TN), and positive with EC and total dissolved solids (TDS). For extracellular enzyme activity, CO_2 flux had a very strong positive correlation with β-D-glucosidase (BG), as did CH_4 with N-acetyl-β-D-glucosaminidase (NAG). Carbon burial rate was low making the pond a carbon source and inefficient at burying carbon.

Keywords: pond, greenhouse gas, carbon dioxide, methane, nitrous oxide, flux, ebullition, carbon burial

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REFERAT

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Det finns många osäkerheter vad gäller globala utsläpp av växthusgaser vilket påverkar samhällets förmåga att effektivt motarbeta den globala uppvärmningen. Små dammar har potentiellt förmågan att ha en stor påverkan på klimatet, men mer forskning behövs för att avgöra i vilken utsträckning de fungerar som källor eller sänkor för växthusgaser, samt vilka faktorer som påverkar deras utsläpp eller förmåga att binda kol. Målet med denna studie var att undersöka utsläpp av koldioxid (CO_2), metan (CH_4) och lustgas (N_2O), samt kolbindning i en liten damm i Uppsala, Sverige. Dammen var en nettoutsläppare av CO_2 och CH_4, men en nettoupptagare av N_2O. CH_4 i form av ebullition (bubblor) stod för ungefär 50% av CH_4 utsläppen. CO_2 flödet var högre i områden med växtlighet jämfört med områden med öppet vatten, för CH_4 hittades ingen skillnad mellan dessa områden. Under kallare dagar var CO_2 och CH_4 flödet högre, medan ebullition av CH_4 var högre under varmare dagar. Under vintern skedde minimal ackumulation av CO_2 och CH_4 under istäcket. För vattenkemin hade CO_2 flödet starkast negativ korrelation med elektrisk konduktivitet (EC), nitrat (NO_3^-) och nitrit (NO_2^-), och positiv korrelation med totalfosfor (TP). CH_4 flödet visade det starkaste negativa förhållandet med klorofyll a (chl-a) och totalkväve (TN), och positiv korrelation med EC och totalt upplösta fasta ämnen (TDS). För extracellulär enzymaktivitet hade CO_2 flödet en mycket stark positiv korrelation med β-D-glucosidase (BG), medan CH_4 flödet hade en mycket stark positiv korrelation med N-acetyl-β-D-glucosaminidase (NAG). Kolbegravningshastigheten var låg vilket resulterade i att dammen var en kolkälla med låg förmåga att binda kol.

Nyckelord: damm, växthusgas, koldioxid, metan, lustgas, flöde, ebullition, kolbindning

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PREFACE

This Master's Thesis of 30 credits marks the final part of the M.Sc. program in Environmental and Water Engineering at Uppsala University (UU) and the Swedish University of Agricultural Sciences (SLU). The supervisor was Michael Peacock and the subject reviewer was Martyn Futter, both from the Department of Aquatic Sciences and Assessment at SLU.

First I would like to wholeheartedly thank both Michael and Martyn for giving me the opportunity to work on this project and most of all for all your support and patience. I want to thank my supervisor Michael for always taking time to answer my questions and give me feedback, and for teaching me how fun it is to do fieldwork. I wish to thank my subject reviewer Martyn for helping me finalize the thesis and prepare it for the presentation. Furthermore, I am very grateful to Pia Geranmayeh, Department of Aquatic Sciences and Assessment, SLU, who helped me collect the sediment samples. A big thank you to Anna Székely, Department of Aquatic Sciences and Assessment, SLU, who taught me how to prepare microbiology samples in the lab. Finally, I want to thank Fritjof Fagerlund, Department of Earth Sciences, UU, for all his patience and for taking over the role as my examiner last minute.

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Maria Carlson
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POPULÄRVETENSKAPLIG SAMMANFATTNING

Den globala uppvärmningen räknas som en av nutidens största utmaningar och riskerar att leda till allvarliga konsekvenser i framtiden. För att samhället ska kunna lösa klimatkrisen behövs kunskap om var växthusgasutsläpp kommer ifrån och hur dessa utsläpp kan motverkas. Ett område som nyligen väckt stort intresse inom forskningsvärlden är hur små dammar som är mindre än 0,001 km^2 påverkar klimatet. Vattendrag kan producera och släppa ifrån sig koldioxid, metan och lustgas, vilket är de tre viktigaste växthusgaserna som bidrar till global uppvärmning. Vattendrag kan dock även motarbeta global uppvärmning genom att ta upp växthusgaser, och kol kan sjunka till botten och lagras i sedimentet där det med tiden blir otillgängligt för bildandet av ny koldioxid och metan. Det har visat sig att jämfört med andra vattendrag har små dammar ofta högre utsläpp av växthusgaser, medan i andra fall kan de tvärtom vara mer effektiva på att ta upp växthusgaser och lagra kol. Det höga antalet små dammar i världen gör att sammanlagt kan de ha klart större påverkan på klimatet än vad man tidigare trott.

I nuläget finns det dock inte tillräckligt med forskning för att effektivt kunna uppskatta på vilket sätt och hur mycket små dammar faktiskt påverkar klimatförändringarna. Därför behövs fler studier som undersöker koldioxid, metan, lustgas och kol i små dammar. Genom att även studera hur olika faktorer påverkar växthusgaserna samt lagring av kol är hoppet att man i framtiden ska kunna anpassa små dammar på ett sådan sätt att de har så låga utsläpp som möjligt. Bättre nog vore om de kunde anpassas så att de i huvudsak tar upp växthusgaser samt lagrar kol och kan därmed användas som ett verktyg för att bekämpa klimatförändringarna.

Målet med denna studie var att bidra till forskningen genom att mäta flödet av koldioxid, metan och lustgas från en liten naturlig damm i Uppsala, samt att beräkna hastigheten som kol lagras i dammen. Koldioxid bildas genom respiration med syre och därmed tillverkas till största del i vattnet där det finns mycket syre. Metan tillverkas däremot genom respiration av mikrober där det inte finns syre, bland annat i sedimentet. Metanutsläpp sker därmed ofta i form av bubblor från sedimentet, vilket kallas ebullition, och mättes också. Under vintern frös dammen i fem månader. För att kunna mäta hur mycket koldioxid och metan som ackumulerades under istäcket borrades hål i isen i december och i februari. För koldioxid och metan studerades dessutom säsongs- och temperaturvariationer, och även faktorer som vegetation, vattenkemi och extracellulär enzymaktivitet.

Resultatet visade att dammen släppte ut både koldioxid och metan, men absorberade lustgas. Koldioxid- och metanutsläppen var högre än för andra små dammar i Sverige, däremot var metanutsläppen i form av ebullition mindre än vad som observerats i andra studier. Inga mätningar utfördes under sommaren vilket är då koldioxid- och metanutsläpp från dammar ofta är som högst. Detta innebär att utsläppen troligen hade varit ännu högre om sommarmätningar också utförts. Lustgas mättes enbart i september och oktober och det kan därför hända att dammen inte enbart tar upp lustgas utan släpper ut lustgas under andra tider av året. För de månader som mättes så var koldioxid- och metanutsläpp generellt högre under kallare dagar, vilket var motsatt till det som förväntades. Enbart metanutsläpp i form av

ebullition var högre under varmare dagar. Troligen var det andra faktorer än temperatur som spelade större roll under vissa av mätningsdagarna.

Bland annat kan vegetation påverka både koldioxid och metangas. Växter tar upp koldioxid och använder gasen för fotosyntes, och metan kan transporteras från sedimentet till luften genom växter. I studien mättes skillnaden mellan utsläpp i områden med vegetation och områden utan vegetation. Högre utsläpp i områden med vegetation hittades för koldioxid men ingen skillnad hittades för metangas, vilket var ej vad som förväntats. Då växter tar upp koldioxid förväntades lägre koldioxidutsläpp från dessa områden, medan för metangas förväntades högre utsläpp då växter kan hjälpa till med att transportera metangas från sedimentet. En möjlig förklaring till detta är att växter producerar och transporterar syre och kan därmed ha syresatt vattnet och sedimentet. Då koldioxid produceras i syrerika förhållanden medan metangas produceras bäst i syrefattiga förhållanden skulle produktionen av koldioxid öka i områden med mycket vegetation och syre medan produktionen av metan skulle minska.

Istäcket kan troligen också haft stor påverkan på utsläppen under och efter isperioden. Under isen skedde mycket liten ackumulation av koldioxid och metangas. Då syrehalten var väldigt låg under isen ledde detta troligen till att produktionen av koldioxid också var låg, till skillnad från metangas där produktionen borde ha varit hög. Metangas kan eventuellt ha använts upp av mikrober, ackumulerat i sedimentet eller fryst fast som bubblor i isen och släppts ut i april när isen smält. Utsläpp kan även ha skett där hål bildats i isen på grund av till exempel vegetation. Ackumulation av koldioxid och metan under istäcken har främst studerats i sjöar och större vattenmassor, det skulle därför vara intressant med fler studier på små dammar för att se om de eventuellt inte ackumulerar så mycket växthusgaser under perioder med is.

Då mätningar enbart utfördes ett fåtal gånger under året gav detta få mätpunkter att studera, vilket gjorde det svårt att dra slutsatser kring trenderna mellan koldioxid, metangas och vattenkemi. Här studerades dessutom enbart en damm medan de flesta andra studier studerat ett stort antal dammar, detta gjorde det också svårare att jämföra resultaten med andra studier och att förklara trender. Generellt stämde inte de hittade trenderna i den här studien med andra studier. Det är även ont om forskning vad gäller utsläpp och extracellulär enzymaktivitet i vattendrag, därför var det svårt att förklara trender mellan utsläpp och enzym. Dock hittades en tydlig relation mellan enzymet β-D-glucosidase (BG) och koldioxid. Enzymet BG assisterar i bildandet av glukos vilket ingår i produktionen av koldioxid, detta resulterade i att mer aktivitet av BG ledde till högre utsläpp av koldioxid.

Slutligen beräknades det hur snabbt dammen lagrar kol, det vill säga hur mycket kol som lagras per år. Det visade sig att dammen lagrar klart mindre kol per år jämfört med andra dammar som studerats. Dammens låga förmåga att lagra kol kombinerat med de höga utsläppen av koldioxid och metan gör att dammen mestadels bidrar till den globala uppvärmningen, även om den tar upp en liten mängd lustgas. Dammen kan därför ej räknas som ett bra exempel på en damm som skulle kunna användas för att bekämpa klimatförändringarna.

ABBREVIATIONS

BG	β-glucosidase enzyme
CH_4	Methane
chl-a	Chlorophyll-a
CO_2	Carbon dioxide
DO	Dissolved oxygen
DOC	Dissolved organic carbon
EC	Electrical conductivity
GC	Gas chromatograph
GHG	Greenhouse gas
GWP	Global warming potential
IC	Inorganic carbon
NAG	N-acetyl-β-D-glucosaminidase enzyme
NH_4^+	Ammonium
N_2O	Nitrous oxide
NO_2^-	Nitrite
NO_3^-	Nitrate
O_2	Oxygen
OC	Organic carbon
OM	Organic matter
PHOS	Phosphatase enzyme
PO_4^{3-}	Phosphate
SO_4^{2-}	Sulfate
TDS	Total dissolved solids
TN	Total nitrogen
TP	Total phosphorous

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1 INTRODUCTION

Ponds have been shown to play a major role in the global carbon cycle, acting as carbon hotspots as microbes break down organic matter (OM) and greenhouse gases (GHGs) are released to the atmosphere, but also acting as carbon sinks by burying and storing carbon in the sediment. Artificial ponds are now included in the IPCC Guidelines for National Greenhouse Gas Inventories (IPCC 2019) and have been shown to have higher GHG emissions than natural ponds (Peacock et al. 2021). However, it is likely that heavily modified natural ponds also have elevated GHG emissions yet are not included in the IPCC inventories despite being influenced by human activity (Peacock et al. 2021). Small ponds have likewise been shown to be especially important. According to Holgerson and Raymond (2016), 40.6% of all diffusive methane (CH_4) emissions and 15.1% of all carbon dioxide (CO_2) emissions stem from small ponds with a surface area less than 0.001 km^2, even though small ponds only make up 8.6% of the total global area of lakes and ponds. Taylor et al. (2019) further shows the importance of small ponds in the carbon cycle and found that when comparing the burial rates of ponds to grasslands, woodlands, and many other types of habitat, the burial rates were 20-30 times higher in ponds. Other natural wetlands were also found to have lower burial rates compared to ponds. These studies demonstrate that small ponds have the potential to play a large role not only in the global carbon cycle, but also in global warming. Whether their release of GHGs or their ability to store carbon balance each other or one outweighs the other, small ponds could either contribute to global warming, be neutral or have a positive effect on global warming.

However, the research on small ponds as GHG sources and as carbon sinks is insufficient, even more so research that covers both. Due to their small size as well as large number, it is difficult to quantify smaller ponds, the spatial data is therefore low (Chumchal et al. 2016). Despite an increase in existing studies on GHG emissions from small ponds, direct flux measurements are lacking and data on ebullitive emissions (bubble emissions) even more so as ebullition is often excluded. The exclusion of ebullition could be an issue as some studies have found ebullition to be especially important for CH_4 emissions from ponds (Grinham et al. 2018, Peacock et al. 2021). Nitrous oxide (N_2O) is also often excluded from studies despite being a powerful GHG (Fan et al. 2022). Some studies even show that small ponds can be sinks for N_2O (Webb et al. 2019; Audet et. al. 2020). Furthermore, the majority of studies focus on either sampling many waterbodies once or sampling one waterbody many times over a period of time. This means there is not enough temporal and spatial replication (Peacock et al. 2021). Vegetation (Jeffrey 2019) and water chemistry such as nutrients (Davidson et al. 2018, DelSontro et al. 2018) can influence emissions from ponds. Extracellular enzyme activity has also been found to influence emissions (Fenner et al. 2005), but few studies have been made in aquatic environments. Understanding what factors play a role and how they affect emissions from ponds is helpful in better estimating emissions. As for carbon burial in small ponds, studies are scarce. After comparing both GHG emissions and carbon burial, Taylor et al. (2019) concluded that small ponds can be used as carbon sinks to combat global warming. Due to the few studies, however, more data is needed to accurately estimate carbon storage of small ponds and to compare these to GHG emissions.

A study on the global CH_4 budget (Saunois et al. 2019) compared top-down and bottom-up approaches of estimating global CH_4 emissions. A top-down approach estimates CH_4 emissions by looking directly at atmospheric concentrations measured by for example aircrafts in combination with models and other methods. A bottom-up approach focuses

instead on the CH_4 sources at ground level and uses measurements and models of the different sources to estimate CH_4 emissions. These two approaches resulted in highly different global estimates, 576 Tg CH_4 y^{-1} for top-down and 737 Tg CH_4 y^{-1} for bottom-up, hence, the bottom-up estimate was nearly 30% larger. Due to the top-down approach providing a total source constraint for the globe, it was concluded that some of the bottom-up estimates had to have been overestimated. Emissions from inland water systems such as ponds were brought up as one of the main sources of uncertainty for the bottom-up estimate and improved quantification was deemed a priority.

It is evident from the top-down and bottom-up study that there are a lot of uncertainties when it comes to the sources of global CH_4 emissions. This is a huge issue as it affects society's ability to respond effectively to the challenges of climate change. The lack of data and knowledge gap of emissions and carbon storage in ponds is part of the problem. Studies, therefore, call out the importance of researching emissions from ponds and the factors affecting these emissions, in order to better understand what role ponds play in climate change (Downing 2010; Peacock et al. 2021).

1.1 OBJECTIVES AND RESEARCH QUESTIONS

The objective of the study was to investigate whether small ponds have an effect on global warming. This was done by measuring CO_2, CH_4 and N_2O emissions from one waterbody and calculating carbon burial rate by measuring the carbon stored in the pond sediment. The trade-off between carbon storage and emissions was then analyzed to see to what extent they counterbalance one another. Spatial variations in emissions were studied by looking at emission differences between vegetated areas and open water. Temporal variations in emissions were studied by taking measurements over a period of a few months. Water chemistry and extracellular enzyme activity was also measured to study their possible effects on emissions.

The following research questions were investigated:

1. Is the pond a source or sink for CO_2, CH_4 and N_2O?
2. How much does CH_4 ebullition contribute to emissions?
3. How do CO_2 and CH_4 emissions vary between vegetated area and open water?
4. How do CO_2 and CH_4 emissions vary seasonally and how does ice coverage affect emissions?
5. How does water chemistry and extracellular enzyme activity affect CO_2 and CH_4 emissions?
6. What is the annual carbon burial rate and how does it compare to the annual carbon emissions from CO_2 and CH_4?

2 THEORY AND BACKGROUND

2.1 CO_2 IN PONDS

CO_2 is a the most important GHG (NOAA 2022c), it is long-lived yet does not have a specific atmospheric lifetime. This is due to the continuous cycle of CO_2 between the atmosphere, biosphere and oceans. The removal of CO_2 from the atmosphere depends therefore on a large number of processes and their different time scales (IPCC 2007a). The global warming potential (GWP) of CO_2 is 1 as CO_2 is the reference gas for GWP (IPCC 2014). GWP compares the amount of energy absorbed by one ton of a gas to that absorbed by one ton of CO_2 over a given time period. This is based on radiative efficiencies and residence times of the different GHGs (Vallero 2019). The atmospheric levels of CO_2 have increased by more than 50% since pre-industrial times (1750), which has caused a 30% increase in ocean acidity, a pH drop by 0.1 units (NOAA 2022a, 2022b). Between 2001 and 2021 global atmospheric levels of CO_2 increased by 12% (Lan 2022a).

2.1.1 Production, consumption, and emissions

CO_2 is one of the species of inorganic carbon (IC) together with carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). In aqueous systems, the chemical relationship between the dissolved species can be described by the bicarbonate equilibrium (Dodds 2002) shown below in eq. (1).

$$\mathbf{CO_2} + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-} \quad (1)$$

Where H_2O is water and H^+ is hydrogen ions. Which species of IC dominate depends on the pH. In freshwater, CO_2 and carbonic acid dominate at pH levels under around 6 and are completely taken over by bicarbonate around pH 8 (Middelburg 2019).

IC can either be allochthonous or autochthonous. Allochthonous IC originates from external sources and has been transported to the pond from lateral inputs, surrounding soil and the atmosphere. Autochthonous IC originates from the pond and is produced during aerobic biodegradation of organic carbon (OC) in for example OM by heterotrophs, organisms that obtain their carbon from other organisms (Tranvik et al. 2009; Gudasz et al. 2010). Aerobic means oxygen (O_2) is used as part of organism respiration when consuming nutrients and therefore occurs in oxic (containing oxygen) sediment and water. Biodegradation can also be referred to as mineralization, when a compound is degraded to its mineral components, complete biodegradation (Knapp and Bromley-Challoner 2003). CO_2 is a product of aerobic respiration of organisms during the mineralization process of OC, eq. (2), where $C_6H_{12}O_6$ is glucose (McGowan 2016; Kaiser 2022).

$$C_6H_{12}O_6 + O_2 \rightarrow \mathbf{CO_2} + H_2O \quad (2)$$

CO_2 is also a product of anaerobic respiration, as described in 2.2.2. Nevertheless, CO_2 in the water can be consumed. Primary production through photosynthesis, eq. (3), uses CO_2 in a process similar but opposite to the mineralization process (McGowan et al. 2016; Kaiser 2022). Primary production is when autotrophic organisms such as plants and algae turn energy and inorganic compounds into OM.

$$6\mathbf{CO_2} + 12H_2O \rightarrow C_6H_{12}O_6 + 6O_2 + 6H_2O \quad (3)$$

The balance between respiration and photosynthesis largely determines the net production of CO_2 (McGowan et al. 2016).

CO_2 is almost completely emitted by diffusive flux. CO_2 is highly soluble in water, therefore many ponds are supersaturated with CO_2 relative to the atmosphere. This causes CO_2 to diffuse from the pond to the atmosphere (Casper et al. 2000; Holgerson 2015)

2.1.2 Emission estimates

Studies on temperate ponds have estimated CO_2 fluxes to be everything from about 50 - 3500 mg m^{-2} d^{-1}. From these studies Sweden showed the lowest emissions of 50 - 1100 mg m^{-2} d^{-1} (Natchimuthu et al. 2014; Peacock et al. 2019; Peacock et al. 2021) while ponds in Denmark and the Netherlands had higher emissions of 2300 and 3500 mg m^{-2} d^{-1} respectively (Audet et al. 2020; Van Bergen et al. 2019). Fluxes from subtropical ponds were estimated to 1100 - 1500 mg m^{-2} d^{-1} (Gorsky et al. 2019; Ollivier et al. 2019a) and tropical ponds to ~3000 mg m^{-2} d^{-1} (Panneer Selvam et al. 2014). A global study on ponds, most of which were in northern regions, by Holgerson and Raymond (2016) estimated CO_2 emissions from ponds to ~1550 mg m^{-2} d^{-1}.

2.2 CH_4 IN PONDS

CH_4 is the second most important GHG (NOAA 2022c) with a lifetime of 12.4 years and a GWP of 28 over 100 years, and as much as 84 GWP over 20 years (IPCC 2014). Although the lifetime of CH_4 is short compared to CO_2, CH_4 absorbs much more energy. CH_4 also plays a role in enhancing stratospheric H_2O and tropospheric ozone, as well as production of CO_2. All of this is reflected in the GWP causing it to be much higher than the GWP for CO_2 (IPCC 2007b). Since pre-industrial times, atmospheric levels of CH_4 have increased by 162% (NOAA 2022c) and accounted for 30% of global warming (UNEP 2021). Between 2001 and 2021 global atmospheric levels of CH_4 increased by 7% (Lan 2022a).

2.2.1 Production and consumption

In wetlands, the majority of CH_4 is produced in anoxic (containing no oxygen) sediments where anaerobic biodegradation of OC in for example OM occurs (Grasset et al. 2018). Anaerobic means electron acceptors other than O_2 are used as part of an organism respiration when consuming nutrients (McLaughlin 2016). Anaerobic degradation of OC is made up of several steps, and CH_4 is produced during the final step called methanogenesis (Bastviken 2009). Methanogenesis is a form of anaerobic respiration by methanogens, which belong to the domain archaea (Lyu et al. 2018). The main types of methanogenesis are acetotrophic and hydrogenotrophic. In acetotrophic methanogenesis acetate (CH_3COO^-) acts as the electron acceptor, eq. (4), acetic acid (CH_3COOH) is broken up into CO_2 and CH_4, while in hydrogenotrophic methanogenesis CO_2 acts as the electron acceptor, eq. (5), hydrogen (H_2) and CO_2 (IC) react to form CH_4 and H_2O (Bastviken 2009; Whalen 2005).

$$\mathrm{CH_3COOH} \rightarrow \mathbf{CO_2} + \mathbf{CH_4} \tag{4}$$

$$4\mathrm{H_2} + \mathbf{CO_2} \rightarrow \mathbf{CH_4} + 2\mathrm{H_2O} \tag{5}$$

A large degree of the CH_4 does not make it into the atmosphere as emissions, and instead gets consumed in the oxic sediment and water column by aerobic CH_4 oxidizing bacteria, methanotrophs. In this process CH_4 is oxidized with O_2 and CO_2 is produced. About 45-100%

of produced CH_4 gets oxidized, therefore the balance between the production and oxidation of CH_4 largely determines the wetland's emission of CH_4 (Bastviken 2009; Whalen 2005).

2.2.2 Emission pathways

There are four emission pathways for CH_4: diffusive flux, ebullitive flux, flux through aquatic vegetation, and storage flux. Diffusive flux occurs when the CH_4 diffuses from the sediment into the water and eventually diffuses from the water into the atmosphere. The difference between the concentration of CH_4 in the water and CH_4 in the atmosphere determines the diffusive flux, therefore the diffusive flux is largely affected by the oxidation of CH_4 (Bastviken et al. 2004a). If CH_4 diffuses from the sediment at a slower rate than the gas is produced, dissolved CH_4 might become oversaturated in the pore-water of the sediment. The build up of CH_4 may cause bubbles to form and be episodically released, which is known as ebullition (Langenegger et al. 2019). Flux through aquatic vegetation occurs when plant stems containing aerenchyma act as chimneys transporting CH_4 from the sediment to the atmosphere. The purpose of the aerenchyma is to transport O_2 in the atmosphere to the roots, which is done either by diffusion or a pressurized gradient built up by the plant. Transportation of other gases can also occur, and pressurized ventilation can be facilitated by exchanging atmospheric O_2 with CH_4 in the sediment (Berg et al. 2020; Jeffrey 2019). Storage flux occurs in stratified lakes with an anoxic layer of water where CH_4 can build up. The stored CH_4 is released during lake overturn in for example spring and autumn (Bastviken et al. 2004a).

As the anoxic layer decreases with decreasing lake size, and shallow wetlands often lack seasonal turnovers, storage flux is less important in shallow ponds. (Branco & Torgersen 2009). Ebullitive flux, on the other hand, is of particular importance in shallow waters as the hydrostatic pressure is lower due to the shorter water column height, therefore the ebullition is often rapid and the CH_4 goes directly to the atmosphere with minimal oxidation (Bastviken et al. 2004a). Furthermore, ebullition has been found to be the dominant emission pathway in ponds (Grinham et al. 2018; Peacock et al. 2021). Plant pathways have also been found to be important for CH_4 emissions, with one study finding 59% of annual CH_4 emissions to be plant-mediated, and ebullition and diffusion only accounting for 20% (Jeffrey 2019). Different types of vegetation have also been found to vary in their efficiency of transporting CH_4, a wetland's emissions may therefore depend on which type of plants it contains (Bhullar et al. 2013, Villa et al. 2020). There is, however, a lack of data on ebullitive and plant-mediated flux (Peacock et al. 2021; Bhullar et al. 2013). Diffusion tends to be less important for CH_4 due to CH_4 being relatively insoluble (Casper et al. 2000). However, small ponds have been found to be prime for CH_4 supersaturation, due to their shallow nature as well as low O_2 and high carbon content (Holgerson 2015). This means diffusion might play a larger role in small ponds.

2.2.3 Emission estimates

In the 2019 IPCC refinement average CH_4 emission from constructed ponds is estimated with an emission factor of 50 mg m^{-2} d^{-1} (IPCC 2019). Studies on temperate ponds have estimated diffusive CH_4 fluxes to be 20-30 mg m^{-2} d^{-1} (Audet et al. 2020; Van Bergen et al. 2019; Peacock et al. 2021; Peacock et al. 2019) with the exception of a study on German ponds with 120 mg m^{-2} d^{-1} (Herrero Ortega et al. 2019). Diffusive fluxes from subtropical ponds were estimated to 120-360 mg m^{-2} d^{-1} (Ollivier et al. 2019a; Gorsky et al. 2019) and tropical ponds at ~50 mg m^{-2} d^{-1} (Panneer Selvam et al. 2014). The global study on ponds by Holgerson and Raymond (2016) estimated diffusive emissions to ~40 mg m^{-2} d^{-1}. Studies on

ebullition showed that most of CH_4 emissions were emitted as ebullitive flux. Temperate ponds were estimated to have an ebullitive flux of 120-300 mg m^{-2} d^{-1}, where ebullition stood for 71-91% of CH_4 emissions from these ponds (Natchimuthu et al. 2014; Van Bergen et al. 2019; Herrero Ortega et al. 2019). Subtropical ponds had a winter ebullitive flux of ~140 mg m^{-2} d^{-1} (Ollivier et al. 2019b) and tropical ponds had an ebullitive flux of ~240 mg m^{-2} d^{-1} (Panneer Selvam et al. 2014) which together made up 83-97% of total CH_4 emissions.

2.3 N_2O IN PONDS

N_2O is the third most important GHG (NOAA 2022c). It has a lifetime of 121 years in the atmosphere and a GWP of 264 over 20 years and 265 over 100 years (IPCC 2014). Not only does N_2O have a very high GWP, but it is also the dominant ozone-depleting emission out of all the emissions by human activities (Ravishankara et al. 2009). In the stratosphere, N_2O reacts with excited oxygen atoms to form nitrogen oxides NO_x ($NO + NO_2$), which in turn contribute to the ozone loss in the stratosphere (Stolarski et al. 2015). The global atmospheric N_2O levels have increased by 23% since pre-industrial times (WMO 2021). Between 2001 and 2021 global atmospheric levels of N_2O increased by 6% (Lan et al. 2022a).

2.3.1 Production, consumption and emissions

Nitrogen (N) in the form of organic or inorganic compounds is carried to wetlands through surface water. Organic compounds of N are in particulate or dissolved form, and inorganic N is mainly in solution as ammonium (NH_4^+) or nitrate (NO_3^-) (DeBusk 1999). Organic N can be broken down (N mineralization) by microorganisms to form NH_4^+. This process is part of decomposition of OM and is called ammonification (DeBusk 1999; Hopkinson 2008). NH_4^+ and NO_3^- are used in nitrification and denitrification, microbial processes in which N_2O is a by-product. Nitrification is when $NH_4^+$is aerobically oxidized to nitrite (NO_2^-) and NO_3^-. Denitrification is when NO_3^- is reduced to nitrogen (N_2) through anaerobic dissimilatory reduction (Ivens et al. 2011). While NO_3^- in denitrification can come from surface water or nitrification, N_2 can also be produced directly from NO_2^- in the nitrification process, this is known as nitrifier denitrification (DeBusk 1999; Megonigal et al. 2003). These processes and resulting N_2O emissions are demonstrated in Figure 1 below, where NH_3 is ammonia, NH_2OH is hydroxylamine, and NO is nitric oxide.

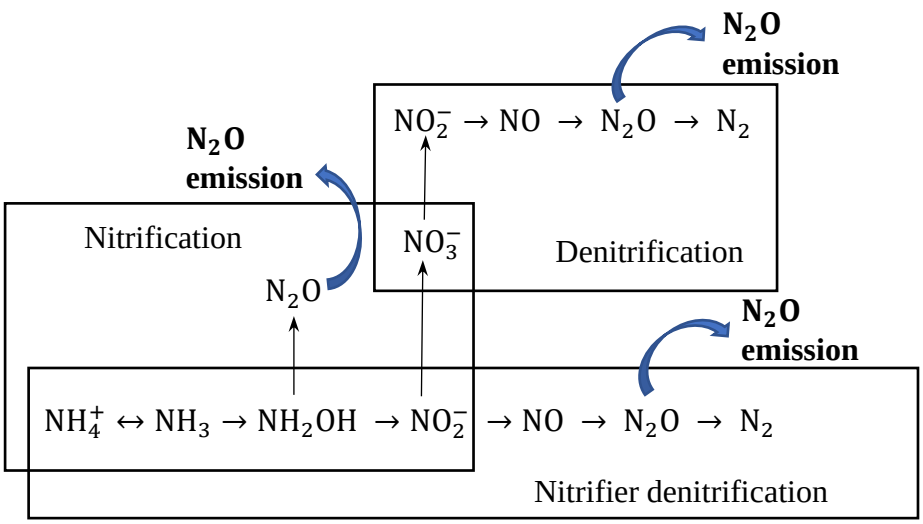

Figure 1. The chemical processes of nitrification and denitrification and resulting N_2O emissions (Thakur & Medhi 2019; Megonigal et al. 2003).

Nitrification is performed by chemoautotrophic bacteria nitrosomonas which converts NH_4^+ into NO_2^- and nitrobacter which turns NO_2^- into NO_3^- (Pepper and Gerba 2015). Chemoautotrophs get their energy and carbon from inorganic compounds (Covich 2013). Denitrification is generally a respiratory process and is performed by many different groups of bacteria. These bacteria are aerobes and can use O_2 for respiration but when there is little or no O_2 they switch to NO_3^- or sometimes NO_2^- as electron acceptor (McGonigal et al. 2003). Surface waters and surface layers of sediment that are high on O_2 promote nitrification, while waters and sediments that are anoxic or hypoxic (low on O_2) promote denitrification (Ivens et al. 2011).

Due to the high solubility of N_2O in water, ebullition is not an important pathway. Diffusion is therefore the main pathway for N_2O (Scranton and de Angelis 2001; Gao et al. 2013; Sturm et al. 2014).

2.3.2 Emission estimates

Studies on temperate ponds have estimated N_2O fluxes to be on average -0.25-1.25 mg m^{-2} d^{-1}. The studies in Canada and Finland showed the lowest average emissions of -0.25 and 0.011 mg m^{-2} d^{-1} (Jensen et al. 2022; Huttunen et al. 2002), while the studies in Denmark and Minnesota, USA, had higher emissions of 0.6 and 1.25 mg m^{-2} d^{-1} respectively (Audet et al. 2020; Rabaey and Cotner 2022). Fluxes from subtropical ponds were estimated to 0.1-0.13 mg m^{-2} d^{-1} (Gorsky et al. 2019; McPhillips and Walter 2015; Ollivier et al. 2019b), with the exception of one study from China which estimated N_2O emissions to 0.56 mg m^{-2} d^{-1} (Fan et al. 2022). A study done on a tropical pond in India estimated fluxes to 0.27 mg m^{-2} d^{-1} (Singh et al. 2005). Multiple studies found ponds with negative fluxes. In Audet et al. (2020) 35% of the ponds had negative fluxes, however, the fluxes were all close to zero. According to a study on small farm ponds in Canada, as much as 67% of the ponds acted as N_2O sinks (Webb et al. 2019a). Jensen et al. (2022) found that only 20% of the sites were net sources of N_2O, and the remaining 80% were either sinks or in equilibrium with the atmosphere.

2.4 TEMPERATURE AND ICE COVERAGE

2.4.1 Temperature and emissions

Some studies have found CO_2 fluxes in ponds to be positively correlated to temperature (Audet et al. 2020) and highest during summer (Peacock et al. 2021). Natchimuthu et al. (2014), however, found that CO_2 flux was negatively correlated to temperature and solar radiation in ponds. It was believed that this was due to the balance between respiration and photosynthesis. During warm sunny summer days, CO_2 consumption through photosynthesis was likely higher than CO_2 production through respiration as the day time fluxes were mostly negative. Therefore, it was suggested that pond morphometry as well as the types of primary producers which dominate might play a large role in determining CO_2 flux during the summer.

On the other hand, studies agree that CH_4 flux and temperature have a positive relationship and that CH_4 flux is highest during the summer (Natchimuthu et al. 2014; van Bergen et al. 2017; Ollivier et al. 2019b; Audet et al. 2020; Peacock et al. 2021). Ebullition of CH_4 has also been found to be strongly related to temperature (Natchimuthu et al. 2014; van Bergen et al. 2017; Peacock et al. 2021). Natchimuthu et al. (2014) found that 47% of the variation in total CH_4 flux was due to variations in air temperature, as well as 45% of the variation in ebullition. One possible reason is that methanogenesis has been shown to be highly dependent on temperature, with lower temperatures inhibiting it (Segers 1998; van Hulzen et al. 1999). Furthermore, there is generally a seasonal variation in substrate supply. High temperatures and solar radiation typically coincide with growth season when primary production by macrophytes is high, which provides easily available organic substrates that can be used for methanogenesis (Natchimuthu et al. 2014).

N_2O flux has also been found to be positively correlated with temperature (Ollivier et al. 2019B; Audet et al. 2020). Which can, according to Ollivier et al. (2019B), be explained by the biological dependence nitrifying and denitrifying bacteria have with temperature (Dobbie and Smith 2001, Holtan-Hartwig et al. 2002, Saggar et al. 2004, Saleh-Lakha et al. 2009, Xia et al. 2013).

Factors such as photosynthesis and substrate supply from primary production are temperature dependent and influence emissions, therefore temperature affects emissions indirectly through these factors. Audet et al. (2020) suggested that changes in nutrient processes or in ecological status due to temperature might also play a large role in changes in CO_2, CH_4 and N_2O emissions (Davidson et al. 2015, 2018). Ecological status is the state of a surface water's biological, physical and chemical characteristics. Hence, it is difficult to determine to what extent temperature directly affects emissions and how much it indirectly affects emissions through other temperature dependent factors.

2.4.2 Ice coverage and emissions

In boreal and temperate climates ice may form and cover ponds and aquatic systems during the winter months. The ice coverage acts as a lid, preventing CO_2 and CH_4 from escaping into the atmosphere. CO_2 and CH_4 builds up under the ice and is later released when the ice melts. Denfeld et al. (2018a) compiled data from 25 studies and found that the ice-melt period represented 17% of annual CO_2 emissions and 27% of annual CH_4 emissions in northern lakes. This shows that annual emissions may be largely underestimated if GHGs produced under the winter ice are excluded. However, studies have also shown that accumulation of CO_2 and CH_4 is complex and depends on many factors. No studies on emissions from ice

covered ponds could be found, therefore the information below focuses on lakes and might not be the most representative of ponds.

Photosynthesis has been found to occur under ice and is affected by ice thickness and snow cover (Room et al. 2014). Ice coverage and snow can limit how much light reaches the water, which in turn can lead to a decrease in photosynthesis (Hampton et al. 2017). A decrease in photosynthesis means less CO_2 is consumed and could contribute to higher CO_2 levels. However, a decrease in photosynthesis also means that less O_2 is produced, and as the ice prevents the transfer of O_2 from the atmosphere to the water, the inflow of new O_2 is limited. Since heterotrophs consume the O_2, the O_2 levels decrease further, which might lead to a gradient from surface to bottom that is hypoxic to anoxic. The lack of O_2 would decrease aerobic respiration and the production of CO_2, and instead increase anaerobic respiration and the production of CH_4 (Garcia et al. 2019).

However, it has been found that oxidation by methanotrophs is of the same magnitude during ice coverage, 0.20 mol CH_4 m^{-2}, as during ice-free periods, 0.22 mol CH_4 m^{-2}. Only 20% of the annual CH_4 that diffused from the sediment was released to the atmosphere, ~80% was oxidized (Kankaala et al. 2006). During ice-free periods, CH_4 in ebullition experiences minimal oxidation, however, during periods with ice, ebullition bubbles of CH_4 can get trapped by the ice. Greene et al. (2014) studied seasonal lake ice and found that 80% of CH_4 that gets trapped under the ice as bubbles dissolves into the water column. Of the 80%, about half is oxidized. The CH_4 bubbles that remain are either trapped and accumulate under the ice or encapsulated by downward-growing ice and stored in the lake until the ice melts, which can take several months. This “ice bubble storage” (IBS) released during ice melt only makes up 7% of annual CH_4 ebullition according to Greene et al. (2014). Thus, oxidation of diffusive CH_4 might remain roughly the same during ice coverage, but oxidation of CH_4 ebullition likely increases.

Garcia et al. (2019) looked at the effects of increased light after removing snow coverage on a frozen lake. The results showed that there was a decrease in methanotrophs and consequently a decrease in oxidation, which led to an increase in CH_4. It was also shown that heterotrophs increased after the snow removal; it was suggested that methanotrophs might have been outcompeted by heterotrophs as methanotrophs grow slowly in comparison. Furthermore, algae activity increased, which might have led to a phosphate (PO_4^{3-}) shortage. Low PO_4^{3-} concentrations have been shown to limit growth of methanotrophs (Denfeld 2016). The decrease in methanotrophs and oxidation might therefore be explained by either an increase in heterotrophs or a decrease in PO_4^{3-}. The increase in algae activity, chlorophyll, in Garcia et al. (2019), meant an increase in primary production, and in turn an increase in O_2. However, this increase in O_2 did not persist. It was suggested that the newly produced O_2 was consumed by the heterotrophs. The increase in heterotrophs likely meant an increase in CO_2 production. Thus, removing the snow cover resulted in an increase in CH_4, but also possibly led to an increase in CO_2 as well.

Studies have shown that due to incomplete water mixing during ice-melt 15-34% of the accumulated CO_2 (Denfeld 2016) and 40-46% of the accumulated CH_4 (López Bellido et al. 2009) remained in the studied lakes, mainly in bottom waters. It is not yet known what happens to the CO_2 and CH_4 that remains stored, if it gets processed or emitted to the atmosphere eventually. However, this means that measurements made during winter and ice-melt might not be representative for how much CO_2 and CH_4 is actually stored in a lake. Denfeld (2016) also estimated that during ice-melt 28-36% of the CO_2 emissions were from

external sources. It was suggested that the external CO_2 came from stream and catchment melt water. This means external inputs of CO_2 and CH_4 as the ice is melting could add to the emissions during ice-melt (Denfeld et al. 2018b). Internal production during the ice-melt period might also contribute to higher emissions when the ice melts (Denfeld et al. 2018b). Thus, accumulated emissions from lakes at ice-melt might be underestimated due to some accumulated CO_2 and CH_4 remaining in the lakes, or emissions might be overestimated due to external sources and production during ice-melt.

Small shallow lakes have been found to have the highest accumulation of CO_2 and CH_4 under the ice (Denfeld 2016; Juutinen et al. 2009). In ice-covered lakes, low O_2 and high nutrients, such as phosphorus and nitrogen have been linked to high CO_2 and CH_4 concentrations (Denfeld 2016; Juutinen et al. 2009; Sobek et al. 2003). This might explain the high accumulation of GHGs in small shallow lakes as they have also been found to have the highest nutrients (Denfeld 2016). A study by MacIntyre et al. (2018), however, found that among the studied lakes, the shallow lake had the least accumulated CO_2. They speculated that the colder temperatures above the sediment might be causing lower aerobic respiration rates, leading to less CO_2 production. The study also suggested that the small volume might lead to a relatively larger anoxic area, and therefore less aerobic respiration and less CO_2. CH_4 can escape through openings in the ice, such as vegetation that is emerging through the ice (Larmola et al. 2004), or cracks in the ice caused by for example CH_4 bubbling or inflows (Greene et al. 2014; Phelps et al. 1998), both likely having a greater effect on a small shallow lake. If the entire water column freezes, from surface to sediments, which is more likely in small shallow lakes, CO_2 and CH_4 build-up is less likely (Jammet et al. 2015; Manasypov et al. 2015; Denfeld. et al. 2018a).

2.5 WATER CHEMISTRY

Electrical conductivity (EC) measures the ability of the water to conduct electricity. The higher the EC, the higher the concentration of dissolved ions, electrically charged atoms or molecules, in the water. Total dissolved solids (TDS) is a measurement of organic and inorganic substances dissolved in the water. All atoms and molecules dissolved in the water that are not H_2O count as TDS. It can also be seen as a measurement of the amount of ions in the water. pH measures whether the water is acidic (less than 7), basic (more than 7) or neutral (equal to 7). Dissolved oxygen (DO) is a measurement of the amount of O_2 dissolved in the water. Dissolved organic carbon (DOC) is the OC that can pass through a filter with pore size between 0.22 and 0.7 µm. The OC remaining in the filter is referred to as particulate organic carbon (POC). DOC is a source of energy and carbon for heterotrophs. Chlorophyll is the green pigment in photosynthetic organisms such as plants, algae and cyanobacteria. Measuring chlorophyll-a (chl-a) gives an estimate of how much algae is in the water and in turn how much primary production is occurring. Common macronutrients in aquatic ecosystems are phosphorus and nitrogen. Total phosphorous (TP) is the sum of all phosphorous in phosphorus containing compounds in the water, both dissolved and particulate. PO_4^{3-} is a common form of phosphorous and is derived from phosphoric acid (H_3PO_4). Total nitrogen (TN) is the total amount of nitrogen, which is the sum of nitrogen in NO_3^-, NO_2^-, NH_4^+ and organically bound nitrogen.

2.5.1 Water chemistry and CO_2

Peacock et al. (2021) found that EC had a positive effect on CO_2 concentrations in small waterbodies. A possible explanation for this is that EC is positively correlated to sulfate (SO_4^{2-}) (Jensen et al. 2022), and SO_4^{2-} is sometimes positively correlated to dissolved CO_2

concentrations in ponds (Audet et al. 2020). EC can therefore be seen as a proxy for the SO_4^{2-} concentration.

In inland waters, pH has a negative correlation with CO_2 concentrations/emissions (Peacock et al. 2021; Hao et al. 2021; Yang et al. 2015; Jensen et al. 2022). When pH > 8, emissions of CO_2 are close to zero. This reflects the effect of the bicarbonate equilibrium on CO_2, where bicarbonate and carbonate dominate over CO_2 at high pH, see section 2.1.1 (Schrier-Uijl et al., 2011; Sets et al. 2017).

A positive correlation between CO_2 fluxes and DO has been found in ponds by Yang et al. (2015). However, Jensen et al. (2022) and Audet et al. (2020) found a negative correlation between DO and CO_2 concentrations. Primary production may have been the cause of the negative relationship as CO_2 is consumed and O_2 is created (Jensen et al. 2022).

Yang et al. (2015) found both a positive and a negative relationship between CO_2 emissions and chl-a. A high chl-a is equivalent to high algal growth, which in turn also means high production of autochthonous OM. This OM could then be mineralized producing CO_2, thus, explaining the positive relationship (Huttunen et al. 2003). However, high algal growth can also result in high primary production and the consumption of CO_2, explaining the negative relationship (Yang et al. 2015).

CO_2 fluxes often positively correlate with DOC in ponds (Peacock et al. 2021) and other inland waters (Hope et al, 1996 Sobek et al. 2003). An increase in inputs of DOC would likely lead to higher levels of OC mineralization by heterotrophs and therefore more production of CO_2 (Larsen et al. 2011).

Higher aquatic nutrients tend to lead to more primary production and therefore lower CO_2 as it is consumed (Pacheco et al. 2014). However, Peacock et al. (2021) observed that waterbodies with higher TP levels had significantly greater fluxes of CO_2. DelSontro et al. (2018) argued that TP may act as a proxy for terrestrial inputs of OC and CO_2. Thus, a higher TP value would mean more terrestrial inputs of TP, but also OC and CO_2, which would result in higher CO_2 concentrations. This could therefore explain a positive correlation between TP and CO_2.

TN has a positive relationship with CO_2 concentrations/emissions (Ollivier et al. 2019a; Peacock et al. 2021; Malyan et al. 2022). Algal growth is enhanced by high nitrogen, which means more algal biomass which can settle to the bottom and degrade, leading to emissions (Webb et al. 2019). Just as mentioned above for TP, however, higher algal growth could also mean more primary production and lower CO_2.

2.5.2 Water chemistry and CH_4

As mentioned in 2.5.1, SO_4^{2-} and EC are highly positively correlated. When SO_4^{2-} levels are high, SO_4^{2-}-reducing bacteria inhibit methanogenesis and the production of CH_4 (Webb et al. 2019). This means higher SO_4^{2-} levels lead to lower CH_4 levels. EC therefore has a negative relationship with CH_4. CH_4 content in ebullition bubbles is also negatively correlated with EC (Jensen et al. 2022).

According to Malyan et al. (2022) pH and CH_4 do not have a significant correlation. CH_4-producing bacteria are pH sensitive and produce CH_4 within the range pH 6-8, but as freshwater ponds are within or around this pH range, pH is not an important variable.

A negative relationship has been found between CH_4 concentrations/emissions and DO (Audet et al. 2020; Peacock et al. 2021). Methanogenesis is an anoxic process, so lower DO results in more CH_4 production. CH_4 oxidation within the water column is also limited by lower DO, so less CH_4 is oxidized, further causing higher CH_4 at lower DO (Yang et al. 2013).

A positive relationship between CH_4 flux and chl-a has been observed (Yang et al. 2015; Jensen et al. 2022). A possible explanation is that high algal growth produces new autochthonous OM, supplying substrates for methanogenesis (Palma-Silva et al., 2013).

A significant positive correlation between DOC and CH_4 concentrations was found by Peacock et al. (2021). An increase in DOC would mean more OC available for anaerobic degradation, and therefore more production of CH_4 (Christensen et al. 2003).

Generally it has been observed that ponds and waterbodies with higher TP levels have significantly larger CH_4 fluxes (Peacock et al. 2021, Malerba et al. 2022). This is often only true, however, if other factors are not limiting. Rabaey and Cotner (2022) found a positive correlation between TP and CH_4 diffusion, ebullition rates and concentrations. This agrees with DelSontro et al. (2016) who observed higher CH_4 emissions in more eutrophic, nutrient rich, ponds and lakes. A surplus of phosphorous encourages algal growth and in turn creates more dissolved OM which could be degraded. During degradation of OM, O_2 is also consumed, which is why anoxia is common in eutrophic waters. Eutrophication is therefore beneficial for CH_4 production (Davidson et al. 2018). A positive correlation has been found between PO_4^{3-} and CH_4 emissions from ponds (Audet et al. 2020) as CH_4 emissions increase with increasing algal growth from eutrophication as mentioned above (Davidson et al. 2018, DelSontro et al. 2018). An increase in algae activity due to eutrophication has also been linked with PO_4^{3-} shortage, which is a limiting factor for methanotrophs (Garcia et al. 2019). Therefore, low levels of PO_4^{3-} would limit oxidation and could lead to higher levels of CH_4, giving a negative relationship between PO_4^{3-} and CH_4.

TN has been found to have a positive correlation with CH_4 production in small ponds (Peacock et al. 2021; Malyan et al. 2022). This is also likely due to an increase in OM from increasing algal growth caused by eutrophication (Davidson et al. 2018, DelSontro et al. 2018). A positive relationship between NO_3^- and CH_4 has also been observed (Ollivier et al. 2019a; Webb et al. 2019b), however, some studies have found a negative relationship between NO_3^- and CH_4 emissions in ponds (Audet et al. 2020; Malyan et al. 2022; Yang et al. 2015). This is due to NO_3^- acting as an electron acceptor. O_2 and NO_3^- are more favorable electron acceptors compared to CO_2 and acetate which are used in methanogenesis, therefore CH_4 production is limited until O_2 and NO_3^- have been used up. Thus, NO_3^- may inhibit methanogenesis, lowering CH_4 production (Audet et al. 2020; Köhn et al. 2021).

2.6 EXTRACELLULAR ENZYME ACTIVITY AND EMISSIONS

An enzyme that removes a PO_4^{3-} group from organic molecules is known as a phosphatase (PHOS). Phosphatase uses hydrolysis to break up phosphoric acid monoesters into a PO_4^{3-} ion and a molecule containing a free hydroxyl group (-OH). Hydrolysis is a chemical reaction where a water molecule is used to break one or more chemical bonds (Dunn et al. 2014). More PHOS could therefore result in more PO_4^{3-} and as mentioned in 2.5.2, PO_4^{3-} can both positively and negatively influence CH_4 emissions.

Glucosidase enzymes act as catalysts in breaking the glycosidic linkage between a carbohydrate molecule and another group through hydrolysis. As a result of the hydrolysis, smaller sugars such as glucose are released, which provides energy and carbon sources for microbes in soil. Glucosidases act as cellulases and are therefore involved in degrading plant-derived cellulose. Cellulose can be cleaved to create water-soluble cellodextrins such as cellobiose, and these can be hydrolysed by the glucosidase catalyst enzyme β-glucosidase, also called β-D-glucosidase (BG) (Dunn et al. 2014). This results in the formation of β-D-glucose which is the most common stereoisomer of glucose found in nature (Deng and Popova 2011). Stereoisomers are molecules with the same order of bonded atoms and molecular formula, but different three-dimensional orientation. More BG could therefore result in more glucose and as mentioned in 2.1.1, CO_2 is produced during the aerobic mineralization of glucose. This is strengthened by Fenner et al. (2005) which observed that the optimum temperature for BG corresponded with microbial respiration of CO_2 and Morrissey et al. (2014) which found that CO_2 production rate correlated with cellulose breakdown by BG.

N-acetyl-β-D-glucosaminidase (NAG) is an enzyme involved in breaking down chitin $(C_8H_{13}O_5N)n$. In nature, chitin is the most common polysaccharide after cellulose and is used in for example cell walls of fungi and algae or as exoskeletons of insects (Dunn et al. 2014). A substantial portion of humus-bound nitrogen can be found in chitin in soils of wetlands (Kang et al. 2005). More NAG could therefore result in more nitrogen and nitrogen has been found to have a positive relationship with CO_2 and CH_4 production, see 2.5.1 and 2.5.2.

2.7 CARBON BURIAL IN PONDS

OC may get deposited at the bottom of the pond and become part of the sediment. Some of this OC gets mineralized by microbes to CO_2 or CH_4, but some of it gets buried longterm in the sediment (Sobek et al. 2009). The burial of OC offsets some GHG production as it removes this carbon from the atmosphere and acts as a sink in the global carbon cycle (Mendonça et al. 2017; Sobek et al. 2009). Carbon burial depends on how much OC gets deposited and how much of the deposited OC escapes mineralization. This is described as organic carbon burial efficiency (OC BE), the ratio of OC burial to OC deposition (Sobek et al. 2011). OC BE is largely affected by the amount of autochthonous and allochthonous OC in the pond. The more OC there is, the more gets deposited. However, autochthonous OC, which is internally produced, is more easily mineralized by microorganisms compared to allochthonous OC, which originates in the terrestrial environment. Allochthonous OC is therefore much more likely to accumulate and get buried in the sediment (Burdige 2007; Sobek et al. 2009). According to Downing (2010), geochemical processing is more intense in ponds compared to larger aquatic systems. Ponds are often shallow with a lot of light and tend to have a high nutrient concentration (eutrophic) which leads to more production of autochthonous OC through primary production (Downing et al. 2008; Tranvik et al. 2009). Due to their high ratio of pond edge to area, ponds also have comparably high allochthonous inputs via soil particulate transfer from land, (Gilbert et al. 2014; Downing et al. 2008). These factors contribute to ponds having very high burial rates. Vegetation type has also been found to play a major role in carbon burial, where some species enhance carbon burial while others restrict it (Taylor et al. 2019).

2.7.1 Estimates of carbon burial in ponds

Studies have estimated carbon burial in ponds to be on average between 142-152 g C m^{-2} y^{-1} (Taylor et al. 2019; Gilbert et al. 2014; Ljung and Lin 2023). Goeckner et al. (2022) looked at

stormwater ponds in Florida and estimated carbon burial to be 114 g C m^{-2} y^{-1}, a little lower than the other studies. Out of the four studies, only Gilbert et al. (2014) looked at small natural ponds, however, there was little difference between the natural and artificial ponds. Taylor et al. (2019) and Goeckner et al. (2022) both found that carbon burial increased with pond age. Ljung and Lin (2023) found no correlation between carbon burial and pond age. When looking at carbon emissions and carbon burial, Taylor et al. (2019) found the studied ponds to be net carbon sinks, but Goeckner et al. (2022) and Ljung and Lin (2023) found ponds to be net carbon sources. Taylor et al. (2019) had the smallest ponds, about 30 cm deep and an area of about 1 m^2, yet the carbon burial rate was about the same as that of the other studies. CO_2 emissions in these ponds were at times negative and at times comparable to that of studies mentioned in 2.1.2, and CH_4 emissions were low (Gilbert et al. 2017; Taylor et al. 2019). Perhaps the very small size contributed to the ponds acting as carbon sinks, however, more data would be needed to draw such a conclusion. It is also important to mention that carbon burial is accounted for in carbon emissions in closed systems such as ponds (Prairie et al. 2018).

3 METHOD

3.1 STUDY SITE

Fieldwork took place from September 2021 until May 2022 in a small shallow pond on SLU campus in the city of Uppsala, Sweden. The region is considered hemiboreal and in 2021 had a mean annual temperature of 7.2 °C and annual precipitation of 499 mm (SMHI n.d.a). The pond has an area of 1331 m^2 (Peacock et al. 2021) and is believed to be natural in origin, possibly a kettlehole left from the last ice age. However, it has been used for cultivation of crucian carp around the 18th century (Bonow and Svanberg 2014) and has likely been influenced by the agricultural and semi-rural environment over the centuries. The pond was last dredged in 1990 and has been mostly untouched since with the exception of duckweed collection once a year for the past five years.

Measurements and sampling were performed on the 28th of September, 25th of October, 18th of April, and 19th of May. Floating chambers for measurement of ebullition were deployed on these dates and left for 24 hours to be sampled and collected the day after. The pond was covered by ice from mid-November until mid-April, during which measurements and sampling was performed on the 6th of December and 24th of February. Floating chambers were not used during these dates. The sediment coring was done on the 19th of October.

3.2 DISSOLVED CH_4 AND N_2O

Samples were collected for analysis of dissolved concentrations of CH_4 and N_2O. This was done using the headspace method (Hope et al. 2004) where 30 mL pond water and 30 mL ambient air was collected in a 60 mL syringe and shaken together for 60 s. This causes the CH_4 and N_2O that is dissolved in the pond water to enter the gaseous phase and mix with the ambient air in the syringe, creating an equilibrium concentration of CH_4 and N_2O between the pond water and the ambient air. From the headspace of the syringe, 22 mL of gas was transferred into a pre-evacuated glass vial. The concentrations in the samples were analyzed on a Perkin Elmer Clarus 500 gas chromatograph (GC) equipped with an electron capture

detector. The dissolved N_2O concentrations were compared to the atmospheric concentrations to determine whether the gases were undersaturated or oversaturated in the pond water, making the pond a sink (undersaturated) or source (oversaturated) for N_2O. For CH_4 the dissolved concentrations were used to calculate ebullition and flux captured in the 24 hour chambers. Air temperature and pressure used in calculations were either measured using the Hanna Instruments or taken from SMHI (SMHI n.d.b). Concentrations are assumed to be constant across the pond.

3.3 GHG EMISSIONS

3.3.1 CO_2 and CH_4 fluxes

A floating chamber was used to measure diffusive fluxes of CH_4 and CO_2 at six different locations along the edge of the pond. Three measurements were made in the vegetated area and three in the open water. As described in Peacock et al. (2021), the design of the floating chamber was adapted from Bastviken et al. (2015) and had a circular base with a 31.5 cm diameter. The total volume of the chamber was 9.56 L. To reflect sunlight and to keep heating effects to a minimum, the floating chamber was covered in aluminum foil. CH_4 and CO_2 concentrations in the chamber were measured in real time using cavity ring-down spectroscopy by a Picarro GasScouter G4301 which was connected in a closed loop to the chamber by two plastic tubes. Each flux was measured until there was a linear increase or no change in the concentrations. If, however, the flux was too noisy, the chamber was removed and air ventilated, and the flux measurement was reattempted.

Calculations of fluxes were done using linear regression between the change in time of the selected data and the concentration of GHGs, also taking into account the air pressure and temperature at the time of measurement. Significant ($p < 0.05$) fluxes with low values of R^2 were accepted while all regressions with $p > 0.05$ were assumed to be zero fluxes. (Peacock et al. 2017, 2021)

3.3.2 CH_4 ebullition

Ebullitive emissions of CH_4 were measured by placing six clusters of floating chambers in the littoral zone around the pond, each cluster containing two to three chambers. This was done on the same day as the flux measurements. The chambers were left overnight and gas samples were collected from the chambers after 24 hours. The collection was executed by connecting a syringe to a chamber, the headspace of the chamber was mixed by extracting and reinserting 30 mL of gas, then 30 mL of gas was extracted and 22 mL was transferred into a pre-evacuated glass vial. For September and October, CH_4 concentrations in the samples were analyzed a GC. For April, the concentrations were analyzed by injecting 2 mL of gas sample into the Picarro GasScouter fitted with a sampling loop (Wilkinson et al. 2018).

Ebullition was calculated using a method developed by David Bastviken at Linköping (Bastviken et al. 2004b, 2010). Firstly, the k value (piston velocity) for each chamber is calculated using eq. (6). The piston velocity is a measurement of the physical exchange rate of CH_4 between the atmosphere and the water.

$$F = k \times (C_w - C_{fc}) \quad (6)$$

F is the flux (moles m^{-2} d^{-1}), k is the piston velocity (m d^{-1}), C_w is the measured concentration of CH_4 in the water (moles m^{-3}), and C_{fc} is the concentration of CH_4 in the water when it is in equilibrium with the CH_4 partial pressure in the floating chamber. The k values are then transformed into k600 values, which is k for a gas that has a Schmidt number of 600 and is the Schmidt number of CO_2 in freshwater at 20 °C (Bade 2009). This allows for comparison of k values for any gas and temperature (Bastviken et al. 2004b). Schmidt number is defined as the ratio between kinematic viscosity and particle diffusivity, low Schmidt number means the particles are very small, diffuse easily and are not affected much by viscosity (Camuffo 2019). Chambers that have received ebullition have higher apparent k600 values compared to chambers that have only received diffusive flux, this makes it possible to calculate ebullition and diffusive flux separately. The separation was done by dividing each chamber's k600 by a minimum k600, which was based on diffusive flux only. If the ratio was 2 or greater, it was determined that ebullition had occurred. An average k600 was calculated from the chambers which only received diffusive flux. This average k600 was used to estimate the diffusive flux in the chambers which had also received ebullition. With the diffusive flux calculated, the remaining CH_4 flux was assumed to be ebullition which could then be calculated (Bastviken et al. 2004b).

3.3.3 N_2O fluxes

Concentrations for N_2O were obtained from analyzing the gas samples from the 24h chambers using a GC. The N_2O concentration was compared to the atmospheric concentration and a linear change was assumed over the 24 hours. From this the flux was calculated, taking into account the atmospheric temperature and pressure. The resulting fluxes were then studied to determine whether the water was undersaturated, making the pond an N_2O sink, or oversaturated, making the pond an N_2O source. From the two sampling months, a mean and median daily flux of N_2O was calculated. To obtain an annual average, the daily average was multiplied by the number of ice-free days. As ice coverage lasted for about five months, the ice-free days were estimated to be about 210 days. The resulting estimates of N_2O emissions were compared to literature.

3.3.4 Temperature and ice coverage

Data for air temperature and air pressure during time of measurement was either measured using the Hanna Instruments or taken from SMHI (SMHI n.d.b). Seasonal and temperature variations in emissions could then be studied. In mid-November 2021 the pond froze and remained frozen until mid-April. In order to measure the CH_4 accumulation under the ice, and therefore potential ice-out emissions, a hole was bored in the ice using a hand ice auger. This was done once in December and once in February. A static chamber was instantly placed over the hole and the flux arising as the CH_4 escaped from under the ice was measured using the Picarro GasScouter. The initial pulse of GHG was considered the moment in which the trapped gas was released, and the flux was only calculated for the increase of this pulse. After the pulse, no clear flux could be measured, even after picking up and resetting the floating chamber. As the area of the bored hole was smaller than the area of the floating chamber, this was adjusted in the calculation. A borer radius of 0.07 m was used giving a hole area of 0.0153 m^2. The fluxes for CH_4 and CO_2 were then calculated using the same method as mentioned in 3.3.1. From these daily fluxes the actual CH_4 and CO_2 flux occurring during the pulse could be calculated. As the flux is given in mg m^{-2} d^{-1}, day was first converted into

seconds by dividing the flux by the number of seconds in a day, 86400 s. The flux was then multiplied by the number of seconds the pulse increased. The resulting CH_4 and CO_2 flux occurring during the pulse was then compared to the pond's total annual emissions in 2018, which were 540 g CO_2 m^{-2} y^{-1} and 44 g CH_4 m^{-2} y^{-1}, found as site 2 in Table 1 of Peacock et al. (2021).

3.3.5 Emission estimates

Annual carbon emissions were calculated by upscaling the measured fluxes and ebullition from the September, October, April and May samplings to the entire year. From the four sampling dates, a mean and median daily flux of CH_4 and CO_2 was calculated. Both vegetated fluxes and open water fluxes were used in the calculation. It was assumed that the vegetated area and open water area made up about 50% each of the area of the pond. An average daily ebullition of CH_4 was calculated from the three sampling dates. To calculate the annual averages, the daily averages were multiplied by the number of ice-free days, 210 days. The estimates of CH_4 and CO_2 emissions were compared to other literature as well as the emissions in 2018 (Peacock et al. 2021). In order to compare to the carbon burial, annual CH_4 and CO_2 emissions were converted into carbon emissions using eqs. (7) and (8).

$$CO_2\text{: } mass\ of\ C = mass\ of\ CO_2\ emission \cdot \frac{12\ (mass\ of\ C)}{44\ (mass\ of\ CO_2)} \tag{7}$$

$$CH_4\text{: } mass\ of\ C = mass\ of\ CH_4\ emission \cdot \frac{12\ (mass\ of\ C)}{16\ (mass\ of\ CH_4)} \tag{8}$$

Finally, the total annual carbon released by the pond through CH_4 and CO_2 emissions was calculated by adding the carbon emissions and multiplying with the pond area, 1331 m^2. This could then be compared to the annual carbon emissions in 2018, 150 g CO_2-C m^{-2} y^{-1} and 33 g CH_4-C m^{-2} y^{-1} (Peacock et al. 2021) which adds up to 244 kg C y^{-1}.

3.4 WATER CHEMISTRY

A Hanna Instruments Multiparameter Meter Hi 9829 was used in situ to measure EC, pH, TDS, DO and water temperature. Chl-a was measured in situ with a Turner Designs FluoroSense Handheld Fluorometer. Water samples were collected and sent to the SWEDAC-accredited Geochemical Laboratory at the Swedish University of Agricultural Sciences in Uppsala where they were analyzed for DOC, TP, TN, NO_3^- and NO_2^-. Water chemistry was compared to CO_2 and CH_4 diffusive fluxes to determine possible relationships between the variables. CH_4 ebullition was not included in these comparisons as ebullition is created and stored in the sediment. Water chemistry and sediment chemistry might differ, therefore, comparing ebullition to water chemistry might not be accurate.

3.5 EXTRACELLULAR ENZYME ACTIVITY

Water samples of 250 mL were collected and sent to the Department of Limnology, Uppsala University, for analysis of hydrolytic enzymes PHOS, BG and NAG, using standard methods and fluorogenic 4-methylumbelliferone labeled substrates (Heffernan et al. 2021). The potential enzyme activity selected for the report was measured at 200 µMol substrate

concentration. Enzyme activity was then compared to CO_2 and CH_4 fluxes to determine possible relationships. CH_4 ebullition was not included in these comparisons.

3.6 CARBON BURIAL

A Willner sediment corer was used to take six sediment cores from the pond, two from the littoral zone, and four by boat from the center of the pond. The depth of the accumulated organic sediment in each core was measured and then sliced and transferred into plastic containers. To speed up the drying process as the sediment was very wet and fluffy, water was removed from each sediment using a sieve. Each container was weighed and then placed in a preheated Dry-Line drying oven set to 50 °C. Sediments were weighed periodically to measure mass loss. On the 1st of November, about two weeks after the coring, the sediments were no longer losing water weight and were taken out for the final weighing. Each core was homogenized into smaller parts and mixed. Samples of roughly 10 g were collected from each core, with the exception of the two cores from the littoral zone, core 5 and 6, for which only one sample of 8 grams could be prepared by mixing the two cores together. Cores 1 and 2 gave four samples each and cores 3 and 4 gave one and two samples respectively. The samples were sent for analysis of carbon content in the SLU Soil Department lab.

Given the weights of the cores before and after drying, as well as the height of the accumulated sediment, the moisture content and the dry bulk density (DBD) of each sediment core was calculated using the method by Gilbert et al. (2021). The moisture content (%) was calculated using eq. (9).

$$moisture\ content\ (\%) = \frac{wet\ weight - dry\ weight}{wet\ weight} * 100 \quad (9)$$

DBD (g cm^{-3}) of the sediment was calculated using eq. (10) where the dry weight and volume was that of the accumulated sediment for the entire core.

$$DBD = \frac{dry\ weight}{volume} \quad (10)$$

The carbon burial rate (g m^{-2} y^{-1}) was calculated by dividing the average pond carbon stock (g m^{-2}) by the time since the pond was dredged. Only the four center cores, 1 to 4, were used to calculate the average carbon stock. The pond was dredged 1990, which makes the time since dredging 32 years. The obtained carbon burial rate was then compared to other literature.

4 RESULTS

4.1 EMISSIONS

4.1.1 CO_2 and CH_4 flux

The CO_2 and CH_4 fluxes are shown in Figure 2 and 3, where all flux measurements for the four sampling dates are plotted together with means in (a) and mean fluxes are further shown in (b) for clarification.

The CO_2 flux varied greatly within the pond as a large spread can be seen between the measured CO_2 fluxes for each measuring date in Figure 2 (a), the mean on the other hand varied only slightly between the different dates (b). The mean increased from September to

October 25, which had the highest mean at 2608 (±296) mg CO_2 m^{-2} d^{-1}. The mean then decreased from October till April and is the lowest after ice melt on April 18, at 2405 (±473) mg CO_2 m^{-2} d^{-1}. Finally, the mean increased between April and May. May had the two highest measured fluxes at 5214 and 4948 mg CO_2 m^{-2} d^{-1}.

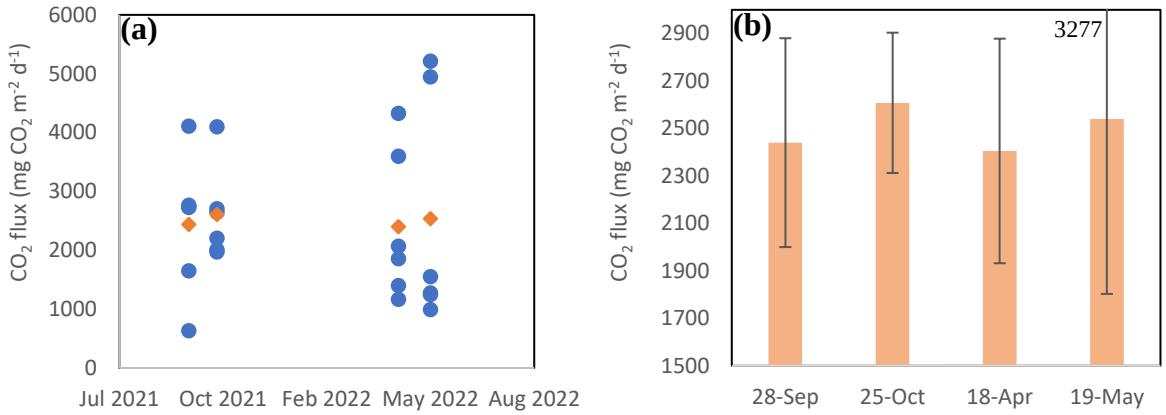

Figure 2. Scatter plot of CO_2 fluxes (a) and mean (± standard errors) CO_2 flux for each measuring date (b). Mean is also shown in peach color in (a).

The CH_4 flux also largely varied within the pond for each measuring date, Figure 3 (a). In (b) the CH_4 flux increased from September to October, and further increased slightly from October to April, after ice melt, and then decreased to a lowest in May. April had the highest mean of 68.5 (±27.8) mg CH_4 m^{-2} d^{-1}, October on the other hand had only a slightly lower flux at 67.4 (±16.6) mg CH_4 m^{-2} d^{-1}. May had the lowest mean flux at 22.4 (±8.24) mg CH_4 m^{-2} d^{-1}. The highest flux was measured in April, 211 mg CH_4 m^{-2} d^{-1}, see (a).

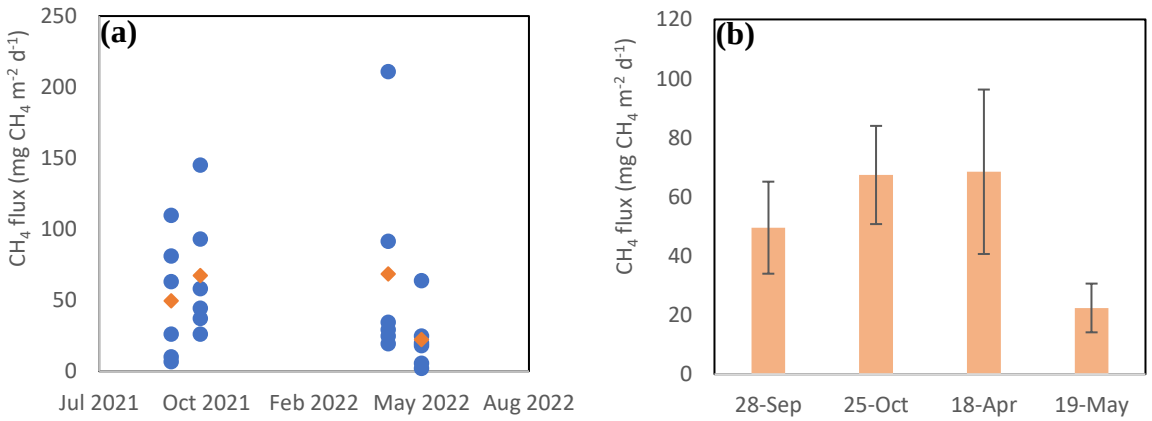

Figure 3. Scatter plot of CH_4 fluxes (a) and mean (± standard errors) CH_4 flux for each measuring date (b). Mean is also shown in peach color in (a).

4.1.2 CH_4 ebullition

CH_4 ebullition is shown in Figure 4, where all ebullition measurements for the three sampling dates are plotted together with means in (a) and mean ebullition is further shown in (b) for clarification. Mean ebullition was the lowest in September and October, with October slightly lower at 33.2 (±3.49) mg CH_4 m^{-2} d^{-1}, see (b). April 18 after ice melt had the highest mean

ebullition of 54.5 (±7.13) mg CH_4 m^{-2} d^{-1}. April also showed the largest spread in data as well as the highest measurement of 121 mg CH_4 m^{-2} d^{-1}, see (a). Some measurements in (a) were 0 mg CH_4 m^{-2} d^{-1}, which means no ebullition was captured by those floating chambers.

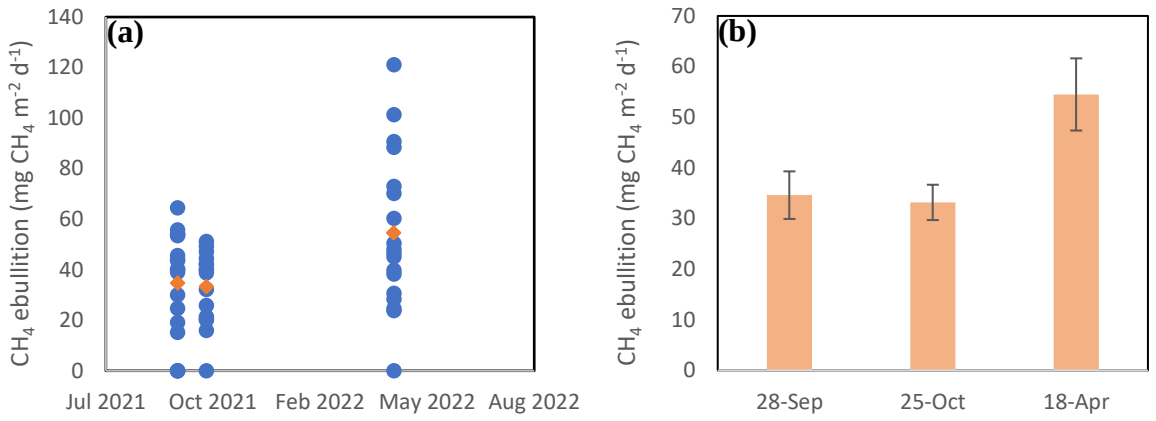

Figure 4. Scatter plot of CH_4 ebullition (a) and mean (± standard errors) CH_4 ebullition for each measuring date (b). Mean is also shown in peach color in (a).

4.1.3 Vegetation

Figure 5 compares the mean (± standard errors) CO_2 (a) and CH_4 (b) flux measured at vegetated area and open water area.

In Figure 5 (a) the mean CO_2 flux in vegetated area and open water area were very similar in September, 2490 (±584) and 2390 (±213) mg CO_2 m^{-2} d^{-1} respectively. However, mean vegetated flux increased from September until it peaked in May at 3720 (±787) mg CO_2 m^{-2} d^{-1}. Meanwhile, the mean open water flux increased slightly between September and October, and then proceeded to decrease to its lowest in May at 1361 (±56.9) mg CO_2 m^{-2} d^{-1}. The biggest difference between vegetated flux and open water flux therefore occurred in May when vegetated flux was at its highest and open water flux at its lowest. The mean flux for all the measuring months shows that CO_2 flux was generally higher in the vegetated area than in the open water area, 3080 (±593) and 1920 (±249) mg CO_2 m^{-2} d^{-1} respectively. Furthermore, the mean vegetated CO_2 flux was higher than the mean open water flux for all measuring dates. A t-test gave a p-value = 0.0275, which is less than 0.05 and therefore the result is statistically significant and there is likely to be a difference between vegetated and open water CO_2 flux.

In Figure 5 (b) the mean CH_4 flux in vegetated area increased from September and hit a peak in April after ice melt at 112 (±30.0) mg CH_4 m^{-2} d^{-1}. It then dropped drastically to its lowest in May at 9.23 (±3.14) mg CH_4 m^{-2} d^{-1}. The mean open water flux increased slightly from September to October, which had the highest mean of 71.9 (±21.4) mg CH_4 m^{-2} d^{-1}. It then proceeded to drop hitting its lowest in April at 24.6 (±1.63) mg CH_4 m^{-2} d^{-1}, and then increased slightly in May. Thus, April had the biggest difference in mean CH_4 flux between the vegetated and open water area when vegetated flux was at its highest and open water flux at its lowest. The mean flux for all the measuring months shows that CH_4 flux was only slightly higher in the vegetated area than in the open water area, 54.1 (±22.8) and 49.8 (±16.5) mg CH_4 m^{-2} d^{-1} respectively. The open water flux was higher than the vegetated area flux for September, October, and May. Only in April was the vegetated flux higher than the open water flux, and then the difference was large. A t-test gave a p-value = 0.837, which is

greater than 0.05 and therefore the result is not statistically significant. This means there is not enough evidence to conclude that there is a difference between vegetated and open water CH_4 flux.

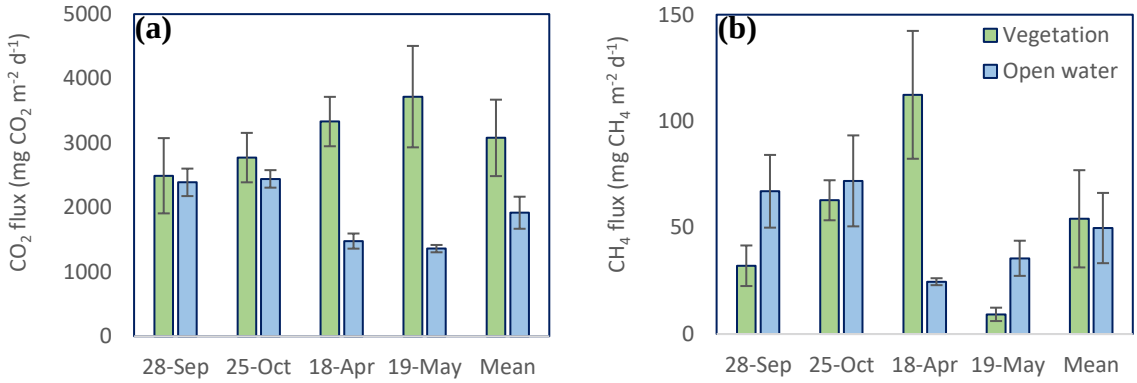

Figure 5. Comparison of monthly mean (± standard errors) CO_2 (a) and CH_4 (b) flux measured at vegetated area and open water area. Mean flux for all months is also shown.

4.1.4 N_2O flux

The N_2O fluxes are shown in Figure 6, where all flux measurements for the two sampling dates are plotted together with means in (a) and mean fluxes are further shown in (b) for clarification. The N_2O flux varied greatly within the pond as a large spread can be seen between the measured N_2O fluxes for each measuring date in (a). As seen in (b) the mean N_2O flux decreased from September to its lowest in October, from -126 (±12.33) to -237 (±23.4) µg N_2O m^{-2} d^{-1}. For the two measuring dates, all N_2O fluxes were negative, see (a).

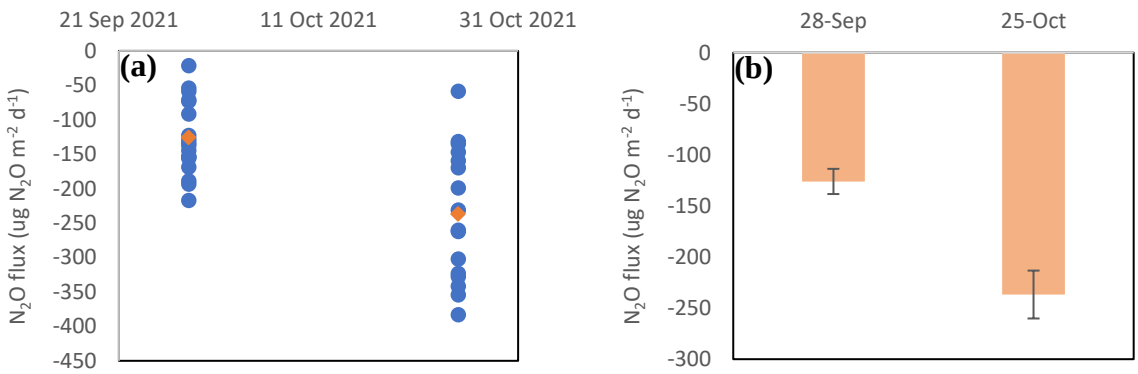

Figure 6. Scatter plot of N_2O fluxes (a) and mean (± standard errors) N_2O flux for each measuring date (b). Mean is also shown in peach color in (a).

4.2 TEMPERATURE AND ICE COVERAGE

4.2.1 Temperature and emissions

Air and water temperature is plotted in Figure 7 and 8 respectively and compared to mean CO_2 (a-b), mean CH_4 (c-d) flux and mean CH_4 ebullition (e-f).

In Figure 7 (a), (c) and (e) the air temperature decreased after September, hitting its lowest in December, -15 °C. In February the air temperature had increased again and continued to

increase until April. On April 18 and May 19 the temperature was 17 °C. No clear trend could be found between air temperature and CO_2 or CH_4 flux in (a) and (c). When the air temperature decreased between September and October, both CO_2 and CH_4 increased. When the air temperature was the same in April and May, CO_2 increased while CH_4 decreased. In (b) and (d) a moderate and weak negative relationship is shown between air temperature and CO_2 and CH_4. Air temperature and CH_4 ebullition (e) on the other hand both decreased between September and October and increased between October and April, which can be seen as a strong positive relationship in (f).

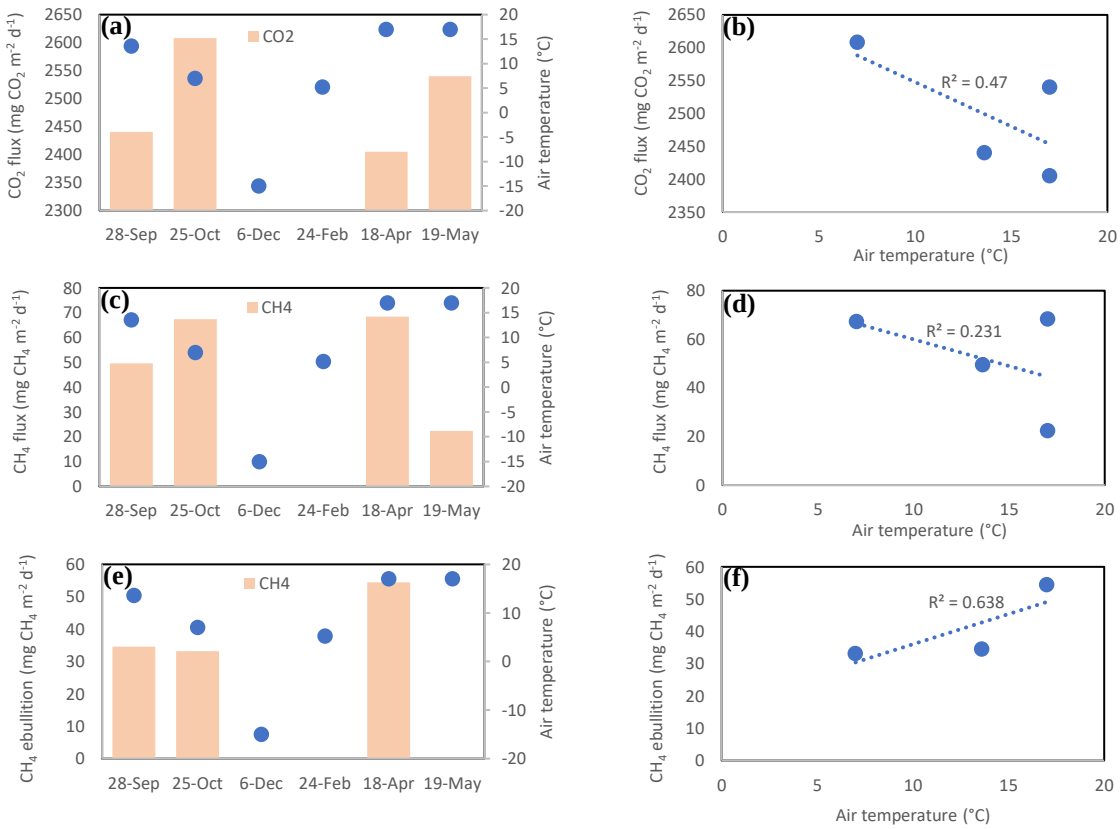

Figure 7. Scatter plots of air temperature and mean CO_2 flux (a-b), mean CH_4 flux (c-d) and mean CH_4 ebullition (e-f). In (a), (c) and (e) CO_2 and CH_4 are shown as columns. As no flux was measured in December and February due to ice, these dates are not included in (b), (d) and (f). Trendlines are used to show general negative or positive trends, actual trends might not be a straight line.

In Figure 8 (a), (c) and (e) the water temperature decreased after September, hitting its lowest on February 24 at 0.68 °C. In April the water temperature had increased again and continued to increase until May. In (a) the water temperature and CO_2 both increased in April and May, however, between September and October the water temperature decreased and CO_2 increased. In (b) no relationship can be found between water temperature and CO_2. When the water temperature decreased between September and October in (c), CH_4 increased and when the water temperature increased between April and May, CH_4 decreased. This possible negative relationship is further strengthened in (d) which shows a very strong linear relationship with $R^2 = 0.966$. No clear trend could be found between water temperature and CH_4 ebullition in (e) and (f).

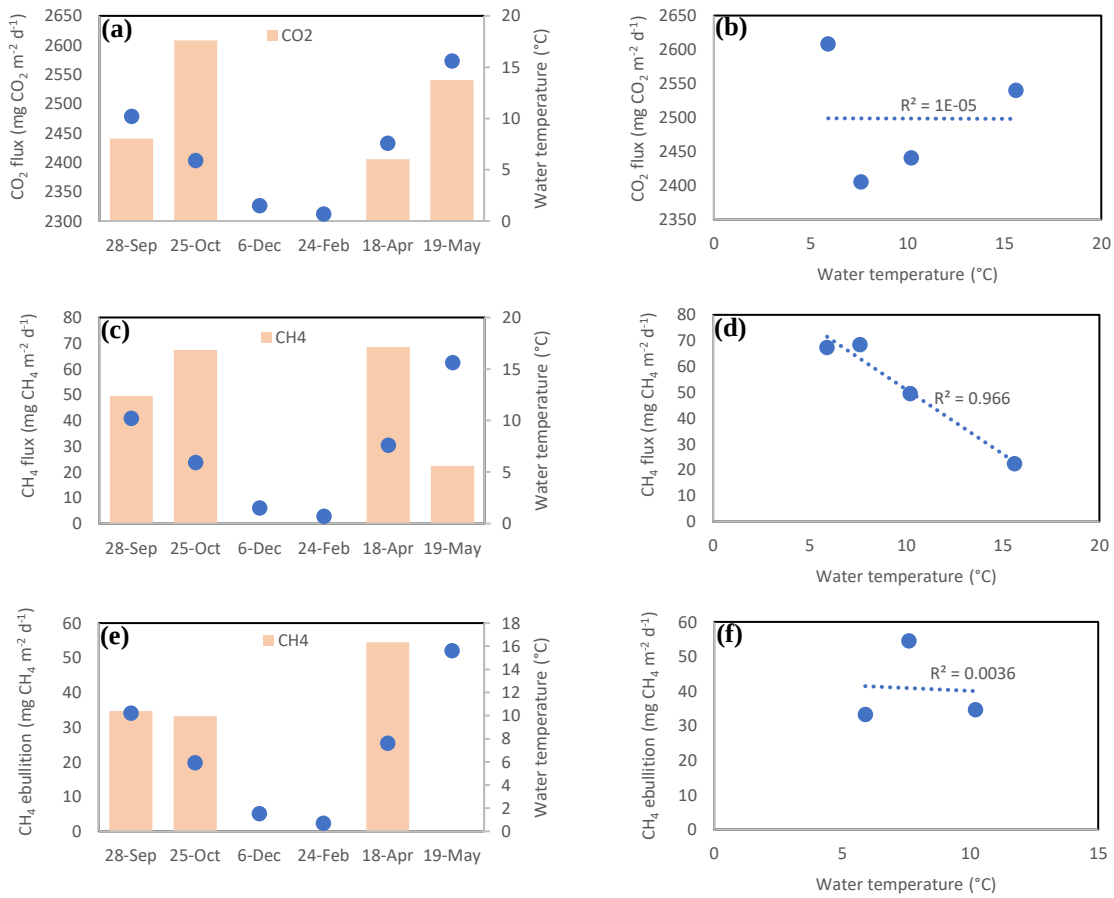

Figure 8. Scatter plots of water temperature and mean CO_2 flux (a-b), mean CH_4 flux (c-d) and mean CH_4 ebullition (e-f). In (a), (c) and (e) CO_2 and CH_4 are shown as columns. As no flux was measured in December and February due to ice, these dates are not included in (b), (d) and (f). Trendlines are used to show general negative or positive trends, actual trends might not be a straight line.

4.2.2 Ice coverage and emissions

In December and February, a hole was bored in the ice and the CO_2 and CH_4 which had accumulated under the ice was measured in the form of a pulse. The time and total flux of the pulses are shown in Table 1. Also shown is the comparison of the pulses to the annual flux measured in 2018 when there was no ice. In December the pulse lasted for two minutes and 17 seconds and amounted to about 0.02% of the 2018 flux for both CO_2 and CH_4. In February the pulse lasted for 15 minutes and 5 seconds and amounted to 0.18% and 0.26% of the 2018 CO_2 and CH_4 flux respectively.

Table 1. Time and total flux of pulse as accumulated CO_2 and CH_4 escaped from under the ice for December and February. The total flux of the pulses was also compared to the pond's annual flux measured in 2018.

Date	Time of pulse (s)	Total flux of pulse (mg m^{-2})		% of 2018 annual flux	
		CO_2	CH_4	CO_2	CH_4
6 Dec 2021	137	116	7.99	0.022	0.018
24 Feb 2022	905	989	114	0.18	0.26

4.3 EMISSION ESTIMATES

The estimated daily and annual CO_2, CH_4 and N_2O fluxes and CH_4 ebullition is shown in Table 2. Average annual carbon emissions are shown in Table 3. Both mean and median are shown for comparison.

As seen in Table 2, the mean daily fluxes were 2499 ± 256 mg CO_2 m^{-2} d^{-1}, 52 ± 10 mg CH_4 m^{-2} d^{-1}, and -0.178 ± 0.016 mg N_2O m^{-2} d^{-1} and the mean daily CH_4 ebullition was 41.1 ± 3.4 mg CH_4 m^{-2} d^{-1}. The mean annual fluxes were 525 g CO_2 m^{-2} y^{-1}, 10.9 g CH_4 m^{-2} y^{-1}, and -0.0374 g N_2O m^{-2} y^{-1} and the mean annual CH_4 ebullition was 8.62 g CH_4 m^{-2} y^{-1}. The median is lower in all cases which means the data distributions are all skewed to the right. CH_4 flux had the biggest difference between mean and median, while the mean and median for CH_4 ebullition was very similar. The mean CH_4 emission from flux and ebullition was 93.1 mg CH_4 m^{-2} d^{-1}. Taking both mean and median into account, roughly 50% of CH_4 emissions were from diffusive fluxes and 50% were from ebullition.

Table 2. Daily and annual mean and median of CO_2, CH_4 and N_2O fluxes and CH_4 ebullition.

	Daily (mg m^{-2} d^{-1})		Annual (g m^{-2} y^{-1})	
	Mean (±SE)	Median (Q1, Q3)	Mean	Median
CO_2 flux	2499 (± 256)	2141 (1519, 2977)	525	450
CH_4 flux	52 (± 10)	31.9 (19.8, 68.2)	10.9	6.69
CH_4 ebullition	41.1 (± 3.4)	40.1 (24.6, 50.6)	8.62	8.43
N_2O flux	-0.178 (± 0.016)	-0.155 (-0.228, -0.130)	-0.0374	-0.0325

In Table 3, the annual carbon emissions were 143 g CO_2-C m^{-2} y^{-1} and 14.6 g CH_4-C m^{-2} y^{-1} (8.18 g m^{-2} y^{-1} from flux and 6.47 g m^{-2} y^{-1} from ebullition) which amounted to a total annual carbon emission of 158 g C m^{-2} y^{-1}. The carbon emission from CO_2 flux made up

about 91% of the total carbon emission and was much larger than the carbon emission from CH_4 flux and ebullition, which made up roughly 9%. In total the pond emitted about 210 kg C y^{-1}.

Table 3. Average annual carbon emissions from annual CO_2 flux and annual CH_4 flux and ebullition, both separately and added together as a total. The pond's total annual carbon emission is also displayed. Averages are shown as means and medians.

Emission (g C m^{-2} y^{-1})	Mean	Median
CO_2-C	143	123
CH_4-C	14.6	11.3
Total C	158	134
Total pond emission (kg C y^{-1})	Mean	Median
Total C	210	178

4.4 WATER CHEMISTRY

Figure 9 shows scatter plots of water chemistry over time and Figure 10, Figure 11 shows mean CO_2 and mean CH_4 flux plotted against water chemistry.

In Figure 9 water chemistry is plotted over time. EC (a) and TDS (b) were the highest in December and lowest in May. pH (c) was the lowest in December and February. In April it had increased and continued to increase to a max in May. DO (d) was very low for December and February. In April it had increased substantially and hit a max. Chlorophyll (e) was lowest in December. It had a small peak in February, and later in May it had increased considerably and reached a max. DOC (f) was the highest in December and lowest in April. EC, TDS, and DOC show similarities in their variations. TP (g) was fairly low for September, October and April. In December it had increased and hit a max later in February. TN (h) showed a similar trend. NO_2^-– N and NO_3^-– N (i) also showed a similar trend to TP and TN, but the decrease between February and April was less drastic with April being more similar to December.

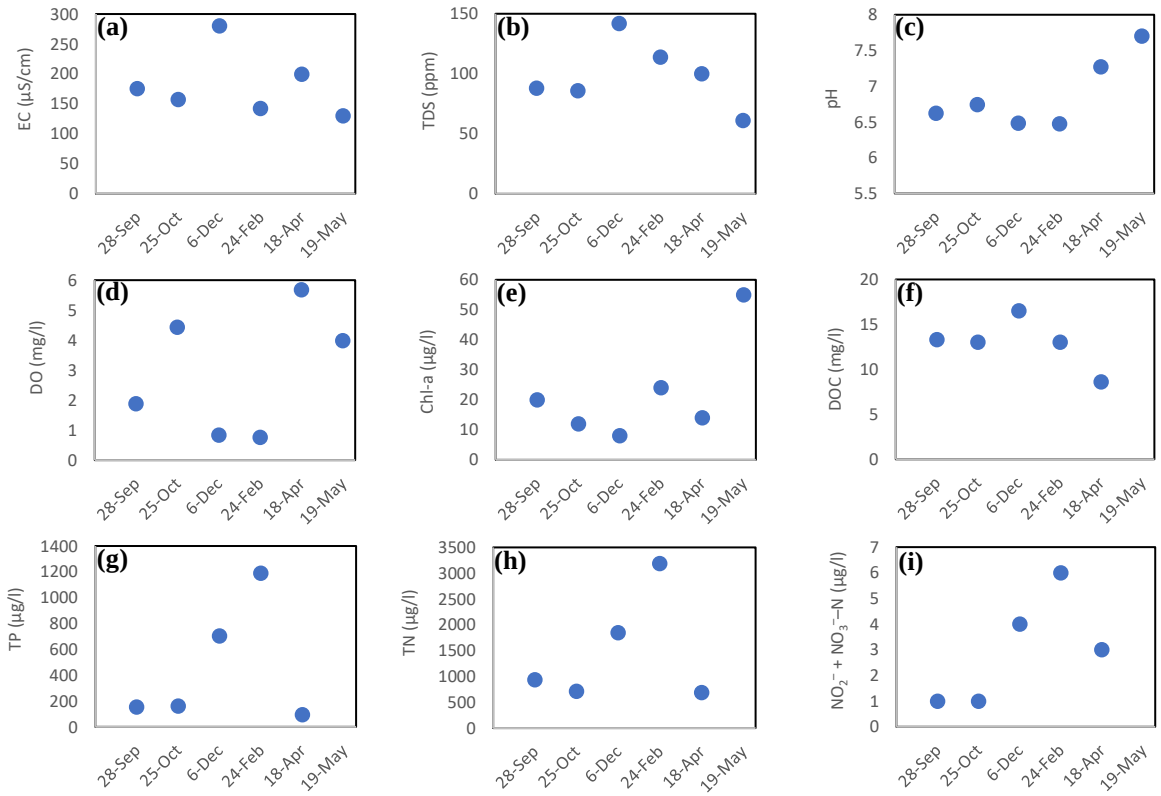

Figure 9. Scatter plots of EC (a), TDS (b), pH (c), DO (d), chl-a (e), DOC (f), TP (g), TN (h), NO_2^-– N and NO_3^-– N (i). No value exists for DOC, TP, TN, NO_2^-– N and NO_3^-– N in May.

In Figure 10 mean CO_2 flux is plotted against water chemistry. As no flux measurements were made in December and February due to ice coverage, these dates are excluded from the following comparisons. May is also excluded for DOC, TP, TN and NO_2^-– N and NO_3^-– N. A negative relationship was found between EC and CO_2 (a) and a weak negative relationship between TDS and CO_2 (b). pH and CO_2 (c) had a very weak negative relationship or no relationship. DO and CO_2 (d) had a very weak positive relationship or no relationship. A very weak positive relationship was found between chl-a and CO_2 (e). DOC and CO_2 (f) had a weak positive relationship. TP and CO_2 (g) had a positive relationship. A very weak negative relationship was found between TN and CO_2 (h) and a negative relationship between NO_2^-– N and NO_3^-– N and CO_2 (i).

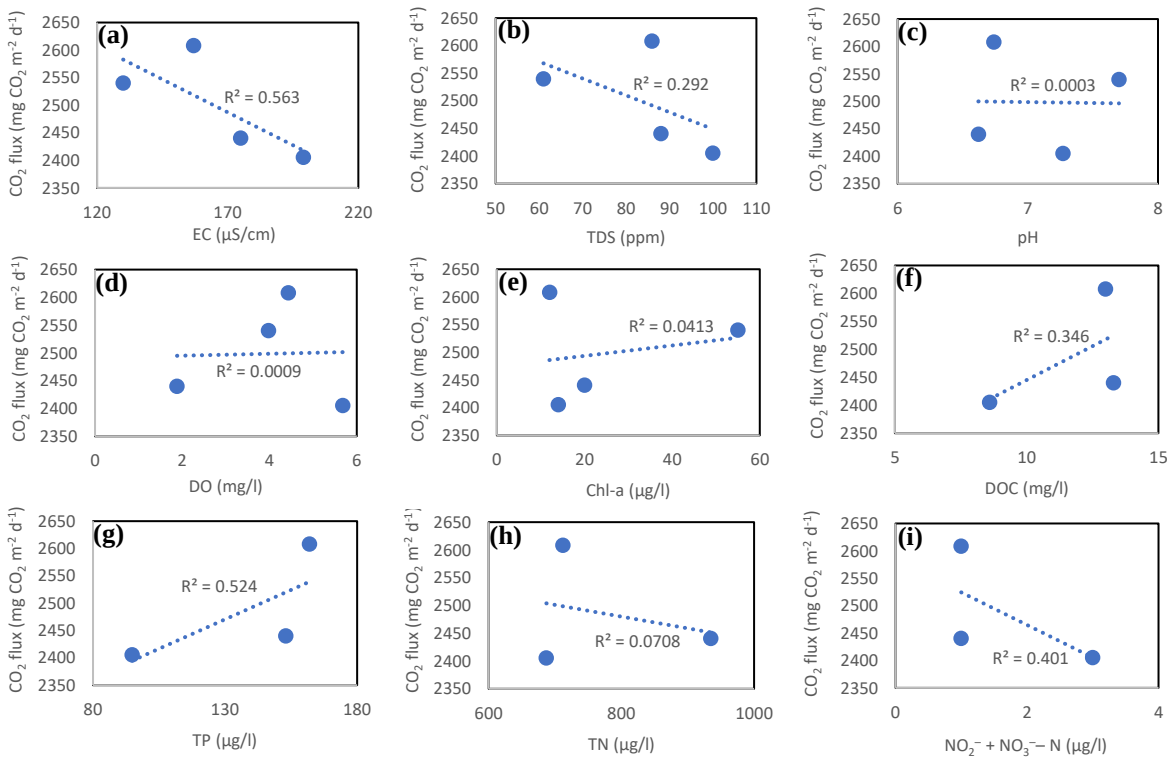

Figure 10. Scatter plots of mean CO_2 flux with EC (a), TDS (b), pH (c), DO (d), chl-a (e), DOC (f), TP (g), TN (h), NO_2^-– N and NO_3^-– N (i). No flux was measured in December and February due to ice, these dates are therefore not included. No value exists for DOC, TP, TN, NO_2^-– N and NO_3^-– N in May. Trendlines are used to show general negative or positive trends, actual trends might not be a straight line.

In Figure 11 mean CH_4 flux is plotted against water chemistry. As no flux measurements were made in December and February due to ice coverage, these dates are excluded from the following comparisons. May is also excluded for DOC, TP, TN and NO_2^-– N and NO_3^-– N. A positive relationship was found between EC and CH_4 (a) and a very strong positive relationship between TDS and CH_4 (b). pH and CH_4 (c) had a weak negative relationship. DO and CH_4 (d) had a very weak positive relationship. A strong negative relationship was found between chl-a and CH_4 (e), $R^2 = 0.936$. DOC and CH_4 (f) had a weak negative relationship. TP and CH_4 (g) had a very weak negative relationship. A very strong negative relationship was found between TN and CH_4 (h), $R^2 = 0.998$. NO_2^-– N and NO_3^-– N and CH_4 (i) showed a weak positive relationship.

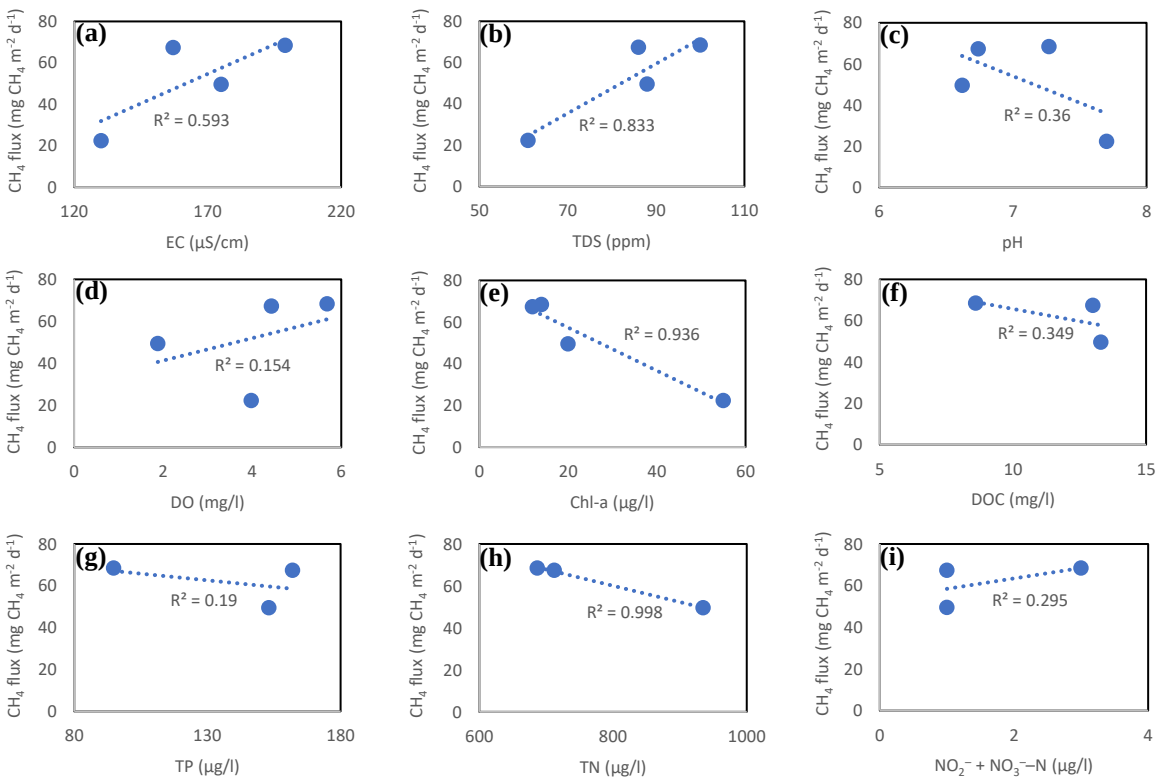

Figure 11. Scatter plots of mean CH_4 flux with EC (a), TDS (b), pH (c), DO (d), chl-a (e), DOC (f), TP (g), TN (h), NO_2^-– N and NO_3^-– N (i). No flux was measured in December and February due to ice, these dates are therefore not included. No value exists for DOC, TP, TN, NO_2^-– N and NO_3^-– N in May. Trendlines are used to show general negative or positive trends, actual trends might not be a straight line.

4.5 EXTRACELLULAR ENZYME ACTIVITY

Figure 12 shows the measured enzyme activities as scatter plots (a, c, e) and mean enzyme activities for each measuring date as columns (b, d, f). Scatter plots are used in Figure 13 to compare CO_2 flux and CH_4 flux to enzyme activities.

In Figure 12 enzyme activity is shown over time. PHOS (a-b) stayed almost the same between September and October, which was also when it was at its highest. It hit a minimum in December, then increased between December and February and further in April. BG (c-d) was the lowest in September where it was only slightly below zero. It was the highest in October and had decreased again in December. October and February had similar enzyme activities, as did December and April. NAG (e-f) increased from September to October, hitting a lowest in December. It had increased in February and was the highest in April.

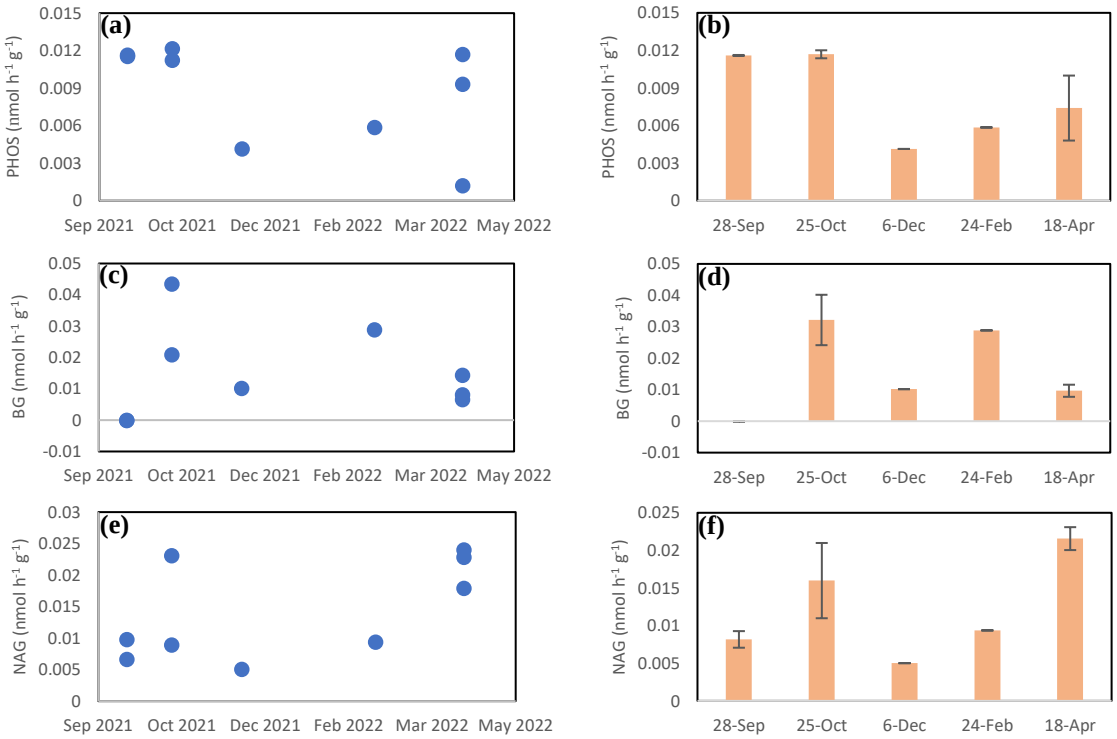

Figure 12. Scatter plots of measured enzyme activities for PHOS (a), BG (c) and NAG (e), and mean (± standard errors) enzyme activity for each measuring date for PHOS (b), BG (d) and NAG (f).

In Figure 13, PHOS had a positive relationship with CO_2 flux (a), and a weak negative relationship with CH_4 flux (d). A positive relationship can be seen between BG and both CO_2 flux (b) and CH_4 flux (e), where CO_2 and BG had a very strong positive relationship. NAG and CO_2 flux (c) showed a very weak negative relationship, while NAG and CH_4 flux (f) had a very strong positive relationship.

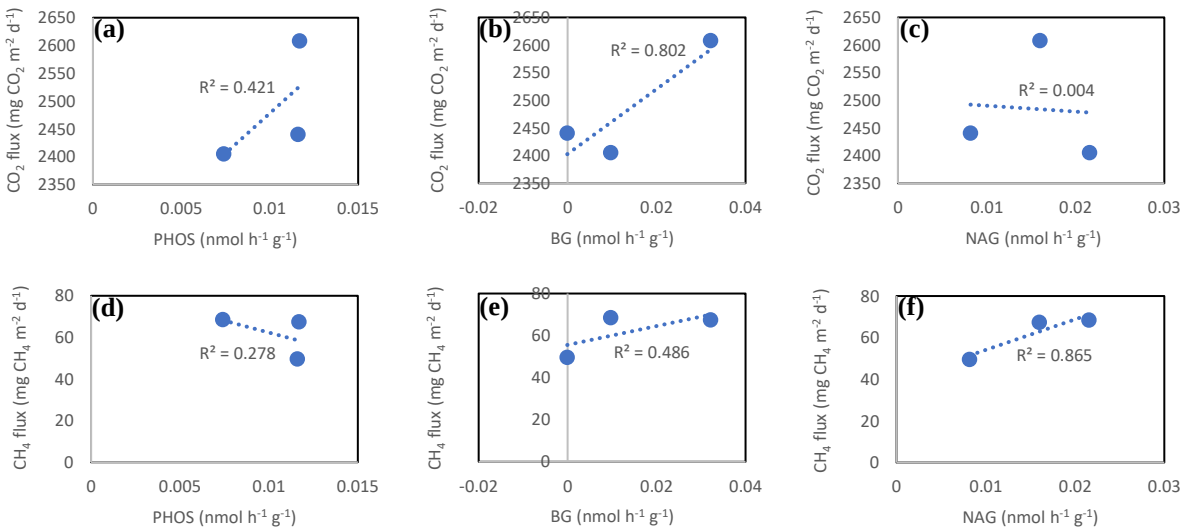

Figure 13. Scatter plots of mean CO_2 flux (a-c) and mean CH_4 flux (d-f) plotted against mean enzyme activity for PHOS, BG and NAG. No flux was measured in December and February due to ice, these dates are therefore not included. Trendlines are used to show general negative or positive trends, actual trends might not be a straight line.

4.6 CARBON BURIAL

Mean moisture content, DBD, total carbon and carbon stock for the six sediment cores are shown in Figure 14 and carbon burial rate for the pond is presented in Table 4.

In Figure 14, the sediment cores had a high moisture content (a) of 86-94%, where core 6 contained the least moisture. DBD (b) was 0.013-0.055 g cm^{-3} and total carbon (c) was 16-21%. The carbon stock (d) was 0.15-2.65 kg C m^{-2}. Sediment cores 5 and 6 had the lowest carbon stock.

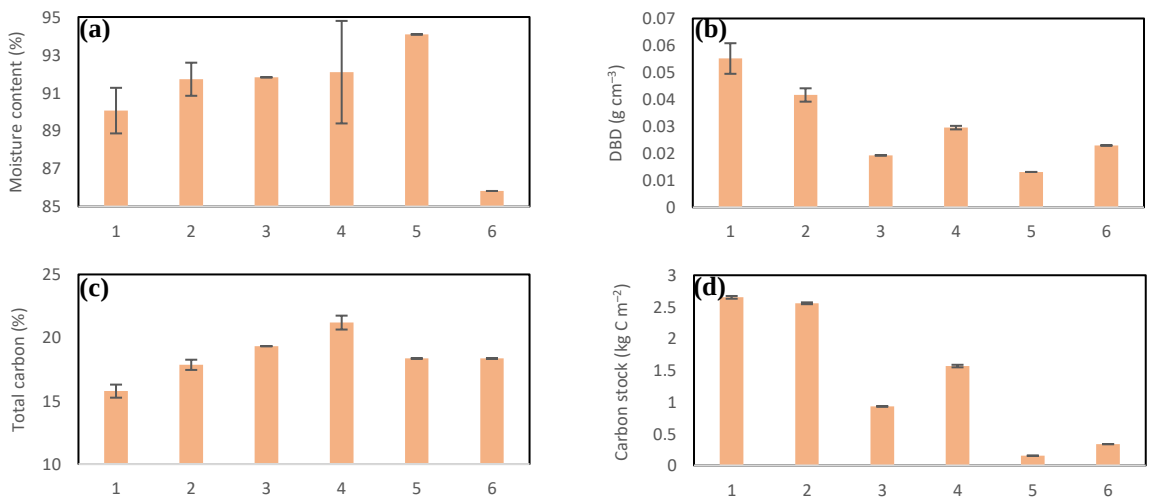

Figure 14. Mean (± standard errors) moisture content (a), DBD (b), total carbon (c) and carbon stock (d) of the six sediment cores.

The mean carbon burial rate in Table 4 was estimated to 60.2 ± 11.2 g C m^{-2} y^{-1} and the entire pond was estimated to bury carbon at a rate of 80.2 kg C y^{-1}. The mean for the burial rate is lower than the median, thus, the distribution is skewed to the left.

Table 4. Annual mean and median carbon burial rate per m^2 and for the entire pond.

	Mean (±SE)	Median (Q1, Q3)
Carbon burial rate (g C m^{-2} y^{-1})	60.2 (±11.2)	64.5 (44, 80.7)
Carbon burial rate for pond (kg C y^{-1})	80.2	85.2

5 DISCUSSION

The results are discussed below with the goal of answering the research questions in 1.1. Daily and annual emissions are presented and compared to estimates from previous studies as well as the measured pond fluxes from 2018. Fluxes from the vegetated area and open water area are also compared and discussed. Seasonal and temperature variations as well as accumulated ice emissions are examined. Furthermore, possible relationships between emissions, water chemistry and extracellular enzyme activity is explored. Finally, carbon burial rate is looked at and compared to previous studies and to the annual carbon emissions from the pond.

5.1 EMISSIONS

Mean daily fluxes were 2499 ± 256 mg CO_2 m^{-2} d^{-1}, 52 ± 10 mg CH_4 m^{-2} d^{-1}, and -0.178 ± 0.016 mg N_2O m^{-2} d^{-1} and the mean daily CH_4 ebullition was 41.1 ± 3.4 mg CH_4 m^{-2} d^{-1}. This resulted in mean annual fluxes of 525 g CO_2 m^{-2} y^{-1}, 10.9 g CH_4 m^{-2} y^{-1}, and -0.0374 g N_2O m^{-2} y^{-1} and a mean annual CH_4 ebullition of 8.62 g CH_4 m^{-2} y^{-1}. The pond was a net emitter of both CO_2 and CH_4, but a sink for N_2O. 91% of the annual carbon emissions came from CO_2 flux which was 143 g CO_2-C m^{-2} y^{-1} and 9% came from CH_4 flux and ebullition which was 14.6 g CH_4-C m^{-2} y^{-1}. This amounted to a total annual carbon emission of 158 g C m^{-2} y^{-1}. In total the pond emitted about 210 kg C y^{-1}.

The mean daily CO_2 flux 2499 mg m^{-2} d^{-1} was comparable to that of other studies, but more similar to ponds in Denmark, 2300 mg m^{-2} d^{-1} (Audet et al. 2020), than to other Swedish ponds, 50 - 1100 mg m^{-2} d^{-1} (Natchimuthu et al. 2014; Peacock et al. 2019; Peacock et al. 2021). Furthermore, the pond had a higher CO_2 flux than in Holgerson and Raymond's (2016) global study, ~1550 mg m^{-2} d^{-1}, likely due to most of the sites in their study being northern ponds in natural ecosystems with lower nutrient inputs. The mean daily CH_4 flux 52 mg m^{-2} d^{-1} was also comparable to that of previous estimates. The 2019 IPCC refinement estimated a CH_4 emission factor for constructed ponds to be 50 mg m^{-2} d^{-1} (IPCC 2019), which is very similar to the estimate in this thesis. Tropical ponds were likewise similar, ~50 mg m^{-2} d^{-1} (Panneer Selvam et al. 2014), while other temperate pond estimates were slightly lower, 20-30 mg m^{-2} d^{-1} (Audet et al. 2020; Van Bergen et al. 2019; Peacock et al. 2021;

Peacock et al. 2019). The CH_4 flux was higher than Holgerson and Raymond's (2016) estimate, ~40 mg m^{-2} d^{-1}. The mean daily N_2O flux -0.178 mg m^{-2} day^{-1} was most comparable to estimates from ponds in Canada, -0.25 mg m^{-2} d^{-1} (Jensen et al. 2022), and slightly less than Finnish ponds, 0.011 mg m^{-2} d^{-1} (Huttunen et al. 2002). However, as N_2O flux was only measured for September and October, it is possible that flux is positive during other times of the year. The estimated daily CH_4 ebullition 41.1 mg m^{-2} d^{-1} was a lot smaller than other estimates, 120-300 mg m^{-2} d^{-1} (Natchimuthu et al. 2014; Panneer Selvam et al. 2014; Van Bergen et al. 2019; Herrero Ortega et al. 2019; Ollivier et al. 2019b).

The studies above estimated 71-97% CH_4 emissions to be from ebullition, in this thesis it was found that only about 50% came from ebullition, mean and median included. A possible explanation for why CH_4 ebullition might have been underestimated is due to the lack of summer measurements, which is when ebullition tends to be the highest (Natchimuthu et al. 2014; van Bergen et al. 2017; Peacock et al. 2021). However, CH_4 flux is also normally higher during the summer (Natchimuthu et al. 2014; van Bergen et al. 2017; Ollivier et al. 2019b; Audet et al. 2020; Peacock et al. 2021), yet the estimated CH_4 flux fell within the range of other estimates. Perhaps if summer had been included this pond would have had a higher annual CH_4 flux more comparable to German ponds, 120 mg m^{-2} d^{-1} (Herrero Ortega et al. 2019), or subtropical ponds, 120-360 mg m^{-2} d^{-1} (Ollivier et al. 2019a; Gorsky et al. 2019). On the other hand, maybe CH_4 ebullition is more affected by temperature than CH_4 flux and if summer had been included ebullition would have made up a larger portion of the CH_4 emissions.

The annual CO_2 flux 525 g CO_2 m^{-2} y^{-1} was approximately the same as the 2018 emission of 540 g CO_2 m^{-2} y^{-1} (Peacock et al. 2021). The difference was possibly due to the lack of summer measurements in this thesis, which is sometimes when CO_2 flux is the highest (Audet et al. 2020; Peacock et al. 2021). Meanwhile the annual CH_4 flux 10.9 g CH_4 m^{-2} y^{-1} was a lot lower than the 2018 estimate of 44 g CH_4 m^{-2} y^{-1}, which was more comparable to that of the studies on German and subtropical ponds mentioned above. Even with ebullition included an emission of 19.6 g CH_4 m^{-2} y^{-1} is quite a bit lower than the 2018 estimate. The 2018 estimate only included diffusive flux and no ebullition. Because of the lower estimates, the ponds annual carbon emission was also a bit lower, 210 kg C y^{-1} compared to 244 kg C y^{-1}. Perhaps most CH_4 flux and ebullition occurs during summer and not much during the rest of the year. The difference could also have been caused by a difference in nutrients as the average TP in 2018 was 1000 µg/l compared to 340 µg/l for this thesis. The main difference in TP could be seen during the summer in 2018 which was much higher than the rest of that year. Thus, it is likely the high temperatures and high TP for 2018 summer contributed to the higher mean CH_4 emissions.

A difference between vegetated and open water flux was found for CO_2 but not for CH_4. Vegetated flux was always higher for CO_2, with May having the highest vegetated flux and lowest open water flux. Vegetated area and open water area was assumed to be 50% each of the pond area, however, most of the open water area in the pond also showed signs of vegetation and only a very small part was completely open with no vegetation. Therefore, by assuming that the vegetated area was only 50%, the calculated daily and annual CO_2 emissions might have been underestimated. However, the vegetation in the middle of the

pond was not as dense as the vegetation in the littoral zone where the flux measurements were taken. Most of the pond could therefore perhaps be considered a mix between open water and vegetation making the 50% assumption slightly more accurate. For CH_4 the open water flux was generally higher except in April when vegetated flux was unusually high and open water flux was the lowest. This was different from the expected results where vegetation would be an important pathway for CH_4. One possible explanation might be that the chambers only covered some of the small emergent macrophytes and floating plants, while many of the larger plants were excluded. Therefore, not all forms of plant flux were covered and since CH_4 transportation varies between different types of plants (Bhullar et al. 2013, Villa et al. 2020) this might have influenced the results. Perhaps CH_4 mainly travelled through the larger or taller plants and not so much through the smaller plants.

In April the plants likely became more active after the winter which would lead to more CH_4 getting transported by plants (Berg et al. 2020; Jeffrey 2019) and could be the reason for the peak in CH_4. Furthermore, perhaps there was a lot of CH_4 stored in the sediment and bottom waters after the ice season (López Bellido et al. 2009), especially in the vegetated area where a lot of dead plant matter can be found. The activation of plants may then have facilitated the release of this CH_4. With the plants getting more active, there would also be an increase in photosynthesis. Thus, the macrophytes oxygenized the water and sediment through photosynthesis and aerenchyma transportation (Berg et al. 2020; Jeffrey 2019). This increase in DO would lead to a growth in heterotrophs and aerobic respiration, and thus an increase in production of CO_2 in the vegetated area, which can also be seen for April. In May CH_4 decreased considerably while CO_2 hit a max, which could be due to high levels of DO in the vegetated area both in the water and in the sediment. This oxygenation of the vegetated area could also be a possible explanation as to why CH_4 production was generally lower in the vegetated area than in the open water area, as the area would be more suitable for aerobic degradation and less so for anaerobic degradation. There would also be more oxidation in that area, further decreasing CH_4 levels. However, DO was not studied in the vegetated area, so whether there is a difference between open water and vegetation is unknown.

5.2 TEMPERATURE AND ICE COVERAGE

No clear seasonal variation could be seen for CO_2 flux as there was little difference between the mean fluxes for the different measuring dates. October had the highest mean while May had the two highest measured fluxes, and April had the lowest mean. A negative relationship was found between air temperature and CO_2, which is the same result as Natchimuthu et al. (2014). The negative relationship could be explained by higher rates of photosynthesis during the warmer measuring dates, thus decreasing CO_2 fluxes by counterbalancing respiration rates. This might be why October had the highest mean flux as photosynthesis had likely decreased. However, CO_2 flux in April was lower compared to May, despite photosynthesis also likely being lower. Perhaps heterotrophs decreased during the winter due to the lack of DO under the ice. The low number of heterotrophs would then have limited CO_2 production in April after ice melt. DO was the highest in April and had decreased in May, which might be a result of the growing heterotrophs consuming DO. An increase in heterotrophs would explain why CO_2 flux was higher in May compared to April. It is possible that the negative relationship between CO_2 and air temperature would have been different if the summer

months had also been studied. No relationship was found between CO_2 flux and water temperature.

CH_4 flux was the highest in April and only slightly lower in October. In May CH_4 flux was the lowest. The seasonal variation therefore appeared to be that CH_4 flux was higher towards the winter and lower in Autumn and Spring. This resulted in a weak negative relationship between air temperature and CH_4 flux, which is the opposite result of other studies (Natchimuthu et al. 2014; van Bergen et al. 2017; Ollivier et al. 2019b; Audet et al. 2020; Peacock et al. 2021). CH_4 ebullition, however, showed the opposite trend of being lower towards the winter and higher in Autumn and Spring, resulting in a strong positive relationship with air temperature. CH_4 ebullition therefore corresponded well with the results of previous studies (Natchimuthu et al. 2014; van Bergen et al. 2017; Peacock et al. 2021). There were likely other factors influencing and causing this difference. It is possible that CH_4 flux would have showed a positive relationship with air temperature if summer emissions had been included. However, a very strong negative relationship was found between water temperature and CH_4 flux, which strengthens the negative relationship with temperature. CH_4 ebullition and water temperature on the other hand showed no clear relationship. The found relationships are very uncertain, however, due to small sample size. The five months of ice may also have had a big influence on emissions in April and influenced the results.

The CO_2 and CH_4 which had accumulated under the ice did not amount to much. In December the accumulated flux was only about 0.02% of the 2018 flux. In February it amounted to a little more, 0.18% and 0.26% of the 2018 CO_2 and CH_4 flux respectively. This, however, is much smaller than the results of Denfeld et al. (2018a), which found that the ice-melt period represented 17% of annual CO_2 emissions and 27% of annual CH_4 emissions in northern lakes. DO was the lowest in December and February, below 1 mg/l, which likely limited aerobic respiration and in turn CO_2 production. There might also have been some photosynthesis occurring, consuming CO_2 (Room et al. 2014). Despite the low DO, CH_4 production through anaerobic respiration was also low. One possible explanation is that the CH_4 produced got oxidized by methanotrophs (Kankaala et al. 2006). TP was the highest in December and February, which means it is possible that PO_4^{3-} was high too and was perhaps not a limiting factor for methanotrophs (Garcia et al. 2019). However, the low DO content might have limited oxidation. It is also possible that CH_4 ebullition got trapped as bubbles in the ice and were missed in the ice measurement (Greene et al. 2014). Moreover, the shallow nature of the pond could have affected how much CO_2 and CH_4 accumulated under the ice. Much of the littoral zone was frozen from surface to sediment, so these areas likely did not contribute much to the accumulated emissions (Jammet et al. 2015; Manasypov et al. 2015; Denfeld. et al. 2018a). There was also a lot of emergent vegetation protruding through the ice, which means CO_2 and CH_4 could have escaped through these openings throughout the winter limiting accumulation (Larmola et al. 2004). Additionally, accumulation of CO_2 and CH_4 in bottom waters and sediment might have occurred and remained when ice measurements were taken (Denfeld 2016; López Bellido et al. 2009), which could explain the high CH_4 emissions in April after ice melt as mentioned previously. The results of this thesis might show that emissions do not accumulate as much in ponds as in lakes.

5.3 WATER CHEMISTRY

Given the few monthly data points available for analysis, the trendlines obtained between GHG emissions and water chemistry are highly uncertain and might only be a coincidence. The real relationships may look very different and may also not be straight lines. Therefore, trendlines are used as a guide to help see potential negative or positive relationships based on the few data points available. R^2 is also presented as weaker trendlines may show that there was no correlation between the variables. Furthermore, it was assumed that stronger trendlines, R^2 closer to 1, increased the probability that there was an actual relationship between the variables. If the actual trend, however, is not that of a straight line, the R^2 value could be misleading.

A negative relationship was found between EC and CO_2, which differs from Peacock et al. (2021) where EC had a positive effect on CO_2 due to acting as a proxy for SO_4^{2-} (Jensen et al. 2022). As SO_4^{2-} was not measured it is not possible to draw any conclusions about SO_4^{2-} and CO_2. A weak negative relationship was found between TDS and CO_2 which might reflect the relationship TDS has to EC as both can be seen as a measure of the concentration of dissolved ions. pH and CO_2 had a very weak negative relationship or no relationship. Previous research has also shown that pH and CO_2 have a negative relationship (Peacock et al. 2021; Hao et al. 2021; Yang et al. 2015; Jensen et al. 2022) and that it reflects the bicarbonate equilibrium (Schrier-Uijl et al., 2011; Sets et al. 2017). However, in this thesis the relationship was so weak it does not really confirm previous research. Since only one site was studied the pH range was not very wide throughout the year, between pH 6.5-7.7. This small range was likely not enough to influence the fluxes much and observe a relationship. DO and CO_2 had a very weak positive relationship or no relationship. The positive relationship corresponds with the results of Yang et al. (2015), however, the results here are so weak they cannot be used to confirm the relationship. Perhaps primary production, although quite low during winter, was enough to weaken the positive relationship (Jensen et al. 2022). It is also possible that due to the very low DO levels during the ice period, there were not a lot of heterotrophs left in April compared to in October, which could have been the reason for the lower CO_2 emissions in April despite the high DO levels. As mentioned earlier, DO decreased in May, perhaps due to the growing number of heterotrophs consuming DO, which could explain the increase in CO_2 emissions in May.

A very weak positive relationship was found between chl-a and CO_2, which is not strong enough to draw many conclusions. Yang et al. (2015) found both a positive and a negative relationship between CO_2 emissions and chl-a as high algal growth can both produce OM for aerobic degradation and CO_2 production (Huttunen et al. 2003), but also increase photosynthesis which consumes CO_2 (Yang et al. 2015). It is possible that both these factors played a role. DOC and CO_2 had a weak positive relationship, which is the same result as for previous research (Hope et al, 1996 Sobek et al. 2003; Peacock et al. 2021). More DOC would likely lead to higher OC mineralization by heterotrophs and more CO_2 production. TP and CO_2 had a positive relationship which is the same as Peacock et al. (2021). According to DelSontro et al. (2018) TP may act as a proxy for terrestrial inputs of OC and CO_2 which could explain a positive relationship between TP and CO_2. A very weak negative relationship was found between TN and CO_2 and a negative relationship between NO_3^-, NO_2^- and CO_2. This is opposite to the positive relationship found by many studies (Ollivier et al. 2019a;

Peacock et al. 2021; Malyan et al. 2022) where high nitrogen increases algal growth and OM for degradation (Webb et al. 2019). A possible explanation for the negative relationship could be that primary production increased due to higher nutrients (Pacheco et al. 2014). This, however, does not correlate to the positive relationship between TP and CO_2.

A positive relationship was observed between EC and CH_4 flux. This is opposite of Webb et al. (2019) and Jensen et al. (2022) who found a negative relationship due to SO_4^{2-}-reducing bacteria inhibiting methanogenesis and the production of CH_4. As SO_4^{2-} was not measured it is not possible to draw any conclusions about SO_4^{2-} and CH_4. A very strong positive relationship was observed between TDS and CH_4 flux which reflects the close relationship between EC and TDS. pH and CH_4 flux had a weak negative relationship. CH_4 producing bacteria are pH sensitive, but the measured pH was within the range of pH 6-8, therefore pH should not be an important variable according to Malyan et al. (2022). Other factors than pH may have been involved, but it may also be a coincidence, especially considering the low number of data points. In May when pH was nearly 8, CH_4 was lower, but this could also be a coincidence. DO had a very weak positive relationship with CH_4 flux, which is opposite of previous studies (Audet et al. 2020; Peacock et al. 2021) as methanogenesis is an anaerobic process and more DO also means more oxidation (Yang et al. 2013). There were likely other factors involved. A strong negative relationship was found between chl-a and CH_4 flux. This is opposite of previous studies (Yang et al. 2015; Jensen et al. 2022) where higher CH_4 might be explained by high algal growth creating OM (Palma-Silva et al., 2013). Perhaps chl-a and CH_4 have a connection elsewhere, or perhaps other factors have more influence. DOC and CH_4 flux had a weak negative relationship, which is opposite to Peacock et al. (2021) as more OC would generally mean more anaerobic degradation (Christensen et al. 2003). DOC was the lowest in April, which might be because it got used up during the ice period. Despite this CH_4 was high, but this could be for other reasons such as CH_4 escaping after having accumulated during the ice period.

TP and CH_4 flux had a very weak negative relationship. This is opposite of most literature (DelSontro et al. 2016; Peacock et al. 2021, Malerba et al. 2022; Rabaey and Cotner 2022) which found a positive relationship, possibly due to the increase in algal growth and OM production with increasing nutrients (Davidson et al. 2018). A potential explanation for a negative relationship is that an increase in algae activity has been linked with a PO_4^{3-} shortage, which is a limiting factor for methanotrophs and thus oxidation (Garcia et al. 2019). This could potentially explain a negative relationship between TP and CH_4, as well as between chl-a and CH_4. TP and chl-a both had a peak in February and both variables had decreased in April. Chl-a might have increased due to the high levels of TP, and TP might then have decreased due to this increase in algae activity causing chl-a to also decrease. The low TP level may have limited oxidation and contributed to the high CH_4 emissions in April. However, there is not enough evidence to show that chl-a and TP share this relationship here, moreover PO_4^{3-} is not studied, so it is also probable that other factors influence the results. A very strong negative relationship was found between TN and CH_4, which is opposite to previous studies (Peacock et al. 2021; Malyan et al. 2022) that have observed a positive relationship between nutrients and OM and therefore CH_4. NO_3^-, NO_2^- and CH_4 on the other hand showed a weak positive relationship which agrees with Ollivier et al. (2019a) and Webb et al. (2019b).

The strongest relationships were between CO_2 and EC, TP, NO_3^- and NO_2^-, and between CH_4 and EC, TDS, chl-a and TN. CO_2 flux correlated better with previous research compared to CH_4 flux. CO_2 and pH, DO, DOC, chl-a and TP all showed similar trends to previous studies, however, most of them were very weak or not much of a relationship. TP was the only variable that correlated with CH_4 in a way that could be explained by the literature, otherwise CH_4 flux did not show the same trends with water chemistry as previous studies. This could be due to CH_4 being mostly produced in the sediment, therefore comparing CH_4 emissions to sedimentary chemistry would probably have been preferable. The lack of data could also be a cause for the difference, and it makes the results highly uncertain. Furthermore, factors affecting emissions are very complicated as many variables, not just water chemistry, influence both emissions and each other at the same time. It is also likely that the ice period affected emissions and the water chemistry both during and after the ice period. EC, TDS and DOC all had a peak in December, pH and DO were both lowest in December and February, chl-a had a peak in February, as did TP, TN, NO_3^- and NO_2^-, which were also elevated in December. Unfortunately, flux could not be measured for these months and therefore they had to be excluded from the comparisons. However, it is very possible that the changes seen during ice period affected the April fluxes and water chemistry to an extent where the trends also were affected. So perhaps if there had not been an ice period, the results might have been more similar to that of other studies. Finally, this thesis looked at variations of GHGs and water chemistry within one site while the studies which were compared to generally looked at many sites (Ollivier et al. 2019a; Audet et al. 2020; Peacock et al. 2021). Having multiple sites might provide a larger variation in the water chemistry which can make correlations between water chemistry and GHGs clearer.

5.4 EXTRACELLULAR ENZYME ACTIVITY

The trendlines obtained between GHG emissions and extracellular enzyme activity are highly uncertain and may only be a coincidence due to the few available data points, same as mentioned in 5.3.

PHOS had a positive relationship with CO_2 flux and a weak negative relationship with CH_4 flux. No relationship was found in the literature between CO_2 and PO_4^{3-}. The negative relationship between PHOS and CH_4 on the other hand could perhaps be explained by PO_4^{3-}'s effect on oxidation as low levels of PO_4^{3-} limits oxidation and therefore leads to higher levels of CH_4 (Denfeld 2016). PHOS was lower during December and February, which could mean that PO_4^{3-} and oxidation of CH_4 was also lower. This does not, however, correlate with TP which was highest during these months. Without measurements for PO_4^{3-} it is therefore difficult to draw conclusions.

A positive relationship can be seen between BG and both CO_2 and CH_4 flux, where CO_2 and BG had a very strong positive relationship. As BG helps produce glucose and CO_2 is produced during the aerobic mineralization of glucose, it is very reasonable that BG and CO_2 would have a positive relationship. No relationship between CH_4 and glucose was found in the literature. BG correlated well with CO_2 over the months. Both BG and CO_2 were lower in September and higher in October, and April they were both lower again. Thus, BG could be an interesting variable to use when looking at CO_2 emissions.

NAG and CO_2 flux showed a very weak negative relationship, while NAG and CH_4 flux had a very strong positive relationship. NAG helps in the production of nitrogen and nitrogen is generally linked to algal growth, which results in more OM and in turn more degradation and production of both CO_2 and CH_4 (Webb et al. 2019; Davidson et al. 2018, DelSontro et al. 2018). This positive relationship was seen between NAG and CH_4. However, this cannot be explained by the negative relationship between chl-a and CH_4. For CO_2 it is possible that more nitrogen and algal growth lead to more photosynthesis and thus a negative relationship between NAG and CO_2 (Pacheco et al. 2014), but this also cannot be explained by the positive relationship between chl-a and CO_2. NAG did not correlate well with TN as NAG was lower in December and February while TN was the highest during these months. TN therefore seems to be mostly affected by other factors, so using NAG as a way of comparing nitrogen and flux might not be very useful.

Due to the lack of previous research on these enzymes and emissions from water bodies it is difficult to draw conclusions about the trends. Here the enzymes relationships with water chemistry were used to draw correlations between the enzymes and emissions, but this might not be very accurate. The enzymes may influence emissions in other ways that were not mentioned in this thesis, and trends might therefore have other explanations.

5.5 CARBON BURIAL

The sediment cores had a high moisture content of 86-94%, this resulted in a large decrease in mass of the cores after drying. DBD was 0.013-0.055 g cm^{-3} and total carbon was 16-21%. The final calculated carbon stock was 0.15-2.65 kg C m^{-2} where sediment cores 5 and 6 from the littoral zone had the lowest carbon stock. These cores were not included in the carbon burial calculation. Carbon burial rate was estimated to 60.2 ± 11.2 g C m^{-2} y^{-1}. This is much less than estimates by other studies which had carbon burial rates of 142-152 g C m^{-2} y^{-1} (Taylor et al. 2019; Gilbert et al. 2014; Ljung and Lin 2023), except for Goeckner et al. (2022) with 114 g C m^{-2} y^{-1}. The entire pond was estimated to bury carbon at a rate of 80.2 kg C y^{-1} and compared to the ponds total annual carbon emission of 210 kg C y^{-1} it is also very small. Keep in mind that carbon burial is accounted for in carbon emissions in closed systems such as ponds (Prairie et al. 2018). So not only is the pond a carbon source, but it is also poor at burying carbon in comparison to how much it emits.

The vegetation could possibly explain the low carbon burial rate. The littoral zone is quite heavily vegetated, the center of the pond is also partially covered in floating plants and during the summer the open water is completely covered in duckweed. All the vegetation likely results in a high production of autochthonous OC. Autochthonous OC, which is more easily mineralized (Burdige 2007; Sobek et al. 2009), might therefore outweigh allochthonous OC. It is also possible that not much allochthonous OC enters this pond. It could have been interesting to study the vegetation types in the pond as some kinds of vegetation have been shown to enhance carbon burial while others have been shown to restrict it (Taylor et al. 2019). Other factors likely also play a role in how efficient a pond is at burying carbon.

6 CONCLUSION

Mean daily fluxes were 2499 mg CO_2 m^{-2} d^{-1}, 52 mg CH_4 m^{-2} d^{-1}, and -0.178 mg N_2O m^{-2} d^{-1} and the mean daily CH_4 ebullition was 41.1 mg CH_4 m^{-2} d^{-1}. The pond was a net emitter of both CO_2 and CH_4, but a sink for N_2O. Mean CO_2, CH_4 and N_2O fluxes were all comparable to other studies, however, the daily CH_4 ebullition was a lot smaller compared to previous studies. The mean CH_4 emissions were also smaller than the 2018 mean, perhaps due to the lack of summer measurements. About 50% of CH_4 emissions came from ebullition, which was a smaller portion compared to other studies. CO_2 flux was higher in the vegetated area than in the open water, while no difference was found between CH_4 flux in vegetated and open water area. No clear seasonal variation could be seen for CO_2 flux, but a negative relationship was found between air temperature and CO_2, perhaps due to higher rates of photosynthesis during the warmer measuring dates. CH_4 emissions were expected to be highest during warmer months and thus have a positive correlation with temperature. This, however, was only found for CH_4 ebullition and not for flux. The CO_2 and CH_4 which had accumulated under the ice did not amount to much. In December the accumulated flux was about 0.02% of the 2018 flux. In February it was 0.18% and 0.26% of the 2018 CO_2 and CH_4 flux respectively. The results of this thesis might show that emissions do not accumulate as much in ponds as in lakes, however, it is also possible that CH_4 did accumulate in the sediment and was released in April after ice melt.

A negative relationship was found between CO_2 flux and EC, TDS, pH, TN, NO_3^- and NO_2^-, while a positive relationship was observed with DO, chl-a, DOC, and TP. For CH_4 flux, a negative relationship was found with pH, chl-a, DOC, TP, and TN, and a positive relationship with EC, TDS, DO, NO_3^- and NO_2^-. CO_2 fluxes correlated strongest with EC, TP, NO_3^- and NO_2^-, and CH_4 fluxes with EC, TDS, chl-a and TN. CO_2 flux and water chemistry correlated better with previous research compared to CH_4 flux. As for extracellular enzyme activity, CO_2 and BG had a very strong positive relationship which agrees with previous studies and reflects the relationship between BG, glucose, and CO_2. The negative relationship between PHOS and CH_4 could potentially be explained by low PHOS activity causing low levels of PO_4^{3-} and in turn less oxidation and more CH_4. NAG and CH_4 flux had a very strong positive correlation, but the relationship between NAG, TN, CO_2 and CH_4 could not be explained well with the literature, so using NAG as a way of comparing nitrogen and flux might not be very useful.

Carbon burial rate was 60.2 g C m^{-2} y^{-1}, which was much lower compared to other studies. The entire pond buries carbon at a rate of 80.2 kg C y^{-1}, which is accounted for in the ponds total annual carbon emission of 210 kg C y^{-1}. Thus, not only is the pond a carbon source, but it is also inefficient at burying carbon. In conclusion, the findings here show that although small ponds may be able to bury some carbon in their sediment, they are generally net emitters of carbon and therefore mainly contribute to global warming.

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