



Differences in ebullitive methane release from small, shallow ponds present challenges for scaling



A.A.P. Baron^{a,b}, L.T. Dyck^{a,b}, H. Amjad^c, J. Bragg^d, E. Kroft^c, J. Newson^d, K. Oleson^c, N.J. Casson^c, R.L. North^d, J.J. Venkiteswaran^e, C.J. Whitfield^{a,b,*}

^a School of Environment and Sustainability, University of Saskatchewan, Saskatoon, SK S7N 3H5, Canada

^b Global Institute for Water Security, University of Saskatchewan, Saskatoon, SK S7N 3H5, Canada

^c Department of Geography, University of Winnipeg, Winnipeg, MB R3B 2E9, Canada

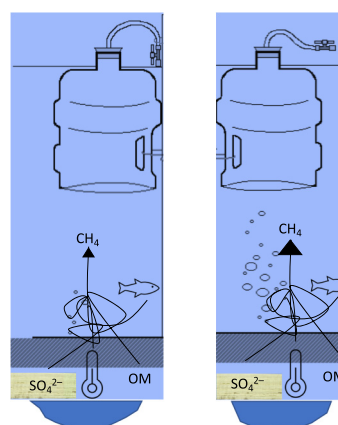
^d School of Natural Resources, University of Missouri, Columbia, MO 65211, United States of America

^e Department of Geography and Environmental Studies, Wilfrid Laurier University, Waterloo, ON N2L 3C5, Canada

HIGHLIGHTS

- Great Plains shallow pond ebullitive CH₄ release varied by four orders of magnitude.
- Warm season CH₄ release reached 40 mmol m⁻² d⁻¹, higher than previously reported.
- CH₄ release at 15 sites across three regions was only weakly linked to temperature.
- Site-specific factors (e.g. SO₄²⁻ or pond management) appear to suppress CH₄ release.
- Caution is needed in efforts to scale these emissions according to temperature.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 March 2021

Received in revised form 16 July 2021

Accepted 11 August 2021

Available online 14 August 2021

Editor: Wei Shi

Keywords:

Ebullition
Greenhouse gas
Organic matter
Shallow water
Sulphate
Temperature

ABSTRACT

Small, shallow waterbodies are potentially important sites of greenhouse gas release to the atmosphere. The role of ebullition may be enhanced here relative to larger and deeper systems, due to their shallow water, but these features remain relatively infrequently studied in comparison to larger systems. Herein, we quantify ebullitive release of methane (CH₄) in small shallow ponds in three regions of North America and investigate the role of potential drivers. Shallow ponds exhibited open-water season ebullitive CH₄ release rates as high as 40 mmol m⁻² d⁻¹, higher than previously reported for similar systems. Ebullitive release of CH₄ varied by four orders of magnitude across our 15 study sites, with differences in flux rates both within and between regions. What is less clear are the drivers responsible for these differences. There were few relationships between open water-season ebullitive flux and physicochemical characteristics, including organic matter, temperature, and sulphate. Temperature was only weakly related to ebullitive CH₄ release across the study when considering all observation intervals. Only four individual sites exhibited significant relationships between temperature and ebullitive CH₄ release. Other sites were unresponsive to temperature, and region-specific factors may play a role. There is some evidence that where surface water sulphate concentrations are high, CH₄ production and release may be suppressed. Missouri sites ($n = 5$) had characteristically low ebullitive CH₄ release; here bioturbation could be important. While this work greatly expands the number of open-water season ebullition rates for small and

* Corresponding author at: School of Environment and Sustainability, University of Saskatchewan, Saskatoon, SK S7N 3H5, Canada.
E-mail address: colin.whitfield@usask.ca (C.J. Whitfield).

shallow ponds, more research is needed to disentangle the role of different drivers. Further investigation of the potential thresholding behaviour of sulphate as a control on ebullitive CH₄ release in lentic systems is one such opportunity. What is clear, however, is that efforts to scale emissions (e.g., as a function of temperature) must be undertaken with caution.

© 2021 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Inland freshwater ecosystems are an active component of the global carbon (C) cycle and are receiving sites for C of both allochthonous and autochthonous origin. Consequently, a variety of freshwater systems are often considered C sinks in terms of potential for C sequestration via sediment deposition and plant biomass (e.g. Bridgman et al., 2006). Lakes, reservoirs and wetlands, however, are also known as sources of biogenic greenhouse gas (GHG) release to the atmosphere, including methane (CH₄), carbon dioxide (CO₂), and nitrous oxide (N₂O) (Bastviken et al., 2004; Cole et al., 2007; Tranvik et al., 2009; Baulch et al., 2011; Tranvik et al., 2018). Considerable effort has been made to derive estimates of the annual release of different GHG from water bodies at large scales, including CO₂, CH₄ and N₂O from reservoirs (Deemer et al., 2016), CO₂ from inland waters (Raymond et al., 2013), CH₄ from wetlands (Bridgman et al., 2006; Denman et al., 2007), CH₄ from streams and rivers (Stanley et al., 2016), CH₄ from beaver ponds (Whitfield et al., 2015), and CO₂ and CH₄ from small ponds (Holgerson and Raymond, 2016). One of the challenges in all such efforts is devising meaningful ways to address the inherent variability in GHG emissions from the water body type investigated. Although not always quantified, uncertainty in estimates is large, often exceeding 100% (e.g., Bastviken et al., 2011; Bridgman et al., 2006).

In the case of CH₄, where both lotic (Stanley et al., 2016) and lentic (Bastviken et al., 2011; Whitfield et al., 2011) water bodies are predominantly supersaturated, there are added challenges. Release of CH₄ to the atmosphere from lentic water bodies is known to occur via diffusion from the water column, plant-mediated transport (e.g., aquatic-atmosphere exchange of gas through plant aerenchyma), and ebullition (bubble-mediated transport). The presence and density of aquatic vegetation (Oliveira Junior et al., 2020) along with water depth, organic matter loading, availability of labile organic matter, and seasonal fluctuations in water and sediment temperature (Chanton, 2005) can determine the relative importance of CH₄ emission pathways.

In shallow water with organic-rich sediments and high CH₄ production rates, CH₄ emissions are often dominated by ebullition (Weyhenmeyer, 1999; Joyce and Jewell, 2003; Venkiteswaran et al., 2013). There is a growing body of literature reporting the timing and quantity of bubble release, as well as their drivers, including sediment temperature and particle size, and changes in hydrostatic pressure of the overlying water column, and nutrients (Weyhenmeyer, 1999; DelSontro et al., 2010; Bartosiewicz et al., 2015; DelSontro et al., 2016; Aben et al., 2017; Beaulieu et al., 2019). Similarly, the amount of sulphate (SO₄²⁻) available for reduction can also be an important determinant of methanogenesis rates (Watson and Nedwell, 1998). Among these drivers, temperature has perhaps received the most focus, and has been identified as an important driver of wetland CH₄ release (Knox et al., 2021). Methane production and bubble formation in sediments, and release to overlying water have all been shown to be temperature dependent (DelSontro et al., 2016).

Identifying patterns, predictors, and rates of ebullition in small water bodies nonetheless remains difficult due to high spatial and temporal variability of the underlying processes, both within and among water bodies. Investigations of ebullition require considerably more effort than sampling for dissolved CH₄ concentrations, and despite the importance of ebullition as an emission pathway, dissolved CH₄ data are often used to derive some of the aforementioned flux estimates, without explicitly quantifying the potential importance of ebullitive

CH₄ release in small and/or shallow water bodies. This points to a need for data collection and improved understanding of the rates of CH₄ release via ebullition in these systems as well as investigation of the potential physicochemical drivers of this release pathway.

This study investigates CH₄ release via ebullition across surface water in shallow ponds in three regions in Canada and the United States. Our focus is on ponds as they have been identified as distinct from wetlands (Holgerson and Raymond, 2016), and the surface area of these small systems is important globally (Downing et al., 2006), but ebullition for these systems is rarely quantified. We quantified shallow water ebullitive CH₄ release rates during two open-water seasons (2017 and 2018) and explored patterns of across site variability. We hypothesized that temperature would be an important driver of emissions at individual sites, and investigated ebullition patterns across a gradient of SO₄²⁻ concentrations and organic matter (OM) content. This work provides a foundation to better quantify ebullition rates and associated GHG fluxes from shallow ponds in these regions, where seasonal to annual records documenting the role of ebullition in water-atmosphere CH₄ exchange are sparse. Moreover, by looking across regions, we can build on the foundation of work that identifies key drivers like temperature within a site or region, and better understand how or why some systems behave differently.

2. Methods

2.1. Study sites

Study ponds were chosen on the basis of having predominantly natural or semi-natural surrounding landcover (e.g., urban park, semi-natural prairie, conservation area; Table 1) and landowner permission. Between 2017 and 2018, 15 shallow freshwater ponds were sampled in three locations in Saskatchewan (SK) and Manitoba (MB), Canada and Missouri (MO), USA (Table 1). In SK, three semi-permanent ponds in a semi-arid prairie pothole region in the City of Saskatoon were investigated. One of the SK ponds was located within a conservation area and nearby (~150 m) a residential neighbourhood. Another site in SK is situated upslope of, and adjacent to, the South Saskatchewan River with cropped fields and parkland forming the contributing area. The third SK pond is surrounded by cropped fields at the site of a former livestock husbandry research facility. In MB, seven permanent ponds with shoreline dominated by *Typha* spp. and underlain by clayey glaciolacustrine deposits were located within two conservation areas, one located in the City of Winnipeg (5 ponds), and another 20 km north of Winnipeg near Stonewall, MB (2 ponds). In MO, five sites situated in the Ozark border ecoregion around the city of Columbia, were selected. Two MO sites are small ponds situated on private pastureland, one is in a prairie conservation area, one is within a woodland conservation area that is a reclaimed coal mine, and the other is largely surrounded by an urban park.

Saskatchewan and MB sites are situated in close proximity to the northern (SK) and eastern (MB) edges of the (Canadian) Prairies ecoregion with cold semi-arid (SK) and humid continental (MB) climates. Mean annual air temperature for these regions is 3.3 and 3.0 °C, respectively. The MO sites are located in a climate region characterised as humid continental but with a mean annual air temperature of 12.9 °C (Table 1). Ice-free open-water periods are typically limited to May–October in SK and MB, whereas MO water bodies may only experience intermittent ice cover in December and January of some years.

Table 1
Study site IDs, region (Canadian province or US state), geographic coordinates, land-use surrounding the ponds, dates of sampling, and mean annual air temperatures.

Site	Region	Latitude	Longitude	Land-use	Sampling dates	Air temperature (°C)
MB1	MB	49.82	-97.22	Woodland conservation	2017-08-24–2017-10-30, 2018-05-23–2018-10-10	3.0
MB2	MB	49.82	-97.22	Woodland conservation	2017-08-24–2017-10-30, 2018-05-23–2018-10-10	3.0
MB3	MB	49.82	-97.22	Woodland conservation	2017-08-24–2017-10-30, 2018-05-23–2018-10-10	3.0
MB4	MB	49.82	-97.22	Woodland conservation	2017-08-24–2017-10-30, 2018-05-23–2018-10-10	3.0
MB5	MB	49.82	-97.22	Woodland conservation	2017-08-24–2017-10-30, 2018-05-23–2018-10-10	3.0
MB6	MB	50.18	-97.13	Semi-natural prairie	2018-06-11–2018-10-09	3.0
MB7	MB	50.18	-97.13	Semi-natural prairie	2018-06-11–2018-10-09	3.0
MO1	MO	38.90	-92.34	Urban park	2017-08-27–2017-11-22, 2018-06-08–2018-10-26	12.9
MO2	MO	39.19	-92.29	Pasture	2017-09-17–2017-12-02	12.9
MO3	MO	39.08	-92.32	Woodland conservation	2017-09-30–2017-12-14	12.9
MO4	MO	39.14	-92.28	Pasture	2017-10-07–2017-12-02	12.9
MO5	MO	38.89	-91.74	Prairie conservation	2018-06-15–2018-11-13	12.9
SK3	SK	52.18	-106.56	Prairie conservation, residential	2017-08-14–2017-11-04, 2018-05-07–2018-10-15	3.3
SK4	SK	52.17	-106.62	Agricultural	2017-08-14–2017-11-04, 2018-05-07–2018-10-15	3.3
SK5	SK	52.12	-106.67	Urban park, agricultural	2017-08-15–2017-10-30, 2018-05-24–2018-10-15	3.3

2.2. Field sampling

At each site, 2–4 bubble traps featuring a pair of collection chambers (Matthews et al., 2005; Baulch et al., 2011; Venkiteswaran et al., 2013) were deployed in the shallow (< 1.2 m) water margins of each pond during the 2017 and/or 2018 open-water seasons. Traps were used to quantify ebullitive fluxes of greenhouse gases and were distributed within each pond to capture spatial variability. Each bubble trap contained two open-bottomed chambers (e.g., water cooler jugs with ~0.26 m average diameter) attached to a steel stake. A rubber stopper was inserted into the top end of each jug, providing an airtight seal. Sampling was generally limited to the ice-free months (~May–October) in Canada, while this was not a limitation at MO sites. Wildlife disturbance to the traps was common at some sites, and where fewer than four observations were available for a single year, the data were excluded from the analyses. Seven of 15 sites included in this analysis (Table 1), had data available for both years.

Gas volumes accumulated between sampling intervals (~2–3 weeks) were measured by drawing air from the bubble traps with a 60 mL syringe. This process was repeated until all gas was expelled from the chamber (water appeared at the top of the stopper), and total volume was recorded. For large volumes, an inverted water-filled graduated cylinder was used to determine the air volume via displacement (Baulch et al., 2011). When necessary, due to fluctuations in water level, traps were repositioned nearby and reset.

Greenhouse gas concentrations in fresh bubbles accumulating in the sediments were collected by manually disturbing sediments (i.e., forced ebullition) while moving along a transect (typically three transects at each site per site visit). Gases were collected with an inverted funnel attached to the body of a 60 mL syringe sealed with a Luer lock. Short transects of a few meters were often sufficient for gas collection, although longer transects were required in areas with low ebullition rates. Where sufficient gas volume for analysis was not collected after 10 min, sample collection was terminated. Methane concentrations of gas collected using these methods is not statistically different from gas collected in chambers near the surface of the water (Helmle, 2019). Collected gas samples were immediately transferred to Exetainer® vials (6 or 12 mL). In 2017, Exetainers were unevacuated, and following revision to our analytical method that facilitated analysis of high CH₄ concentrations for 2018, evacuated Exetainers were used.

Sediment samples were collected using an Ekman dredge (AJAX AMS Ekman dredge sampler) at all sites in 2017 and in 2018. Samples were collected adjacent to transects where bubble gas samples were obtained. A single sediment grab was collected for each transect, and a sample (~40–100 g) from the centre of each grab (to minimize potential loss of finer particles from sediment outwash when removing the dredge from the water) was kept for analysis. Individual sediment samples for each transect were bagged and refrigerated until further analysis.

Water temperature, electrical conductivity (EC), and pH were measured at depth during each site visit (YSI Environmental, Inc., or Oakton Instruments, Inc.). Temperature at the sediment-water interface was measured every 10 min at two SK sites (SK3, SK4) using HOBO Pendant Temperature/Light 8 K Data Loggers from June–October 2018. Bulk water samples in 500–1000 mL HDPE bottles were obtained at least once per season at all sites and stored cool for transport to the laboratory.

2.3. Laboratory analysis

Bulk water samples were analyzed for a suite of chemical parameters. Total dissolved phosphorus (TDP), and sulphate (SO₄²⁻) were analyzed in duplicate using a SMARTCHEM® discrete analyzer (MB and SK sites). For the MO sites, TDP was analyzed spectrophotometrically and SO₄²⁻ was analyzed on a Lachat QuikChem Flow Injection Analyzer. Dissolved organic carbon (DOC) was analyzed on a Shimadzu® TOC-L. Total dissolved nitrogen (TDN) was analyzed on a Shimadzu® TOC-L with TNM-L module (SK sites), using a SMARTCHEM® discrete analyzer (MB sites), or spectrophotometrically using the second derivative spectroscopy method (MO sites; Crumpton et al., 1992). Methane concentrations were analyzed by gas chromatography (GC) with a Scion 456 Gas Chromatograph (Bruker, Ltd.) either by flame ionization detector (FID), or where concentrations were sufficient to saturate the FID signal, via thermal conductivity detector (TCD).

Sediment samples were air-dried, disaggregated, and sieved to 2 mm, then analyzed to determine organic matter content (OM) and particle size. Organic matter content was determined via loss-on-ignition (LOI) by heating oven-dried (105 °C) subsamples (~5 g) at 400 °C for 16 h in a muffle furnace (Schumacher, 2002). Post-

combustion samples were analyzed in triplicate for particle size via laser ablation (Horiba Partica LA-950) after soaking overnight (16 h) in a dispersing agent.

2.4. Data and statistical analysis

Littoral volumetric ebullitive fluxes ($\text{mL m}^{-2} \text{d}^{-1}$) for individual bubble trap chambers were quantified using accumulated ebullition volume (mL), chamber area (m^2), and length of accumulation period (d), where accumulation period was taken as number of days between site visits. To facilitate comparison of fluxes across season and sites, accumulated volumes were normalized to standard temperature and pressure (STP; 273.15 K, 1 atm) according to the combined gas law:

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} \quad (1)$$

where V_2 (mL) is the normalized gas volume, V_1 (mL) is collected gas volume, P_1 (atm) is local atmospheric pressure, T_1 (K) is water temperature at time of sample collection, and P_2 and T_2 are standard pressure and temperature. Because there were two collection chambers at each location (bubble trap) within a site, measurements for the chambers were averaged to yield a flux measurement for the bubble trap for each sampling period.

The ideal gas law was applied to quantify littoral ebullitive GHG fluxes (e.g., $\text{mol CH}_4 \text{ m}^{-2} \text{d}^{-1}$) for each chamber:

$$n_g = \frac{P_1 V_2}{RT_1} \quad (2)$$

where n_g (mol) is amount of gas in each chamber, P_1 , and T_1 are standard temperature and pressure, and R ($\text{L atm mol}^{-1} \text{K}^{-1}$) is the ideal gas constant. Moles of CH_4 released for each interval (n_{CH_4}) were then calculated using average CH_4 concentration of gas samples collected from sediments ($[\text{CH}_4]$; ppmv).

$$n_{\text{CH}_4} = \frac{[\text{CH}_4]}{10^6} \times n_g \quad (3)$$

Gas samples collected in 2017 required a correction to account for mixing with ambient atmospheric air in unevacuated vials:

$$C_2 = \frac{C_T V_T - C_1 V_1}{V_2} \quad (4)$$

where C_1 , C_2 , and C_T refer to ambient atmospheric, corrected, and GC-analyzed CH_4 concentrations, respectively. Total volume (V_T) corresponds to the sum of the unevacuated vial volume (V_1 , 6 or 12 mL) and the gas volume collected via forced ebullition (V_2 , 14 or 20 mL). Measured ambient atmospheric concentrations (C_1) in the Exetainers were 1.85 ppmv CH_4 . Finally, sampling interval length (d) and chamber area (m^2) were used to quantify the flux rate.

Calculations, statistical tests, and data visualisations (ggplot2 package, Wickham, 2016) were performed using R (R Core Team, 2020). Visual inspection of histograms and quantile-quantile plots, and Levene's test (car package, leveneTest function, Fox and Weisburg, 2019) were used to investigate normality and homogeneity of variance. The data were non-normal and heteroscedastic. A non-parametric Kruskal-Wallis test (stats package, kruskal.test function, R Core Team, 2020) was used to compare overall differences in CH_4 flux rates and concentrations, due to its flexibility of variance (e.g., does not require equal variance between groups) and distributional assumptions (Konietschke et al., 2015). We note that a significant result, if obtained, should be interpreted with caution, as the data do not duly satisfy the parametric nor non-parametric tests' assumptions. To compare between-site differences post-hoc Dunn's test (dunn.test package, dunn.test function, Dinno, 2017) for multiple comparisons with Benjamini-Yekutieli p -value adjustment was used, with an alpha value

of 0.05. Inter-year differences for individual sites were not tested, owing to the different timing of sample collection between years. Spearman rank correlations (stats package, cor.test function, R Core Team, 2020) were used to assess relationships between (median) ebullitive CH_4 release rates for each site and site physicochemical characteristics, including water temperature, SO_4^{2-} and OM; the alpha value of 0.05 was adjusted for multiple comparisons as described above. Our analysis focussed on these three parameters, as they have the potential to be directly linked to ebullitive CH_4 release, whereas nutrient concentrations may only be indirectly related. We also investigated generalized additive models (GAM; mgcv package, Wood, 2017) as an approach for identifying multivariate drivers (temperature, SO_4^{2-} , OM) of ebullitive CH_4 release. Where CH_4 release data were available for two years, we used the mean of these observations. We used a GAM to fit models with temperature, SO_4^{2-} , and OM as individual predictors and also explored additive models with and without grouping, with the Canadian and US sites each forming a group (cold and warm climates, respectively), and transformations (log, square root) were explored in an effort to normalize data, as necessary. This grouping may also account for other (non-climate) differences between these regions (see discussion). Model fitting was performed using the restricted maximum likelihood penalization method. We used diagnostic plots to check our models (gratia package; Simpson, 2021) and AIC, coefficient of determination and deviance explained were used to compare models.

3. Results

Ebullition fluxes were monitored with average monitoring periods of 6 and 18 weeks in 2017 and 2018, respectively; seven sites were monitored in both years. The sites represented a wide range in chemical character (Table 2) and land-use (Table 1). Average water temperatures during the monitoring periods at individual sites ranged from 8.4 to 26.4 °C, with sites monitored in both years having higher temperatures in 2018, attributed principally to an earlier start and end to the observation period. The sites were circumneutral or slightly basic and EC ranged by approximately two orders of magnitude (51–4040 $\mu\text{S cm}^{-1}$). Sulphate concentrations across the sites also exhibited a wide range (6–2820 mg L^{-1}) but were below 100 mg L^{-1} at most sites, corresponding closely to EC levels. Total dissolved phosphorus and DOC (select sites) were also variable. Sediment geometric mean particle size was similar across the sites, ranging from silt (11 sites) to very fine sand (3 sites), while OM was more variable, ranging from 4 to 30% (Table 2).

3.1. Ebullition fluxes

Open-water season rates of ebullitive CH_4 release were measurable at all sites, but were highly variable. In 2017, median rates for the 10 sites spanned more than four orders of magnitude (3.33×10^{-4} –26.4 $\text{mmol m}^{-2} \text{d}^{-1}$). In 2018 (12 sites) the pattern was similar (Fig. 1) and ebullitive CH_4 release was highly variable, but the lowest observed rates were somewhat higher, in part because data for MO sites with low ebullitive flux were not available in 2018 (median rates: 1.67×10^{-2} –40.4 $\text{mmol m}^{-2} \text{d}^{-1}$). With the exceptions of the MO sites and SK3, median CH_4 fluxes did not exceed a 10-fold difference across sites. There were statistically significant differences in CH_4 flux rates among sites in both 2017 ($\chi^2 = 20.8$, $\text{df} = 9$, $p < 0.05$) and 2018 ($\chi^2 = 27.5$, $\text{df} = 11$, $p < 0.01$). Despite clear differences in magnitude between sites (Fig. 1), post-hoc results did not identify significant differences, possibly due to a large number of comparisons, and small group sizes (maximum of 4 bubble traps per pond).

Methane concentrations from gas collected directly from the sediments (Fig. 2) exhibited a similar pattern to CH_4 fluxes (Fig. 1), which is expected given that these CH_4 concentration observations were used to calculate fluxes. Fresh bubble CH_4 concentrations were found

Table 2

Physicochemical characteristics of the study sites during the observation periods in 2017 and 2018. Organic matter and mean particle size represent measurements on sediments (both years) while all other parameters represent mean surface water conditions. Concentrations below detection limits are denoted by <DL.

Site	Year	Water temperature (°C)	pH	EC ($\mu\text{S cm}^{-1}$)	SO_4^{2-} (mmol L^{-1})	TDN ($\mu\text{mol L}^{-1}$)	TDP ($\mu\text{mol L}^{-1}$)	DOC (mmol L^{-1})	Organic matter (%)	Mean particle size (μm)
MB1	2017, 2018	12.2, 19.1	8.8, 9.8	1140, 988	—, 0.36	—, 93	—, 0.21	—	9.6	32.4
MB2	2017, 2018	10.7, 16.2	8.4, 8.0	975, 964	—, 0.07	—, 64	—, 0.32	—	11.5	36.6
MB3	2017, 2018	9.8, 15.5	8.0, 7.9	1040, 980	—, 0.11	—, 64	—, 1.8	—	8.5	41.3
MB4	2017, 2018	8.5, 15.2	7.9, 7.8	1040, 981	—, 0.49	—, 35	—, 2.0	—	16.2	64.7
MB5	2017, 2018	9.3, 15.8	7.9, 7.9	1090, 993	—, 0.51	—, 38	—, 1.4	—	13.1	48.4
MB6	2018	17.1	8.4	924	1.0	120	0.07	—	29.5	53.7
MB7	2018	16.6	8.0	1290	0.68	80	0.13	—	27.1	71.7
MO1	2018	28.6	8.7	126	0.06	—	0.84	0.73	4.3	48.2
MO2	2017	15.6	7.6	339	<DL	60	1.2	0.72	11.6	47.0
MO3	2017	11.4	7.4	1883	3.9	36	0.23	0.40	11.3	19.3
MO4	2017	8.9	8.2	79	<DL	51	0.57	0.68	9.6	62.8
MO5	2018	24.8	8.0	51	0.02	—	0.39	0.73	—	—
SK3	2017, 2018	11.3, 16.2	7.7, 8.1	4040, 3870	28, 29	160, 180	0.81, 1.3	2.3, 2.3	18.7	36.8
SK4	2017, 2018	14.0, 17.1	8.9, 8.6	506, 534	0.95, 0.92	46, 120	—, 2.2	0.81, 1.1	6.9	46.4
SK5	2018	17.2	9.1	1130	4.2	200	16	2.1	7.8	31.8

to be significantly different between sites in both 2017 ($\chi^2 = 80.2$, $df = 9$, $p < 0.001$) and 2018 ($\chi^2 = 167$, $df = 11$, $p < 0.001$). Observed CH_4 concentrations of fresh gas collected directly from the sediments were notably lower at the MO sites and SK3, which also had lower ebullitive CH_4 release rates (Fig. 2). Median CH_4 concentrations for these five sites were less than 50,000 ppmv, while the remaining sites (MB sites, SK4 and SK9) exhibited median concentrations greater than 500,000

ppmv. Post-hoc tests identified that these differences between sites were significant in many cases. This included across region differences; for example, MO4 and SK3 had significantly lower CH_4 concentrations than all MB sites in 2017 ($p < 0.05$). There were also within region differences; for example, SK4 CH_4 concentrations were higher than SK3 in 2017 ($p < 0.05$), and MB2, MB3 and MB5 were higher than MB6 in 2018 ($p < 0.05$).

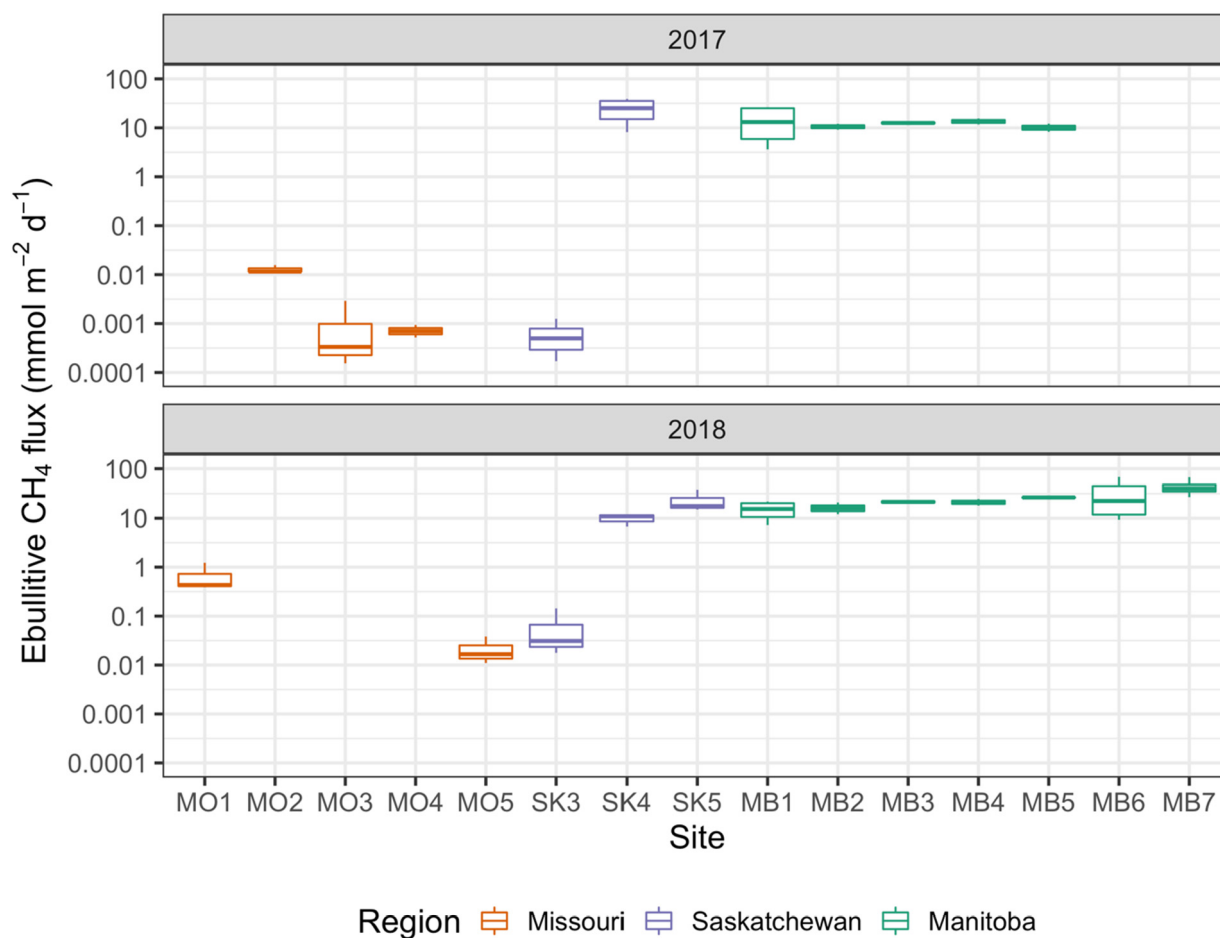


Fig. 1. Littoral ebullitive CH_4 flux rates for study sites in MO (MO1, MO2, MO3, MO4, MO5), SK (SK3, SK4, SK5), and MB (MB1, MB2, MB3, MB4, MB5, MB6, MB7) during 2017 and 2018 open-water seasons. (Note that while a log scale is used here for clarity, no flux rates were zero).

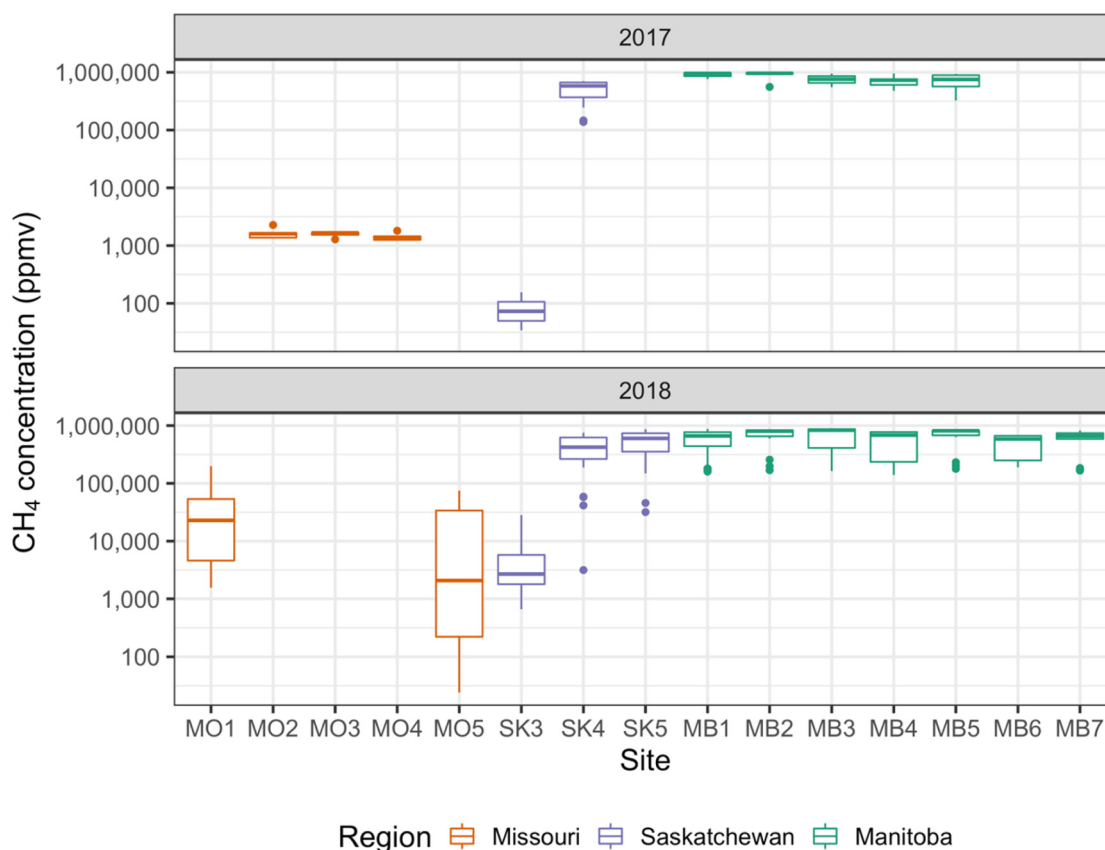


Fig. 2. Fresh bubble CH₄ concentrations from study sites in MO (MO1, MO2, MO3, MO4, MO5), SK (SK3, SK4, SK5), and MB (MB1, MB2, MB3, MB4, MB5, MB6, MB7) during 2017 and 2018 open-water seasons.

3.2. Physicochemical conditions

Across our study, median ebullitive CH₄ release rates were not significantly related to potential drivers including temperature ($r = 0.27, p = 0.23$) and OM ($r = 0.24, p = 0.42$; Fig. 3). At our sites in MB, ebullitive CH₄ release was consistently high, despite contrasting temperatures and OM among sites. We also observed that sites with both very low (e.g., MO sites) and very high SO₄²⁻ were found to have very low

ebullitive CH₄ release rates (Fig. 4), and SO₄²⁻ was not related to ebullitive CH₄ release across the study sites ($r = 0.099, p = 0.70$). We did, however, observe high variability in CH₄ release at lower SO₄²⁻ concentrations (~0–1 mmol L⁻¹), whereas for the lone site with very high SO₄²⁻ (SK3: >25 mmol L⁻¹), volumes collected in the ebullition traps and CH₄ concentrations (Fig. S1) were both consistently low (both years).

Average pond temperature and efflux rates were not significantly correlated at the site level (over the period of observation; Fig. 3)

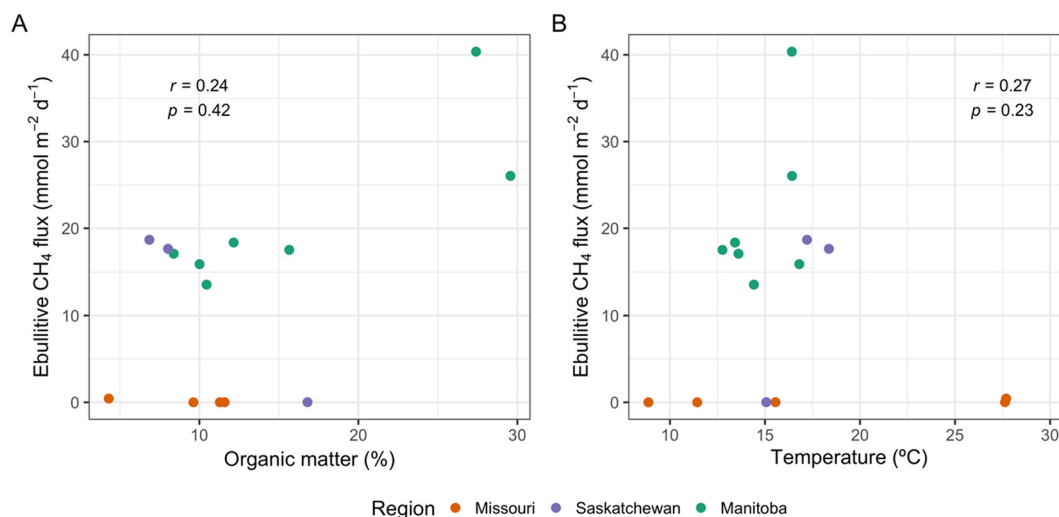


Fig. 3. Median ebullitive CH₄ flux for A) organic matter content and B) water temperature.

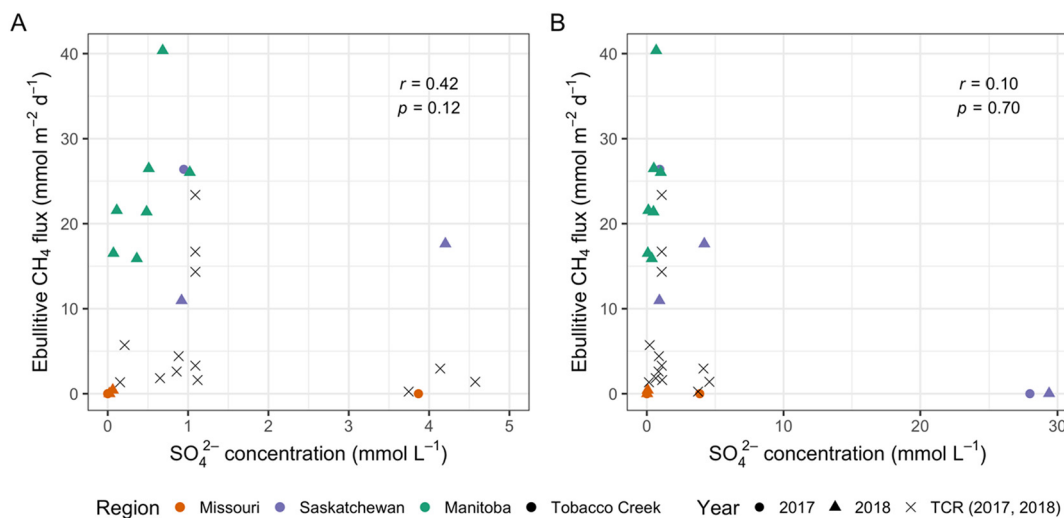


Fig. 4. Median ebullitive CH₄ flux for different surface water SO₄²⁻ concentrations for A) study sites with SO₄²⁻ concentrations below 5 mmol L⁻¹, B) all study sites. Correlation statistics for the study sites are shown. Data points representing small agricultural reservoirs in Tobacco Creek (TCR), southern Manitoba, generated using methods analogous to the current study, are also shown.

suggesting that temperature is not a driver of inter-site differences. When considering all ebullition observations and the temperatures of their respective observation intervals (and thus temporal variability), we did find a significant, albeit weak, positive correlation ($r = 0.26$, $p < 0.001$). When investigating temperature and CH₄ release at individual sites, significant correlations were observed for only four of the 15 sites (Fig. 5). For some of the sites where correlations were not significant (e.g., MB1 and SK4), ebullition remains elevated for weeks after temperature begins dropping toward minima (below 10 °C; Fig. S1). At other sites, periods of maximum ebullition occurred at moderate temperatures (e.g., MB5, MB7). In contrast, ebullitive CH₄ release rates were low and relatively static across the period of observation for some sites (MO1 through MO5, SK3), and ebullition appears to be largely independent of temperature. Analysis of CH₄ concentration

and temperature across the sites and observation periods indicated they were not significantly correlated ($r = -0.085$, $p = 0.11$).

A multivariate GAM including temperature, SO₄²⁻, and OM was not significant; however, when grouping the sites according to warm and cold region (Canada and US sites, respectively), we found a model with a significant coefficient for region, and significant smooth terms for SO₄²⁻ and OM (Fig. S2; adjusted $r^2 = 0.88$; deviance explained = 91%, edf = 1). This model had the strongest performance of the models tested (including a model with region, temperature, SO₄²⁻, and OM; Table S1); however, the distributional assumptions were not met (Fig. S3), and we were unable to meet the assumptions by transforming the data. Thus, while the model is interpretable from a mechanistic standpoint, its robustness has not been confirmed.

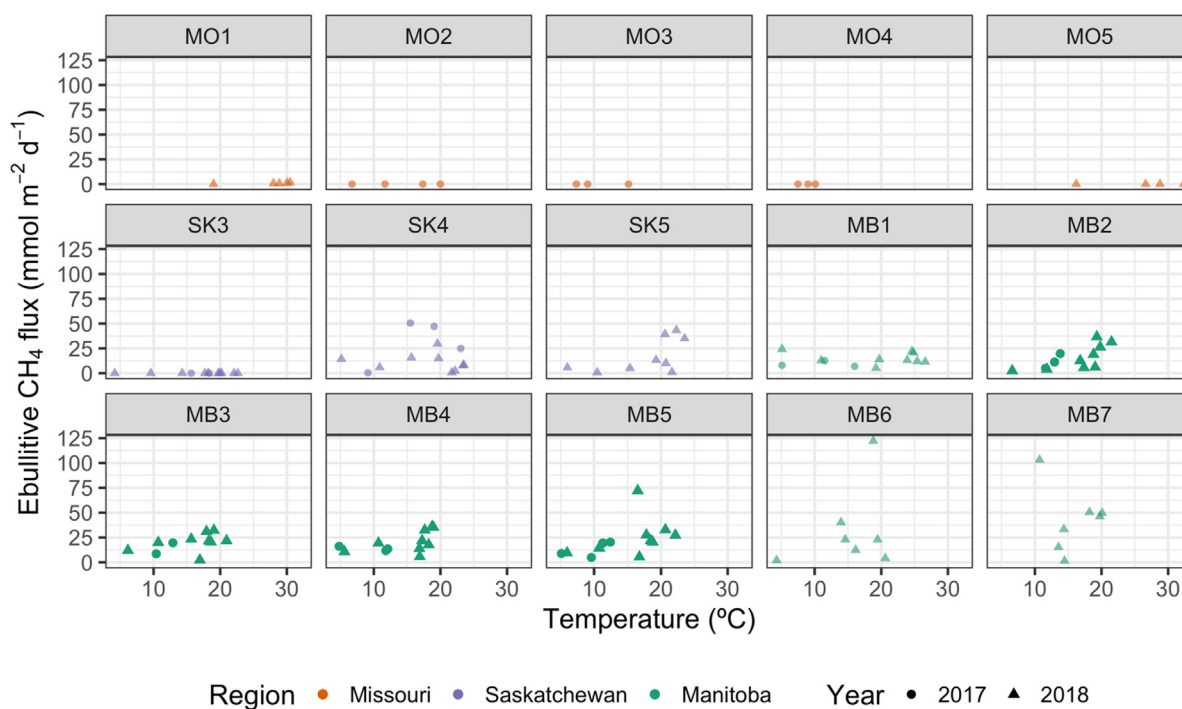


Fig. 5. Median CH₄ release rates according to average water temperature of individual sampling intervals for all sites and both years. Correlations for sites with semi-transparent points are non-significant. Sites with non-transparent points (MB2, MB3, MB4, and MB5) indicate significant Spearman correlations ($r > 0.6$, $p < 0.05$).

4. Discussion

This work quantifies multi-season ebullitive CH₄ fluxes in 15 ponds in three regions across the Great Plains and bordering landscapes. Most studies to date focus on individual ponds, or similar ponds within a single region or landscape type. Our study quantifies open-water season ebullitive CH₄ release rates with a view to contrasting rates across different regions and physicochemical pond characteristics. This work illustrates local and regional between-pond variability in ebullitive fluxes, while also suggesting that temperature is not a dominant driver across the range of system behaviour observed. The results also suggest that CH₄ release is suppressed at high SO₄²⁻. Likewise, other potential controls including OM were not clearly linked to differences in ebullitive CH₄ release, as the study sites demonstrated considerable differences in behaviour.

4.1. Methane emission

Small, shallow ponds like those investigated herein have been identified as important sources of CH₄ (Holgerson and Raymond, 2016; Davidson et al., 2018). Much of the work on CH₄ release from small ponds has been on natural systems in the boreal ecoregion, and there is a particular need for measurements from productive systems and

those located in urban or agriculturally impacted regions (DelSontro et al., 2018). Small ponds are often compared to or miscategorized as wetlands, owing to limitations of remote signal interpretation (Lehner and Döll, 2004). Nonetheless, processes occurring in small ponds are distinct (Holgerson and Raymond, 2016), and we have focussed on ponds rather than a broader suite of aquatic systems. Studies of CH₄ emissions from ponds often employ methods that collect discrete samples over short time periods (e.g., Bansal et al., 2016). Low temporal resolution sampling is likely to underestimate emissions (Wik et al., 2016), as these methods do not adequately account for ebullition from open water, which can be event-based and a dominant flux pathway for CH₄ (Weyhenmeyer, 1999; Venkiteswaran et al., 2013). As such, these fluxes remain poorly quantified.

The data reported in this study add to the sparse but growing number of measurements of CH₄ ebullition from ponds globally, and suggest that both rates of ebullition and controls on this process are extremely variable. The CH₄ ebullition rates from 15 sites in three distinct regions span a wider range (3.3×10^{-4} –40 mmol m⁻² d⁻¹) than previously reported for similar pond systems (~0–27 mmol m⁻² d⁻¹; Table 3). The seven ponds in MB exhibited consistently high ebullitive CH₄ release (Fig. 1), the five ponds in MO had characteristically low ebullitive CH₄ release, while sites in SK demonstrated a wide range in ebullitive CH₄ release. Mean flux rates for both MB (21.7 mmol m⁻² d⁻¹

Table 3

Ebullitive CH₄ release rates for open-water ponds reported in the literature^a as well as details on the nature of the sampling and study sites. Only studies of freshwater ponds with repeat measurements over an extended period (e.g., totalling >1 month, either continuously, or via regular multi-day sampling intervals that collectively span >1 month) were included. Other water bodies (lakes, reservoirs, tailings ponds) and wetland sites where water is not ponded above the surface were excluded.

Pond type	Ebullitive CH ₄ flux (mmol m ⁻² d ⁻¹)	Location	Sites	Traps (per site)	Measurements (total)	Ponded water depth(s) (m)	Pond area(s) (ha)	Contributing Area/Land cover	Source
Mesotrophic ponds	0.22–0.47 (range for all sites)	Finland	2	1	–	1.8–3.2	1.0	Boreal forest, peatland	Huttunen et al. (2003)
Northern boreal ponds	4.6 ± 4.1 (mean ± SD for all sites)	Québec, Canada	10	1	77	0.6–0.8	0.12–4.2	Mixed boreal forest	DelSontro et al. (2016)
Northern boreal beaver pond	1.32, 7.14 (means; vegetated, open water)	Thompson, Manitoba, Canada	1	–	–	0.5–2.3	5.0	Boreal forest, peatland	Dove et al. (1999)
Boreal beaver pond	1.42 ± 1.04 (mean ± SD)	Ontario, Canada	1	9	–	1.4	3.8	Mixed boreal forest	Weyhenmeyer (1999)
Thaw ponds	0–3.34; 1.25 (range; mean for all sites)	Abisko, Sweden	8	2–4	2063	0.18–0.85	0.0013–0.045	Sporadic permafrost peatland complex	Burke et al. (2019)
Ombrotrophic bog	0–15.8; 0.686 (range; median)	Siikaneva peatland, Finland	1	11–13	50	1	–	Peatland	Männistö et al. (2019)
Emergent freshwater marsh	0.07 (0.03–0.09); 1.03 (0.78–1.36) (median, Q ₁ –Q ₃ for each site)	Sacramento Delta, California, USA	2	6	588	1–2	121	Restored wetland; previously agricultural peatland	McNicol et al. (2017)
Farm ponds, swamp	22 ± 12; 27 ± 13; 22 ± 12 (mean ± SD of multiple day intervals for three sites)	Michigan, USA	3	1	32	1	0.0025; 0.015; 8.8	Agricultural	Baker-Blocker et al. (1977)
Permanent ponds	10.2–40.4; 21.7 ± 15.4 (range; mean ± SD)	Winnipeg, Manitoba, Canada	7	2–4	244	1–2	0.014–147	Woodland conservation; semi-natural prairie	This study
Semi-permanent pothole ponds	5.0·10 ⁻⁴ –26.4; 12.5 ± 13.9 (range; mean ± SD)	Saskatoon, Saskatchewan, Canada	3	3	149	1–2	0.16–1.31	Prairie conservation, residential; Agricultural; Urban park, agricultural	This study
Pasture, woodland or urban ponds	3.33·10 ⁻⁴ –0.43; 0.144 ± 0.332 (range; mean ± SD)	Columbia, Missouri, USA	5	3	114	1–2	0.26–2.7	Urban park; Pasture; Woodland conservation	This study

^a Keywords used in Web of Science search were methane, ebullition, and pond OR wetland.

¹) and SK ponds ($12.5 \text{ mmol m}^{-2} \text{ d}^{-1}$) were higher than in all regions previously reported, with the exception of farm ponds in Michigan (Table 3). With few exceptions, including tropical reservoirs (Keller and Stallard, 1994; DelSontro et al., 2011) and sites that feature CH_4 seeps (Spulber et al., 2010; Walter Anthony et al., 2010), the seven MB sites as well as SK4 and SK9 are among the highest reported ebullitive CH_4 flux rates for open-water seasons, with MB7 ($40 \text{ mmol m}^{-2} \text{ d}^{-1}$) having the highest known rate of ebullitive CH_4 release for a freshwater pond.

Ebullitive CH_4 release from MO ponds (mean: $0.14 \text{ mmol m}^{-2} \text{ d}^{-1}$) were comparable to other sites with low CH_4 production, including mesotrophic ponds in Finland (Huttunen et al., 2003). This ran counter to initial predictions, given that these sites are warm and nutrient-rich. In contrast to the MB and SK sites, MO sites do not undergo a prolonged period of ice-cover, which could contribute to lower but less (temporally) variable rates over the course of a full year. Nonetheless, we note that CH_4 concentrations were significantly different between systems (Fig. 2), and the MO sites featured significantly lower CH_4 concentrations than most MB and SK sites. Methane concentrations at the four MO sites and SK3 are lower than reported in previous studies (Walter Anthony et al., 2010; Baulch et al., 2011). We found a weak ($r = 0.43$, $p < 0.001$) but significant relationship between CH_4 concentration and volumetric flux across the study (Fig. S4), suggesting that the CH_4 concentration of gases collected in sediments could be used as a coarse proxy for indicating the relative potential for shallow sites to release CH_4 .

4.2. Drivers of methane emission

We did not observe consistent relationships between temperature and CH_4 fluxes; only four of the sites had significant positive relationships with temperature, and in some cases these sites were adjacent to ones where no relationship with temperature was observed. This is despite the sites in MB and SK having temperature ranges of $>15 \text{ }^\circ\text{C}$ during the observed open-water periods. The MO sites had consistently low fluxes, despite sustained high temperatures during the observation period for some sites.

While some studies have found clear exponential increases in CH_4 fluxes with temperature in a variety of freshwater systems (Aben et al., 2017; van Bergen et al., 2019), others have reached similar conclusions to ours, namely that the effects of rising temperatures are mediated by other environmental factors. There are a number of studies that have found an interaction between eutrophication and temperature, suggesting that substrate availability may be more limiting to CH_4 ebullition than temperature in some ponds (DelSontro et al., 2016), while there may be synergistic effects of eutrophication and temperature in highly productive ponds (Davidson et al., 2018). Results from urban ponds are mixed and at times conflicting, suggesting that in systems with substantial human influence, teasing apart individual drivers may be more difficult than in more pristine systems. There are examples of a clear relationship between CH_4 flux and temperature (Natchimuthu et al., 2014; McPhillips and Walter, 2015), and where no clear temperature relationship was observed (Gorsky et al., 2019). In the current study, pond management practices such as fish stocking or redox constraints (see below) may be more important than temperature in controlling CH_4 fluxes at individual sites. We suggest that these factors may constrain CH_4 release and may result in ebullition flux being unresponsive to temperature at select sites. For similar reasons, site-specific factors governing CH_4 production could confound our ability to detect a temperature relationship across sites.

There is some indication from our data that seasonal patterns of CH_4 concentration in sediments and bubble formation may not be entirely synchronous. At the SK and MB sites, where there was a marked seasonal pattern in air temperatures, the sediment CH_4 concentrations remained high through the end of the season, while volumetric

ebullitive flux tended to decrease as water temperatures cooled down in the fall. Both CH_4 production and bubble formation and release have been shown to be temperature dependent, especially in ponds (DelSontro et al., 2016). Bubble release is affected by myriad biological, physical, and chemical processes, many of which depend on temperature to greater or lesser degrees (Wik et al., 2018). While this analysis did not investigate factors such as hydrostatic pressure due to changing water levels, water level drawdown was notable for only two sites (SK3 and SK9). For SK3, which had among the highest temperatures and OM, ebullitive CH_4 release was uniformly low, suggesting that another top-down control plays a role. Part of the challenge of identifying relationships between temperature and ebullitive CH_4 flux is that the temperature dependence of each of the component processes may be more or less important, depending on other environmental drivers (DelSontro et al., 2016).

Previous work from a wide variety of systems has suggested that SO_4^{2-} concentrations can mediate CH_4 emissions as sulphate-reducing bacteria can be superior competitors for substrates used by methanogens (Abram and Nedwell, 1978). High SO_4^{2-} concentrations as a result of hydrological inputs (Bansal et al., 2016) or soil characteristics (Dunmola et al., 2010) have been related to low CH_4 emissions from Prairie ponds. The ponds in our study featured a wide range in SO_4^{2-} (Table 2), and ebullitive CH_4 flux was highly variable at low SO_4^{2-} concentration, including at levels previously suggested to be potentially CH_4 limiting ($0.031 \text{ mmol L}^{-1}$, Pennock et al., 2010). We demonstrate that relatively high ebullitive CH_4 release can occur at SO_4^{2-} concentrations approaching 4 mmol L^{-1} . Our analysis featured sites with both low and high ebullitive CH_4 release across this SO_4^{2-} range ($0\text{--}4 \text{ mmol L}^{-1}$). In contrast, while our analysis featured only one site with very high SO_4^{2-} concentration ($>25 \text{ mmol L}^{-1}$), ebullitive CH_4 release at this site was very low ($<0.1 \text{ mmol m}^{-2} \text{ d}^{-1}$). Sulphate was significant in the GAM, but the single high SO_4^{2-} site may have been overly influential on this relationship given the relatively small number of sites (Fig. S2). Likewise, while OM was also included in the best GAM, we caution that a group of sites exhibiting such a diversity of ebullition behaviour and physicochemical character as shown here can present a challenge for multivariate analyses generally, as the strength of multivariate analysis lies in having very large numbers of observations to explain complex underlying patterns; datasets of this nature for ebullition in these small systems do not yet exist. Nonetheless, the behaviour for the high SO_4^{2-} pond (SK3) could suggest that SO_4^{2-} acts as a top-down control when at sufficiently high levels. This may be important for the Prairie Pothole Region where pothole pond dissolved CH_4 is strongly related to SO_4^{2-} concentration (L.T. Dyck unpublished data). Using our data, along with those from Helmle et al. (In review) for small ($<1 \text{ ha}$) agricultural reservoirs in southern MB suggests that SO_4^{2-} may only be important as a control at relatively high concentrations ($>4 \text{ mmol L}^{-1}$). This result highlights the still poorly understood role of SO_4^{2-} as a methanogenesis suppressant in pond systems, and more data from SO_4^{2-} rich ponds are needed to investigate this mechanism. For the MO sites that exhibit a range of SO_4^{2-} ($<\text{DL}$ to 3.9 mmol L^{-1}), but consistently low ebullitive CH_4 release, other factors may also be important.

Urban ponds are typically highly managed systems, and these management practices can interfere with typical controls on CH_4 emissions observed in more natural systems. Mesocosm experiments have shown that ebullitive CH_4 emissions decreased by 67% as a result of the addition of benthivorous fish (i.e., carp), where increased sediment oxidation was attributed to bioturbation by the carp, resulting in fish-induced reduction in ebullition (Oliveira Junior et al., 2019). The MO ponds were likely all stocked with carp, as this practice is very common in ponds in MO (Jones et al., in review). Notably, the MO1 pond was stocked with thirty 20–25 cm long grass carp (*Ctenopharyngodon idella*) in September 2017 to control aquatic vegetation (Pers Comm, Darby Niswonger, Fisheries Management Biologist, Missouri Department of

Conservation, Columbia, MO). We hypothesize that this fish management practice enhanced CH₄ oxidation, contributing to the low CH₄ ebullitive emissions in MO ponds. Vegetation management practices in these MO ponds may also have enhanced sediment aeration; like many ponds and reservoirs in the Midwest, the MO ponds were stocked with American water willow (*Justicia americana*) in order to improve fish habitat (Jones et al., in review; Strakosh et al., 2005). This emergent macrophyte can substantially alter the sediment structure (Fritz and Feminella, 2003), and its aerenchymous stems may alter pathways of CH₄ emissions (Waldo et al., 2019). Water hyacinth (*Eichhornia crassipes*) is ubiquitous in MO, and has also been implicated in altering CH₄ emissions (Oliveira-Junior et al., 2018). These results point to the complexity of unraveling competing drivers in highly managed systems and the need to include site-specific factors when estimating CH₄ emissions from small ponds.

5. Conclusions

The results of this study have several important implications for estimating CH₄ ebullition from small ponds. Our study is unique in its focus on capturing open-water season rates for multiple years across three distinct regions of the Great Plains. This diverse set of study sites exhibits a wide range in rates of ebullitive CH₄ release. Identifying clear drivers of differing behaviour among the sites proved difficult. While temperature is significantly related to ebullitive CH₄ emissions at some sites, this relationship is far from universal. Other factors including trophic status and OM availability (DelSontro et al., 2016; Dalcin Martins et al., 2017; Davidson et al., 2018) have been identified in other studies as important in mediating this temperature-CH₄ relationship; however, this was less clear in the present dataset. Rather, redox constraints from SO₄²⁻ concentrations and management practices seem to have resulted in low CH₄ emissions at some sites where OM levels were moderate, even at higher temperatures. These results have several important implications. First, the results affirm that rates of CH₄ emissions from small ponds can be very high, and given the importance of these water bodies globally, should be carefully considered in estimates of CH₄ emissions from aquatic systems. Second, given the range of ebullitive CH₄ emissions within regions, accurate scaling, for example to quantify regional emissions from water bodies, will be predicated on having sufficient and representative data. Third, caution must be exercised when using observed relationships with temperature to extrapolate to other water bodies, even within the same region, as other environmental drivers can disrupt this relationship. Finally, these results suggest that the effects of rising global temperatures on CH₄ emissions from ponds will not be uniform, and investigations into site-specific controls are critical for predicting the trajectory of CH₄ emissions from ponds.

CRedit authorship contribution statement

A.A.P. Baron: Data curation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **L.T. Dyck:** Data curation, Investigation, Writing – review & editing. **H. Amjad:** Data curation, Investigation. **J. Bragg:** Data curation, Investigation. **E. Kroft:** Data curation, Investigation. **J. Newson:** Data curation, Investigation. **K. Oleson:** Data curation, Investigation. **N.J. Casson:** Resources, Writing – original draft, Writing – review & editing. **R.L. North:** Resources, Writing – original draft. **J.J. Venkiteswaran:** Resources, Writing – review & editing. **C.J. Whitfield:** Methodology, Resources, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors wish to thank students and technicians who assisted with fieldwork and laboratory analyses at UW, US and MU, and two anonymous reviewers who provided constructive feedback on the work. Fieldwork at US and GHG analyses for the project were funded through an NSERC-DG awarded to CJW. Fieldwork and analysis at UW were funded through an NSERC-DG awarded to NJC. Fieldwork and nutrient analysis at MU were funded by the Prairie Fork Charitable Endowment Trust to RLN.

Appendix A. Supplementary information

Supplementary information to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.149685>.

References

- Aben, R.C.H., Barros, N., van Donk, E., Frenken, T., Hilt, S., Kazanjian, G., Lamers, L.P.M., Peeters, E.T.H.M., Roelofs, J.G.M., de Senerpont Domis, L.N., Stephan, S., Velthuis, M., Van de Waal, D.B., Wik, M., Thornton, B.F., Wilkinson, J., DelSontro, T., Kosten, S., 2017. Cross continental increase in methane ebullition under climate change. *Nat. Commun.* 8, 1682. <https://doi.org/10.1038/s41467-017-01535-y>.
- Abram, J.W., Nedwell, D.B., 1978. Inhibition of methanogenesis by sulphate reducing bacteria competing for transferred hydrogen. *Arch. Microbiol.* 117, 89–92. <https://doi.org/10.1007/BF00689356>.
- Baker-Blocker, A., Donahue, T.M., Mancy, K.H., 1977. Methane flux from wetlands areas. *Tellus* 29, 245–250. <https://doi.org/10.1111/j.2153-3490.1977.tb00731.x>.
- Bansal, S., Tangen, B., Finocchiaro, R., 2016. Temperature and hydrology affect methane emissions from prairie pothole wetlands. *Wetlands* 36, 371–381. <https://doi.org/10.1007/s13157-016-0826-8>.
- Bartosiewicz, M., Laurion, I., MacIntyre, S., 2015. Greenhouse gas emission and storage in a small shallow lake. *Hydrobiologia* 757, 101–115. <https://doi.org/10.1007/s10750-015-2240-2>.
- Bastviken, D., Cole, J., Pace, M., Tranvik, L., 2004. Methane emissions from lakes: dependence of lake characteristics, two regional assessments, and a global estimate. *Glob. Biogeochem. Cycles* 18. <https://doi.org/10.1029/2004GB002238>.
- Bastviken, D., Tranvik, L.J., Downing, J.A., Crill, P.M., Enrich-Prast, A., 2011. Freshwater methane emissions offset the continental carbon sink. *Science* 331, 50.
- Baulch, H.M., Dillon, P.J., Maranger, R., Schiff, S.L., 2011. Diffusive and ebullitive transport of methane and nitrous oxide from streams: are bubble-mediated fluxes important? *J. Geophys. Res. Biogeosci.* 116, 1–15.
- Beaulieu, J.J., DelSontro, T., Downing, J.A., 2019. Eutrophication will increase methane emissions from lakes and impoundments during the 21st century. *Nat. Commun.* 10, 1375. <https://doi.org/10.1038/s41467-019-09100-5>.
- Bridgman, S.D., Megonigal, J.P., Keller, J.K., Bliss, N.B., Trettin, C., 2006. The carbon balance of North American wetlands. *Wetlands* 26, 889–916. [https://doi.org/10.1672/0277-5212\(2006\)26\[889:TCBONA\]2.0.CO;2](https://doi.org/10.1672/0277-5212(2006)26[889:TCBONA]2.0.CO;2).
- Burke, S.A., Wik, M., Lang, A., Contosta, A.R., Palace, M., Crill, P.M., Varner, R.K., 2019. Long-term measurements of methane ebullition from thaw ponds. *J. Geophys. Res. Biogeosci.* 124, 2208–2221. <https://doi.org/10.1029/2018JG004786>.
- Chanton, J.P., 2005. The effect of gas transport on the isotope signature of methane in wetlands. *Stable Isot. Appl. Methane Cycle Stud.* 36, 753–768. <https://doi.org/10.1016/j.orggeochem.2004.10.007>.
- Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Downing, J.A., Middelburg, J.J., Melack, J.M., 2007. Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems* 10, 171–184.
- Crumpton, W.G., Isenhardt, T.M., Mitchell, P.D., 1992. Nitrate and organic N analyses with second-derivative spectroscopy. *Limnol. Oceanogr.* 37, 907–913. <https://doi.org/10.4319/lo.1992.37.4.0907>.
- Dalcin Martins, P., Hoyt, D.W., Bansal, S., Mills, C.T., Tfaily, M., Tangen, B.A., Finocchiaro, R.G., Johnston, M.D., McAdams, B.C., Solensky, M.J., Smith, G.J., Chin, Y.P., Wilkins, M.J., 2017. Abundant carbon substrates drive extremely high sulfate reduction rates and methane fluxes in prairie pothole wetlands. *Glob. Change Biol.* 23, 3107–3120. <https://doi.org/10.1111/gcb.13633>.
- Davidson, T.A., Audet, J., Jeppesen, E., Landkildehus, F., Lauridsen, T.L., Søndergaard, M., Svåvånta, J., 2018. Synergy between nutrients and warming enhances methane ebullition from experimental lakes. *Nat. Clim. Chang.* 8, 156–160. <https://doi.org/10.1038/s41558-017-0063-z>.
- Deemer, B.R., Harrison, J.A., Li, S.Y., Beaulieu, J.J., DelSontro, T., Barros, N., Bezerra-Neto, J.F., Powers, S.M., dos Santos, M.A., Vonk, J.A., 2016. Greenhouse gas emissions from reservoir water surfaces: a new global synthesis. *Bioscience* 66, 949–964. <https://doi.org/10.1093/biosci/biw117>.
- DelSontro, T., McGinnis, D.F., Sobek, S., Ostrovsky, I., Wehrli, B., 2010. Extreme methane emissions from a Swiss hydropower reservoir: contribution from bubbling sediments. *Environ. Sci. Technol.* 44, 2419–2425. <https://doi.org/10.1021/es9031369>.
- DelSontro, T., Kunz, M.J., Kempton, T., Wüest, A., Wehrli, B., Senn, D.B., 2011. Spatial heterogeneity of methane ebullition in a large tropical reservoir. *Environ. Sci. Technol.* 45, 9866–9873. <https://doi.org/10.1021/es2005545>.

- DelSontro, T., Boutet, L., St-Pierre, A., del Giorgio, P.A., Prairie, Y.T., 2016. Methane ebullition and diffusion from northern ponds and lakes regulated by the interaction between temperature and system productivity: productivity regulates methane lake flux. *Limnol. Oceanogr.* 61, S62–S77. <https://doi.org/10.1002/lno.10335>.
- DelSontro, T., Beaulieu, J.J., Downing, J.A., 2018. Greenhouse gas emissions from lakes and impoundments: upscaling in the face of global change. *Limnol. Oceanogr. Lett.* 3, 64–75. <https://doi.org/10.1002/lo2.10073>.
- Denman, K.L., Brasseur, G., Chidthaisong, A., Ciais, P., Cox, P.M., Dickinson, R.E., Hauglustaine, D., et al., 2007. Couplings between changes in the climate system and biogeochemistry. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, pp. 499–588 Cambridge, United Kingdom and New York, NY, USA.
- Dinno, A., 2017. *DunnTest: Dunn's Test of Multiple Comparisons Using Rank Sums (Version 1.3.5)*.
- Dove, A., Roulet, N., Crill, P., Chanton, J., Bourbonniere, R., 1999. Methane dynamics of a northern boreal beaver pond. *Écoscience* 6, 577–586. <https://doi.org/10.1080/11956860.1999.11682548>.
- Downing, J.A., Prairie, Y.T., Cole, J.J., Duarte, C.M., Tranvik, L.J., Striegl, R.G., McDowell, W.H., Kortelainen, P., Caraco, N.F., Melack, J.M., Middelburg, J.J., 2006. The global abundance and size distribution of lakes, ponds and impoundments. *Limnol. Oceanogr.* 51, 2388–2397.
- Dunmola, A.S., Tenuta, M., Moulin, A.P., Yapa, P., Lobb, D.A., 2010. Pattern of greenhouse gas emission from a prairie pothole agricultural landscape in Manitoba, Canada. *Can. J. Soil Sci.* 90, 243–256. <https://doi.org/10.4141/CJSS08053>.
- Fox, J., Weisburg, S., 2019. *An R Companion to Applied Regression. Third ed.* Sage, Thousand Oaks, CA.
- Fritz, K.M., Feminella, J.W., 2003. Substratum stability associated with the riverine macrophyte *Justicia Americana*. *Freshw. Biol.* 48, 1630–1639. <https://doi.org/10.1046/j.1365-2427.2003.01114.x>.
- 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, 100218. <https://doi.org/10.1016/j.ancene.2019.100218>.
- Helmle, R.E.J., 2019. *An Analysis of Ebullition Dynamics in Agricultural Reservoirs Using Novel Automated Sensors. University of Saskatchewan*, p. 126 Master of Environment and Sustainability.
- Holgeron, M.A., Raymond, P.A., 2016. Large contribution to inland water CO₂ and CH₄ emissions from very small ponds. *Nat. Geosci.* 9, 222–226. <https://doi.org/10.1038/ngeo2654>.
- Huttunen, J.T., Alm, J., Liikanen, A., Juutinen, S., Larmola, T., Hammar, T., Silvola, J., Martikainen, P.J., 2003. Fluxes of methane, carbon dioxide and nitrous oxide in boreal lakes and potential anthropogenic effects on the aquatic greenhouse gas emissions. *Chemosphere* 52, 609–621. [https://doi.org/10.1016/S0045-6535\(03\)00243-1](https://doi.org/10.1016/S0045-6535(03)00243-1).
- Jones, J.R., Obrecht, D., North, R.L. Influence of fisheries management on limnological characteristics of three Missouri reservoirs. In review at *Inland Waters*.
- Joyce, J., Jewell, P.W., 2003. Physical controls on methane ebullition from reservoirs and lakes. *Environ. Eng. Geosci.* 9, 167–178. <https://doi.org/10.2113/9.2.167>.
- Keller, M., Stallard, R.F., 1994. Methane emission by bubbling from Gatun Lake, Panama. *J. Geophys. Res. Atmos.* 99, 8307–8319. <https://doi.org/10.1029/92JD02170>.
- Knox, S.H., Bansal, S., McNicol, G., Schafer, K., Sturtevant, C., Ueyama, M., Valach, A.C., Baldocchi, D., Delwiche, K., Desai, A.R., Euskirchen, E., Liu, J., Lohila, A., Malhotra, A., Mellling, L., Riley, W., Runkle, B.R.K., Turner, J., Vargas, R., Zhu, Q., Alto, T., Fluet-Chouinard, E., Goeckede, M., Melton, J.R., Sonnentag, O., Vesala, T., Ward, E., Zhang, Z., Feron, S., Ouyang, Z., Alekseychik, P., Aurela, M., Bohrer, G., Campbell, D.I., Chen, J., Chu, H., Dalmagro, H.J., Goodrich, J.P., Gottschalk, P., Hirano, T., Iwata, H., Jurasinski, G., Kang, M., Koebisch, F., Mammarella, I., Nilsson, M.B., Ono, K., Peichl, M., Peltola, O., Ryu, Y., Sachs, T., Sakabe, A., Sparks, J., Tuittila, E.-S., Vourlitis, G.L., Wong, G.X., Windham-Myers, L., Poulter, B., Jackson, R.B., 2021. Identifying dominant environmental predictors of freshwater wetland methane fluxes across diurnal to seasonal time scales. *Glob. Change Biol.* <https://doi.org/10.1111/gcb.15661>.
- Konietschke, F., Placzek, M., Schaarschmidt, F., Hothorn, L.A., 2015. nparcomp: an R software package for nonparametric multiple comparisons and simultaneous confidence intervals. *J. Stat. Soft.* 64 (1), 1–17. <https://doi.org/10.18637/jss.v064.i09>.
- Lehner, B., Döll, P., 2004. Development and validation of a global database of lakes, reservoirs and wetlands. *J. Hydrol.* 296, 1–22. <https://doi.org/10.1016/j.jhydrol.2004.03.028>.
- Männistö, E., Korrensalo, A., Alekseychik, P., Mammarella, I., Peltola, O., Vesala, T., Tuittila, E.-S., 2019. Multi-year methane ebullition measurements from water and bare peat surfaces of a patterned boreal bog. *Biogeosciences* 16, 2409–2421. <https://doi.org/10.5194/bg-16-2409-2019>.
- Matthews, C.J.D., Joyce, E.M., Schiff, S.L., Venkiteswaran, J.J., Hall, B.D., Beaty, K.G., Bodaly, R.A. (Drew), St. Louis, V.L., 2005. Carbon dioxide and methane production in small reservoirs flooding upland boreal forest. *Ecosystems* 8, 267–285. <https://doi.org/10.1007/s10021-005-0005-x>.
- McNicol, G., Sturtevant, C.S., Knox, S.H., Dronova, I., Baldocchi, D.D., Silver, W.L., 2017. Effects of seasonality, transport pathway, and spatial structure on greenhouse gas fluxes in a restored wetland. *Glob. Change Biol.* 23, 2768–2782. <https://doi.org/10.1111/gcb.13580>.
- McPhillips, L., Walter, M.T., 2015. Hydrologic conditions drive denitrification and greenhouse gas emissions in stormwater detention basins. *Ecol. Eng.* 85, 67–75. <https://doi.org/10.1016/j.ecoleng.2015.10.018>.
- Natchimuthu, S., Panneer Selvam, B., Bastviken, D., 2014. Influence of weather variables on methane and carbon dioxide flux from a shallow pond. *Biogeochemistry* 119, 403–413. <https://doi.org/10.1007/s10533-014-9976-z>.
- Oliveira Junior, E.S., Temmink, R.J.M., Buhler, B.F., Souza, R.M., Resende, N., Spanings, T., Muniz, C.C., Lamers, L.P.M., Kosten, S., 2019. Benthivorous fish bioturbation reduces methane emissions, but increases total greenhouse gas emissions. *Fresh. Biol.* 64, 197–207. <https://doi.org/10.1111/fwb.13209>.
- Oliveira Junior, E.S., van Bergen, T.J.H.M., Nauta, J., Budiša, A., Aben, R.C.H., Weideveld, S.T.J., de Souza, C.A., Muniz, C.C., Roelofs, J., Lamers, L.P.M., Kosten, S., 2020. Water hyacinth's effect on greenhouse gas fluxes: a field study in a wide variety of tropical water bodies. *Ecosystems* <https://doi.org/10.1007/s10021-020-00564-x>.
- Oliveira-Junior, E.S., Tang, Y., van den Berg, J.J.P., Cardoso, S.J., Lamers, L.P.M., Kosten, S., 2018. The impact of water hyacinth (*Eichhornia crassipes*) on greenhouse gas emission and nutrient mobilization depends on rooting and plant coverage. *Aquat. Bot.* 145, 1–9.
- Pennock, D., Yates, T., Bedard-Haughn, A., Phipps, K., Farrell, R., McDougal, R., 2010. Landscape controls on N₂O and CH₄ emissions from freshwater mineral soil wetlands of the Canadian prairie pothole region. *Geoderma* 155, 308–319. <https://doi.org/10.1016/j.geoderma.2009.12.015>.
- R Core Team, 2020. *R: A Language and Environment for Statistical Computing*.
- Raymond, P.A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R.G., Mayorga, E., Humborg, C., Kortelainen, P., Durr, H., Meybeck, M., Ciais, P., Guth, P., 2013. Global carbon dioxide emissions from inland waters. *Nature* 503, 355–359. <https://doi.org/10.1038/nature12760>.
- Schumacher, B.A., 2002. *Methods for the determination of total organic carbon (TOC). Soils and Sediments. United States Environmental Protection Agency*.
- Simpson, G.L., 2021. Gratia: graceful 'ggplot'-based graphics and other functions for GAMs fitted using 'mgcv' R package version 6.0.6.0. <https://CRAN.R-project.org/package=gratia>.
- Spulber, L., Etiope, G., Baciu, C., Malos, C., Vlad, S.N., 2010. Methane emission from natural gas seeps and mud volcanoes in Transylvania (Romania). *Geofluids* 10, 463–475. <https://doi.org/10.1111/j.1468-8123.2010.00301.x>.
- Stanley, E.H., Casson, N.J., Christel, S.T., Crawford, J.T., Loken, L.C., Oliver, S.K., 2016. The ecology of methane in streams and rivers: patterns, controls, and global significance. *Ecol. Monogr.* 86, 146–171. <https://doi.org/10.1890/15-1027.1>.
- Strakosh, T.R., Eitzmann, J.L., Gido, K.B., Guy, C.S., 2005. The response of water willow *Justicia Americana* to different water inundation and desiccation regimes. *North Am. J. Fish. Manag.* 25, 1476–1485. <https://doi.org/10.1577/m05-051.1>.
- Tranvik, L.J., Downing, J.A., Cotner, J.B., Loiselle, S.A., Striegl, R.G., Ballatore, T.J., Dillon, P.J., Finlay, K., Fortino, K., Knoll, L.B., Kortelainen, P.L., Kutser, T., Larsen, S., Laurion, I., Leech, D.M., McAllister, S.L., McKnight, D.M., Melack, J.M., Overholt, E., Porter, J.A., Prairie, Y.T., Renwick, W.H., Roland, F., Sherman, B.S., Schindler, D.W., Sobek, S., Tremblay, A., Vanni, M.J., Verschoor, A.M., von Wachenfeldt, E., Weyhenmeyer, G.A., 2009. Lakes and reservoirs as regulators of carbon cycling and climate. *Limnol. Oceanogr.* 54, 2298–2314.
- Tranvik, L.J., Cole, J.J., Prairie, Y.T., 2018. The study of carbon in inland waters—from isolated ecosystems to players in the global carbon cycle. *Limnol. Oceanogr. Lett.* 3, 41–48. <https://doi.org/10.1002/lo2.10068>.
- van Bergen, T.J.H.M., Barros, N., Mendonça, R., Aben, R.C.H., Althuisen, I.H.J., Huszar, V., Lamers, L.P.M., Lüring, M., Roland, F., Kosten, S., 2019. Seasonal and diel variation in greenhouse gas emissions from an urban pond and its major drivers. *Limnol. Oceanogr.* 64 (5), 2129–2139. <https://doi.org/10.1002/lno.11173>.
- Venkiteswaran, J.J., Schiff, S.L., St. Louis, V.L., Matthews, C.J.D., Boudreau, N.M., Joyce, E.M., Beaty, K.G., Bodaly, R.A., 2013. Processes affecting greenhouse gas production in experimental boreal reservoirs. *Glob. Biogeochem. Cycl.* 27 (2), 567–577. <https://doi.org/10.1002/gbc.2004>.
- Waldo, N.B., Hunt, B.K., Fadely, E.C., Moran, J.J., Neumann, R.B., 2019. Plant root exudates increase methane emissions through direct and indirect pathways. *Biogeochemistry* 145, 213–234. <https://doi.org/10.1007/s10533-019-00600-6>.
- Walter Anthony, K.M., Brosius, L., Chapin III, F.S., Zimov III, S.A., Zhuang III, Q., Vas Dragos, A., 2010. Estimating methane emissions from northern lakes using ice-bubble surveys. *Limnol. Oceanogr. Methods* 8, 592–609. <https://doi.org/10.4319/lom.2010.8.0592>.
- Watson, A., Nedwell, D.B., 1998. Methane production and emission from peat: the influence of anions (sulphate, nitrate) from acid rain. *Atmos. Environ.* 32, 3239–3245. [https://doi.org/10.1016/S1352-2310\(97\)00501-3](https://doi.org/10.1016/S1352-2310(97)00501-3).
- Weyhenmeyer, C.E., 1999. Methane emissions from beaver ponds: rates, patterns, and transport mechanisms. *Glob. Biogeochem. Cycl.* 13, 1079–1090. <https://doi.org/10.1029/1999GB900047>.
- Whitfield, C.J., Ahern, J., Baulch, H.M., 2011. Controls on greenhouse gas concentrations in polymictic headwater lakes in Ireland. *Sci. Total Environ.* 410, 217–225.
- Whitfield, C.J., Baulch, H.M., Chun, K.P., Westbrock, C.J., 2015. Beaver-mediated methane emission: the effects of population growth in Eurasia and the Americas. *Ambio* 44, 7–15. <https://doi.org/10.1007/s13280-014-0575-y>.
- Wickham, H., 2016. *GGPlot2: Elegant Graphics for Data Analysis*.
- Wik, M., Thornton, B.F., Bastviken, D., Uhlback, J., Crill, P.M., 2016. Biased sampling of methane release from northern lakes: A problem for extrapolation. *Geophys. Res. Lett.* 43, 1256–1262. <https://doi.org/10.1002/2015gl066501>.
- Wik, M., Johnson, J.E., Crill, P.M., DeStasio, J.P., Erickson, L., Halloran, M.J., Fahnestock, M.F., Crawford, M.K., Phillips, S.C., Varner, R.K., 2018. Sediment characteristics and methane ebullition in three Subarctic Lakes. *J. Geophys. Res. Biogeosciences* 123, 2399–2411. <https://doi.org/10.1029/2017JG004042>.
- Wood, S.N., 2017. *Generalized Additive Models: An Introduction With R. 2nd edition.* Chapman and Hall/CRC.