

Regulation of carbon dioxide and methane in small agricultural reservoirs: Optimizing potential for greenhouse gas uptake

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Abstract. Small farm reservoirs are abundant in many agricultural regions across the globe and have the potential to be large contributing sources of carbon dioxide (CO₂) and methane (CH₄) to agricultural landscapes. Compared to natural ponds, these artificial waterbodies remain overlooked in both agricultural greenhouse gas (GHG) inventories and inland water global carbon (C) budgets. Improved understanding of the environmental controls of C emissions from farm reservoirs is required to address and manage their potential importance. Here, we conducted a regional scale survey (~235,000 km²) to measure CO₂ and CH₄ concentrations and diffusive fluxes across 101 small farm reservoirs in Canada's largest agricultural area. A combination of abiotic, biotic, hydromorphologic, and landscape variables were modelled using generalized additive models (GAMs) to identify regulatory mechanisms. We found that CO₂ concentration was best estimated by a combination of internal metabolism and groundwater-derived alkalinity (65.7% deviance explained), while multiple lines of evidence support eutrophication-driven CH₄ (74.1%). Fluxes ranged from -21 to 466 and 0.14 to 92 mmol m⁻² d⁻¹ for CO₂ and CH₄, respectively, with CH₄ contributing an average of 74% of CO₂-equivalent (CO₂-e) emissions. Approximately 19% farm reservoirs were found to be net CO₂-e sinks. From our models, we show that the GHG impact of farm reservoirs can be greatly minimised with optimal design and management.

1 Introduction

Small waterbodies have recently been recognised as substantial contributors to global carbon emissions from inland waters. Current assessments estimate that small ponds ($<0.001 \text{ km}^2$) account for 15% and 40% of global CO_2 and CH_4 emissions respectively from lakes (Holgerson and Raymond, 2016). Other estimates suggest emissions from small lakes and impoundments (0.001 to 0.01 km^2) could constitute 40% of global CO_2 emissions and 20% of global CH_4 emissions from lentic ecosystems (DelSontro et al., 2018). Extreme CO_2 and CH_4 supersaturation is characteristic of small waterbodies due to greater contact with the sediment and littoral zone (Downing et al., 2008; Holgerson, 2015), often making them disproportionately important in landscape carbon (C) budgets (Hamilton et al., 1994; Premke et al., 2016; Kuhn et al., 2018).

Conversely, ponds may have the capacity to store landscape-significant amounts of carbon, with burial rates 20–30 times higher than wetlands and large lakes (Gilbert et al., 2014; Taylor et al., 2019). While these assessments have stimulated a growing area of research on small waterbodies, much work is still needed to revise estimates of their carbon emissions due to limited knowledge on their regional distribution and variability, as well as their overall global extent (Verpoorter et al., 2014). This is particularly true for greenhouse gas (GHG) emissions from human-created small waterbodies.

The expansion of agriculture and urban land use has introduced a new type of lentic system that remains relatively unexplored – small artificial waterbodies (Clifford and Heffernan, 2018). These artificial aquatic systems have been created through human modification of the hydrological landscape and include small farm reservoirs and urban ponds. Farm reservoirs are earthen excavations designed to store water for later use (BC Ministry of Agriculture, 2013). The global abundance of these systems remains uncertain (Verpoorter et al., 2014), but statistical extrapolation suggest there may be around 16 million worldwide (Lehner et al., 2011). Regional-scale inventories indicate that upwards of 8 million farm reservoirs exist in the USA (Brunson, 1999; Smith et al., 2002), China (Chen et al., 2019), India (Anbumozhi et al., 2001), South Africa (Mantel et al., 2017), and Australia alone (Lowe et al., 2005; MDBA, 2008; Grinham et al., 2018a). The density of farm reservoirs can exceed 30% of agricultural area in some regions such as China where food demand is high (Chen et al., 2019). Small agricultural reservoirs are estimated to cover $77,000 \text{ km}^2$ globally and are being created at rates up to 60% of standing stock per annum in some regions (Downing et al., 2008). Given their abundance, these artificial systems may contribute substantially to landscape biogeochemical cycles, including fluxes of GHG. In particular, very little is known of the capability of these systems to act as GHG sinks to partially offset the otherwise strong carbon efflux associated with intensive agriculture (Robertson et al., 2000).

Understanding the controls and rates of carbon fluxes from small artificial waterbodies is the first step required to understand their landscape and eventually global importance. Farm reservoirs have the potential to be potent sources of CO_2 and CH_4 due to their highly eutrophic nature (Downing et al., 2008) and high degree of heterotrophy (Holgerson and Raymond, 2016). Further, estimates of CO_2 and CH_4 flux are complicated by high variation among reservoirs and regions in the importance of groundwater, littoral macrophytes, and local land use practises (Pennock et al., 2010; Badiou et al., 2019). Currently, only three studies have comprehensively assessed C fluxes from small agricultural reservoirs and these support

60 the notion that they are important landscape sources of GHGs (Panneer Selvam et al., 2014; Grinham et al., 2018a; Ollivier et al., 2019). All studies found large fractions of CH₄ being released, and large mean CO₂ emissions on the order of 24 and 99 mmol m⁻² d⁻¹, comparable to the global average flux rate of very small natural ponds (35 mmol m⁻² d⁻¹, Holgerson and Raymond, 2016). However, carbon fluxes from farm reservoirs remain unaccounted in agricultural GHG inventories and global inland water carbon budgets. To facilitate their inclusion in agricultural and global budgets, we need to further
65 constrain flux rates and mechanisms across a broad geographic area.

Here, we present a large-scale assessment of CO₂ and CH₄ fluxes from small farm reservoirs in the Northern Great Plains, the largest agricultural region in Canada. The hydroclimate, lithology and edaphic features are vastly different compared to previous studies of agricultural areas (Australia, India, USA), with factors that favour CO₂ uptake by alkaline surface waters (Finlay et al., 2009; Finlay et al., 2015) and lead to high variability in CH₄ fluxes from regional wetlands (Pennock et al.,
70 2010; Badiou et al., 2019). Our aim was to identify the key environmental conditions regulating CO₂ and CH₄ fluxes, and to evaluate the potential for reservoir design to minimize CO₂-equivalent (CO₂-e) emissions. To achieve this goal, we carried out an extensive survey of CO₂ and CH₄ concentrations across 101 farm reservoirs and used generalized additive models (GAMs) to assess the effects of abiotic, biotic, hydromorphological and land use properties. Our findings show that farm dams were not always strong sources of carbon emissions and in certain cases can be carbon neutral or sinks in terms of
75 CO₂-e emissions. By identifying the driving characteristics of farm dams that support reduced C emissions, our findings provide the first step to developing management strategies to help minimise farm carbon emissions.

2 Methods

2.1 Study site

Farm sites were surveyed across the agricultural region of Saskatchewan, Canada (Fig. 1). This region covers an area of
80 235,000 km² in the southern half of the province, where agriculture accounts for ~80% of land use. The region has a sub-humid to semi-arid climate (Köppen *Dfb* classification), with short warm summers (~18°C) and long winters (~-17°C) resulting in 4.5 to 5.5 months of ice cover on surface waters (Finlay et al., 2015).

Small farm reservoirs (known locally as ‘dugouts’) are a prominent feature of the landscape, with densities up to 10 per km² (Fig. 1B). Up until 1985, over 110,000 farm reservoirs had been constructed in Saskatchewan (Gan, 2000), although
85 subsequent densities are unknown. We sampled 101 farm reservoirs between July and August 2017, ranging in surface area from 158 – 13,900 m² (Table 1), including basins in pasture (n = 80) and cropland (n = 21) sites. Saskatchewan farm reservoirs are typically uniform in shape and morphometry, dug to a depth of 4 to 6 m with steep sides (1.5:1 slopes). Most shallow wetlands and lakes in the region exhibit water balances dominated by evaporation and limited inflow from winter precipitation or groundwater (Conly and van der Kamp, 2001; Pham et al., 2009). Farm reservoirs differ from small natural
90 waterbodies in that they have a higher ratio of water volume to surface area, designed to minimise evaporation losses. Despite this feature, arid conditions persisted during the sampling year, with reduced (34-65%) annual rainfall such that

many reservoirs were only half their designed depth. Natural waterbodies also tend to be high pH hard-water systems, owing to the soils which consist of glacial till high in carbonates (Last and Ginn, 2005). The same was observed for the majority of farm reservoirs, with an average pH of 8.75 (Table 1).

95 2.2 CO₂ and CH₄ measurements

Dissolved gas samples were collected using the in-field headspace extraction method (Webb et al., 2019). Briefly, water was collected from ~30 cm below the surface using a submersible pump which filled a 1.2-L glass-serum bottle, ensuring the bottle overflowed and no air bubbles were present. The bottle was sealed with a rubber stopper fitted with two three-way stopcock valves. Using two 60-mL air-tight syringes, atmospheric air was added to the bottle whilst simultaneously
100 extracting 60-mL of water. The bottle was then shaken for 2 minutes to ensure gas equilibration in the headspace. Two analytical replicates were extracted and stored in 12-mL evacuated Exetainer vials with double-wadded caps. Headspace concentrations of CO₂ and CH₄ were measured using gas chromatography with a Scion 456 Gas Chromatograph (Bruker Ltd.) and calculated using standard curves. Dry molar fractions were corrected for dilution and converted to concentrations according to solubility coefficients (Weiss, 1974; Yamamoto et al., 1976).

105 Carbon dioxide and methane fluxes were estimated for each water body using water column concentrations (C_{water}) and average farm reservoir gas transfer velocity (k_c) using the following equation:

$$f_c = k_c(C_{\text{water}} - C_{\text{air}}), \quad (1)$$

where f_c is the flux of CO₂ or CH₄ (mmol m⁻² d⁻¹) and C_{air} is the ambient air concentration. The average global mixing ratios for the sampling period of 406 and 1.85 µatm were used for ambient concentrations for CO₂ and CH₄ respectively (Mauna
110 Loa NOAA station, June to August 2017). Site-specific gas transfer velocity (k_c) was determined from 30 individual floating- chamber (area = 0.23 m², volume = 0.046 m³) measurements carried out on a subset of 10 reservoirs. During each 10-minute incubation, changes in gas concentrations were measured at 2.5-min intervals by taking samples using syringes and dispensing gases into pre-evacuated 12-mL vials. The flux (mmol m⁻² d⁻¹) was calculated from the observed rate of change in the dry mole fraction of the respective gas (Lorke et al., 2015). The gas transfer velocity normalised to a Schmidt
115 number of 600 (k_{600}) for each respective gas was then determined using measured flux, *in situ* gas concentrations, atmospheric concentration, Henry's constant, and Schmidt numbers, assuming a Schmidt exponent of 0.67. The average k_{600} calculated from the floating chamber incubations was 1.50 ± 1.34 m d⁻¹ and 1.68 ± 1.26 m d⁻¹ for CO₂ and CH₄, respectively.

2.3 Abiotic and biotic variables

A range of abiotic and biotic parameters were measured at each site. Water quality variables including temperature (°C), pH,
120 dissolved O₂ (DO; mg O₂ L⁻¹), conductivity (µS cm⁻²), and salinity were measured at 0.5-m intervals from the surface to the bottom using a YSI (Yellow Springs Instruments, OH, USA) multi-probe meter. Surface (0.5 m) samples for water chemistry were collected using a submersible pump. Upon collection, samples for dissolved nitrogen (NO₃+NO₂, NH₄, total

dissolved N; $\mu\text{g N L}^{-1}$), soluble reactive phosphorus (SRP; $\mu\text{g P L}^{-1}$) and total dissolved P (TDP; $\mu\text{g P L}^{-1}$), dissolved organic and inorganic carbon (DOC, DIC; mg C L^{-1}), alkalinity ($\text{OH} + \text{HCO}_3 + \text{CO}_3$; mg L^{-1} as CaCO_3), and water isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$; ‰) were filtered through a 0.45- μm pore membrane filter. Nutrient and dissolved carbon samples were stored in a dark bottle at 4°C until analysis. Chlorophyll *a* (Chl-*a*) samples were collected on GF/C glass-fiber filters (nominal pore size 1.2 μm) and frozen (-10°C) until analysis. Sediment samples were collected at the centre of each reservoir, the uppermost 10 cm using an Ekman grab sampler, and were frozen at -10°C until analysis.

Most analyses were carried out at the University of Regina Institute of Environmental Change and Society (IECS). Water nutrient and dissolved carbon concentrations were measured on a Lachat QuikChem 8500 and Shimadzu model 5000A total carbon analyzer, following standard analytical procedures, respectively (Patoine et al., 2006; Finlay et al., 2009). Alkalinity was measured using standard methods of the US Environmental Protection Agency (EPA) on a SmartChem 200 Discrete Analyser (WestCo) and estimated as the concentration of CaCO_3 (EPA, 1974). Chl-*a* was analysed using standard trichromatic methods (Finlay et al. 2009). The total carbon and nitrogen content (% dry weight) of freeze-dried sediment samples were determined on a NC2500 Elemental Analyzer (ThermoQuest, CE Instruments).

2.4 Hydromorphology

Morphometric parameters of reservoirs were estimated for each site. The depth of each farm reservoir was measured during using a portable ultrasonic depth sounder, taken at the deepest section in the centre of the reservoir. Surface area was determined using Google Earth satellite imagery. Reservoir volume was calculated using the formula for a prismoid by assuming that all sites maintained their original shape, including slopes of 1.5:1 ratio (Andresen et al., 2015). From these measurements, an Index of Basin Permanence (IBP) was calculated (Kerekes, 1977).

The degree of water-column mixing or vertical stratification was determined by calculating the squared Brunt-Väisälä buoyancy frequency (N^2 , s^{-2}). The strongest density gradient was calculated based on vertical temperature measurements at 0.5-m depth intervals using the package *rLakeAnalyzer* (Read et al., 2012) in R (version 3.5.2; R Core Team 2018).

The hydrology of farm reservoirs was estimated through analysis of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope values of water. Samples were collected from 0.5 m below the surface, filtered (0.45- μm pore) and stored in amber borosilicate jars at 4°C until analysis using a Picarro L2120-I cavity ring-down spectrometer (CRDS). Hydrological parameters, including evaporation to inflow ratio (E/I), residence time (years), and inflow volume (m^3), deuterium (^2H) excess (d-excess), and $\delta^{18}\text{O}$ inflow (δ_i) values, were calculated using the coupled isotope tracer method (Yi et al., 2008) and conventional isotopic water-balance methods (Gibson et al., 2001). All methods assumed that reservoirs were headwater systems in hydrological steady-state (Yi et al., 2008). Model inputs included information about the local water meteoric line (LWML), the trajectory of evaporation along a local evaporative line (LEL), and regional meteorological conditions. From here, the water mass balance of a given waterbody can be quantified based on its relative position along the LEL (Gibson et al., 2001).

Briefly, the isotopic inflow values were estimated by the intercept between the LWML and site-specific LEL as determined by $\delta^{18}\text{O}$ evaporation value (δ_E) and $\delta^{18}\text{O}$ reservoir water value at each site (Yi et al., 2008). The E/I ratio was calculated by using headwater isotopic models of the water mass balance ($(\delta_I - \delta_L) * (\delta_E - \delta_L)^{-1}$). Hydrologic residence time was estimated from the reservoir volume and the water isotopic values of waterbodies, inflow, and evaporation. Deuterium excess (d-excess ‰ = $\delta^2\text{H} - 8 * \delta^{18}\text{O}$) was calculated as an additional indicator of evaporation losses, where lower values (< -10‰) indicate isotopic enrichment from precipitation (Brooks et al., 2014).

2.5 Landscape properties

Landscape soil data was obtained from The National Soil DataBase, Government of Canada (<http://sis.agr.gc.ca/cansis/nsdb/dss/v3/index.html>) using ArcGIS to extract the soil attributes at each site. Extracted variables included soil salinity, soil pH, soil organic carbon content, saturated hydraulic conductivity (K_{sat}), cation exchange capacity (CEC), and the total composition of soil from sand, silt, and clay fractions (%). Reservoir elevation (m, a.s.l.) was determined using ArcGIS and the Canadian Digital Elevation Model (CDEM, v1.1). Local land use in the immediate area surrounding each reservoir was categorised into three types based on local observations at the time of sampling. Categories included pasture land used for either livestock grazing or hay harvesting, pasture where livestock have direct access to the waterbody, and crop fields.

2.6 Statistical analyses

Environmental variables were selected based on known or presumed influence on CO_2 and CH_4 concentrations in lakes and small waterbodies. Both biotic and abiotic predictors that influence production or consumption of CO_2 and CH_4 were selected, including DO, alkalinity, NO_x , NH_4 , dissolved inorganic nitrogen (DIN), TDN, TDP, Chl-*a*, DOC, conductivity, pH, and sediment organic C:N ratio. The influence of reservoir hydrology and morphology were also examined, including measures of surface area, basin permanence, hydrologic regime (E/I), water source (δ_I), and degree of mixing (or stratification). Finally, potential effects of the surrounding terrestrial landscape were estimated in models using soil properties, elevation, and land use practises to account for any localised landscape drivers. Before testing relationships, all predictors were transformed as needed using either \log_{10} or square root to remove skewness.

The relationships between covariates and CO_2 and CH_4 were estimated using generalised additive models (GAMs). GAMs provide an ideal approach to model non-linear associations between predictor variables and responses, using the sum of unspecified smooth functions to estimate trends. GAMs were developed with a gamma distribution for the response and the log link function. Each model included covariates that represented hydromorphological, abiotic and biotic, and landscape controls. To avoid multicollinearity, correlation coefficients between pairs from Pearson linear correlation tests was used to guide covariate choice before model fitting (Table S1-3). Candidate variables were then selected for each model to test which variables best estimate variability in CO_2 and CH_4 concentrations. All model coefficients were estimated using

185 restricted marginal likelihood with the *mgcv* package (Wood, 2011; Wood et al., 2016) for R (version 3.5.2; R Core Team 2018).

3 Results

The region experienced a drier than average year during sampling, with recorded average annual precipitation ~60% less than the long-term climate average of 390 mm in Regina, Saskatchewan (Government of Canada, 190 <http://climate.weather.gc.ca>). Consequently, while most farm reservoirs were constructed to ~5 m depth the mean water-column depth was 2.1 m (0.2-5.1, Table 1). Despite this, isotopic analysis of water revealed that 93% of waterbodies exhibited an E/I < 1.0, suggesting that reservoirs were gaining more water than was lost via evaporation. In general, water residence time was ~8 months, although the range in this value was large (29 days to 2.5 years). Estimates of inflow $\delta^{18}\text{O}$ (δ_{I}) indicated variable water sources, with 79% derived from rain (>-15.66‰), 6% from snowmelt or groundwater (<-17.9‰), 195 and 15% intermediate between sources (-17.9 to -15.6‰).

Carbon dioxide and methane concentrations spanned three orders of magnitude across surveyed reservoirs, with concentrations ranging between 1.3 to 326.1 and 0.1 to 54.5 μM for CO_2 and CH_4 , respectively (Table 1). Most waterbodies were alkaline, with a mean pH of 8.8 (7.0 to 10.2) and carbonate alkalinity between 71 and 755 mg L^{-1} . Many waters were highly eutrophic, with means for Chl-*a* of 99 $\mu\text{g L}^{-1}$ (range 2 to 344 $\mu\text{g L}^{-1}$), total nitrogen of >3,000 $\mu\text{g N L}^{-1}$ (418 to 200 14,280), and total phosphorus of 285 $\mu\text{g P L}^{-1}$ (9 to 648). Dissolved O_2 in the surface layer varied by three orders of magnitude among basins with 32% exhibiting oversaturation (>100%).

3.1 Models

Regional variation in CO_2 concentrations were best estimated in a GAM including pH alone, with 86.3% of deviance explained and a strongly declining CO_2 at pH above 8 (Fig. S1). Exclusive of the model with pH, the detailed mechanistic 205 GAM for estimating CO_2 concentrations across farm reservoirs included a combination of DO saturation, alkalinity, NO_x , thermal stratification (buoyancy frequency), basin hydrology (the interaction between δ_{I} and WRT), and landscape features (soil CEC, elevation, soil salinity) (Fig. 2). Overall, the model explained 65.7% of deviance in CO_2 concentrations (Table S4). All covariates had a significant effect except soil salinity, with DO, alkalinity, and the interaction between δ_{I} and WRT being the strongest predictors ($p < 0.001$). CO_2 concentrations displayed a positive response with increasing alkalinity, NO_x , 210 buoyancy frequency, and soil CEC, with a generally negative response to increasing DO and elevation. The effect of DO on CO_2 was particularly distinct between 25 and 100% O_2 saturation (Fig. 2A). The interactive effect of hydrology parameters suggests that sites with elevated rain inflows ($\delta^{18}\text{O} > -12.5\text{‰}$) and longer WRT will exhibit undersaturated CO_2 concentrations.

Variation in CH_4 concentrations among waterbodies were explained by a combination of DO saturation, sediment C/N ratio, 215 DIN, conductivity, the interaction between δ_{I} and WRT, and local land use (Fig. 3), with buoyancy frequency, soil K_{sat} , and

elevation not significant. Overall, the GAM explained 74.1% of the deviance in CH₄ (Table S5). Concentrations of CH₄ increased with sediment C/N and DIN and decreased with conductivity. The significant unimodal relationship with DO indicates that the highest observed CH₄ concentrations occurred under both anoxic and supersaturated O₂ environments (Fig. 3A), while low CH₄ levels were seen when inflow was more composed of snowmelt or groundwater (depleted isotope values) and WRT was long (Fig. 3F). In contrast to the CO₂ model, soil properties and elevation were not significant drivers, yet local land use was significant, with crop sites having significantly higher CH₄ compared to pastures.

4 Discussion

Our comprehensive spatial analysis revealed wide variations among CO₂ and CH₄ concentrations between farm reservoirs. Significant modelled environmental drivers suggested CO₂ was primarily controlled by pH, with strong independent models indicating mechanisms associated with primary productivity, the hydrological regime, and landscape elevation. In contrast, CH₄ was most correlated by internal abiotic and biotic mechanisms. We discuss these potential drivers in detail and from our evidence suggest management strategies that may help reduce the net GHG effect of these farm reservoirs.

4.1 Environmental drivers of CO₂ concentrations

As seen in other hardwater ecosystems, variations in CO₂ were strongly coupled to differences among sites in water-column pH (Finlay et al., 2015; Müller et al., 2016). We demonstrate this with the strong correlation observed between CO₂ and pH in a separate GAM of only water pH as a covariate, explaining 86.3% of deviance (Fig. S1). As expected, the role of pH in regulating CO₂ content is most pronounced at values between 8.6-9.0, the transition point where the predominant species of DIC shifts from free CO₂ to HCO₃⁻ (Duarte et al., 2008; Finlay et al., 2015). Above this value, carbonate buffering increasingly regulates pH and restricts CO₂ to only trace fractions of total DIC (Stumm and Morgan 1970). However, direct changes in CO₂ concentrations can also alter water-column pH, such as biological metabolism (Talling, 2010). Therefore, given the direct chemical relationship between pH and CO₂ concentrations (Stumm and Morgan, 1970), we opted to leave pH out of our model to further investigate the underlying biological, chemical, hydrological, and land use mechanisms.

The detailed GAM showed that variance in CO₂ concentrations among farm reservoirs was estimated (65.7% of deviance) by a combination of predictors related to water-column productivity and microbial metabolism (DO saturation, alkalinity, NO_x), thermal stratification (buoyancy frequency), basin hydrology (the interaction between δ_1 and WRT), and landscape features (soil CEC, elevation) (Fig. 2), but not local soil salinity. This was shown by the DO, alkalinity, δ_1 and WRT covariates having the most significant effect at $p < 0.001$, while CO₂ concentrations did not vary significantly between different soil salinity levels (Table S4, Fig. 2).

Carbon dioxide and dissolved oxygen are closely linked by biological metabolism in aquatic systems and diverge when other chemical or physical processes occur. Here, we see evidence for both linked and divergence (Fig. 2A). The tight linear relationship between CO₂ and O₂ at 25 to 100% saturation indicates close coupling between the gases. This likely represents

control via metabolic processes such as net ecosystem production (NEP) or chemical oxidation of reduced species (Stets et al., 2017). In contrast, relationships between CO₂ and O₂ were less well defined at both high and low oxygen saturations, conditions which may indicate a greater contribution from anaerobic production of CO₂ (Torgersen and Branco, 2008; Holgerson, 2015). Alternatively, alkalinity buffering can mediate the effect of NEP on CO₂ concentrations at both extreme ranges of the DO spectrum (Marcé et al., 2015). Alkalinity buffering is most likely to affect CO₂-DO relationships in waters where alkalinity is >2000 µeq L⁻¹ (Stets et al., 2017) which was the case for ~90% of our sites (Table 1; Fig. 2).

Stratification can also weaken the impact of DO as a driver for CO₂ by regulating the effect of sediment respiration on epilimnetic chemistry (Huotari et al., 2009; Holgerson, 2015). Our model shows that those sites that were most stratified (elevated buoyancy frequency) exhibited higher CO₂ concentrations (Fig. 2D). This pattern contrasts those observed in other small lentic systems where elevated epilimnetic CO₂ concentrations were observed during and after breakdown of water-column stratification (Huotari et al., 2009; Glaz et al., 2016). Preliminary seasonal studies of some farm reservoirs in 2018 show that stratification is strong and persistent throughout the summer, with no obvious diurnal mixing events. Such strong stratification can maintain anoxic conditions throughout most of the water column, which supports intense anaerobic respiration and CO₂ production. Here, the higher CO₂ concentrations observed at high stratification may simply represent an accumulation of benthic-derived respiratory CO₂ during summer that eventually diffuses into the epilimnion.

The positive association between NO_x and CO₂ found in our reservoirs is consistent with similar patterns seen with dissolved inorganic N species in other artificial waterbodies (Ollivier et al., 2019; Peacock et al., 2019) and regional prairie lakes (Wiik et al., 2018). In some lakes, high N loading favoured elevated heterotrophy, despite simultaneous boosts in primary production which draws down free CO₂ (Huttunen et al., 2003; Cole et al., 2000). The effect of a high N influx on CO₂ may be heightened in smaller or shallow lentic waters which are more influenced by sedimentary processes (Torgersen and Branco, 2008). Further, high N availability can increase algal biomass and the deposition of fresh OM made increasingly available for bacterial respiration (Cole et al., 2000). As a result, the effect increased benthic respiration offsets CO₂ uptake by primary producers, while extremely high influx of dissolved N can also favour microbial processes such as nitrification and denitrification which increase CO₂ evolution (Bogard et al., 2017).

Hydrological controls are known to be important regulators of water chemistry in small lentic systems (Reverey et al., 2016; Nitzsche et al., 2017; Peacock et al., 2019). Here we show that sites which received most of their inflow from snowmelt or groundwater, and which had short WRT supported supersaturated CO₂ concentrations (Fig. 2F). Such patterns may reflect increased inputs of groundwater which are typically supersaturated with CO₂ (Macpherson, 2009). Long WRT is associated with larger, deeper systems. These sites are usually less influenced by the terrestrial-aquatic interface, take longer to concentrate the effect of any catchment-derived solutes (Junger et al., 2019), and have higher biotic assimilation of nutrients (Devito and Dillon, 1993; Fairchild and Velinsky, 2006). Larger waterbodies may also be able to better mediate stream or groundwater C inputs through longer chemical processing times and transformations. For example, agricultural reservoirs with the highest WRTs tended to be hydrologically closed systems (E/I > 1) and any watershed derived DIC delivered from previous water sources is likely to be consumed by primary production which encourages atmospheric CO₂ uptake (Macrae

et al., 2004) Additionally, smaller waterbodies with shorter WRT can support higher rates of internal CO₂ production due to higher rates of allochthonous DOC mineralisation (Weyhenmeyer et al., 2015; Vachon et al., 2017).

Groundwater delivery of DIC-rich porewater is the most likely hydrological source resulting in CO₂ enrichment of small farm reservoirs. This mechanism is also suggested by the observation that higher reservoir CO₂ concentrations are predicted in high CEC soils. Alkaline high CEC soils retain more calcium ions within clay particles which releases carbonates and bicarbonates into soil porewater (Kelley and Brown, 1934). Although regional snowmelt and groundwater have similar isotopic signatures (Pham et al., 2009; Jasechko et al., 2017), the positive correlation of CO₂ with alkalinity suggests groundwater as the main source. Edaphic sources of inorganic carbon can result in farm waterbodies accumulating dissolved CO₂, bicarbonates, and carbonates, and therefore alkalinity, from the surrounding soils via groundwater discharge (Miller et al., 1985). Other studies have found strong evidence for groundwater inputs driving CO₂ supersaturation in small lentic systems (Perkins et al., 2015; Peacock et al., 2019) and watershed-derived alkalinity driving CO₂ supersaturation in lakes (Marcé et al., 2015).

Finally, landscape elevation had a significant external effect on reservoir CO₂ and may represent diverse weak controls related to landscape setting. Lower CO₂ concentrations at higher elevations are common in ‘perched’ ecosystems with smaller contributing catchment areas (Diem et al., 2012) and low rates of allochthonous carbon influx (Rose et al., 2015). Conversely, waterbodies low in the landscape may receive more watershed C via groundwater influx due to topographical gradient (Winter and LaBaugh, 2003; van der Kamp and Hayashi, 2009). The effect of elevation could also be related to changes in vegetation composition within the local landscape, with the lowest lying catchments exhibiting higher abundance of marginal wetland vegetation (Zhang et al., 2010) which favours higher inputs of terrestrial C (Magnuson et al., 2006; Abril et al., 2014).

4.2 Environmental drivers of CH₄ concentrations

The GAM suggested that CH₄ concentrations were primarily related to by internal biogeochemical processes and the influence of the hydrological regime. For example, factors related to water column productivity (DO, sediment C/N, DIN, conductivity) had the most significant effect ($p < 0.01$), while some of the broader landscape features such as soil K_{sat} and elevation had no significant effect on CH₄ levels. The nutrient status of waterbodies is often a primary driver of high CH₄ emissions in lakes, impoundments, and ponds (DelSontro et al., 2018; Peacock et al., 2019). Consequently, high nutrient availability is likely fuelling elevated values in both O₂ saturation and CH₄ (Fig. 3A). High CH₄ concentrations at low O₂ saturation reflects the development of anoxic habitats which favours methanogenesis (Huttunen et al., 2003; Bastviken et al., 2004). This is likely the result of rapid biomass production which both enriches epilimnion with O₂ and depletes O₂ in the hypolimnion by providing fresh labile organic matter for decomposition.

In support of eutrophication-driven CH₄ production, our model indicated that high proportions of autochthonous organic matter in sediments were associated with elevated concentrations of CH₄ (Fig. 3B). Overall, sedimentary C/N ratios were in the range (8.5 to 13.4) expected for both phytoplankton and submerged macrophytes (Liu et al., 2018). This suggests that *in*

situ rather than terrestrial organic matter (OM), was the main source of C fuelling methanogenesis in these reservoirs. Strong associations of labile autochthonous C and CH₄ production in sediments (Due et al., 2010; Crowe et al., 2011) also suggests a direct link between eutrophication and CH₄ production in small farm waterbodies.

Unexpectedly, thermal stratification of the water column did not significantly influence CH₄ concentrations in small farm reservoirs (Fig. 3E). This finding contrasts with observations from other small waterbodies where limited mixing favours CH₄ accumulation (Kankaala et al., 2013). Although some small systems exhibit diurnal mixing patterns with turnover at night (Glaz et al., 2016), the wide range of buoyancy frequency values (0.00 to 0.16) suggests that at least some farm reservoirs are continuously stratified, particularly in deeper ponds (Kankaala et al., 2013), as noted for CO₂ distributions (see above and Fig. 2D). Taken together, our findings suggest that variability in the biological production of CH₄ likely exerts a stronger influence over CH₄ concentrations across farm reservoirs than does physical mixing, and further supports the hypothesis that the prevailing sediment and water chemistry are the primary controls of CH₄ concentrations.

Although the hydrological regime of small water bodies is rarely measured, we find that water source (rain, snow/groundwater) and reservoir retention time interact to influence CH₄ concentrations (Fig. 3F). In particular, CH₄ concentrations were lowest when WRT was long (>1 year) and water was derived mainly from snow or groundwater sources ($\delta^{18}\text{O}$ depleted). This may be due to a combination of reasons, including the prevalence of sulfate delivered from groundwater (Pennock et al., 2010), dilution of waterbody from snow melt inflow, and sediments depleted in labile carbon due to longer biogeochemical processing times in the dams. The effect potential effect of sulfate limiting methanogenesis is in agreement with the strong negative relationship found between CH₄ and conductivity in our model (Fig. 3D). Sulfate makes up a large portion of the ionic composition of groundwater in the Prairie Pothole Region due to pyrite oxidation (Goldhaber et al., 2014). Clearly, the biological influence on CH₄ concentrations is less pronounced in these larger, low-flow dams.

In contrast to the external drivers found for CO₂, local land use had a significant effect on CH₄ concentrations in farm reservoirs (Fig. 3I), with significantly higher CH₄ levels in cropland waterbodies than those in pasture. This finding contrasts with those from Australian farm reservoirs where diffusive CH₄ fluxes were 250% higher in reservoirs with livestock compared to crops, although the mechanisms responsible for observed differences were inconclusive (Ollivier et al., 2019). Catchment land use regulates the physioco-chemical properties of ponds (Novikmec et al., 2016) by influencing the degree of local vegetative cover and associated influx of allochthonous C to waterbodies (Whitfield et al., 2011). Similarly, regions with crops undergo more intensive agricultural modification, with fertilisation, crop rotations, and mechanical disturbance of soil which all lead to greater nutrient runoff and soil erosion. In this case it's likely that CH₄ levels are more influenced by nutrient loading from the landscape which stimulates eutrophication (Huttunen et al., 2003), as suggested by the biotic variables in our model (Fig. 3).

345 **4.3 Emissions from farm reservoirs compared to other small waterbodies**

To date, small waterbodies on farms have been shown to be large emitters of both CO₂ and CH₄ (Fig. 4). However, in our study we show that this is not always the case. Diffusive fluxes varied -21 to 466 and 0.14 to 92 mmol m⁻² d⁻¹ for CO₂ and CH₄, respectively. These findings are consistent with other small artificial waterbodies which are strong CH₄ sources that exhibit a large range of variability from 0.02-33 mmol m⁻² d⁻¹ (Grinham et al., 2018a; Ollivier et al., 2019). The negative
350 fluxes observed in our farm dams represents one of the few studied small waterbodies that exhibit CO₂ sink behaviour, with most showing net heterotrophy (Fig. 4). Although other studies have noted CO₂ sink behaviour in artificial ponds and reservoirs (Peacock et al., 2019; Ollivier et al., 2019), this is the first study to capture such a high proportion (>52%) of CO₂ uptake in such systems.

When CO₂ and CH₄ fluxes from small artificial waterbodies are compared with natural small waterbodies, no apparent trend
355 exists in which group produces more or less carbon emissions (Fig. 4). Natural ponds and constructed waterbodies have a similar range in variability of mean fluxes for both gases, while wetlands exhibit some of the greatest within-study variability. Constructed waterbodies often have lower net CO₂ efflux, suggesting that these systems more often switch between net autotrophy and heterotrophy than small natural systems. Small artificial waterbodies have disproportionately higher CO₂ and CH₄ emissions than other natural waterbodies due to the direct impact of agricultural and urban land use
360 (Wang et al., 2017). However, analysis of the limited literature shows that is not the case. We suggest that the lack of a clear distinction between constructed and naturally-occurring small water bodies arises because of geographical variation in the relative importance of the diverse factors regulating carbon metabolism (Figs 2, 3).

When assessing the GHG impact of constructed waterbodies, it is important to consider the relative contribution to CO₂-equivalent (CO₂-e) fluxes between CO₂ and CH₄. Here, CH₄ fluxes were converted to CO₂-e fluxes using the sustained-flux
365 global warming potential over 100 years (Neubauer and Magonigal, 2015). Small natural ponds and wetlands have some of the highest CO₂-e emission rates, with particular importance of contributions from CH₄ (Fig. 5). On average our farm reservoirs had one of the highest CH₄ contribution to CO₂-e fluxes (74%), in agreement with the one other farm reservoir study (83%) of CH₄ contribution (Ollivier et al., 2019). This large contribution from CH₄ is similar to patterns recorded from lakes and impoundments globally, where large freshwater bodies contribute to 75% of all CO₂-e efflux (DelSontro et al.,
370 2018). Fortunately, because the factors that regulate CH₄ emissions are becoming better identified (Fig. 3), there exists the possibility that artificial wetlands can be constructed to minimize CH₄-related CO₂-e emissions and mitigate the overall large rate of CO₂-e emissions from agriculture (Robertson et al., 2000).

4.4 Minimising emissions: potential management solutions

A combination of factors, including landscape position, construction, and management, could optimize features to minimize
375 carbon emissions from reservoirs and potentially enhance the carbon storage on farms. From our models, we suggest that key variables including the degree of water column stratification (buoyancy frequency), WRT, water source, land use, and

elevation are all suitable parameters for management. For example, strategizing landscape positioning to favour groundwater influx of sulfate to reduce methanogenesis. Creating deeper reservoirs will promote primary production through increased water clarity (Dirnberger and Weinberger, 2005), facilitate CH₄ oxidation through the water column (Bastviken et al., 2008),
380 and reduce the impact of watershed-derived solutes, terrestrial OM and benthic respiration. Additionally, deeper and larger artificial waterbodies tend to have lower nutrient concentrations due to longer processing times (Chiandet and Xenopoulos, 2016). Finally, modest increases in pH may further enhance CO₂ capture (Supporting Information), while having limited effect on CH₄ fluxes (Fig. 3).

Agricultural and urban waterbodies are highly susceptible to nutrient enrichment due to their direct proximity to intensified
385 land uses. Reducing nutrient loading from the landscape will likely have one of the greatest impacts in minimising C emissions from farm dams given that both CO₂ and CH₄ were strongly predicted by inorganic N-species. In Australian farm reservoirs, for example, a 25% reduction of nitrates can reduce CO₂-e emissions by 50% (Ollivier et al., 2019). Similarly, removing direct livestock access to farm waterbodies will improve water quality overall through reducing direct DIN inputs and dam infilling.

390 Nitrogen loading can also have a direct influence on nitrous oxide (N₂O), the third most potent greenhouse gas that can contribute substantially to CO₂-e emissions in farm systems (Robertson et al., 2000). The flux of N₂O was constrained in our earlier study (Webb et al., 2019), which found a small CO₂-e sink (-89 to -3 mg CO₂ m⁻² d⁻¹) for the majority of these farm reservoirs despite high N concentrations. Similar to our CO₂ model, stratification and primary production were important regulators in driving N₂O uptake (Webb et al., 2019). Therefore, the potential to achieve net GHG sinks weighs mostly on
395 the ability to reduce CH₄ emissions in these systems.

It is important to note that the CH₄ contribution to CO₂-e emissions is likely underestimated here as ebullition emissions were not measured. In farm reservoirs, ebullition flux can contribute >90% of total CH₄ emissions and is often highest in the smallest size classes (Grinham et al., 2018a). This reinforces that design and management strategies that focus on reducing all pathways of CH₄ emissions will be most effective in curbing total CO₂-e emissions. Deeper farm dams with steep side
400 slopes will likely be effective in reducing ebullition events due to a limited macrophytes, reduced bottom water temperature in summer, and suppressed bubble release with higher water pressure (Joyce and Jewell, 2003; Natchimuthu et al., 2014; Grinham et al., 2018b).

5 Conclusion

Until recently, carbon emissions from small farm reservoirs have been an overlooked, yet potentially important source of
405 CO₂ and CH₄ emissions within agricultural carbon budgets. To date, development of management strategies to reduce GHG emissions from waterbodies has been limited by lack of knowledge about the mechanisms regulating CO₂ and CH₄ production in these systems. By utilising adaptive modelling techniques across a broad range of environmental variables (abiotic, biotic, hydromorphological, landscape properties), we were able to explain a high degree of deviance in reservoir

CO₂ and CH₄ concentrations. We found that *in situ* water chemistry and local hydrological regime had the strongest impact on CO₂ and CH₄ concentrations. In agreement with previous studies, CH₄ fluxes were the largest contributor to CO₂-e emissions. However, in 19 reservoirs the net CO₂-e emissions were found to be sinks. We suggest that with optimal reservoir design and management the climatic impact of farm reservoir C-emissions has the potential to be a carbon net sink. To further develop farm reservoir management practices that are locally effective, we express a need for more widespread farm waterbody GHG measurements across the globe to cover other continents and land uses.

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Data availability: All data used in the models is available online in a GitHub repository (<https://github.com/JackieRWebb/Dugouts-CO2-CH4>). Public access to this repository will be made available upon publication and a DOI will be generated at this time.

420 **Supplement:** The supporting information related to this study will be published online.

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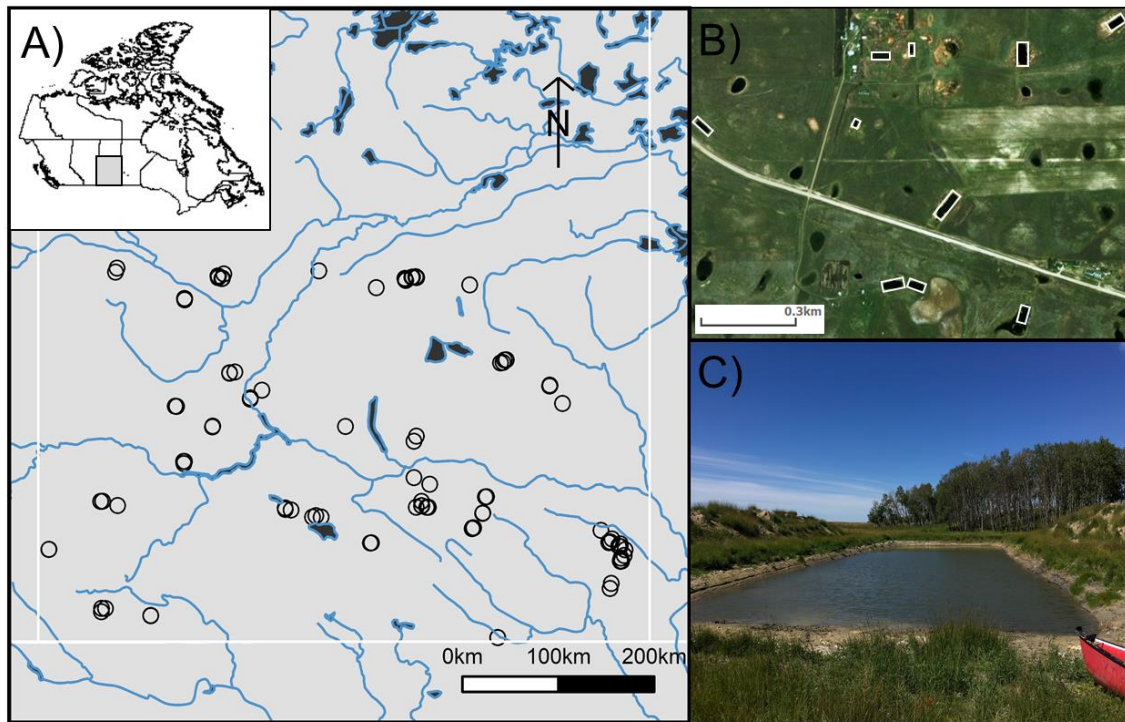
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Tables and Figures

Table 1: Farm reservoir and landscape physical, hydrological, and chemical characteristics of the study sites (n = 102)

	<i>Units</i>	<i>N</i>	<i>Mean</i>	<i>Median</i>	<i>Min</i>	<i>Max</i>
Area	m ²	101	1,312	1,040	158	13,900
Depth	m	102	2.08	2.10	0.18	5.10
Buoyancy frequency	s ⁻²	99	0.01	0.005	0.00	0.03
δ ¹⁸ O inflow	‰	101	-13.37	-13.33	-19.39	-8.40
Evaporation to inflow		101	0.46	0.43	0.04	1.58
Water residence time	Years	100	0.76	0.66	0.08	2.51
CO ₂	μM	101	42.2	14.6	1.3	326.1
CH ₄	μM	101	4.3	1.9	0.1	54.5
Temperature	°C	102	20.1	19.9	15.7	29.5
Dissolved O ₂	%	102	92.6	88.9	2.3	344.0
Salinity	ppt	102	0.9	0.5	0.1	8.6
pH		102	8.75	8.75	6.95	10.19
Chlorophyll a	μg L ⁻¹	102	99.1	36.9	2.2	2,483
NH ₃	μg N L ⁻¹	100	354.7	100.0	10.0	5,930
NO _x	μg N L ⁻¹	98	196.6	34.1	1.2	3,188
TP	μg P L ⁻¹	98	285.2	80.0	8.7	6,480
TN	μg N L ⁻¹	98	3,082	2,360	417.5	14,280
DOC	mg C L ⁻¹	99	31.8	29.3	4.6	90.4
Sediment organic carbon	%	101	5.2	3.9	0.6	31.4
Sediment organic nitrogen	%	101	0.6	0.4	0.1	2.8
Alkalinity	mg L ⁻¹	96	245.4	219.2	71.0	755.5
Soil CEC	M-eq 100g ⁻¹	98	24	24	10	180
K _{sat}	cm hr ⁻¹	102	9.9	5.0	0.0	39.7
Elevation	m	102	627.6	598.0	484.0	997.0



660 **Figure 1: A) Map of southern Saskatchewan in Canada showing the distribution of studied farm reservoirs, B) aerial image showing 10 farm reservoirs delineated by white rectangles within a 1 km² area, and C) general size and shape of farm reservoirs with two characteristic side mounds of excavated materials.**

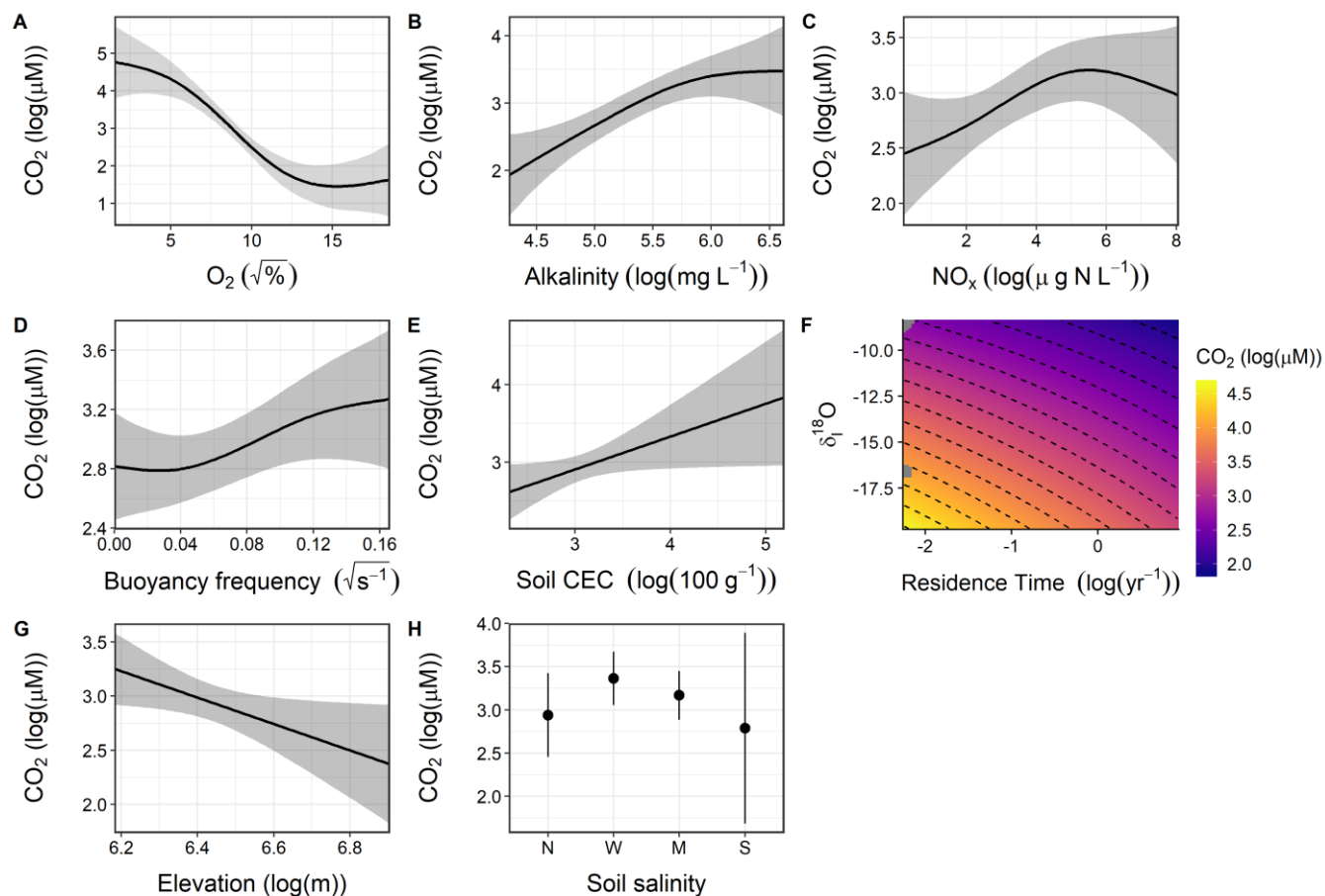


Figure 2: Response patterns farm reservoir CO_2 concentrations with abiotic, biotic, hydromorphological, and landscape variables based on GAMs. CO_2 was best estimated by a combination of a) DO saturation, b) alkalinity, c) NO_x , d) buoyancy frequency, e) interaction between $\delta^{18}\text{O}$ and WRT, f) soil CEC, g) and elevation, with soil salinity (h) not significant. Model deviance explained was 65.7%. The response patterns shown are the partial effect splines from the GAM and shaded area indicated 95% credible intervals. See Table S4 for summary of model statistics.

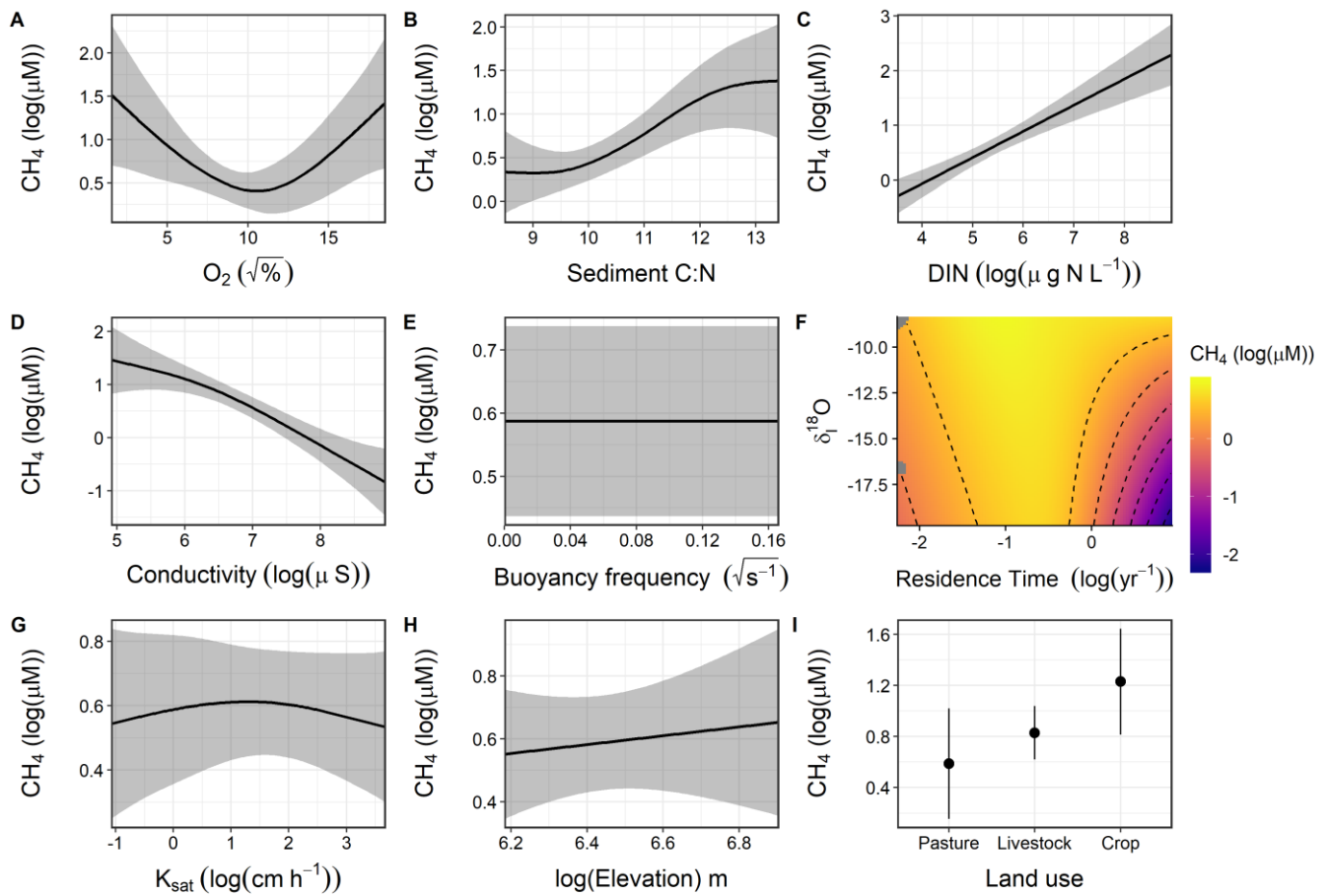


Figure 3: Response patterns farm reservoir CH_4 concentrations with abiotic, biotic, hydromorphological, and landscape variables based on generalised additive models (GAMs). CH_4 was explained by a combination of a) DO saturation, b) sediment C/N, c) DIN, d) conductivity, e) buoyancy frequency (not significant), f) interaction between $\delta^{18}\text{O}$ and WRT, g) soil K_{sat} (not significant), h) elevation (not significant), and i) local land use. Model deviance explained was 74.1%. The response patterns shown are the partial effect splines from the GAM and shaded area indicated 95% credible intervals. See Table S5 for summary of model statistics.

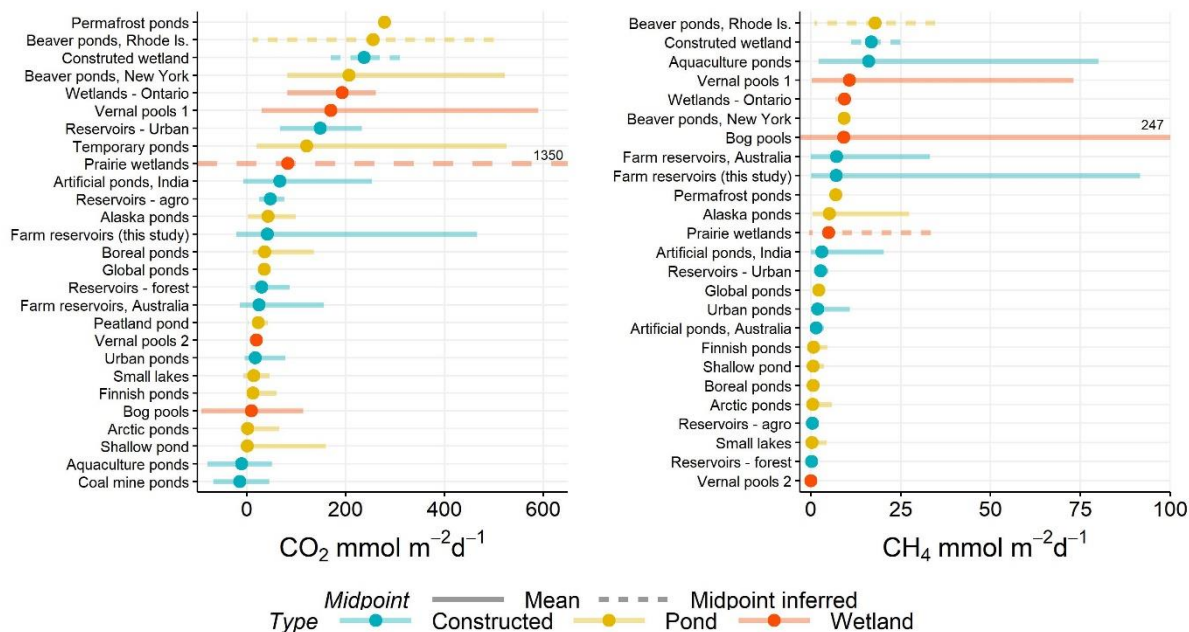


Figure 4: Range of CO₂ and CH₄ (diffusive) fluxes observed in natural and constructed small (<0.01 km²) waterbodies, including this study (farm reservoirs). Dots represent the mean reported in each study and error bars the range. If no mean value was reported, then the midpoint was inferred as the middle of range (dashed lines). All data is from the published literature and references can be found in the Table S6.

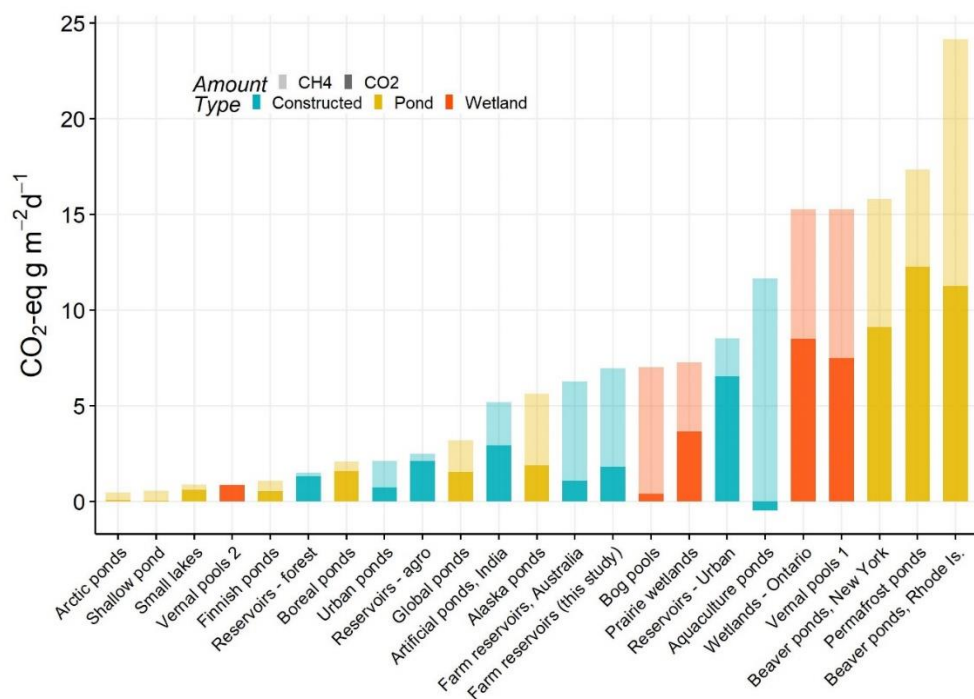


Figure 5: Total CO₂ equivalent fluxes of CO₂ and CH₄ (diffusive) measured in natural and artificial small waterbodies (<0.01 km²). CO₂-e fluxes were calculated based on 100 year sustained-flux global warming potentials in Neubauer and Megonigal (2015). Relative proportions of each gas are indicated by shading, and waterbody type is given by colour. All data is from the published literature and references can be found in the Table S6.