Burping Wetlands: Quantifying greenhouse gas ebullition rates across a range of sediment types and characteristics, water quality variables, and land use

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Abstract

Aquatic ecosystems are a source of greenhouse gases (GHG) to the atmosphere. One pathway of this GHG release is ebullition, or bubbling, from aquatic sediments. The contribution of ebullition is often underestimated in global GHG budgets, as it is rarely included in GHG emission measurements. The ebullition pathway can account for up to 67% of methane emissions from water bodies. We aim to determine the factors that influence ebullition of methane (CH_4), carbon dioxide (CO_2), and nitrous oxide (N_2O), including sediment characteristics, water quality characteristics, and land use. Our study ponds are in urban, agricultural, and woodland areas. We found that N_2O flux rates are significantly lower than CH_4 and CO_2 flux rates across all study ponds. We also found that urban areas have higher GHG flux rates, which is correlated with low organic matter content. Understanding the factors influencing GHG ebullition from aquatic ecosystems will give us a broader understanding of the significance of their contribution to global GHG budgets in a changing climate.

Key words: Greenhouse gas, ebullition, freshwater, wetlands, carbon dioxide, nitrous oxide, methane

Introduction

Aquatic ecosystems are abundant on the terrestrial landscape yet are not included in the terrestrial greenhouse gas (GHG) budget (Bastviken et al., 2017; Crawford et al., 2014; Harrison et al., 2017; Huttunen et al., 2003). Around the world, water bodies such as lakes, reservoirs, and wetlands play a significant role in balancing global GHG emissions (Baulch et al., 2011; Descloux et al., 2017; West et al., 2016). This is done through bubble-mediated fluxes, diffusion, or plant-mediated transport (Poissant et al., 2007). Gases such as methane (CH_4), carbon dioxide (CO_2), and nitrous oxide (N_2O) are released from aquatic sediments of inland water bodies and enter the atmosphere. Though all water bodies contribute to the global GHG budget, smaller water bodies are hot spots for GHG release and are underrepresented in current estimates (Aben et al., 2017; Bastviken et al., 2017; Crawford et al., 2014; T. Delsontro et al., 2015; Juutinen et al., 2008). The potential to link quantities of GHG release from small water bodies, such as wetlands, with climate and land use data can inform land management decisions, improve global GHG budgets, and forecast future changes to these budgets.

Ebullition, also called bubbling, is the release of gases from aquatic sediments in lakes and shallow water systems (Joyce et al., 2003). It occurs when gas bubbles become buoyant enough to surpass forces holding them in the water column (Kellner et al., 2006), and can be triggered by shear stress, lowering the water table, or decreasing atmospheric pressure (Aben et al., 2017; Baulch et al., 2011; Flury et al., 2015; Joyce et al., 2003). Ebullition is one pathway for gases in aquatic systems to escape the water body and enter the atmosphere. These gases include CH_4, N_2O, and CO_2. These gases contribute to climate change by trapping heat in the

troposphere and thus resulting in increasing global temperatures over time. Although various studies recognize the importance of CH_4 ebullition to the atmosphere (Bastviken et al., 2017; Sepulveda-Jauregui et al., 2015; Walter, et al., 2006), the factors that control ebullition rates are still poorly understood (Joyce et al., 2003). Data on ebullition is limited, and estimates are hard to achieve due to its episodic nature (Bastviken et al., 2017; Fechner-Levy et al., 1996). Sampling over longer periods of time, with higher frequency, and more spatial variation will be necessary to accurately profile ebullition (Crawford et al., 2014). Including ebullition in gas flux pathway analyses will give a better estimate of how GHG emissions from aquatic systems factor into the anthropogenic GHG budget.

Diffusion, or surface aeration, is the movement of dissolved gas from sediment through the water column and into the atmosphere. When lake sediments are overlain with anoxic water, gasses are easily released from sediments, and when mixing occurs, gasses can be oxidized or escape into the atmosphere (Delsontro et al., 2011). Diffusion is another way for GHGs to escape aquatic systems into the atmosphere. Previous studies assumed that diffusive transport was the primary method of transport for GHGs, which left a gap in the knowledge on ebullition (Baulch et al., 2011). Although diffusion is an important pathway, ebullition usually accompanies it. Diffusion is recognized as the dominant pathway for CO_2 (Casper et al., 2000; Poissant et al., 2007) Lake size, water temperature, and nutrient availability have been found to be good predictors of diffusion rates (West et al., 2016). Diffusion has been found to occur more in deeper, productive lakes with colder water temperatures (Joyce et al., 2003). In addition, shallow, nutrient rich calcareous lakes have higher rates of diffusion (Juutinen et al., 2008).

GHG emissions from freshwater systems have been estimated and compared to anthropogenic GHG emissions. CO_2 freshwater emissions have been estimated to be equivalent

to 0.4–4% of anthropogenic CO_2 emissions (Descloux et al., 2017; Huttunen et al., 2003). CH_4 freshwater emissions have been estimated to be equivalent to 5–18% of anthropogenic CH_4 emissions and 10–15% of natural CH_4 emissions (Delsontro et al., 2011; Descloux et al., 2017; Huttunen et al., 2003). N_2O freshwater emissions are negligible compared to anthropogenic N_2O emissions (Descloux et al., 2017). Ebullition alone accounts for 1% of freshwater CO_2 emissions, 20–67% of freshwater CH_4 emissions, and <0.1% of freshwater N_2O emissions (Baulch et al., 2011).

CO_2 is a GHG produced in aquatic systems by aerobic respiration, denitrification, and acetate fermentation (Baulch et al., 2011). CO_2's global warming potential (GWP) is 1, and other GHG GWP's are measure relative to CO_2 (EPA, 2018). Aquatic systems are regarded as carbon sinks, but there are emissions from these systems as well (Bastviken et al., 2017; West et al., 2016).

CH_4 is a GHG with a GWP 25 times that of CO_2 (EPA, 2010). CH_4 in water bodies is produced by acetate fermentation or H_2 dependent methanogenesis (Baulch et al., 2011). When CH_4 is produced in water bodies, it is either oxidized to CO_2, or it escapes into the atmosphere. Methanotrophic bacteria in the water column successfully oxidize the majority of CH_4 diffusely released from sediments, however bubbles (ebullition) escaping to the atmosphere are not similarly oxidized (Bastviken et al., 2017; West et al., 2016). Ebullition occurs rapidly, and CH_4 dissolved from rising bubbles is dependent on lake depth, water temperature, CH_4 concentration in the water, and the initial size of the bubble (Delsontro et al., 2011). CH_4 has a low solubility, which makes ebullition a more likely pathway (Crawford et al., 2014). Estimates on CH_4 emissions from aquatic systems show that it could offset as much as one-fourth of the continental carbon sink (West et al., 2016). In shallow water bodies, CH_4 released from sediments is of a

larger magnitude than CH_4 released from deep lakes (West et al., 2016). This is due to CH_4 bubbles dissolving as they rise to the top of the water column. A review of previous studies on CH_4 emissions found that nearly all recorded concentrations of CH_4 were super saturated with relation to the atmospheric equilibrium and that the general effect of anthropogenic change to fluvial systems results in CH_4 enrichment (Stanley et al., 2016).

N_2O is a GHG produced in aquatic systems by denitrification and nitrification. It is released from aquatic sediment typically via diffusion and has 300 times the GWP than that of CO_2 (EPA, 2018). N_2O in aquatic systems has received much study based on the assumption that agriculture and sewage inputs of nitrogen would lead to large N_2O emissions from water bodies (Baulch et al., 2011). Research has shown that CH_4 fluxes typically exceed N_2O fluxes (Baulch et al., 2011), which suggest a better understanding of CH_4 flux is necessary.

This study examines ebullition rates of GHGs in small water bodies at an international scale. This study is a collaboration between researchers at the University of Missouri, the University of Winnipeg, Wilfred Laurier University, and the University of Saskatchewan. The objectives are to determine what controls ebullition in small water bodies and examine variability of GHG flux rates.

We intend to answer the question of what controls GHG ebullition in small water bodies? North America has a range of sediment types, land uses, and water quality characteristics associated with its water bodies. These variables are not homogenous in our study ponds, so there is the potential to identify relationships between them and GHG flux rates. We hypothesize that ebullition in small water bodies is affected by sediment characteristics, land use, and water quality characteristics to varying degrees.

We captured GHG emissions via ebullition with bubble traps for volume and with the inverted funnel method for concentrations of CH_4, CO_2, and N_2O. The bubble traps were deployed in four water bodies in Missouri. Our study ponds represent a variety of land uses, including agriculture, urban, and woodland.

Methods

Study Ponds

Sampling was conducted at four small water bodies in mid Missouri over an eight-week study period. Catchment land uses include woodland area, urban (pervious), and agriculture (pasture) (Table 1). These sites were chosen based on lake depth, proximity to Columbia, Missouri, diversity in land use, and permit accessibility to use the site.

Bethel Lake is within an urban park where anglers, swans, geese, and ducks are often present. Carol's Pond and Jennifer's Pond are on rural private property in an area surrounded by hayfield/cow pasture. Jennifer's Pond also has an abandoned dock on the shore and deer tracks have been spotted here as well. Finger Lakes is in a forested conservation area where we have observed algal blooms several times throughout the study period. This lake is use for recreation and was reclaimed after strip mining operations ended.

Field Methods

We captured GHG emissions via ebullition with bubble traps. The bubble traps consist of two jugs, approximately 27 cm in diameter. Gas was withdrawal from the jugs through attached tubing with a syringe. The bubble traps were deployed in four water bodies in Missouri. Traps were anchored into sediments near the shoreline in the littoral zone, thus measurements were limited to shallower profiles. Upon installation at each study pond (August-October), we took a

water sample from the surface. Gas volumes from the bubble traps and EXO3-YSI profiles of the lake water columns were taken and recorded biweekly (approximately every two weeks) at each site. Temperature, pH, dissolved oxygen (DO), and conductivity were recorded from YSI profile. Water depth was recorded biweekly with either a YSI or a meter stick. Triplicate sediment samples and duplicate gas concentration samples were collected biweekly near shore using an Eckman dredge and inverted funnel, respectively.

Lab Methods

Water samples were analyzed for concentrations of total phosphorus (TP), total dissolved phosphorus (TDP), total nitrogen (TN), total dissolved nitrogen (TDN), ammonia (NH_4^+), nitrate (NO_3^-), sulfate (SO_4^{2-}), and dissolved organic carbon (DOC). TP and TDP concentrations were analyzed on a spectrophotometer, following Standard Methods 4500-P E. (Eaton et al., 1995). TN and TDN concentrations were analyzed on a spectrophotometer using a second derivative method after persulfate digestion (Crumpton et al., 1992). NH_4^+ concentrations were analyzed on Lachat Flow Injection Analyzer following Lachat's QuikChem Method 10-107-06-1-K (Diamond, 2001). NO_3^- concentrations were analyzed on a Lachat Flow Injection Analyzer following Lachat's QuikChem Method 10-107-04-1-C (Lachat Applications Group, 2008) SO_4^{2-} concentrations were analyzed on a Lachat Flow Injection Analyzer following Lachat QuikChem Method 10-116-10-2-A (Switala, 2003). DOC concentrations were analyzed on a Shimadzu Organic Carbon Analyzer following Standard Methods 5310 B (Eaton et al., 1995). Detection limits were 1 µg L^{-1} for TP and TDP, 60 µg L^{-1} for TN and TDN, 7 mg L^{-1} for SO_4^{2-}, 0.01 mg L^{-1} for NH_2, 0.05 mg L^{-1} for NO_3^-, and 0.2 mg L^{-1} for DOC.

Organic matter content was determined by doing a loss on ignition (LOI) analysis, which consists of air drying, grinding, 2mm sieving, oven drying (100°C for 12 hours), and combusting

(400°C for 16 hours) sediment samples. LOI estimates the organic fraction of the sample. Samples run through the muffle furnace were then used for particle size analysis. The particle size analysis was done using Horiba Partica LA-950 Laser Diffraction Particle Size Analyzer (Whitfield et al., 2011). The particle size analysis gives us the fraction of sand, silt, and clay in the sample, as well as mean particle size. The sizes categories are as follows: 0-2 µm clay, 2-63 µm silt, and 63-2000 µm sand.

Gas concentration samples were analyzed using the Scion 456-GC, a gas chromatography machine. This machine determines gas identity and concentration. The gas chromatograph consists of a thermal conductivity detector, a flame ionization detector, and a micro-electron detector. The thermal conductivity detector measures CO_2 concentrations, the flame ionization detector measures CH_4 concentrations, and the micro-electron detector measures N_2O concentrations. The exetainers containing gas concentration samples were not evacuated, so we adjusted gas concentration data to account for ambient air present in the exetainers. Concentrations present within exetainers were as follows: 1.85 mg L^{-1} CH_4, 407 mg L^{-1} CO_2, and 0.330 mg L^{-1} N_2O.

By combining gas volumes with gas concentrations, we can obtain a gas flux. We recorded gas volumes from each jug on each bubble trap. Dividing the volume per unit area by the period of gas accumulation gives us a jug rate, with units of mL/m^2/d. Multiplying gas concentrations by jug rates, we arrive at flux rates for individual GHGs. Units are converted from mL/m^2/d to µmol/m^2/d.

Statistical Methods

To achieve normal distribution of our data, we transformed variables to achieve a standard bell curve. For organic matter (%), temperature (°C), and pH, we transformed data additively [Value +3]. For average particle size (μm), conductivity (μS cm^{-1}), and dissolved oxygen (mg L^{-1}), we did a logarithmic transformation [Log (value)]. For CH$_4$ flux rates (μmol/m^2/d), N$_2$O flux rates (μmol/m^2/d), and CO$_2$ flux rates (μmol/m^2/d), we did a logarithmic and additive transformation [Log (value+1)]. The addition component within the logarithm was to retain our values of zero.

Using normally distributed data, we did a simple correlation to determine if there were positive or negative relationships between our variables of gas flux, water temperature, sediment organic matter content, average particle size, pH, conductivity, depth, and dissolved oxygen. We did a one-way ANOVA to determine if there was a significant difference between individual GHG flux rates. We also did one-way ANOVAs to determine if land use and sediment type were affecting GHG flux rates.

Results

Water Quality

Average water depth was highest at Finger Lakes, followed by Bethel Lake, Jennifer's Pond, and Carol's Pond (Table 1). All study ponds were oxygenated at the surface; however, Bethel had the lowest average DO concentration (7.635 mg L^{-1}). The other study ponds had average DO concentrations ranging from 9.46–10.58 mg L^{-1}, with Carol's Pond having the highest. Average conductivity was highest at Finger Lakes – the average conductivity at Finger Lakes is approximately 5 times higher than Bethel Lake, 7 times higher than Carol's Pond, and

23 times higher than Jennifer's Pond. All study ponds were slightly basic in pH. Highest average pH was recorded at Jennifer's Pond.

Based on TN and TP concentrations each study pond, trophic statuses are as follows: Bethel Lake-eutrophic, Carol's Pond-hypereutrophic, Finger Lakes-hypereutrophic, and Jennifer's Pond-eutrophic. Trophic statuses were based on TN concentrations and were determined using the trophic state criteria for Missouri reservoirs (Jones et al., 2008). NO_3^- and NH_2 concentrations were negligible at all study ponds (Table 1). Finger Lakes had the lowest average DOC concentration (4.9 mg/L). Average DOC concentrations at other study ponds ranged from 7–8.2 mg L^{-1}, with Carol's Pond having the highest average concentration. SO_4^{2-} was negligible at all study ponds except Finger Lakes, which had a concentration of 371.5 mg L^{-1}. TN was highest at Finger Lakes (6.2 mg L^{-1}), while other study ponds had much lower TN concentrations, ranging from 0.9–1.6 mg L^{-1}. TDN concentrations ranged from 0.51–0.84 mg L^{-1}, with Carol's Pond having the highest. Highest average TP concentration was recorded at Carol's Pond (158 μg L^{-1}), while other study ponds' average concentrations ranged from 18–78 μg L^{-1}, with Finger Lakes having the lowest. Highest average TDP concentration was also recorded at Carol's Pond (36 μg L^{-1}), while other study pond's average concentrations ranged from 7–17.5 μg L^{-1}, with Finger Lakes having the lowest (Table 1).

GHG Volume and Concentration

Highest volume was recorded at Carol's Pond, which also had the largest range for volume data (Table 2). However, Bethel Lake had the highest average volume for the entire study period. Without the outlier of 900 mL at Carol's Pond, Bethel Lake would have the highest recorded volume and largest volume range. Carol's Pond had the second highest average volume, followed by Finger Lakes and then Jennifer's Pond. N_2O concentrations ranged from 0.312–0.324 mg L^{-1},

with Jennifer's Pond having the highest average N_2O concentration. CO_2 concentrations ranged from 1,024.443–1,574.184 mg L^{-1}, with Carol's Pond having the highest average CO_2 concentration. CH_4 concentrations ranged from 3.967–12,745,970 mg L^{-1}, which was the largest range for gas concentrations. Carol's Pond had the highest average concentration of CH_4 (4810.869) (Table 2).

GHG Flux Rates

Highest average flux rates for N_2O were at Bethel Lake (Table 3). Flux rates for N_2O ranged from 0–7.542 µmol/m2/d. CO_2 flux rates ranged from 0–21,916.975 µmol/m2/d, with the highest average flux rate at Bethel Lake (Table 3). CH_4 had the highest average flux rate overall as well as the largest range (0–409,641.136 µmol/m2/d) (Table 3). Highest average CH_4 flux rate was at Carol's Pond (99,104.561 µmol/m2/d) (Table 3). N_2O flux rates were significantly different than CO_2 and CH_4 flux rates ($F_{2, 234} = 71.713$, $p < 0.0005$), as they were consistently lower than CO_2 and CH_4 flux rates (Figure 1). CH_4 and CO_2 flux rates were not significantly different ($p = 0.998$). GHG flux rates in the urban study pond are significantly different than those in the agricultural and wooded area study ponds (Table 4). Flux rates for all GHGs are higher in the urban study pond (Figure 2). The urban study pond's higher flux rates correlated with lower organic matter content ($F_{2, 72} = 127.777$, $p < 0.0005$). We did not find a relationship between GHG flux and sediment type (N_2O: $F_{1, 53} = 1.307$, $p = 0.258$; CO_2: $F_{1, 53} = 0.109$, $p = 0.743$; CH_4: $F_{1, 53} = 1.106$, $p = 0.298$). There was no relationship between GHG flux rates and water temperature, organic matter, conductivity, pH, average particle size, DO, nor water depth (Table 5).

Discussion:

CH_4 and CO_2 dominated the gas flux. Land use impacts GHG flux rates, which is correlated with low organic matter content. Our hypothesis was supported, as ebullition varied with land use. However, we did not see such variation with water quality characteristics nor sediment characteristics (sediment organic matter correlated indirectly, but not directly).

Is water quality affecting GHG flux rates?

Higher conductivity at Finger Lakes was due to higher concentrations of anions, specifically SO_4^{2-}, relative to other study ponds. Higher SO_4^{2-} concentrations are due to a history of strip mining for coal, which can contain inorganic and organic forms of sulfur (Calkins et al., 1992). N_2O had the highest recorded concentration at Carol's Pond, and the highest average concentration at Jennifer's Pond over the entire study period. Variability among concentrations was minimal. The overall lack of N_2O production in our study ponds can be attributed to negligible NO_3^- and NH_2 concentrations. Denitrification and nitrification produce N_2O (Baulch et al., 2011; Ji et al., and our study ponds showed low NO_3^- and NH_2 concentrations throughout, which explains the lack of N_2O production, thus resulting in low N_2O flux rates. High N_2O production has been found in nutrient enriched lakes (Huttunen et al., 2003), however, we did not find this in our dataset. Although most of our study ponds are eutrophic. N_2O production is low. Ebullition has been found to increase with increasing water temperatures (Aben et al., 2017; Marotta et al., 2014; Wik et al., 2014). However, we did not find this relationship significant in our dataset, which may be due to a truncated sample size (Temperature ranged from 18–6.4 °C).

CH_4 production has been found to occur more in shallow waters (Delsontro et al., 2011; Flury et al., 2015; Joyce & Jewell, 2003), which explains more CH_4 production in Carol's Pond

relative to other study ponds, as it had the shallowest depth. High CH_4 production has also been found to occur with higher water temperatures (Joyce & Jewell, 2003; Sepulveda-Jauregui et al., 2015; Walter et al., 2006). CH_4 flux rates appeared to increase with increasing water temperature, however, this was found to be insignificant. Trophic status affects CH_4 production, where nutrient rich waters have higher CH_4 production (Harrison et al., 2017; Sepulveda-Jauregui et al., 2015). We lacked a range of trophic status, so our study ponds could not test this assumption.

Low oxygen can promote N_2O production (Huttunen et al., 2003). Surface oxygen concentrations showed all our study ponds as oxygenated, so this could also explain the lack of N_2O. Oxygen concentrations in sediments influence CO_2 production, however, we did not look at redox conditions of the sediment.

Do sediment characteristics affect GHG flux?

High CH_4 production has been found to occur in lakes that have organic rich, anoxic sediments (Delsontro et al., 2011; Descloux et al., 2017; Harrison et al., 2017; Huttunen et al., 2003; Sepulveda-Jauregui et al., 2015). We did not see this in our dataset, as the relationship between organic matter and CH_4 flux rates, although insignificant, appeared to be an inverse relationship No data was collected on sediment redox conditions.

Does land use affect GHG flux?

GHG flux rates were higher at the urban study pond, which was correlated with low organic matter content. GHG flux and organic matter may be related, but we cannot determine with certainty. Studies have found that more organic matter results in more ebullitive flux (Delsontro et al., 2011; Descloux et al., 2017; Harrison et al., 2017; Huttunen et al., 2003;

Sepulveda-Jauregui et al., 2015; West et al., 2016). We did not see this relationship hold in our dataset.

Conclusion

Land use is an important influence on GHG flux. With urbanization occurring globally, we may have to consider its consequences for the global GHG budget. GHGs do not occur equally, so we must interpret their flux with respect to their individual influencers. Gaining an understanding of GHG ebullition from aquatic ecosystems will reveal their significance for the global GHG budget and assist in land management and forecasting the future of the global GHG budget.

Acknowledgements

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Table 1: Characteristics of study sites in Missouri. Watershed delineation done with ESRI ArcGIS 10.3.1. Values shown are averages for each study pond.

Parameter	Bethel Lake	Carol's Pond	Finger Lakes	Jennifer's Pond
Category	Urban Pervious	Ag Pasture	Woodland	Ag Pasture
GPS	38.9031808, – 92.344332	39.1893805, – 92.2920539	39.07526, – 92.3157444	39.138204, – 92.27907
Max Depth (m)	1.25	0.81	1.30	0.96
DO (mg/L)	7.635	10.58	9.46	10.01
Conductivity ($\mu S\ cm^{-1}$)	250.85	338.65	1882.5	79.4
pH	7.92	7.585	7.42	8.22
DOC ($mg\ L^{-1}$)	7	8.6	4.9	8.2
SO_4^{2-} ($mg\ L^{-1}$)	<7	<7	371.5	<7
TN ($mg\ L^{-1}$)	0.9	1.6	6.2	1.0
TDN ($mg\ L^{-1}$)	0.7	0.84	0.51	0.71
NO_3^- ($mg\ L^{-1}$)	<0.05	<0.05	<0.05	<0.05
NH_2 ($mg\ L^{-1}$)	<0.01	<0.01	<0.01	<0.01
TP ($\mu g\ L^{-1}$)	28	158	18	78
TDP ($\mu g\ L^{-1}$)	12	36	7	17.5
Trophic Status	Eutrophic	Eutrophic	Hypereutrophic	Eutrophic
Sand (%)	54	47	78	57
Silt (%)	44	43	18	39
Clay (%)	2	10	4	4
Organic Matter (%)	4.578	11.585	11.243	9.184
Particle Size (μm)	48.21	47.03	19.29	62.76

Table 2: Averages and ranges of gas volumes and gas concentrations by study pond. Columns show averages and ranges; ranges are shown in parentheses.

Study Pond	Volume (mL)	N_2O Concentrations (mg L^{-1})	CO_2 Concentrations (mg L^{-1})	CH_4 Concentrations (mg L^{-1})
Bethel Lake	201	0.319	1,234.578	2616.190
	(0–512)	(0.315–0.324)	(1,066.087–1397.383)	(31.239–8,528.521)
Carol's Pond	176	0.316	1276.891	4810.869
	(1–900)	(0.312–0.324)	(1,083.235–1574.184)	(3967–12,745.970)
Finger Lakes	23	0.319	1,259.198	432.143
	(0–116)	(0.315–0.322)	(1,257.487–1,262.620)	(1,288.080–1,284.697)
Jennifer's Pond	12	0.320	1,130.918	1,319.793
	(0–72)	(0.315–0.327)	(1,024.443–1,320.589)	(14.912–5,115.397)

Table 3: Averages and ranges of flux rates for N_2O, CO_2, and CH_4 by study pond. Columns show averages and ranges; ranges are shown in parentheses.

Study Pond	N_2O Flux ($\mu mol/m^2/d$)	CO_2 Flux ($\mu mol/m^2/d$)	CH_4 Flux ($\mu mol/m^2/d$)
Bethel Lake	2.030 (0–4.839)	5,437.075 (0–12,549.860)	38,936.122 (0–177,028.667)
Carol's Pond	1.166 (0.006–7.542)	4,660.793 (13.918–21,916.975)	99,104.561 (0.212–409,641.136)
Finger Lakes	0.205 (0–0.985)	552.090 (0–2,781.697)	1,165.654 (0–10,800.3410)
Jennifer's Pond	0.118 (0–0.713)	287.363 (0–2,503.641)	219.781 (0–2,503.641)

Table 4: One-way ANOVA and Tukey-Kramer post hoc comparisons for the effect of land use on GHG flux rates. Post hoc test were conducted if ANOVA factors were identified as significant (p<0.05). The letters for the post hoc comparison indicate statistical significance (p<0.05); the relationship between identical letters is not statistically significant, whereas the relationship between different letters is significant.

Gas	Land Use	Post hoc test		
		Agriculture	Urban	Woodland
N_2O	$F_{2,\,52}$=81.234, p<0.0005	a	b	a
CO_2	$F_{2,\,52}$=18.780, p<0.0005	a	b	a
CH_4	$F_{2,\,52}$=35.964, p<0.0005	a	b	a

Table 5: Correlation matrix for the parameters measured for their effects on N_2O, CO_2, and CH_4 flux rates.

	N_2O (n = 21)	CO_2 (n = 21)	CH_4 (n = 21)
Water temperature	p = 1, r = - 0.230	p = 1, r = - 0.297	p = 1, r = - 0.246
Organic Matter	p = 1, r = 0.169	p = 1, r = 0.326	p = 1, r = -0.187
Conductivity	p = 1, r = 0.199	p = 1, r = 0.386	p = 1, r = - 0.127
pH	p = 1, r = - 0.138	p = 1, r = - 0.141	p = 1, r = 0.321
Average Particle Size	p = 1, r = - 0.209	p = 1, r = - 0.274	p = 1, r = 0.278
Dissolved Oxygen	p = 1, r = - 0.240	p =1, r = 0.145	p = 1, r = 0.183
Depth	p = 1, r = - 0.319	p = 1, r = - 0.160	p = 1, r = - 0.064

Figure 1: Flux rates of individual GHGs. The letters indicate statistical significance (p<0.05); the relationship between identical letters is not statistically significant, whereas the relationship between different letters is significant. Y- axis is on a log scale.
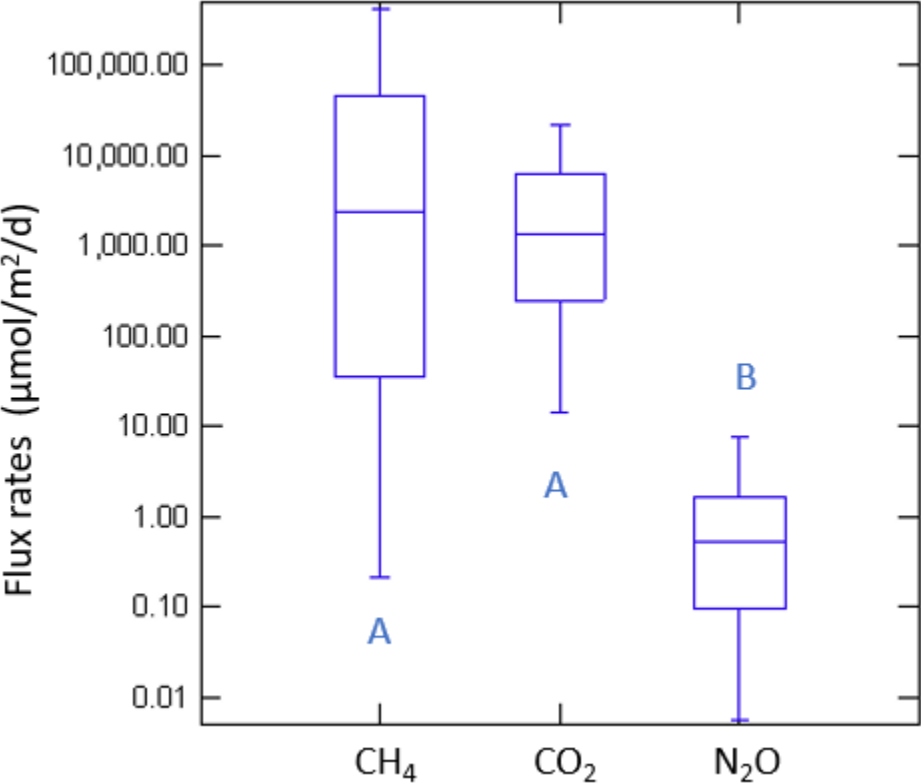
Figure 2: Flux rates of individual GHGs against land use. The letters indicate statistical significance ($p<0.05$); the relationship between identical letters is not statistically significant, whereas the relationship between different letters is significant. Y- axis is on a log scale.