

**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<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), and nitrous oxide (N<sub>2</sub>O), including sediment characteristics, water quality characteristics, and land use. Our study ponds are in urban, agricultural, and woodland areas. We found that N<sub>2</sub>O flux rates are significantly lower than CH<sub>4</sub> and CO<sub>2</sub> 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<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), and nitrous oxide (N<sub>2</sub>O) 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. Delsonetro 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<sub>4</sub>, N<sub>2</sub>O, and CO<sub>2</sub>. 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<sub>4</sub> 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<sub>2</sub> (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<sub>2</sub> freshwater emissions have been estimated to be equivalent

to 0.4–4% of anthropogenic CO<sub>2</sub> emissions (Descloux et al., 2017; Huttunen et al., 2003). CH<sub>4</sub> freshwater emissions have been estimated to be equivalent to 5–18% of anthropogenic CH<sub>4</sub> emissions and 10–15% of natural CH<sub>4</sub> emissions (Delsontro et al., 2011; Descloux et al., 2017; Huttunen et al., 2003). N<sub>2</sub>O freshwater emissions are negligible compared to anthropogenic N<sub>2</sub>O emissions (Descloux et al., 2017). Ebullition alone accounts for 1% of freshwater CO<sub>2</sub> emissions, 20–67% of freshwater CH<sub>4</sub> emissions, and <0.1% of freshwater N<sub>2</sub>O emissions (Baulch et al., 2011).

CO<sub>2</sub> is a GHG produced in aquatic systems by aerobic respiration, denitrification, and acetate fermentation (Baulch et al., 2011). CO<sub>2</sub>'s global warming potential (GWP) is 1, and other GHG GWP's are measure relative to CO<sub>2</sub> (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<sub>4</sub> is a GHG with a GWP 25 times that of CO<sub>2</sub> (EPA, 2010). CH<sub>4</sub> in water bodies is produced by acetate fermentation or H<sub>2</sub> dependent methanogenesis (Baulch et al., 2011). When CH<sub>4</sub> is produced in water bodies, it is either oxidized to CO<sub>2</sub>, or it escapes into the atmosphere. Methanotrophic bacteria in the water column successfully oxidize the majority of CH<sub>4</sub> 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<sub>4</sub> dissolved from rising bubbles is dependent on lake depth, water temperature, CH<sub>4</sub> concentration in the water, and the initial size of the bubble (Delsontro et al., 2011). CH<sub>4</sub> has a low solubility, which makes ebullition a more likely pathway (Crawford et al., 2014). Estimates on CH<sub>4</sub> 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<sub>4</sub> released from sediments is of a

larger magnitude than CH<sub>4</sub> released from deep lakes (West et al., 2016). This is due to CH<sub>4</sub> bubbles dissolving as they rise to the top of the water column. A review of previous studies on CH<sub>4</sub> emissions found that nearly all recorded concentrations of CH<sub>4</sub> were super saturated with relation to the atmospheric equilibrium and that the general effect of anthropogenic change to fluvial systems results in CH<sub>4</sub> enrichment (Stanley et al., 2016).

N<sub>2</sub>O 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<sub>2</sub> (EPA, 2018). N<sub>2</sub>O in aquatic systems has received much study based on the assumption that agriculture and sewage inputs of nitrogen would lead to large N<sub>2</sub>O emissions from water bodies (Baulch et al., 2011). Research has shown that CH<sub>4</sub> fluxes typically exceed N<sub>2</sub>O fluxes (Baulch et al., 2011), which suggest a better understanding of CH<sub>4</sub> 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<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O. 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 used 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 withdrawn 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 ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), sulfate ( $\text{SO}_4^{2-}$ ), 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).  $\text{NH}_4^+$  concentrations were analyzed on Lachat Flow Injection Analyzer following Lachat's QuikChem Method 10-107-06-1-K (Diamond, 2001).  $\text{NO}_3^-$  concentrations were analyzed on a Lachat Flow Injection Analyzer following Lachat's QuikChem Method 10-107-04-1-C (Lachat Applications Group, 2008)  $\text{SO}_4^{2-}$  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  $1 \mu\text{g L}^{-1}$  for TP and TDP,  $60 \mu\text{g L}^{-1}$  for TN and TDN,  $7 \text{mg L}^{-1}$  for  $\text{SO}_4^{2-}$ ,  $0.01 \text{mg L}^{-1}$  for  $\text{NH}_2$ ,  $0.05 \text{mg L}^{-1}$  for  $\text{NO}_3^-$ , and  $0.2 \text{mg L}^{-1}$  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 ( $100^\circ\text{C}$  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  $\mu\text{m}$  clay, 2-63  $\mu\text{m}$  silt, and 63-2000  $\mu\text{m}$  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  $\text{CO}_2$  concentrations, the flame ionization detector measures  $\text{CH}_4$  concentrations, and the micro-electron detector measures  $\text{N}_2\text{O}$  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  $\text{mg L}^{-1}$   $\text{CH}_4$ , 407  $\text{mg L}^{-1}$   $\text{CO}_2$ , and 0.330  $\text{mg L}^{-1}$   $\text{N}_2\text{O}$ .

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  $\text{mL/m}^2/\text{d}$ . Multiplying gas concentrations by jug rates, we arrive at flux rates for individual GHGs. Units are converted from  $\text{mL/m}^2/\text{d}$  to  $\mu\text{mol/m}^2/\text{d}$ .

### *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 ( $\mu\text{m}$ ), conductivity ( $\mu\text{S cm}^{-1}$ ), and dissolved oxygen ( $\text{mg L}^{-1}$ ), we did a logarithmic transformation [ $\text{Log}(\text{value})$ ]. For  $\text{CH}_4$  flux rates ( $\mu\text{mol/m}^2/\text{d}$ ),  $\text{N}_2\text{O}$  flux rates ( $\mu\text{mol/m}^2/\text{d}$ ), and  $\text{CO}_2$  flux rates ( $\mu\text{mol/m}^2/\text{d}$ ), we did a logarithmic and additive transformation [ $\text{Log}(\text{value}+1)$ ]. 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 ( $7.635 \text{ mg L}^{-1}$ ). The other study ponds had average DO concentrations ranging from  $9.46\text{--}10.58 \text{ mg L}^{-1}$ , 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).  $\text{NO}_3^-$  and  $\text{NH}_2$  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<sup>-1</sup>, with Carol's Pond having the highest average concentration.  $\text{SO}_4^{2-}$  was negligible at all study ponds except Finger Lakes, which had a concentration of 371.5 mg L<sup>-1</sup>. TN was highest at Finger Lakes (6.2 mg L<sup>-1</sup>), while other study ponds had much lower TN concentrations, ranging from 0.9–1.6 mg L<sup>-1</sup>. TDN concentrations ranged from 0.51–0.84 mg L<sup>-1</sup>, with Carol's Pond having the highest. Highest average TP concentration was recorded at Carol's Pond (158 µg L<sup>-1</sup>), while other study ponds' average concentrations ranged from 18–78 µg L<sup>-1</sup>, with Finger Lakes having the lowest. Highest average TDP concentration was also recorded at Carol's Pond (36 µg L<sup>-1</sup>), while other study pond's average concentrations ranged from 7–17.5 µg L<sup>-1</sup>, 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.  $\text{N}_2\text{O}$  concentrations ranged from 0.312–0.324 mg L<sup>-1</sup>,

with Jennifer's Pond having the highest average N<sub>2</sub>O concentration. CO<sub>2</sub> concentrations ranged from 1,024.443–1,574.184 mg L<sup>-1</sup>, with Carol's Pond having the highest average CO<sub>2</sub> concentration. CH<sub>4</sub> concentrations ranged from 3.967–12,745,970 mg L<sup>-1</sup>, which was the largest range for gas concentrations. Carol's Pond had the highest average concentration of CH<sub>4</sub> (4810.869) (Table 2).

### *GHG Flux Rates*

Highest average flux rates for N<sub>2</sub>O were at Bethel Lake (Table 3). Flux rates for N<sub>2</sub>O ranged from 0–7.542 μmol/m<sup>2</sup>/d. CO<sub>2</sub> flux rates ranged from 0–21,916.975 μmol/m<sup>2</sup>/d, with the highest average flux rate at Bethel Lake (Table 3). CH<sub>4</sub> had the highest average flux rate overall as well as the largest range (0–409,641.136 μmol/m<sup>2</sup>/d) (Table 3). Highest average CH<sub>4</sub> flux rate was at Carol's Pond (99,104.561 μmol/m<sup>2</sup>/d) (Table 3). N<sub>2</sub>O flux rates were significantly different than CO<sub>2</sub> and CH<sub>4</sub> flux rates ( $F_{2, 234} = 71.713$ ,  $p < 0.0005$ ), as they were consistently lower than CO<sub>2</sub> and CH<sub>4</sub> flux rates (Figure 1). CH<sub>4</sub> and CO<sub>2</sub> 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<sub>2</sub>O:  $F_{1, 53} = 1.307$ ,  $p = 0.258$ ; CO<sub>2</sub>:  $F_{1, 53} = 0.109$ ,  $p = 0.743$ ; CH<sub>4</sub>:  $F_{1, 53} = 1.106$ ,  $p = 0.298$ ). 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<sub>4</sub> and CO<sub>2</sub> 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<sub>4</sub><sup>2-</sup>, relative to other study ponds. Higher SO<sub>4</sub><sup>2-</sup> 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<sub>2</sub>O 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<sub>2</sub>O production in our study ponds can be attributed to negligible NO<sub>3</sub><sup>-</sup> and NH<sub>2</sub> concentrations. Denitrification and nitrification produce N<sub>2</sub>O (Baulch et al., 2011; Ji et al., and our study ponds showed low NO<sub>3</sub><sup>-</sup> and NH<sub>2</sub> concentrations throughout, which explains the lack of N<sub>2</sub>O production, thus resulting in low N<sub>2</sub>O flux rates. High N<sub>2</sub>O 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<sub>2</sub>O 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<sub>4</sub> 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<sub>4</sub> production in Carol's Pond

relative to other study ponds, as it had the shallowest depth. High CH<sub>4</sub> production has also been found to occur with higher water temperatures (Joyce & Jewell, 2003; Sepulveda-Jauregui et al., 2015; Walter et al., 2006). CH<sub>4</sub> flux rates appeared to increase with increasing water temperature, however, this was found to be insignificant. Trophic status affects CH<sub>4</sub> production, where nutrient rich waters have higher CH<sub>4</sub> 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<sub>2</sub>O production (Huttunen et al., 2003). Surface oxygen concentrations showed all our study ponds as oxygenated, so this could also explain the lack of N<sub>2</sub>O. Oxygen concentrations in sediments influence CO<sub>2</sub> production, however, we did not look at redox conditions of the sediment.

#### *Do sediment characteristics affect GHG flux?*

High CH<sub>4</sub> 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<sub>4</sub> 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**

I would like to thank the McNair Scholars Program, University of Missouri Limnology Lab staff Dan Obrecht, Carol Pollard, and Tony Thorpe, students Meaghan Pearson, Erin Petty, Matt Sauer, and Kyle Carson, Jennifer Pollard and Trent University for all their assistance in making this project possible.

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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.

<b>Parameter</b>	<b>Bethel Lake</b>	<b>Carol's Pond</b>	<b>Finger Lakes</b>	<b>Jennifer's Pond</b>
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 ( $\mu\text{S cm}^{-1}$ )	250.85	338.65	1882.5	79.4
pH	7.92	7.585	7.42	8.22
DOC ( $\text{mg L}^{-1}$ )	7	8.6	4.9	8.2
$\text{SO}_4^{2-}$ ( $\text{mg L}^{-1}$ )	<7	<7	371.5	<7
TN ( $\text{mg L}^{-1}$ )	0.9	1.6	6.2	1.0
TDN ( $\text{mg L}^{-1}$ )	0.7	0.84	0.51	0.71
$\text{NO}_3^-$ ( $\text{mg L}^{-1}$ )	<0.05	<0.05	<0.05	<0.05
$\text{NH}_2$ ( $\text{mg L}^{-1}$ )	<0.01	<0.01	<0.01	<0.01
TP ( $\mu\text{g L}^{-1}$ )	28	158	18	78
TDP ( $\mu\text{g L}^{-1}$ )	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 ( $\mu\text{m}$ )	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.

<b>Study Pond</b>	<b>Volume (mL)</b>	<b>N<sub>2</sub>O Concentrations (mg L<sup>-1</sup>)</b>	<b>CO<sub>2</sub> Concentrations (mg L<sup>-1</sup>)</b>	<b>CH<sub>4</sub> Concentrations (mg L<sup>-1</sup>)</b>
Bethel Lake	201 (0–512)	0.319 (0.315–0.324)	1,234.578 (1,066.087–1397.383)	2616.190 (31.239–8,528.521)
Carol’s Pond	176 (1–900)	0.316 (0.312–0.324)	1276.891 (1,083.235–1574.184)	4810.869 (3967–12,745.970)
Finger Lakes	23 (0–116)	0.319 (0.315–0.322)	1,259.198 (1,257.487–1,262.620)	432.143 (1,288.080–1,284.697)
Jennifer’s Pond	12 (0–72)	0.320 (0.315–0.327)	1,130.918 (1,024.443–1,320.589)	1,319.793 (14.912–5,115.397)

**Table 3:** Averages and ranges of flux rates for N<sub>2</sub>O, CO<sub>2</sub>, and CH<sub>4</sub> by study pond. Columns show averages and ranges; ranges are shown in parentheses.

<b>Study Pond</b>	<b>N<sub>2</sub>O Flux (<math>\mu\text{mol}/\text{m}^2/\text{d}</math>)</b>	<b>CO<sub>2</sub> Flux (<math>\mu\text{mol}/\text{m}^2/\text{d}</math>)</b>	<b>CH<sub>4</sub> Flux (<math>\mu\text{mol}/\text{m}^2/\text{d}</math>)</b>
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.

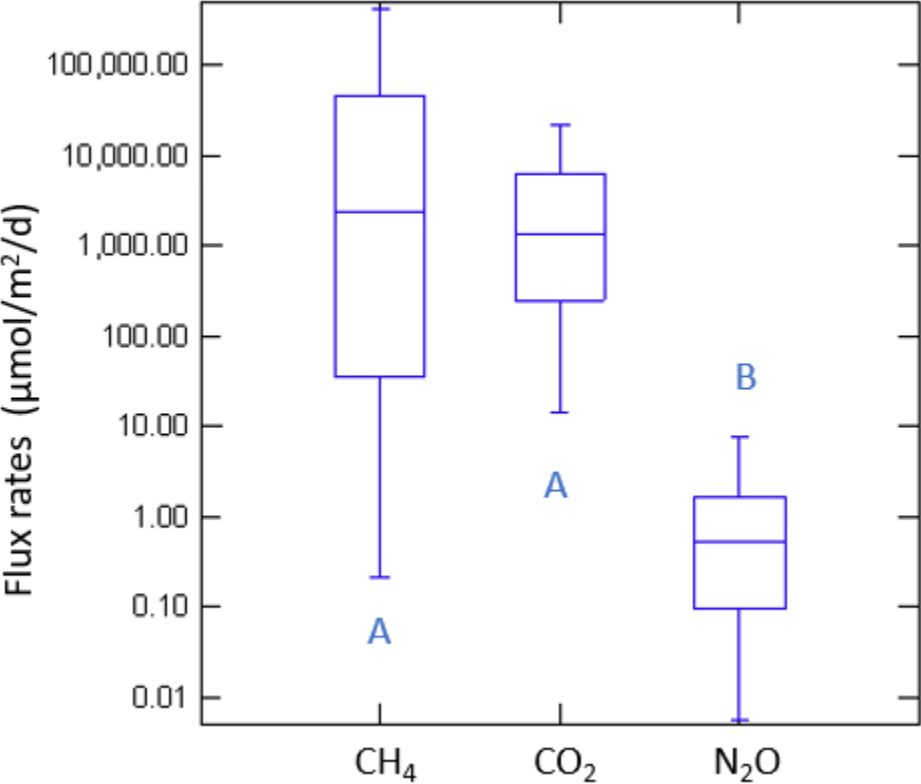
Gas	Land Use	Post hoc test		
		Agriculture	Urban	Woodland
N <sub>2</sub> O	F <sub>2, 52</sub> =81.234, p<0.0005	a	b	a
CO <sub>2</sub>	F <sub>2, 52</sub> =18.780, p<0.0005	a	b	a
CH <sub>4</sub>	F <sub>2, 52</sub> =35.964, p<0.0005	a	b	a



**Table 5:** Correlation matrix for the parameters measured for their effects on N<sub>2</sub>O, CO<sub>2</sub>, and CH<sub>4</sub> flux rates.

	<b>N<sub>2</sub>O (n = 21)</b>	<b>CO<sub>2</sub> (n = 21)</b>	<b>CH<sub>4</sub> (n = 21)</b>
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.

