



UPPSALA
UNIVERSITET



UPTEC W 22008

Examensarbete 30 hp
Maj 2022

Emission of greenhouse gases from constructed wetlands

Nutrient status in relation to methane and
nitrous oxide emission

Christian Lundström

ABSTRACT

Emission of greenhouse gases in constructed wetlands with relation to nutrient status

Christian Lundström

Agricultural land releases large amounts of nitrogen and phosphorus to water bodies which causes eutrophication. Creating wetlands on agricultural land is one way to prevent this major issue. However, constructed wetlands are a large emission source of greenhouse gases. The aim of this study was to quantify the CH₄ and N₂O emissions in 21 constructed wetlands (CWs) around Mälardalen located in mid-Sweden and 19 CWs in the county of Halland along the south-west coast of Sweden and examine if there was any relation between the emissions and the nutrient status. Furthermore, the emission contributed by CH₄ ebullition was evaluated. Synoptic water and gas sampling was done during early and late autumn. Floating chambers were deployed in six wetlands and measured CH₄ ebullition over a 24-hour period. The diffusive CH₄ emissions varied between 0.10–103 mg m⁻² d⁻¹ with a mean value of 13 mg m⁻² d⁻¹. The N₂O emission varied between -0.086–7.8 mg m⁻² d⁻¹ with a mean of 1.4 mg m⁻² d⁻¹. Significant negative correlation between N₂O emission and C:N ratio and a significant positive correlation between N₂O emission and N:P ratio was found. No relation between the CH₄ emission and total organic carbon (TOC) was found which other studies have been able to prove. Only a weak relation between the CH₄ emission and the C:N ratio was found. The ebullition in the six wetlands varied between 0–62 mg m⁻² d⁻¹ and accounted for more than 85 % of the total CH₄ emission in most of the chambers. No significant difference in ebullition was found within the CWs but between the CWs there were found significant differences. The conclusion of this thesis is that CWs in agricultural areas represent a large source of CH₄ and N₂O emissions and that nutrient status has a major influence of the N₂O emissions. Lastly, ebullition seems to be a major pathway for the CH₄ emission.

Keywords: Constructed wetland, greenhouse gas emission, nutrient status, ebullition

REFERAT

Utsläpp av växthusgaser från anlagda våtmarker i relation till näringsstatusen

Christian Lundström

Jordbruksmark släpper ut stora mängder kväve och fosfor till ytvatten vilket orsakar övergödning. Skapandet av våtmarker på jordbruksmark är ett sätt att förhindra detta problem. Dock är anlagda våtmarker stora utsläppskällor av växthusgaser. Målet för den här studien var att kvantifiera utsläppen av CH₄ och N₂O från 21 anlagda våtmarker runt Mälardalen beläget i mitten av Sverige och 19 anlagda våtmarker i Hallands län längs Sveriges sydvästra kust. Vidare var syftet att undersöka om det fanns någon relation mellan utsläppen och näringsstatusen. Försättningsvis, utsläppen av CH₄ genom ebullition utvärderades. Synoptisk vatten- och gasprovtagning utfördes under tidig höst och senhöst. Flytande kamrar sattes ut i sex våtmarker och mätte CH₄ ebullition under en 24-timmars period. Utsläppen av CH₄ genom diffusion varierade mellan 0.10–103 mg m⁻² d⁻¹ med ett medelvärde på 13 mg m⁻² d⁻¹. Utsläppen av N₂O varierade mellan -0.086–7.8 mg m⁻² d⁻¹ med ett medelvärde på 1.4 mg m⁻² d⁻¹. Signifikant negativ korrelation mellan utsläpp av N₂O och C:N-kvoten och en signifikant positiv korrelation mellan utsläpp av N₂O och N:P-kvoten hittades. Ingen relation mellan utsläppen av CH₄ och totalt organiskt kol hittades vilket andra studier kunnat påvisa. Endast en svag relation mellan utsläppen av CH₄ och C:N-kvoten hittades. Ebullitionen i de sex våtmarkerna varierade mellan 0–62 mg m⁻² d⁻¹ och stod för mer än 85 % av det totala CH₄ utsläppen i de flesta kamrarna. Inga signifikanta skillnader i ebullition kunde hittas inom de anlagda våtmarkerna men dock mellan våtmarkerna. Slutsatsen av den här studien är att anlagda våtmarker på jordbruksmark representerar en stor källa av CH₄ och N₂O utsläpp och att näringsstatusen i anlagda våtmarker har en stor inverkan på utsläppen av N₂O. Slutligen, ebullitionen verkar vara en betydande utsläppsväg för CH₄.

Nyckelord: Anlagd våtmark, växthusgasutsläpp, näringsstatus, ebullition

PREFACE

This master thesis corresponds to 30 credits and was written within the Master's Program in Environmental and Water Engineering at Uppsala and the Swedish University of Agricultural Sciences (SLU). Pia Geranmayeh was the main supervisor, Michael Peacock was the co-supervisor and Marcus Wallin was the subject reviewer, all three working at the Department of Aquatic Sciences and Assessment at SLU.

A special thanks to my supervisor Pia for always supporting me and pointed me in the right direction and want to thank my subject reviewer Marcus for helping me with the thesis and giving me hints along the way. I also want to thank Micheal Peacock for helping with equipment, calculations and answer my questions thoroughly. Lastly, I want to thank Gordon Lindau for great company during the first sampling session and help with logistics.

Copyright © Christian Lundström and the Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences.

UPTEC W 22008, ISSN 1401-5765

Digitally published at the Department of Earth Sciences, Uppsala University, Uppsala, 2022.

Populärvetenskaplig sammanfattning

I Sverige är övergödning ett stort problem, speciellt i sjöar och kustvatten. Den underliggande orsaken till övergödningen är stora utsläpp av näringsämnen kväve och fosfor. Det här leder till bland annat ökad förekomst av algbloomning och syrefria botten. Hårdast drabbad är Östersjön där ungefär hälften av allt tillkommande kväve och fosfor ursprungligen kommer från jordbruksmark. Ett sätt att hantera övergödningen är att anlägga våtmarker på jordbruksmarkerna för att avlägsna inkommande näringsämnen. Det här sker framför allt genom sedimentation, där partikelbundet kväve och fosfor sjunker till botten, och denitrifikation, där bakterier bryter ner nitrat till kvävgas och den potenta växthusgasen, lustgas (N_2O). Utöver N_2O bildas även växthusgaserna koldioxid (CO_2) och metan (CH_4) i våtmarker. Bildningen av CH_4 drivs främst av arkéer i våtmarkernas botten. Det finns två huvudsakliga vägar för CH_4 att avges från våtmarker, dels genom diffusion, dels genom att bubblor släpps lös från botten och snabbt frigörs till atmosfären.

Forskningen angående utsläppen av växthusgaser i anlagda våtmarker är idag begränsad och det här projekt ska ge ytterligare förståelse inom området. Syftet med det här projektet var att kvantifiera utsläppen av CH_4 och N_2O från 21 anlagda våtmarker i Mälardalen och 19 anlagda våtmarker i Halland där alla våtmarker var placerade i områden med mycket jordbruksmark. Ett annat syfte var att undersöka hur näringsstatusen i våtmarken påverkade utsläppen av CH_4 och N_2O . Projektet syftade även till att utvärdera utsläppen inom och mellan sex våtmarker gällande bubbelutsläpp av CH_4 från sedimenten. Projektet baserades på provtagning i våtmarkerna under tidig höst och senhöst. Vattenprover togs vid in- och utlopp medan prover av gaser lösta i vattnet togs i mitten av våtmarkerna. För att samla in gasprover gällande bubbelutsläpp placerades nio flytande kamrar ut i 24 timmar. Tre kamrar placerades i respektive inlopp, mitten och utlopp i varje våtmark i den mån det var möjligt. Beräkningar gjordes för att konvertera de lösta gaser i vattnet till utsläpp från våtmarken till atmosfären.

Utsläppen av CH_4 genom diffusion varierade mellan $0.10\text{--}103 \text{ mg m}^{-2} \text{ d}^{-1}$ med ett medelvärde på $13 \text{ mg m}^{-2} \text{ d}^{-1}$ vilket var liknande vad andra studier har uppvisat i tempererade områden. I varmare klimat har studier rapporterat högre värden vilket anses rimligt med tanke på att processen för bildningen av CH_4 fungerar optimalt runt $38 \text{ }^\circ\text{C}$. Resultatet av N_2O -utsläppen visade på en stor variation ($-0.086\text{--}7.8 \text{ mg m}^{-2} \text{ d}^{-1}$) och där ett flertal våtmarker konsumerade N_2O .

Resultatet visade att det fanns relationer mellan utsläppen av växthusgaser från anlagda våtmarker och näringsstatusen. Utsläppen av N_2O kunde framför allt påvisa relationer till näringsstatusen där den starkaste relationen hittades hos C:N-kvoten. Relationen var negativ vilket innebär att vid lägre kolkoncentrationer och högre kvävekoncentrationer kommer bildningen av N_2O öka och därmed även utsläppen från våtmarkerna. Ingen relation mellan utsläppen av CH_4 och totalt organiskt kol hittades vilket andra studier kunnat påvisa. Endast en svag relation mellan utsläppen av CH_4 och C:N-kvoten hittades.

Från provtagningen med kamrarna varierade bubbelutsläppen mellan $0\text{--}62 \text{ mg m}^{-2} \text{ d}^{-1}$. I de flesta kamrarna stod bubbelutsläppet för mer än 85 % av de totala metanutsläppen från våtmarken. Ingen skillnad i ebullition inom våtmarkerna kunde hittas. Däremot var det skillnader i ebullition mellan några våtmarker.

Från resultaten kan slutsatser dras att anlagda våtmarker har en betydande roll när det gäller utsläpp av växthusgaser och att näringsstatusen har betydelse på framför allt utsläppen av N_2O . Det verkar även som om ebullition är en viktig utsläppsväg av CH_4 och verkar skilja sig mellan olika våtmarker.

TABLE OF CONTENTS

1. INTRODUCTION.....	1
1.1 BACKGROUND.....	1
1.2 AIM AND RESEARCH QUESTIONS.....	1
2. THEORY.....	2
2.1 NITROGEN AND PHOSPHORUS REMOVAL.....	2
2.1.1 Nitrification and denitrification.....	2
2.2 CH ₄ PROCESSES AND EMISSION.....	2
3. METHOD.....	3
3.1 SITE DESCRIPTION.....	3
3.2 SAMPLING PERIOD.....	5
3.3 WATER SAMPLING.....	5
3.4 DISSOLVED GHG MEASUREMENT.....	6
3.5 FLOATING CHAMBER MEASUREMENT.....	6
3.6 CALCULATIONS.....	7
3.6.1 Dissolved GHG concentrations.....	7
3.6.2 Diffusive GHG fluxes.....	8
3.6.3 Ebullition and diffusive fluxes.....	9
3.7 STATISTICAL ANALYSIS.....	10
4. RESULTS.....	10
4.1 DISSOLVED CH ₄ AND N ₂ O CONCENTRATIONS.....	10
4.2 DIFFUSIVE EMISSIONS OF CH ₄ AND N ₂ O.....	12
4.3 NUTRIENTS AS INFLUENCING FACTORS ON THE GHG EMISSION.....	14
4.4 CH ₄ EBULLITION.....	15
5. DISCUSSION.....	17
6. CONCLUSION.....	20
REFERENCES.....	21
APPENDIX.....	25

1. INTRODUCTION

1.1 BACKGROUND

Eutrophication in lakes and coastal waters is currently a common issue in Sweden and is a result of an excessive load of nutrients, nitrogen (N) and phosphorus (P), to water bodies. The Baltic Sea is heavily affected which have led to algal blooms and oxygen-free seabed. The primary reason for this is the nutrient losses from agricultural areas where it alone stands for approximately half of the nutrient contribution to the Baltic Sea (Jordbruksverket 2013). Sweden is a part of The Helsinki Convention (HELCOM) together with the other countries around the Baltic Sea. In the Baltic Sea Action Plan (BSAP) the countries have agreed to decrease the nutrient release to such an extent that the Baltic Sea no longer going to suffer from eutrophication (Naturvårdsverket, 2021).

Creating wetlands in the agricultural landscape is one way of dealing with the eutrophication by improving the water quality through nutrient retention. In Sweden there have been subsidy programs directed to farmers to encourage them to create wetlands on their arable land (Weisner et al., 2016). The placement of the constructed wetland (CW) on arable land is important. There are many factors that affect the nutrient transport such as texture of the catchment soil, the average slope of the land and animal density (ibid). However, wetlands are a large emission source of the greenhouse gases (GHGs), carbon dioxide (CO₂), methane (CH₄) (Holgerson and Raymond, 2016) and nitrous oxide (N₂O) (Webb et al., 2019). The nutrient status in CWs have shown to be an important factor for the GHG emissions (Peacock et al., 2017, Peacock et al., 2019, Webb et al., 2021). CH₄ and N₂O are beside CO₂, the most important GHG (Bastviken, 2009). Studies have shown that the CO₂ emission from wetlands stands for the largest emission among the GHGs (Peacock et al., 2019, Holgerson and Raymond, 2016) however, CH₄ is 25 times more potent as a GHG over a 100-year period and N₂O is even more potent (298 times) (Brander, 2012). The CH₄ emission from inland waters account for more than 25 % of the total CH₄ contribution to the atmosphere (Bastviken, 2009). Taking this into consideration it is important to evaluate the benefits and the disadvantages before constructing a wetland.

Swedish University of Agricultural Sciences (SLU) is involved in a research project called WetKit Hydro-ES that is funded by the Swedish Environmental Protection Agency (EPA). The aim for the project is to optimize the size and placement of wetlands around agricultural areas to obtain an optimal nutrient retention while increasing the biodiversity and decreasing the GHG emissions. In this study the emission of GHG from 40 constructed wetlands was quantified and analysed to get an understanding how to construct wetlands with as low GHG emissions as possible. The method used to collect the dissolved CH₄ and N₂O was the headspace method (Hope et al., 2004) which has been used in other studies (Peacock et al., 2019, Peacock et al., 2017).

1.2 AIM AND RESEARCH QUESTIONS

The main aim for this thesis was to quantify the emissions of CH₄ and N₂O from CW in agricultural areas of two different geographical locations with different soil texture. The relation between CH₄ and N₂O emission and the CW nutrient status was examined. Another aim was to evaluate how the CH₄ ebullition varies within and between CWs. This is important to evaluate since CH₄ ebullition have shown to be a major pathway for the CH₄ emission (Grinham et al., 2018, Peacock et al., 2021). For this study the following research questions have been formulated:

1. How does nutrient status affect the emission of CH₄ and N₂O in wetlands?
2. How does the CH₄ ebullition differ within and between CWs?

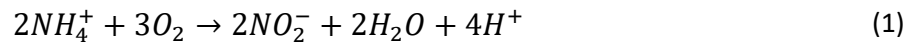
2. THEORY

2.1 NITROGEN AND PHOSPHORUS REMOVAL

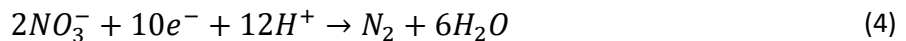
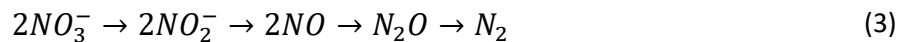
In CWs phosphorus is removed through sedimentation, plant uptake and sorption (Land et al., 2016), while nitrogen is removed by sedimentation, nitrification and denitrification, chemical adsorption and plant uptake (Lee et al., 2009). Through sedimentation, where particles settle at the bottom of the CW, most of the particulate organic nitrogen is removed. However, the most important nitrogen removal in CW in agricultural areas is denitrification since the run-off mostly consists of nitrate (NO_3^-) (Kynkäänniemi, 2014). The nitrogen removal in CW varies between 25-85 % (ibid). The most important drivers for denitrification are nitrate concentration, organic carbon source, temperature, and no present oxygen (ibid).

2.1.1 Nitrification and denitrification

Nitrification is a microbial process that operates during aerobic conditions such as in the sediment's top layers or in flowing water (Liou and Madsen, 2008). The nitrification is performed by bacteria in two steps where the first step is the oxidation of ammonia (NH_4^+) to nitrite (NO_2^-) (Equation 1) and the second step, oxidation of NO_2^- to NO_3^- (Equation 2) (Lee et al., 2009).



Denitrification on the other hand, is a microbial process that operates during anaerobic conditions. Microorganisms called denitrifiers converts NO_3^- and NO_2^- to nitric oxide (NO), N₂O and dinitrogen (N₂) by stepwise reduction (Equation 3) (Skiba, 2008). This process is the largest source of N₂O to the atmosphere (Robertson and Groffman, 2015). The total reduction of NO_3^- to N₂ is shown in the chemical reaction formula (Equation 4).



2.2 CH₄ PROCESSES AND EMISSION

The CH₄ formations are driven by methanogenic archaeobacteria in an anaerobic environment. Acetotrophic methanogenesis and hydrogenotrophic methanogenesis are the two main pathways for CH₄ formation in wetlands (Bastviken, 2009). Acetotrophic methanogenesis decompose acetate (CH₃COO) to CH₄ and carbon dioxide (CO₂) (Equation 5) (Fenchel et al., 2012).



In hydrogenotrophic methanogenesis dihydrogen (H₂) reacts with CO₂ to produce CH₄ and water (H₂O) (Equation 6) (ibid).



These CH₄ formations mainly occur in the sediment (Bastviken, 2009) and the transformation is active between 4–45°C for this kind of methanogenesis with the optimal temperature around 38°C (Zeikus and Winfrey, 1976). From the sediment, CH₄ can be released by either diffusion or ebullition (Bastviken et al., 2004). Dissolved CH₄ emission is driven by diffusion between the water and the air. This process is dependent on the difference in CH₄ concentrations between the water and the air where high surface concentrations lead to increased CH₄ emission. Another factor that influences the diffusion flux is turbulence in the surface water since this increases the contact between the water and the air (Bastviken, 2009). The gas transfer velocity (k) is often used to describe the turbulence and is dependent on the wind speed (Bastviken et al., 2004). Ebullition is when the sediment releases CH₄ as bubbles which travels fast through the water column to the atmosphere. The amount of ebullition is dependent on the CH₄ formations and the hydrostatic pressure. Lower hydrostatic pressure makes it easier for the sediment to release bubbles which means that shallow sediments will have a higher ebullition activity (Bastviken, 2009). This means that especially shallow ponds or near the edges of the ponds, the ebullition flux can be significantly larger than the diffusive flux (Holgerson and Raymond, 2016). Peacock et al. (2021) showed that the air temperature has a strong positive relation to ebullition.

3. METHOD

3.1 SITE DESCRIPTION

In this thesis project 40 CWs located in mid-Sweden around Mälardalen and in the county of Halland along the south-west coast of Sweden were studied, with 21 CWs scattered around Mälardalen (Figure 1) and 19 wetlands in Halland (Figure 2). There were two different types of CWs considered in this study. The first type is a pond with more or less homogenic depth throughout the whole area. The second type is a phosphorus wetland (P-wetland) divided in two parts. The first part at the inlet is a deep area which in most of the cases has a smaller area than the next part that is shallow with emergent vegetation. In Mälardalen only five of the CW (Gra, Sän, LiF, Kur and Tor) are ponds while in Halland all the studied wetlands are ponds. The catchment area for each CW has at least 50 percent agricultural land. Around Mälardalen the CWs are located on clay-silt soils while in Halland they are on postglacial sand, glaciofluvial deposits and moraine (Sveriges geologiska undersökning, 2020).

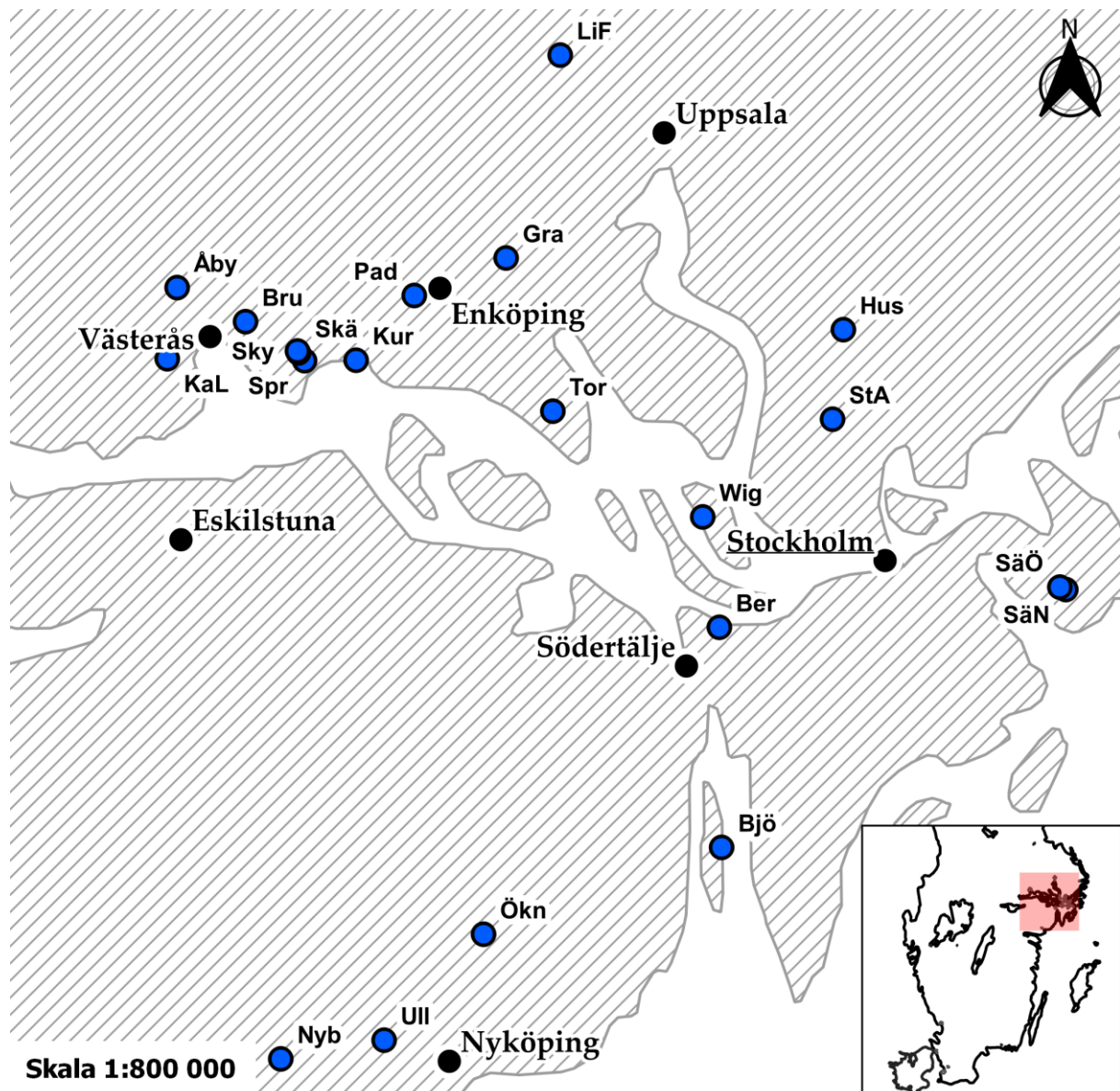


Figure 1. Map presenting the location of the CWs as blue dots in Mälardalen (Lindau, 2021).

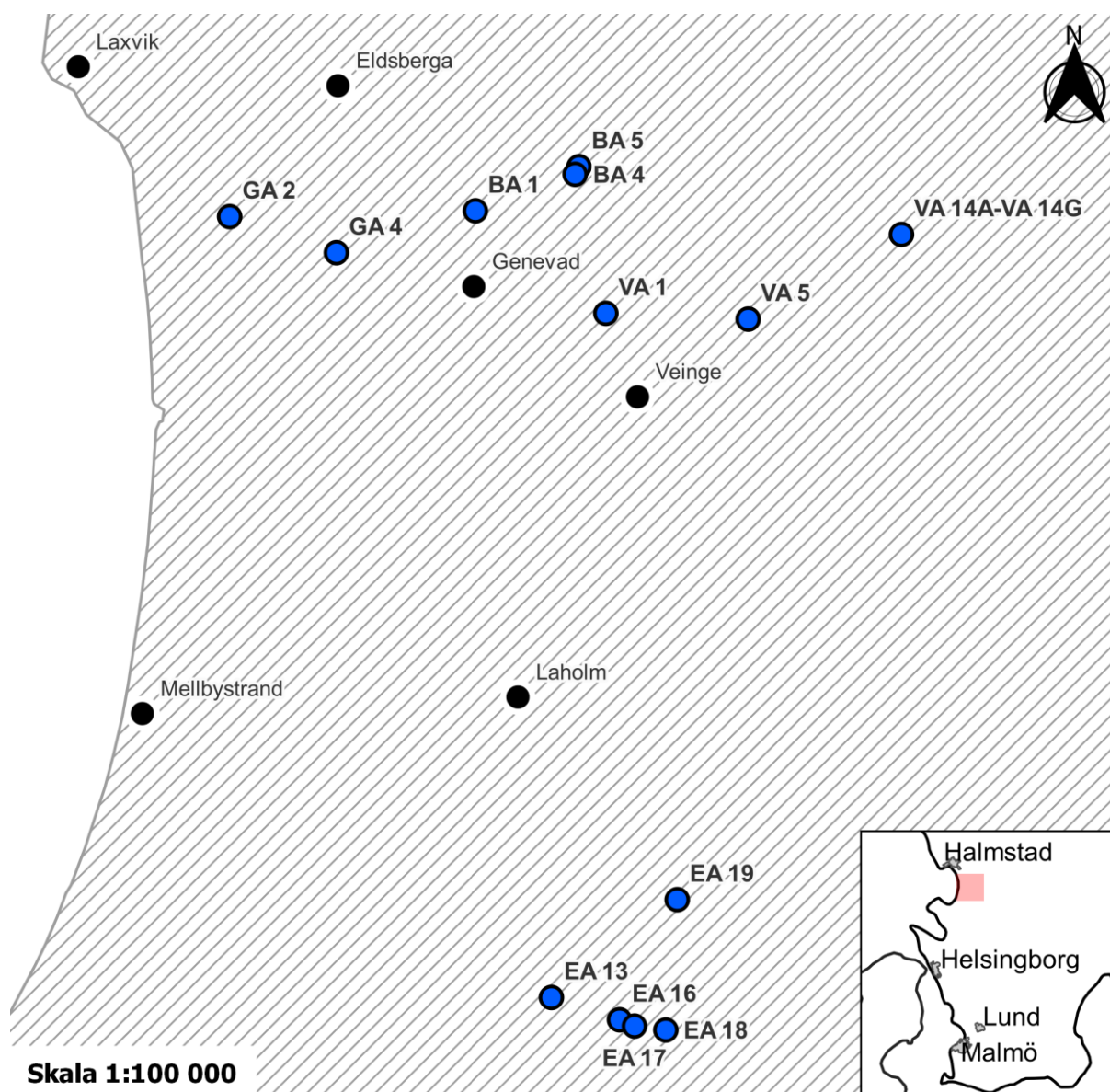


Figure 2. Map presenting the locations of the CWs as blue dots in Halland. VA14A–VA14G contains seven CWs that are connected to each other and therefore marked as one blue dot.

3.2 SAMPLING PERIOD

Synoptic sampling of water and gas were conducted in each wetland in Mälardalen and Halland at two different occasions. In late September to early October 2021, samples were taken in Mälardalen during low flow conditions. In late November to early December new samples were taken in Mälardalen also during low flow. During the latter sampling almost every wetland was more or less covered with ice where the inlet and outlet still had an open surface except Lilla Fågelbo and Graneberg which were totally covered by ice. The shallow areas in some of the P-wetlands were partly ice free. In Halland water and gas sampling was conducted during high flow in the middle of November. The sampling in Halland during low flow had already been done in end of August before this thesis project.

3.3 WATER SAMPLING

In each wetland, four water samples were collected at the inlet and at the outlet. These were sent to the accredited by SWEDAC geochemistry laboratory at SLU (Swedish University of Agricultural Sciences, 2022) for analysis. From the analysis, values from the water chemistry

were received, whereof total phosphorus (TP), total nitrogen (TN) and total organic carbon (TOC) will be of importance to this project. At both the inlet and the outlet a Hanna Instruments Multiparameter Meter Hi 9829 was lowered into the water for a couple of minutes to stabilize. Then water temperature and pressure in the water was measured. To measure the air temperature around the wetland the probe was used on land, a couple of meters from the wetland.

3.4 DISSOLVED GHG MEASUREMENT

To measure the concentration of N_2O and CH_4 dissolved in the water, the headspace technique (Hope et al., 2004) was used and is shortly described in this thesis. With a 60 ml syringe a sample of 30 ml water was taken at a depth of approximately 5 centimeters. Then 30 ml of ambient air was taken a couple of meters away from the CW at shoulder height. A needle with a plastic sheath was then put on the syringe before shaking it vigorously for 1 minute to make sure no air or water would escape the syringe. By shaking the syringe, the GHG in the water was equilibrated with the headspace. After this the sheath was removed and 5 ml was ejected while holding the syringe with the needle upwards so that the water stayed at the bottom. This made sure that water in the needle or end of the syringe was removed. Finally, 22 ml gas was injected into a 22 ml vial while still holding the needle upwards to avoid getting water into the vial. This was done in the middle of the ponds while for the P-wetlands this was done in the middle of both the shallow part and the deep part. The vials were sent to the Gas Chromatography (GC) laboratory at SLU for analyses.

3.5 FLOATING CHAMBER MEASUREMENT

To measure how the emission of CH_4 differs within wetlands, nine floating chambers were used. The chamber consists of a plastic bucket with a plastic tube with a valve going through the top of the bucket. The floating chambers was placed on the water surface over a 24-hour period where they collected the CH_4 that was released from the bottom sediments. When taking the samples from the chambers a syringe was used by connecting it to the valve and extracting 30 ml of gases. Then a needle was quickly placed on the syringe before ejecting 22 ml into a 22 ml vial. As for the dissolved gases the vials were sent to the GC laboratory at SLU for analyses.

The placement of the chambers was arranged so that three chambers were set close to the shore at the inlet, middle and outlet respectively (Figure 3). A plastic stick was driven down to the bottom of the wetland with a thread connected to it and the chambers. This was done to make sure they did not drift away from the shore and each other. In total six wetlands were measured with floating chambers whereof four in Halland (VA1, VA5, GA2 and GA4) and two in Mälardalen (Gra and Bru where the latter is a P-wetland). The initial idea was to measure Gra and Bru twice but there was a too thick ice cover during the second sampling period which prevented deploying the floating chambers.



Figure 3. Floating chamber locations in six of the CWs where the red dots symbolize the chambers, and the blue arrows marks the in- and the outflow. The three chambers in Bru are placed with some distance to the outlet due to vegetation hindering the deployment. In Gra the water near the inlet contained a large amount of water vegetation and the other chambers were placed at a free water surface, therefore the placement further down the wetland.

3.6 CALCULATIONS

3.6.1 Dissolved GHG concentrations

Dissolved GHG concentrations were converted using Henry's law and solubility coefficients, where the Henry's law states that the dissolved gas concentration in a liquid is proportional to the partial pressure of the gas above the liquid (Vallero, 2014). This approach uses Henry's constants and equilibrium solubilities which are dependent on temperature, pressure, and salinity (Weiss, 1974). The solubilities depend on the gas in question and were taken from Wiesenburg & Guinasso (1979) for CH₄ and from Weiss & Price (1980) for N₂O. For the

ponds the water temperature and the pressure were calculated by taking the mean of the inlet and outlet measurements. While for the P-wetlands the water temperature was calculated separately for the deep area and the shallow area to get a more accurate value. This was done by calculating the mean water temperature as for the ponds but for the deep area inlet water temperature was added to the mean and divided by two (Equation 7). For the shallow area the same thing was done but instead of adding the inlet water temperature the outlet water temperature was added (Equation 8).

$$T_{Deep} = \frac{T_{Mean} + T_{Inlet}}{2} \quad (7)$$

$$T_{Shallow} = \frac{T_{Mean} + T_{Outlet}}{2} \quad (8)$$

The pressure was calculated in the same way as for the ponds since it did not differ much between inlet and outlet anyways.

3.6.2 Diffusive GHG fluxes

To calculate an estimate for the diffusive CH₄ fluxes the method of Holgerson and Raymond (2016) was used. This method enables calculations of diffusive CH₄ flux without deploying floating chambers in the CW and only using the gas samples taken in the middle of the CW. The CH₄ flux was calculated with equation 9 with the gas transfer velocity (*k*), the Henry's law constant for methane (*K_h*), the previously calculated concentration of dissolved CH₄ in the water (*C_w*) and the concentration when the CH₄ in the water and the air is in equilibrium (*C_{eq}*). With equation 10 the gas transfer velocity was calculated. The method uses a gas transfer velocity (*k₆₀₀*) which gets bigger with the pond area. The assumption is that smaller ponds are less prone to wind and waves and therefore less turbulent water than bigger ponds which leads to less gas emission. The *k₆₀₀* according to Holgerson and Raymond (2016) are 0.36 m/d for ponds <0.001 km², 0.48 m/d for ponds 0.001–0.01 km² and 0.57 m/d for ponds 0.01–0.1 km². To get the areas of the ponds the area tool was used in Google Earth. This does not give an exact area but a good enough estimation to assign the *k₆₀₀* value in the calculation. The Schmidt number (*S_c*) was calculated with the method used in (Wanninkhof, 1992) and the division with 600 transforms the *k₆₀₀* to a regular *k*.

$$F_{CH_4} = kK_h(C_w - C_{eq}) \quad (9)$$

$$k = k_{600} \left(\frac{S_c}{600} \right)^{-0.5} \quad (10)$$

For the estimation of the N₂O fluxes the method of Audet et al. (2017) was used. With equation 11 the diffusive flux (*F_{N2O}*) was calculated with the gas transfer velocity (*k*), the previously calculated concentration of dissolved N₂O in the water (*C_w*) and the concentration when the water is in equilibrium with the N₂O concentration in the air (*C_{eq}*). To obtain the *k*-value equation 10 was used where the Schmidt number (*S_c*) was calculated with the method used in (Wanninkhof, 1992). The same *k₆₀₀* values as for the CH₄ flux estimation were used.

$$F_{N_2O} = k(C_w - C_{eq}) \quad (11)$$

3.6.3 Ebullition and diffusive fluxes

For the ebullition and diffusive fluxes in the floating chambers the method of Bastviken et al. (2004) were used. With equation 12 the diffusive flux (F) in moles $m^{-2} d^{-1}$ into the floating chamber could be calculated with the gas transfer velocity (k) in $m d^{-1}$, the dissolved CH_4 concentration in the water (C_w) and the concentration in the chamber (C_c) with the unit molarity.

$$F = k(C_w - C_c) \quad (12)$$

To be able to obtain the diffusive flux the k -value needed to be determined and Equation 12 was therefore rewritten (Equation 13).

$$\frac{(P_t - P_0)V}{RTA} = k(P_w K_h - P_0 K_h) \quad (13)$$

The chambers placed at the inlet were calculated with the measured water temperature (T) in Kelvin and pressure values (P_t and P_0) in Pascal at the inlet, where P_0 is the initial pressure in the chamber and P_t is the pressure at time t , in this case 24 hours. The temperature and the pressure at the outlet were used for the chambers placed at the outlet. Chambers placed in the middle of the CW used the mean value of the inlet and the outlet. P_w is the methane pressure in the chamber at equilibrium with C_w . Regarding the dissolved CH_4 concentration all the chambers in the ponds used the same value while the P-wetlands used the value depending on where they were placed, deep or shallow area. The chamber volume (V) used was $9.56 \cdot 10^{-3} m^3$ and the chamber bottom area (A) was $0.0779 m^2$. R is the gas constant and K_h is the Henry's law constant for methane. By rewriting equation 13, the change in pressure over time could be obtained (Equation 14) where K is according to equation 15. Solving equation 14 gave us equation 16.

$$\frac{dP}{dt} = K(P_w - P) \quad (14)$$

Where K is:

$$K = k \frac{K_h RTA}{V} \quad (15)$$

$$(P_w - P) = C e^{(-Kt)} \quad (16)$$

The constant C was determined by using $t = 0$ and k could be determined from equation 15. The k -values were transformed into k_{600} -values to be able to detect if ebullition had occurred in the floating chamber. The k_{600} -value will be considerably higher in the floating chambers that received ebullition compared to the floating chambers which only received diffusive flux. The ratios between the calculated k_{600} -value in each floating chamber and the lowest k_{600} -value in the CW was calculated. This was done to examine if the calculated ratio exceeded the threshold of 2 which was set as a threshold to indicate that it had occurred ebullition into the floating chamber. An average k_{600} -value from the floating chambers where only diffusive flux occurred, was used in equation 12 to obtain an estimation of the diffusive flux from the

floating chambers that exceeded the threshold. The remaining measured CH₄ flux into the floating chamber would therefore be accounted as ebullition. The CH₄ diffusive flux, the CH₄ ebullitive flux and the total CH₄ flux all with the unit mmol m⁻² d⁻¹ was calculated alongside with the ebullition flux percentage of the total flux.

3.7 STATISTICAL ANALYSIS

Statistical analyses were used to examine the correlations between the emissions of the diffusive CH₄ and N₂O and the nutrients in the CW. Furthermore, tests were used to examine if there were any significant differences of GHG emissions between CWs. The statistical tests were mainly computed in Rstudio but in some cases in Excel. The significance level for all the tests was set to 95 % ($p < 0.05$). To examine if there were any influencing factors on the CH₄ and N₂O fluxes in the CWs a correlation test was used. To determine which test to use a Shapiro-Wilk test was used on the data to see whether it was normally distributed or not. Since the data was not normally distributed, a Spearman correlation test was used. The influencing factors that were tested were TOC, TN, TP (which were taken at the inlet of the CWs), C/N, C/P, N/P, and the wetland area. The TOC was used to represent C when calculating the ratios. Regression analyses were performed with the CH₄ and N₂O fluxes as the response variables and the influencing factors as the predictors.

One-way ANOVA tests were computed in Excel of the GHG emission between the CWs to see if there were any significant differences. This was followed up by the Tukey's Honest Significance Difference (HSD) test if any significant differences were found. Mood's median test was used in Rstudio to compare the medians.

4. RESULTS

4.1 DISSOLVED CH₄ AND N₂O CONCENTRATIONS

The dissolved CH₄ concentrations during early autumn ranged between 0.9–345.5 µg L⁻¹ and with a mean concentration of 49.2 µg L⁻¹ (Table 1). During late autumn the dissolved CH₄ concentrations ranged between 0.4–255.6 µg L⁻¹ and a mean concentration of 30.5 µg L⁻¹. The dissolved N₂O concentration during early autumn ranged between 0.4–30.0 µg L⁻¹ and with a mean concentration of 6.0 µg L⁻¹. During late autumn the dissolved N₂O concentrations ranged between 0.7–42.0 µg L⁻¹ and with a mean concentration of 8.0 µg L⁻¹.

Table 1. Dissolved CH₄ and N₂O concentrations in the CWs during early autumn and late autumn. Ponds in Halland are between VAI–GA4, ponds in Mälardalen are between LiF–SäN and P-wetlands in Mälardalen are between Ber–Åby. The dissolved CH₄ and N₂O concentrations in P-wetlands are calculated mean values between the deep and the shallow areas.

CW	Early autumn dissolved CH ₄ (µg L ⁻¹)	Late autumn dissolved CH ₄ (µg L ⁻¹)	Early autumn dissolved N ₂ O (µg L ⁻¹)	Late autumn dissolved N ₂ O (µg L ⁻¹)
VA1	245.1	22.3	10.7	11.5
VA5	0.9	0.8	12.0	30.6
VA14A	19.8	3.8	9.6	3.4
VA14B	10.1	3.9	9.1	5.4
VA14C	46.2	6.6	20.8	5.4
VA14D	21.3	4.5	3.6	4.3
VA14E	39.1	4.1	0.4	1.0
VA14F	18.5	4.1	0.5	1.2
VA14G	17.6	6.3	0.9	3.0
EA13	2.8	2.6	6.7	7.2
EA16	8.8	2.2	4.4	5.7
EA17	13.2	21.7	6.8	12.0
EA18	12.9	10.4	16.4	15.6
EA19	6.0	4.5	5.6	4.6
BA1	1.7	0.4	18.3	12.6
BA4	8.4	112.7	2.5	6.0
BA5	36.7	17.5	1.9	1.7
GA2	8.1	72.1	7.2	1.4
GA4	47.6	3.7	16.3	8.5
LiF	39.4	12.9	0.6	2.4
Tor	14.1	27.0	0.7	4.0
Gra	60.4	21.0	0.5	5.1
Kur	5.1	3.5	10.3	34.3
SäN	67.7	30.2	0.6	42.0
Ber	266.1	3.0	0.5	1.1
Bjö	256.7	255.6	2.6	10.0
Hus	123.3	230.1	0.4	0.2
StA	3.4	138.0	2.4	13.3
SäÖ	19.2	19.4	6.3	7.0
Wig	2.0	4.3	0.4	5.8
Nyb	345.5	44.7	1.1	10.8
Ull	78.8	47.0	0.7	5.2
Ökn	63.3	14.0	2.1	1.7
Pad	1.9	1.7	1.0	1.9
Bru	3.9	2.7	30.0	19.1
KaL	10.5	3.2	9.3	6.9
Sky	6.3	9.2	1.5	1.8
Skä	5.4	4.0	10.9	3.5
Spr	8.2	15.6	2.8	0.7
Åby	3.1	27.5	2.9	2.3

4.2 DIFFUSIVE EMISSIONS OF CH₄ AND N₂O

The diffusive CH₄ and N₂O emissions were compared between early autumn and late autumn to examine the differences in emission during different flow regimes and temperature. The expectation was that the diffusive CH₄ emissions would be larger during early autumn since the CH₄ formation is strongly positive dependent on temperature. There were some variations found in diffusive CH₄ emissions between the sampling occasions (Figure 4), however not statistically significant ($p = 0.071$). The emission from the P-wetlands is the mean value between the deep and the shallow area. Although there was no systematic quantitative difference detected between the early and the late sampling, when ranked the early autumn it showed higher values in 75 % of the cases. Large variations were found in VA1, Ber and Nyb where the CH₄ emission dropped drastically during late autumn. The diffusive CH₄ emission for both sampling occasions in the CWs ranged between 0.10–103.0 mg m⁻² d⁻¹ with a median of 3.8 mg m⁻² d⁻¹ and a mean of 13.1 mg m⁻² d⁻¹. During the early autumn sampling the mean emission was 17.8 mg m⁻² d⁻¹ and for the late autumn sampling the mean was 8.5 mg m⁻² d⁻¹.

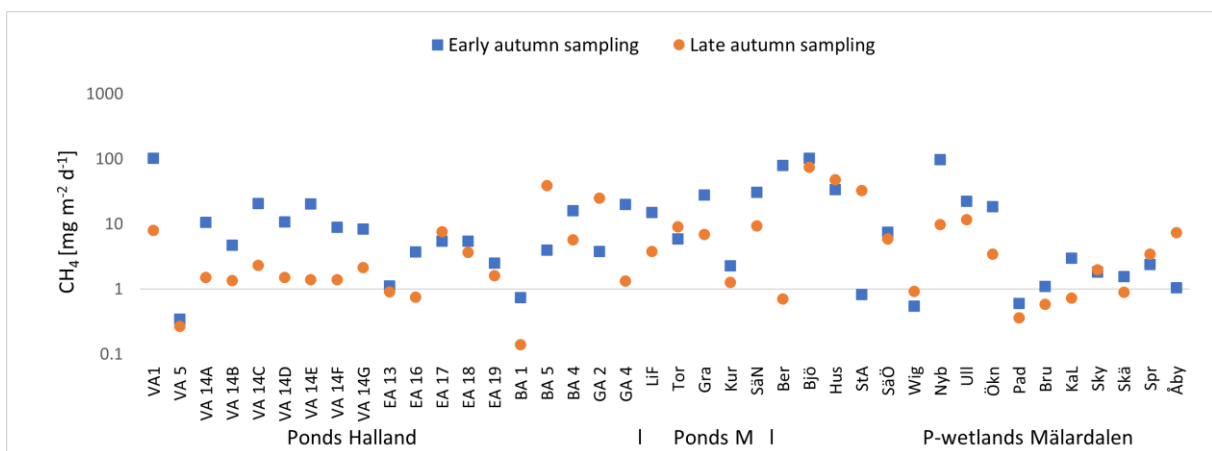


Figure 4. The diffusive CH₄ emission on a logarithmic scale in each wetland at both sampling occasions. “Ponds M” refers to the ponds in Mälardalen. The emission for the P-wetlands is the mean value of the deep and shallow part.

The N₂O emission were different in many of the CWs (Figure 5). Around half of the CWs had higher N₂O emission during early autumn sampling. The three largest N₂O emissions were during the late autumn sampling compared to the CH₄ emission where the four largest were during early autumn. There was no significant difference between the two sampling sessions ($p = 0.88$). The N₂O emission ranged between -0.086–7.8 mg m⁻² d⁻¹ with a median of 0.78 mg m⁻² d⁻¹ and a mean of 1.4 mg m⁻² d⁻¹.

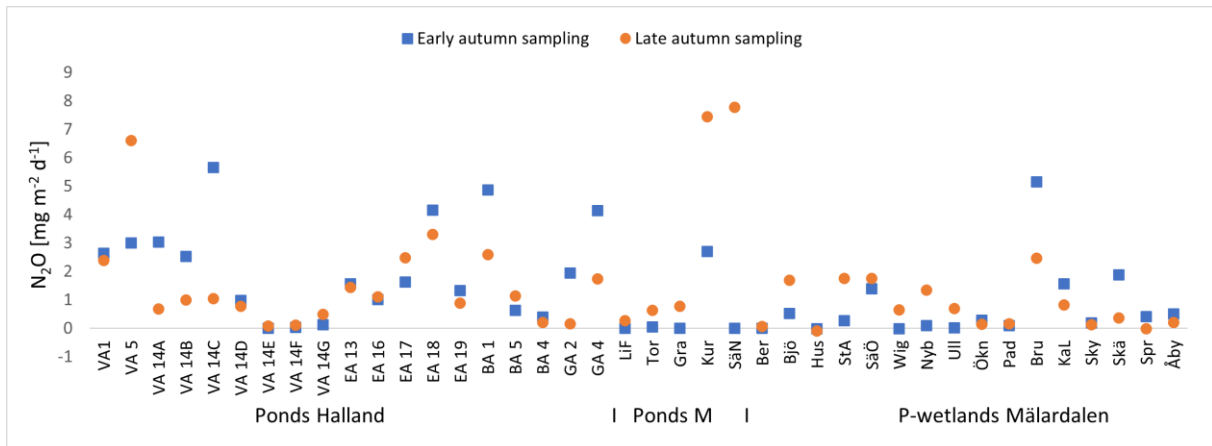


Figure 5. The N₂O emission in each wetland at both sampling occasions. “Ponds M” refers to the ponds in Mälardalen. The emission for the P-wetlands is the mean value of the deep and shallow part.

When grouping the CWs according to wetland type (P-wetland divided into deep and shallow areas) and location no significant difference between the means ($p = 0.097$) could be found (Figure 6). However, the mean value of the CH₄ emission in the shallow areas in P-wetlands ($28 \text{ mg m}^{-2} \text{ d}^{-1}$) was more than twice as high as the others which ranged between $9\text{--}11 \text{ mg m}^{-2} \text{ d}^{-1}$. The larger mean value of the CH₄ emission in the shallow areas in P-wetlands is highly influenced by the four extreme outliers that ranges between $148\text{--}200 \text{ mg m}^{-2} \text{ d}^{-1}$. These outliers respond to the first sampling at Ber and Nyb and on both sampling occasions at Bjö. The medians of the diffusive CH₄ emission from the different CWs ranged from $2\text{--}8 \text{ mg m}^{-2} \text{ d}^{-1}$ but there could not be found any significant differences between the medians ($p > 0.05$). All the ponds were net emitters of CH₄.

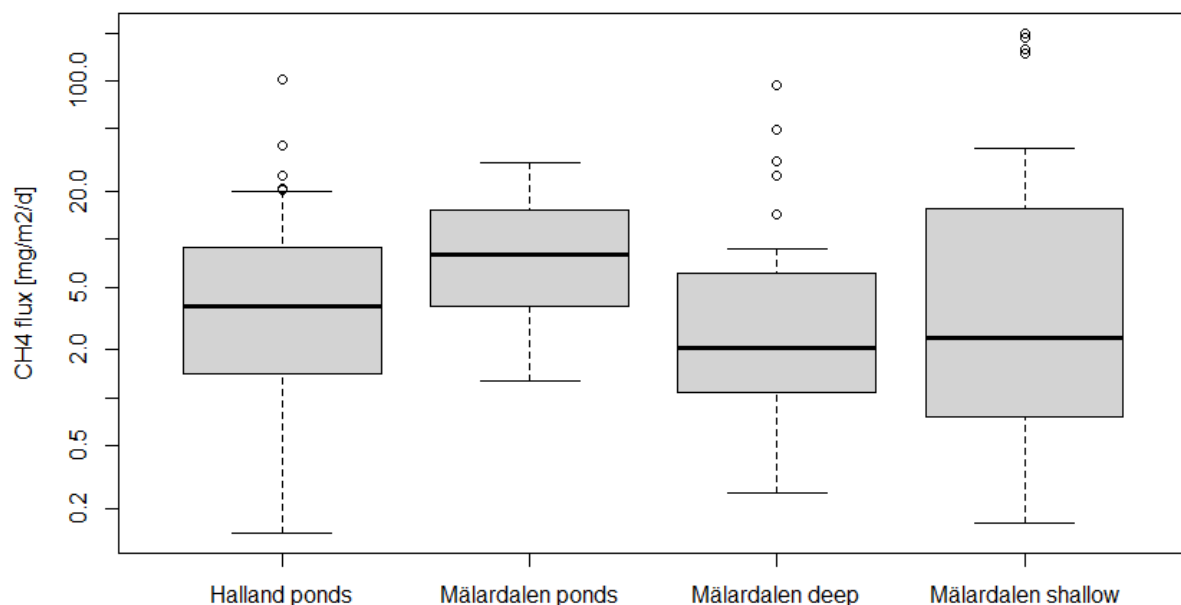


Figure 6. Boxplot showing the diffusive CH₄ emission on a logarithmic scale from the ponds in Halland ($n = 38$), ponds in Mälardalen ($n = 10$) and the P-wetlands divided into deep (0.5–2.0 m) and shallow (<0.5 m) areas ($n = 32$).

The ponds in Halland had a much higher median of N₂O emission, 1.2, 0.46, 0.094, 0.31 mg m⁻² d⁻¹ (medians in the graphs order) (Figure 7) compared to the ponds and P-wetlands in Mälardalen. Despite that fact, no significant differences could be found between the medians. Furthermore, the mean values for the ponds in Halland and Mälardalen were 2.0 and 1.8 mg m⁻² d⁻¹, respectively, compared to the deep and shallow area with lower means of 0.91 and 0.98 mg m⁻² d⁻¹, respectively. However, there were no significant difference of the means ($p = 0.062$). For the N₂O emission there were 40 deep areas that were net emitters and 2 that were consumers. In the shallow areas 25 were net emitters and 7 consumed N₂O. All the ponds were net emitters of N₂O.

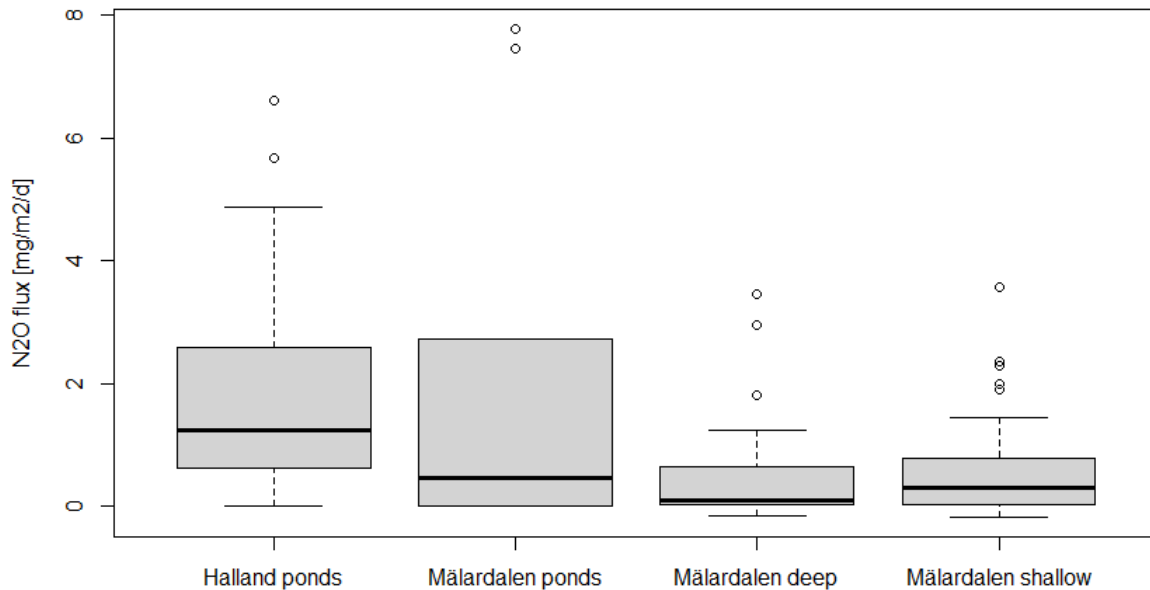


Figure 7. Boxplot showing the N₂O emission from the ponds in Halland ($n = 38$), ponds in Mälardalen ($n = 10$) and the P-wetlands divided into deep (0.5–2.0 m) and shallow (<0.5) areas ($n = 32$).

4.3 NUTRIENTS AS INFLUENCING FACTORS ON THE GHG EMISSION

There were no significant correlations between either CH₄ or N₂O emission with any of the influencing factors when performing the tests on all CWs, where the mean value between the two areas in the P-wetlands was used. While performing the Spearman correlation test with all CWs in Halland and Mälardalen (deep areas represent the P-wetlands in Mälardalen) the emission of CH₄ did only show a significance correlation with the C:N ratio ($\rho = 0.22$, $p = 0.048$). However, significant correlations were found for the N₂O emission with C:N ratio ($\rho = -0.68$, $p < 0.0001$), TN ($\rho = 0.67$, $p < 0.0001$), N:P ratio ($\rho = 0.55$, $p < 0.0001$), TOC ($\rho = -0.37$, $p = 0.0008$) and TP ($\rho = -0.28$, $p = 0.013$). Linear regression analyses between log transformed N₂O emissions and C:N ratio showed a negative relation, $r^2 = 0.40$, $p < 0.0001$, while there was a positive relation between N₂O emissions and N:P ratio, $r^2 = 0.15$, $p < 0.0002$ (Figure 8). Since the N₂O emissions had several negative measurements, a constant was added to all emissions to be able to log transform and receive graph A. This constant was set to the absolute value of the largest negative value with an addition of 0.1 to avoid zero.

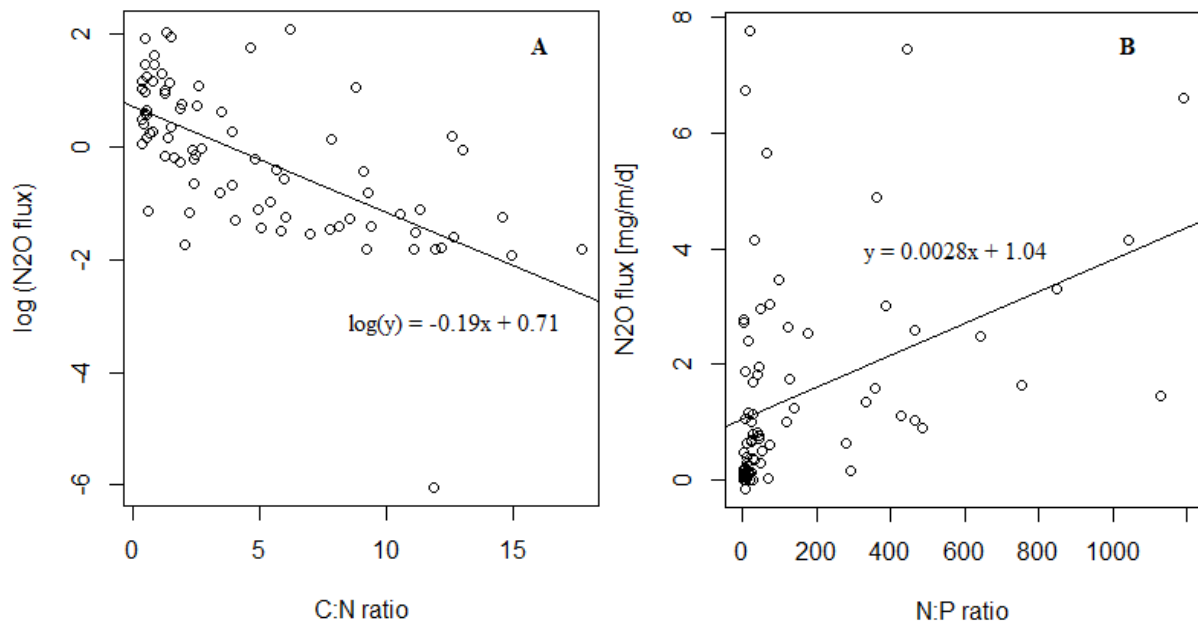


Figure 8. Scatter plots with a linear regression showing significant correlations between the log transformed N₂O emission and the C:N ratio (A), $r^2 = 0.40$, $p < 0.0001$, the N₂O emission and the N:P ratio (B), $r^2 = 0.15$, $p = 0.0002$, for all the CWs in both Mälardalen and Halland ($n = 80$). A constant was added to the N₂O emissions in graph A, to avoid negative and zero values, before log transforming. The equations are the fitted regression line. The P-wetlands are represented here with their deep areas N₂O emission.

4.4 CH₄ EBULLITION

Due to the short time frame of this thesis the limit of ebullition measurements was initially set to eight CWs. However, during late autumn sampling in Mälardalen, the CWs were ice covered and prevented deployment of the floating chambers. Therefore, ebullition was only measured in six CWs. Examination of the CH₄ ebullition within the CWs revealed differences (Figure 9), however not statistically significant. The ebullition at the outlet was the lowest in all the CWs beside in the only P-wetland (Bru). In GA2, no ebullition was detected at the outlet and in VA5 there was no ebullition detected at either location.

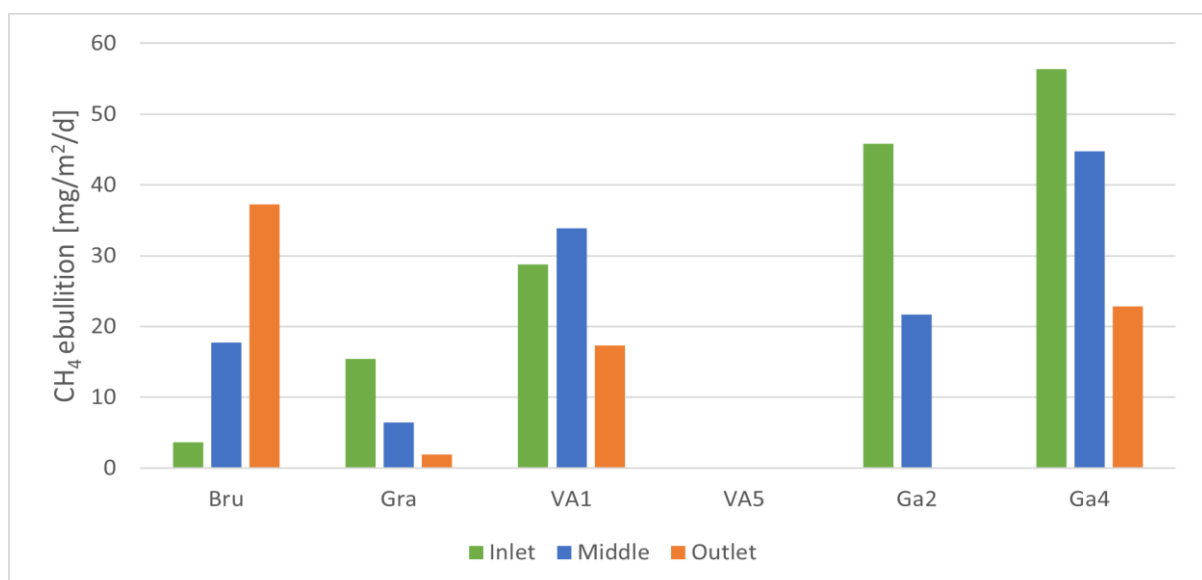


Figure 9. Bar chart showing the mean CH₄ ebullition (n = 3) at the inlet, in the middle and at the outlet in six of the CWs.

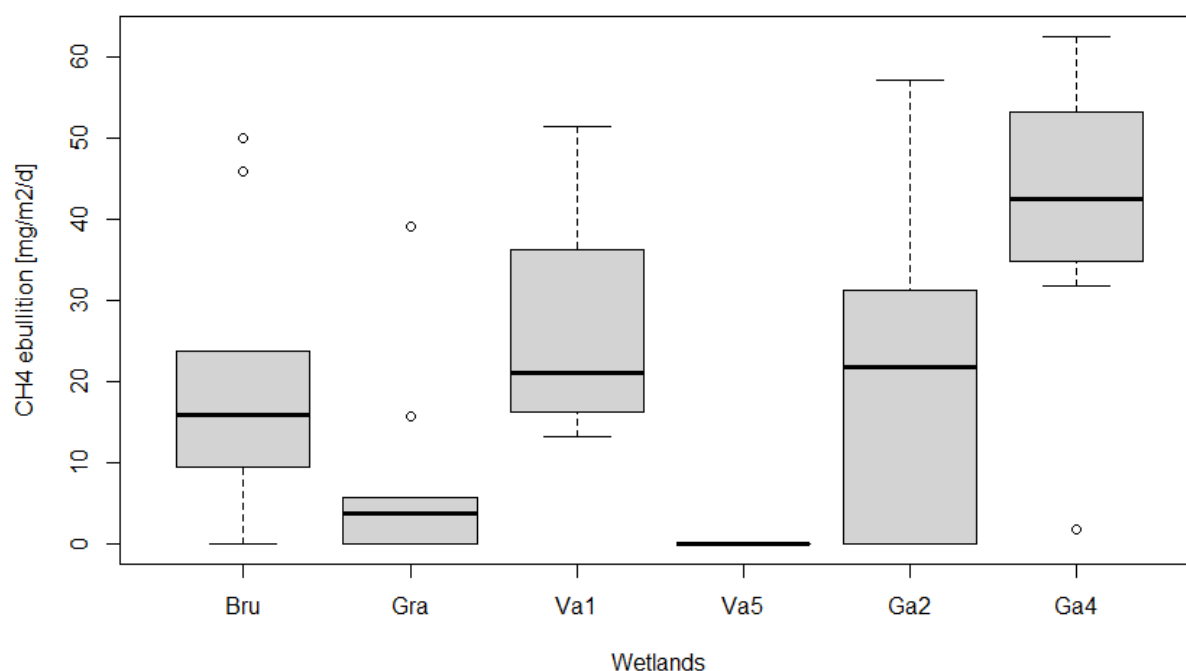


Figure 10. Boxplot showing the CH₄ ebullition in six of the CWs (n = 9).

Variations in CH₄ ebullition were found between different CWs (Figure 10). The CH₄ ebullition had large differences in range, median and mean (Table 2). The variance test showed that there were significant differences between the ebullition for some of the CWs ($p < 0.0001$). The mean value of VA1 was significantly higher than the mean value of VA5. The mean value of GA4 was significantly higher than the mean value of both Gra and VA5, respectively. The floating chambers collected CH₄ emissions through diffusion and ebullition. In most of the floating chambers the emission was either 100 % diffusion or dominated by >85 % ebullition, where the latter accounted for the majority (Appendix). This did not apply in four chambers, where the distribution between diffusion and ebullition was close to fifty-fifty. All of them could be found in Gra, two at the inlet, one in the middle and one at the outlet.

Table 2. CH₄ ebullition for six CWs with the ranges, medians and means [mg m⁻² d⁻¹]. The nutrient concentrations into the CWs [mg L⁻¹] and the ratios are displayed.

	Bru	Gra	VA1	VA5	GA2	GA4
Range	0–50.0	0–39.1	13.2–51.5	0	0–57.2	1.8–62.6
Median	15.9	3.7	21.0	0	21.7	42.6
Mean	19.6	7.9	26.6	0	22.5	41.3
TN	3.2	1.8	9.8	12.6	12.3	11.8
TOC	4.8	21.4	12.1	5.7	7.6	6.3
TP	0.6	0.09	0.6	0.01	0.04	0.09
C:N	1.5	12.0	1.2	0.45	0.6	0.5
C:P	8.7	243.2	20.2	537.8	181.0	68.0
N:P	5.7	20.3	16.3	1188.7	293.0	127.3

5. DISCUSSION

It is well known that freshwaters such as wetlands are large sources of GHG (Li et al., 2021). However, only a few measurements of the emission of GHG from CWs in Sweden has been made. In this study large variations in GHG emission were found. The CH₄ emission varied between 0.10–103.0 mg m⁻² d⁻¹ with an average diffusive CH₄ flux of 13.1 mg m⁻² d⁻¹, including all the measured CWs, which is similar to other studies. During a study of three CWs in southern Sweden the CH₄ emission averaged 10 mg m⁻² d⁻¹ during the summer with temperatures above 15 °C (Stadmark and Leonardson, 2005). However, during water temperatures below 10 °C the emission was 0.6 mg m⁻² d⁻¹ or less. The decrease in CH₄ emissions when the temperature decrease is to be expected due to that the production of CH₄ is inhibited at lower temperatures (Zeikus and Winfrey, 1976). Comparing the two sampling occasions in this study (Figure 4) there is a visible pattern that during early autumn there is higher CH₄ emission than for the sampling during late autumn, however not statistically significant. The average CH₄ emission was more than twice as large during early autumn and late autumn (17.8 mg m⁻² d⁻¹ and 8.5 mg m⁻² d⁻¹). This is not nearly the percentage difference as for Stadmark and Leonardson (2005) that had around 17 times larger CH₄ emissions during summer than winter (10 mg m⁻² d⁻¹ and 0.6 mg m⁻² d⁻¹). This could depend on that in this study, many samplings during early autumn were below 15 °C and a few samplings during late autumn were slightly above 10 °C.

Another important factor is wetland size. In Holgerson and Raymond's (2016) study they found that the mean diffusive CH₄ flux in ponds smaller than 0.001 km² was 36.48 mg m⁻² d⁻¹, ponds between 0.001–0.01 km² (10.4 mg m⁻² d⁻¹) and ponds between 0.01–0.1 (4.48 mg m⁻² d⁻¹). The most common size for the CWs around Halland and Mälardalen was either smaller than 0.001 km² or between 0.001–0.01 km² with nearly the same amount CWs for each. LiF, Kur and Gra were the only CWs with a pond size between 0.01–0.1 km². By taking the average emission from the two smaller size categories (23.44 mg m⁻² d⁻¹), considering the size distribution, the emission was almost twice as large as for the average value of 13 mg m⁻² d⁻¹ in this study. However, this could be explained by the fact that Holgerson and Raymond (2016) included ponds which were globally distributed. The average temperature might have been higher and therefore closer to the optimal temperature for the methanogenesis activity. In India, located in the tropical zone, there were shown to be an average diffusive CH₄ emission of 49.6 mg m⁻² d⁻¹ in ponds (Selvam et al. 2014). Gorsky et al., (2019) studied stormwater ponds in southeastern Virginia, which as the studied CWs in this thesis is located in the temperate zone, and reported a CH₄ emission of 15.1 mg m⁻² d⁻¹.

In this study the CH₄ and N₂O emissions was calculated as the mean value between the deep and the shallow area. This suggests that both areas have equally strong impact on the emissions which should not be the case. Since the shallow area in most of the P-wetlands are considerably larger, they should have a larger impact on the emissions. The mean CH₄ emissions from the shallow area is more than twice as large than the deep area which means that the calculated mean CH₄ emission (13.1 mg m⁻² d⁻¹) might be underestimated. When calculating the GHGs emissions from the concentrations an estimated gas transfer velocity was used and is a major source of error (Audet et al., 2017).

There was a large variation in N₂O emission (-0.086–7.8 mg m⁻² d⁻¹). This could be explained by the different nutrient status in the CWs. With a lower C:N ratio and a larger N:P ratio it seems to enhance the N₂O production and therefore greater emissions (Figure 8). The C:N ratio had the strongest relation to N₂O emission and could be assumed to be the most

important factor. Large variation was shown when comparing the average N₂O emission (1.4 mg m⁻² d⁻¹) with other studies. Mander et al (2014) were examining the GHG emission in three different types of CWs (free water surface, vertical subsurface flow and horizontal subsurface flow). The CWs were globally distributed and treated different types of wastewaters such as from domestic, artificial, dairy farm and agricultural. They found that the average emission for the types ranged from 3.1–5.8 mg m⁻² d⁻¹ which is an order of magnitude higher than the emission found in this thesis. However, the stormwater ponds in southeastern Virginia the N₂O emission was an order of magnitude lower, 0.10 mg m⁻² d⁻¹ (Gorsky et al., 2019). In this study I found that there was a positive significant correlation between N₂O emissions and TN. This could be the reason why the stormwater ponds released less N₂O emissions since they probably receive less TN than the ponds around agricultural areas. The average N₂O emission for both the compared studies differs from the average N₂O emission in this study. However, the average N₂O emission in the compared studies are within the N₂O emission range in this study.

As mentioned earlier, the N₂O emission had a significant negative correlation with the C:N ratio which agree with other studies (Peacock et al., 2017, Webb et al., 2021). However, in their study they used dissolved organic carbon (DOC) instead of TOC and NO₃⁻ instead of TN but since DOC is included in TOC and NO₃⁻ is included in TN it is comparable. This correlation indicates that a high concentration of nitrogen is present at the same time there is a low concentration of TOC during the largest emissions. The reason behind this might be that there need to be concentrations of NO₃⁻ that is high enough to perform denitrification which leads to formation of N₂O. With to high concentrations of C the dominating processes will change to nitrogen assimilation or nitrogen reduction which produces NH₄⁺ and N₂, respectively (Peacock et al., 2017). Furthermore, another study has shown a positive relationship between CH₄ emissions and TOC (Peacock et al., 2019) and a larger CH₄ emission would be expected when the concentration of C increases. However, no significant relationship between them in this thesis was found, only a positive significant relationship between CH₄ emissions and C:N ratio was found. This indicates that the C concentration does have an impact on the CH₄ emission. In summary, decreasing C leads to increased N₂O emission and decreased CH₄ emission. Furthermore, the significance level was set to 95 % (p <0.05) which is a strong significance level. There were relationships in this study that showed a significance level above 90 % but below 95 % and they were assessed as insignificant. However, these relationships should not be overlooked since 90 % significance level means that the probability that the relationship occurred by chance is merely 10 %. When designing a wetland this aspect needs to be taken into consideration to minimize the release of GHGs. Since the relationship between N₂O emissions and C:N ratio proved to be the strongest it would be preferable to choose the placement for the wetland where there is a higher incoming C load. However, more studies should be done on the nutrient status impact on GHG emissions to confirm the previous findings.

An interesting note is that several of the P-wetlands in Mälardalen were consumers of N₂O even though it is commonly known that water bodies in agricultural landscapes with high nitrogen load are large N₂O sources (Baulch et al., 2011). However, in a recent study, more than half of the CWs in Canada with mainly agricultural land showed to be N₂O consumers (Webb et al., 2019). In the P-wetlands the shallow areas accounted for seven out of the nine N₂O consuming occasions. The P-wetlands are characterized to have a shallow area covered by vegetation and that could be the explanation to why these CWs were N₂O consumers. The nitrogen can be removed by plant uptake and therefore lower the NO₃⁻ and NH₄⁺ concentration in the water. This leads to less production of N₂O since nitrification and

denitrification are dependent on NO_3^- and NH_4^+ . The deep area was consuming N_2O in Hus at both sampling occasions. What differed Hus to many other P-wetlands was that the deep area contained a large amount of vegetation in relation to the water surface area.

In this study the dissolved CH_4 concentration showed large variations and ranged between 0.4–345.5 $\mu g L^{-1}$ where a study on urban ponds in Uppsala, Sweden presented a similar variation where the dissolved CH_4 concentrations ranged between 1.73–325 $\mu g L^{-1}$ (Peacock et al. 2019). The dissolved N_2O concentrations did not show as large variation as the dissolved CH_4 concentration. The mean dissolved N_2O concentrations in this study during early autumn (6.0 $\mu g L^{-1}$) and during late autumn (8.0 $\mu g L^{-1}$) was similar to the dissolved N_2O concentration (12.7 $\mu g L^{-1}$) in a study located in northern France on a CW treating agricultural run-off during autumn (Mander et al. 2021). Interestingly, they did not find any dissolved N_2O concentrations during winter. In this study several of the dissolved N_2O samples taken during late autumn when the water surface was covered by ice and still dissolved N_2O concentrations were found in all CWs. The reason behind this could be that the samplings in this study were taken shortly after the water surfaced got ice-covered and therefore concentrations of dissolved N_2O remained from before. Mander et al (2021) took their winter samplings in March which means that the cold period had lasted over a longer time and no N_2O production occurred.

The ebullition in the CWs ranged between 0–62.6 $mg m^{-2} d^{-1}$ (Table 2, Figure 10) which compared to research on lakes in North America showed a similar result (0.25–45 $mg m^{-2} d^{-1}$) (Bastviken et al., 2004). However, other studies have shown an order of magnitude higher mean emission in CWs (257–300 $mg m^{-2} d^{-1}$) (Peacock et al., 2021, Ortega et al., 2019). There has been a suggestion to use at least 11 floating chambers in each CW to get a highly accurate measurement (Wik et al., 2016). Therefore, by using 9 floating chambers can be the reason that the values might be underestimated. Furthermore, when deploying the floating chambers, a plastic stick was driven down to the bottom and connected with a thread to the chambers. This will lead to a new path for bubbles to be released from the sediment and captured in the floating chambers. Another source of error was that in several cases it was required to enter the water to get past the vegetation close to the shore before deploying the floating chambers. The sediment was therefore affected and should result in large emission through ebullition. These sources of errors might lead to an overestimation of the ebullition.

The mean ebullition in four of the six CWs was larger than the mean value for the diffusive fluxes (13.1 $mg m^{-2} d^{-1}$) and 61 % of the chambers ($n = 33$) accounted for >85 % of the total CH_4 emission. This indicates that ebullition is one of the main pathways of the CH_4 emission in CWs which is in an agreement with a study on ditches and ponds (Peacock et al., 2021) and a study on ponds in Queensland, Australia (Grinham et al., 2018).

There could not be found any statistically significant variations of CH_4 ebullition within CWs in this study even though there seemed to be a pattern that the ebullition was lowest at the outlet and largest at the inlet. However, the small amount of measurements might have lowered the significance level. A study on a freshwater reservoir located in Queensland, Australia showed that the ebullition was largest at the inflow due to the shallow depth and the higher amount of organic matter in the sediment (Grinham et al., 2017). The floating chamber locations was supposed to be at the inlet, in the middle and at the outlet in the CWs. This was not done in Gra where the supposed placement at the inlet was moved further down the CW to avoid water vegetation. It was neither done in Bru where the supposed placement at the outlet was moved closer to the middle of the shallow area due to vegetation hindering the

deployment. Bru was the only P-wetland in this study that ebullition was measured, and it showed an exact opposite pattern, the largest ebullition was at the outlet and the lowest at the inlet. P-wetlands have a deep area at the inlet and a shallow area at the outlet this could be the explanation since shallow sediments have higher ebullition activity (Bastviken, 2009). To draw a conclusion whether there are variations within CWs more studies is needed to be done where the floating chamber positions need to be more precisely placed and the comparison should contain more CWs.

While comparing the mean ebullition between CWs there was found statistically significant differences. The mean value of VA1 was significantly higher than VA5, and GA4 was significantly higher than both Gra and VA5. One explanation to why GA4 had higher ebullition than Gra could depend on that Gra had a deeper sediment where the floating chambers were deployed. In addition, the placement of the floating chambers that was supposed to be at the inlet was moved further down the CW. Since it seems to be higher ebullition at the inlet this could have given a lower mean ebullition than it would have gotten if the floating chambers was placed at the inlet. There was no ebullition in VA5 in any floating chambers which might depend on the low C:N ratio. If the organic matter is low in the sediment less ebullition will occur (Grinham et al., 2017). This might also be the case why VA1 had significantly higher ebullition than VA5 since the C:N ratio was almost 3 times as large.

6. CONCLUSION

This thesis supports that CWs in agricultural areas represent an important source of CH₄ and N₂O emissions. Comparing with ponds treating different type of wastewater such as stormwater it seems that CWs in agricultural areas have larger N₂O emissions. Moreover, the N₂O emission is highly influenced by the CWs nutrient status, with a strong negative relationship with the C:N ratio. The ebullition can be considered a major pathway for the CH₄ emissions in CWs. There seems to be a variation in ebullition between and within CWs. However no statistically significant difference was found within CWs. There are only a few studies on GHG emissions from CWs around agricultural areas in Sweden. In the future, more studies should be done to clarify which factors are the most important for the GHG emissions and which importance the ebullition has for the CH₄ emissions from CWs. When measuring ebullition in the future the amount and placement of the floating chambers should be optimized to be able to cover the variations in the CWs.

REFERENCES

- Audet, J., Wallin, M. B., Kyllmar, K., Andersson, S. & Bishop, K. (2017). Nitrous oxide emissions from streams in a Swedish agricultural catchment. *Agriculture, Ecosystems & Environment*. 236, 295-303. <https://doi.org/10.1016/j.agee.2016.12.012>
- Bastviken, D., Cole, J., Pace, M. & Tranvik, L. (2004). Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate. *Global Biogeochemical Cycles*. 18 (4). <https://doi-org.ezproxy.its.uu.se/10.1029/2004GB002238>
- Bastviken, D. (2009). Methane. *Encyclopedia of Inland Waters*, Elsevier. 783–805. <https://doi.org/10.1016/B978-012370626-3.00117-4>
- Baulch, H. M., Schiff, S. L., Maranger, R. & Dillon, P. J. (2011). Nitrogen enrichment and the emission of nitrous oxide from streams. *Global Biogeochemical Cycles*. 25 (4). <https://doi-org.ezproxy.its.uu.se/10.1029/2011GB004047>
- Brander, M. (2012). Greenhouse Gases, CO₂, CO₂e, and Carbon: What Do All These Terms Mean? *Ecometria*. <https://ecometrica.com/assets/GHGs-CO2-CO2e-and-Carbon-What-Do-These-Mean-v2.1.pdf>
- Fenchel, T., King, G. M. & Blackburn, T. H. (2012). Chapter 1 - Bacterial Metabolism. *Bacterial Biochemistry*, 3rd ed., Elsevier. 1–34. <https://doi.org/10.1016/B978-0-12-415836-8.00001-3>
- Gorsky, A. L., Racanelli, G. A., Belvin, A. C. & Chambers, R. M. (2019). Greenhouse gas flux from stormwater ponds in southeastern Virginia (USA). *Anthropocene*. 28. <https://doi.org/10.1016/j.ancene.2019.100218>
- Grinham, A., Dunbabin, M. & Albert, S. (2017). Importance of sediment organic matter to methane ebullition in a sub-tropical freshwater reservoir. *Science of The Total Environment*. 621, 1199–1207. <https://doi.org/10.1016/j.scitotenv.2017.10.108>
- Grinham, A., Albert, S., Deering, N., Dunbabin, M., Bastviken, D., Sherman, B., Lovelock, C. E., and Evans, C. D. (2018). The importance of small artificial water bodies as sources of methane emissions in Queensland, Australia. *Hydrology and Earth System Sciences*. 22, 5281–5298. <https://doi.org/10.5194/hess-22-5281-2018>
- Holgerson, M.A. & Raymond, P.A. (2016). Large contribution to inland water CO₂ and CH₄ emissions from very small ponds. *Nature Geoscience*. 9, 222-226. <http://doi.org/10.1038/ngeo2654>
- Hope, D., Palmer, S. M., Billett, M. F. & Dawson, J. J. C. (2004). Variations in dissolved CO₂ and CH₄ in a first-order stream and catchment: an investigation of soil–stream linkages. *Hydrological Processes*. 18, 3255-3275. <https://doi.org/10.1002/hyp.5657>
- Jordbruksverket (2013). *Actions against Plant Nutrient Losses from Agriculture*. https://www2.jordbruksverket.se/webdav/files/SJV/trycksaker/Pdf_ovrigt/ovr125gbv2.pdf
- Kynkäänniemi, P. (2014). Small Wetlands Designed for Phosphorus Retention in Swedish Agricultural Areas – Efficiency Variations during the First Years after Construction.

(Doctoral Thesis). Swedish University of Agricultural Sciences. Department of Soil and Environment.

Land, M., Granéli, W., Grimvall, A., Hoffmann, C. C., Mitsch, W. J., Tonderski, K. S. & Verhoeven, J. T. A. (2016). How effective are created or restored freshwater wetlands for nitrogen and phosphorus removal? A systematic review. *Environmental Evidence*. 5 (9). <https://doi.org/10.1186/s13750-016-0060-0>

Lee, C., Fletcher, T. D. & Sun, G. (2009). Nitrogen removal in constructed wetland systems. *Engineering in Life Sciences*. 9, 11-22. <https://doiorg.ezproxy.its.uu.se/10.1002/elsc.200800049>

Li, Y., Shang, J., Zhang, C., Zhang, W., Niu, L., Wang, L. & Zhang, H. (2021). The role of freshwater eutrophication in greenhouse gas emissions: A review. *Science of The Total Environment*. 768. <https://doi.org/10.1016/j.scitotenv.2020.144582>

Liou, J. S. -C. & Madsen, E. L. (2008). Microbial Ecological Processes: Aerobic/Anaerobic. *Encyclopedia of Ecology*, Elsevier. 2348–2357. <https://doi.org/10.1016/B978-008045405-4.00254-8>

Lindau, G. (2021). Våtmarksbatymetri – djupmätning av 10 våtmarker i Mälardalen. (Självständigt arbete). Sveriges lantbruksuniversitet. Institutionen för vatten och miljö.

Mander, Ü., Dotro, G., Ebie, Y., Towprayoon, S., Chiemchaisri, C., Nogueira, S. F., Jamsranjav, B., Kasak, K., Truu, J., Tournebize, J. & Mitsch, J. (2014). Greenhouse gas emission in constructed wetlands for wastewater treatment: A review. *Ecological Engineering*. 66, 19–35. <https://doi.org/10.1016/j.ecoleng.2013.12.006>

Mander, Ü., Tournebize, J., Espenberg, M., Chaumont, C., Torga, R., Garnier, J., Muhel, M., Maddison, M., Lebrun, J. D., Uher, E., Remm, K., Pärn, J. & Soosaar, K. (2021). High denitrification potential but low nitrous oxide emission in a constructed wetland treating nitrate-polluted agricultural run-off. *Science of The Total Environment*. 779. <https://doi.org/10.1016/j.scitotenv.2021.146614>

Naturvårdsverket (2021). Miljömålen: Årlig uppföljning av Sveriges nationella miljömål 2021 – Med fokus på statliga insatser. (6968). Stockholm.

Ortega, S. H., González-Quijano, C. R., Casper, P., Singer, G. A. & Gessner, M. O. (2019). Methane emissions from contrasting urban freshwaters: Rates, drivers, and a whole-city footprint. *Global Change Biology*. 25, 4234-4243. <https://doi.org/10.1111/gcb.14799>

Peacock, M., Ridley, L. M., Evans, C. D. & Gauci, V. (2017). Management effects on greenhouse gas dynamics in fen ditches. *Science of The Total Environment*. 578, 601-612. <https://doi.org/10.1016/j.scitotenv.2016.11.005>

Peacock, M., Audet, J., Jordan, S., Smeds, J. & Wallin., M.B. (2019). Greenhouse gas emissions from urban ponds are driven by nutrient status and hydrology. *Ecosphere*. 10 (3). <https://doi.org/10.1002/ecs2.2643>

Peacock, M., Audey, J., Bastviken, D., Cook, S., Evans, C. D., Grinham, A., Holgerson, M. A., Högbom, L., Pickard, A. E., Zieliński, P. & Futter, M. N. (2021). Small artificial

waterbodies are widespread and persistent emitters of methane and carbon dioxide. *Global Change Biology*. 27 (20), 5109-5123. <https://doi.org/10.1111/gcb.15762>

Robertson, G. P. & Groffman, P. M. (2015). Chapter 14 - Nitrogen Transformations. *Soil Microbiology, Ecology and Biochemistry*, 4th ed., Elsevier. 421–446. <https://doi.org/10.1016/B978-0-12-415955-6.00014-1>

Selvam, B.P., Natchimuthu, S., Arunachalam, L. & Bastviken, D. (2014). Methane and carbon dioxide emissions from inland waters in India – implications for large scale greenhouse gas balances. *Global Change Biology*. 20, 3397-3407. <https://doi-org.ezproxy.its.uu.se/10.1111/gcb.12575>

Skiba, U. (2008). Denitrification. *Encyclopedia of Ecology*, Elsevier. 866–871. <https://doi.org/10.1016/B978-008045405-4.00264-0>

Stadmark, J. & Leonardson, L. (2005). Emissions of greenhouse gases from ponds constructed for nitrogen removal. *Ecological Engineering*. 25, 542–551. <https://doi.org/10.1016/j.ecoleng.2005.07.004>

Sveriges geologiska undersökning (2020). *Kartvisaren*. <https://apps.sgu.se/kartvisare/> [2022-04-04]

Swedish University of Agricultural Sciences (2022). *Laboratoriet för geokemi (Vattenkemiska laboratoriet)*. <https://www.slu.se/institutioner/vatten-miljo/laboratorier/vattenkemiska-laboratoriet/> [2022-04-04]

Vallero, D. (2014). Chapter 18 - Air Pollutant Kinetics and Equilibrium. *Fundamentals of Air Pollution (Fifth Edition)*, Elsevier. 437–473. <https://doi.org/10.1016/B978-0-12-401733-7.00018-9>

Wanninkhof, R. (1992). Relationship Between Wind Speed and Gas Exchange Over the Ocean. *Journal of Geophysical Research*. 97, 7373-7382. <https://doi.org/10.1029/92JC00188>

Webb, J. R., Hayes, N. M., Simpson, G. L., Leavitt, P. R., Baulch, H. M. & Finlay, K. (2019). Widespread nitrous oxide undersaturation in farm waterbodies creates an unexpected greenhouse gas sink. *PNAS*. 116, 9814-9819. <https://doi.org/10.1073/pnas.1820389116>

Webb, J. R., Clough, T. J. & Quayle, W. C. (2021). A review of indirect N₂O emission factors from artificial agricultural waters. *Environmental Research Letters*. 16 (4).

Weisner, S. E. B., Johannesson, K., Thiere, G., Svengren, H., Ehde, P. M. & Tonderski, K. S. (2016). National Large-Scale Wetland Creation in Agricultural Areas—Potential versus Realized Effects on Nutrient Transports. *Water*. 8, 544. <https://doi.org/10.3390/w8110544>

Weiss, R. F. (1974). Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Marine Chemistry*. 2, 203-215. [https://doi.org/10.1016/0304-4203\(74\)90015-2](https://doi.org/10.1016/0304-4203(74)90015-2)

Weiss, R.F. & Price, B.A. (1980). Nitrous oxide solubility in water and seawater. *Marine Chemistry*. 8, 347–359. [https://doi.org/10.1016/0304-4203\(80\)90024-9](https://doi.org/10.1016/0304-4203(80)90024-9)

Wiesenburg, D. A. & Guinasso Jr, N. L. (1979). Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water. *Journal of Chemical & Engineering Data*. 24, 356-360. <https://doi.org/10.1021/je60083a006>

Wik, M., Thornton, B. F., Bastviken, D., Uhlbäck, J. & Crill, P.M. (2016). Biased sampling of methane release from northern lakes: A problem for extrapolation. *Geophysical Research Letters*. 43, 1256-1262. <https://doi.org/10.1002/2015GL066501>

Zeikus, J. G. & Winfrey, M. R. (1976). Temperature limitation of methanogenesis in aquatic sediments. *American Society for Microbiology*. 31, 99–107.

APPENDIX

Table 3. The diffusive flux, ebullition flux and the ebullition percentage of the total flux in each floating chamber. For the CWs, A stands for the chambers at the inlet, B for the chambers in the middle and C for the chambers at the outlet.

CW	Diffusive CH ₄ flux [mg m ⁻² d ⁻¹]	CH ₄ ebullitive flux [mg m ⁻² d ⁻¹]	Ebullition percentage of total flux [%]
Bru A	0.192	1.68	89
Bru A	0.208	9.376	98
Bru A	0.192	0	0
Bru B	0.048	16.896	100
Bru B	0.048	12.432	100
Bru B	0.048	23.776	100
Bru C	0.048	45.984	100
Bru C	0.048	50	100
Bru C	0.048	15.92	100
Gra A	2.96	39.056	93
Gra A	2.96	3.84	56
Gra A	2.96	3.44	54
Gra B	3.184	0	0
Gra B	2.96	3.712	56
Gra B	2.96	15.632	84
Gra C	2.96	5.744	66
Gra C	0.896	0	0
Gra C	0.608	0	0
Va1 A	1.056	13.472	93
Va1 A	1.056	51.456	98
Va1 A	1.056	21.296	95
Va1 B	1.056	36.288	97
Va1 B	1.056	16.24	94
Va1 B	1.056	49.088	98
Va1 C	1.056	17.648	94
Va1 C	1.056	13.184	93
Va1 C	1.056	21.024	95
Va5 A	2.096	0	0
Va5 A	2.544	0	0
Va5 A	2.72	0	0
Va5 B	0.128	0	0
Va5 B	0.208	0	0
Va5 B	0.08	0	0
Va5 C	3.184	0	0
Va5 C	1.2	0	0
Va5 C	2.16	0	0
Ga2 A	3.52	49.008	93
Ga2 A	3.52	57.2	94
Ga2 A	3.52	31.184	90

Ga2 B	3.52	21.712	86
Ga2 B	3.52	17.984	84
Ga2 B	3.52	25.424	88
Ga2 C	2.496	0	0
Ga2 C	0.288	0	0
Ga2 C	0.16	0	0
Ga4 A	0.128	62.56	100
Ga4 A	0.128	47.152	100
Ga4 A	0.128	59.44	100
Ga4 B	0.128	42.576	100
Ga4 B	0.128	38.56	100
Ga4 B	0.128	53.2	100
Ga4 C	0.128	1.808	94
Ga4 C	0.128	31.76	100
Ga4 C	0.128	34.896	100
