I need a title here

Draft for review

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# Abstract

Many quantitative relations in the environmental sciences, and specifically in watershed

# 1. Introduction

Wetlands are important global carbon (C) stores, accounting for 20-30% of the total terrestrial C storage in soils despite only covering 4-6% of the Earth’s land surface (refs). While peatlands are responsible for the majority of C stored in wetland soils, freshwater mineral soil (FWMS) wetlands are also globally significant C stores. Furthermore, FWMS wetlands are typically much more productive compared to peat forming wetlands (Mitsch and Gosselink 2000; Rocha and Goulden 2009). Globally, average C sequestration in established temperate FWMSWs is estimated to range between 100 and 250 (Bernal and Mitsch, 2012; Zhang et al., 2016; Lu et al., 2017).

The North American Prairie Pothole Region (PPR) extends from north-west Iowa in the USA into central Alberta in Canada and covers an area of ~800,000 km (Badiou et al., 2011). This region is dotted with millions of FWMS wetlands, generally refereed to as prairie pothole wetlands. Relative to other wetland ecosystems such as swamps, bogs, and northern peatlands, fewer studies have focused on prairie pothole wetlands despite their high C sequestration capacity (Bansal et al., 2016).

Although peatlands account for the majority of wetland area in Canada, it is estimated that ~20 million ha of FWMSWs have been lost in Canada since European settlement (~1800), compared to 1.4 million ha of peatlands (National Wetlands Working Group (NWWG) 1988), resulting in significant emissions of to the atmosphere (refs). Conversely, restoring FWMSWs can reverse soil C loss and sequester atmospheric (refs). Several studies have shown that restored wetlands in the Prairie Pothole Region of North America are particularly proficient at sequestering C (Gleason et al., 2006), with C sequestration rates ranging between 110-305 (Euliss et al., 2006; Badiou et al., 2011; Tangen and Bansal, 2020). These high C sequestration rates are driven by high productivity and low decomposition rates created by anoxic conditions. However, the same conditions which allow PPR wetlands to accumulate large amounts of C also promote the production and emission of methane ().

Methane fluxes from PPR wetlands have been observed to be among the highest reported for freshwater wetlands, although emissions show considerable spatial and temporal variability (Bansal et al., 2016, Badiou et al., 2011, Pennock et al., 2010). Notably, emissions in the PPR are significantly inversely correlated to concentrations of wetland waters (Pennock et al. 2010, Bansal et al., 2016). PPR wetlands have a wide range of sulfate-dominated salinities due to undulating topography and groundwater interactions with sulfur and carbonate rick glacial till (Winter and Rosenberry 1998;Goldhaber et al.2014). Higher sulfate concentrations are typically linked to reduced emissions as sulfate-reducing bacteria out compete methanogens for primary substrates such as acetate and hydrogen (refs).

While there have been a growing number of studies focused on C cycling in the PPR wetlands, to date observations of greenhouse gas (GHG) fluxes in the region have only been conducted using chamber-based methods (e.g., Bansal et al., 2016, more refs). While chambers are advantageous for assessing spatial variability in GHG exchange and treatment effects on fluxes, they are discrete in time, cover only a small area and are challenging to conduct over tall, emergent vegetation which dominate PPR wetlands. These limitations present challenges for estimating robust annual GHG budgets at the ecosystem level (Baldocchi 2003). Conversely, eddy covariance measurements can provide GHG flux estimates that are near-continuous and at ecosystem-scale flux measurements, without interfering with the system they are measuring. This makes this approach well-suited for estimating accurate GHG budgets and informing nature-based climate solutions (Novick et al., 2022). Furthermore, coupling these quasi-continuous flux measurements with ancillary biophysical measurements can provide new insights into the controls on GHG fluxes across a range of temporal scales (Knox et al., 2021)

Here we present the first eddy covariance estimates of carbon dioxide () and fluxes from two geographically isolated freshwater marshes in the grasslands and croplands of the PPR of Canada. Our objectives are to: (1) assess the annual GHG budget of these two wetland sites, and (2) identify the biophysical drivers of and fluxes at these sites and if/how they differ between sites.

# 2. Methods

## 2.1 Site description

MBPPW1, located at 50.3623˚N, -100.20242˚W, is an isolated cropland marsh in the PPR of Manitoba, Canada. This wetland site is entirely dominated by emergent vegetation, primarily populated by Schoenoplectus tabernaemontani and Typha spp. The water chemistry in this wetland is characterized by high sulfate concentrations.

MBPPW2, located at 50.3705˚N, -100.5339˚W, is an isolated grassland marsh about 24 km East of MBPPW1. However, this site is much more heterogeneous than MBPPW1 and is characterized by a combination of open water and emergent vegetation. Large mats of submersed macrophytes are found near the open water surface during the growing season, and the emergent vegetation is dominated by Typha spp. This site is characterized by lower sulfate concentrations.

PICS of sites and footprints?

CLIMATE NORMALS?

## 2.2 Eddy covariance measurements

The eddy covariance method was used to measure continuous, ecosystem-scale fluxes of CO2, CH4, water and energy over the two prairie wetland sites over two full years (June 1, 2021 to June 1, 2023). A flux tower was constructed at each of the sites with sensors mounted at ~4.1m at both sites. These sensors include a 3-dimensional ultrasonic anemometer (RM Young 81000, RM Young Inc.), an open path CO2/H2O infrared gas analyzer (IRGA) (LI-7500A, LI-COR Inc.), and an open path CH4 IRGA (LI-7700, LI-COR Inc.). Data was logged using LI-COR’s Synchronization, Management and Real Time Flux system (Smartflux 3) software and onsite data pre-processing was done using a LI-COR 7550 Analyzer Interface Unit. Final re-processing of the raw flux data measured were processed in EddyPro (LI-COR Inc., US) with an averaging time of 30 minutes. Statistical tests for raw data screening were conducted to remove spikes, data outside plausible limits, skewness and kurtosis (Vickers & Mahrt, 1997). To correct the sonic anemometer tilt relative to the streamline, the double rotation method was applied (Wilczak et al., 2001). Block averaging was used for calculating the turbulent fluctuations, in which the mean values were removed from the scalar timeseries data. Covariance maximization was then used to correct for time lags arising from sensor separation (Fan et al., 1990). Other corrections applied to the data included the WPL correction to account for the effects of air density changes during the averaging period (Webb et al., 1980) and spectral corrections for low-pass and high-pass filtering (Moncrieff et al., 2004).

## 2.3 Supporting measurements

Meteorological variables were measured continuously throughout the study period. Incoming and outgoing shortwave and longwave radiation were measured using a net radiometer (CNR1, Kipp and Zonen, Holland), and incoming and outgoing photosynthetically active radiation (PAR) were measured using a pair of quantum sensors (LI-190, LI-COR, USA) at a height of 3.44 m. Air temperature (TA) and relative humidity (RH) were measured at 2 m (HMP-35 A, Vaisala Oyj, Vantaa, Finland) and precipitation was measured at the EC tower with a tipping bucket rain gauge (TR-525M, Texas Electronics, Dallas, TX, USA). Thermocouples were installed within 3-5 m from the tower to measure soil temperatures (TS) at depths of -10, +10 cm relative to the sediment water -interface. Additionally, a third thermocouple was installed at approximately half the water column depth at each site (HOGG - 25 cm and YOUNG – 40 cm). For the WTD measurements we used Odyssey capacitance water-level loggers (Ody Ltd, 2013). WTD measurements were not collected during the winter while wetlands were frozen. Meteorological measurements were recorded every second (confirm) and averaged over 30-min periods.

## 2.4 Flux data processing

Filtering of the flux and meteorological data first involved removing data that fell outside of realistic minimum and maximum ranges. Next we removed data coming from poor sensor conditions. These included conditions when the Smartflux system voltage fell below 0 V or rose above 30 V, Data Retention Module voltage fell below 0V or above 50V, Data Acquisition Module temperature fell outside of -60 to 60˚C, and when the LI7700 signal strengths fell below 20%. Additionally, we filtered flux data from measurements when wind directions were between 330˚ and 30˚ to remove turbulence interference from the flux towers which are positioned north of the EC sensors.

The half-hourly fluxes output from EddyPro were further filtered to exclude low-quality records and measurements made under conditions in which EC assumptions were not fulfilled. The half-hourly fluxes were marked with quality flags following a standard developed by Foken et al. (2004), and records flagged as “2” were discarded. Finally, a minimum friction velocity threshold was applied to remove EC measurements under insufficient turbulence conditions. Friction velocity thresholds were estimated with moving point tests via the REddyProc v 2.2.0 R package (Wuzler et al., 2018). Half-hourly flux measurements whose friction velocities fell beneath the threshold were removed from the final data set.

NEE, H, and LE, which are strongly controlled by site-level environmental conditions, were gap-filled with the Marginal Distribution Sampling (MDS) technique using REddyProc (Reichstein et al., 2005; Wutzler et al., 2018). Missing measurements in these fluxes were modelled with data calculated by their correlation with their driver variables: Net radiation, TA, and vapour pressure deficit, with gaps in meteorological variables filled by merging data from nearby Environment and Climate Change Canada climate stations. After gap-filling, NEE was partitioned into its two components (i.e., GPP and Reco) using the nighttime partitioning approach implememted using REddyProc (Reichstein et al., 2005; Wutzler et al., 2018).

FCH4 are more complex to model due to their non-stationary behaviour and temporally non-uniform relationships with their driver variables (Knox et al., 2021; Kim et al., 2002). Random forest modelling was used to gap-fill CH4 following the methods described in Kim et al. (2002). The predictor variables used to train the random forest models were friction velocity, net ecosystem exchange (NEE), LE, H, incoming shortwave radiative flux, TA, relative humidity, vapour pressure deficit, day of year, wind direction, and TS at 40 cm above, 10 cm above and 10 cm below the sediment-water interface. The random forest variable importance graph for MBPPW1 (Figure 6) shows that H, NEE, and 10 cm below sediment-water interface TS were found to be the strongest drivers of FCH4 at MBPPW1.

## 2.5 Uncertainty analysis

## 2.6 Net C and GHG balance estimation

### 2.6.1 Water sampling and analysis

Water samples were collected from three different open-water areas within each wetland and then composited into one sample for each wetland site. Samples were collected 10-20 cm below the water surface and care was taken not to sample any sediment or plant material suspended as a result of wading into the sites. The composite sample was split into three fractions that were stored and shipped in coolers. One fraction was sent to ALS laboratories in Winnipeg and analyzed for SO4 using ion chromatography (EPA 300.1 mod) and alkalinity using standard titration procedures (APHA 2320B). The remaining two fractions, one field filtered upon collection using glass fiber filters (GF/C) for dissolved nutrient analysis, and one unfiltered fraction for total nutrient analysis were delivered to the Agriculture and Agri-Food Canada’s Brandon Research and Development Centre in Manitoba, where they were frozen and stored in a cooler until analyzed. A flow analyzer was used to measure NH4+ and NO3- (as NO3- + NO2-) concentrations colorimetically. Total dissolved N and DOC concentrations were determined through the combustion method using a Shimadzu TOC-VCSn analyzer. Total P and TDP concentrations were determined through sulfuric acid/persulfate digestions and colorimetry using the ascorbic acid method. Additionally, water temperature, specific conductivity, dissolved oxygen, pH, and salinity were measured in-situ using handheld multi-probes.

ABS 280 - does higher mean more recalcitrant DOC?

samples were collected on xxx days and linearly interpolated between observations

## 2.7 Statistical methods

All data processing and statistical analyses were conducted using R (R Core Team, 2019). Significant differences in water quality parameters, environmental variables, and fluxes between sites, years and the interaction between site and year were assessed using a two-way ANOVA with Type III Sums of Squares on the rank-transformed data, as ranking can be used to transform data that do not meet the assumptions of normality (ref). Here, each original data value was replaced by its rank, with 1 for the smallest value to N for the largest, where N is the combined data sample size. This rank-based approach is robust to non-normal errors, resistant to outliers, and is effective for many distributions. When comparing differences in variables between sites, years and the interaction between site and year, we only considered the summer period when water quality measurements were available.

Multivariate associations of water quality parameters across sites were analyzed using principal component analysis (PCA). All variables were centered and scaled, and PCA was done using the ‘prcomp’ function in base R.

To investigate the environmental factors controlling differences in FCH4 across sites, we trained random forest (RF) models on daily mean FCH4 using common meteorological and biological drivers, and a subset of water quality parameters. Meteorological variables included daily mean TA, WTD, VPD, u\*, and daily GPP was included as the biological predictor. As certain water quality parameters were highly correlated (Figure [3](#fig-PCA)), to capture the primary differences in water quality parameters between sites, only , TP, , (as (as & )), and pH were included in the RF analysis.

The RF algorithm creates bootstrapped data sets and then generates independent regression trees using randomly sampled variables at each split node. Then, RF aggregates the prediction results of the individual trees. Random forests were fit using the ‘caret’ (Kuhn 2017) and ‘ranger’ (R (Wright & Ziegler, 2017; R Core Team, 2019) packages. Similar to Knox et al. (2021), each RF was trained on all available data from both sites (i.e., the dataset was not split into training and test data), and out-of-bag data were used for hyperparameter tuning. The inclusion of all available data is justified as our goal was to assess dominant predictors of FCH4 across sites rather than develop a predictive model that can be applied to new conditions, and 2) RF is already robust to outliers (Zhang & Lu, 2012). We used an ensemble of 500 trees, and hyperparameter tuning was performed for mtry (the number of predictors randomly sampled at each devision node) and min.node.size. Predictors were ranked using permutation importance, which avoids bias from other approaches (Strobl et al., 2007), and importance values were scaled for comparison between sites (Knox et al., 2021). Additionally, Partial Dependence Plots (PDP), generated using the ‘pdp’ package, were used to investigate the marginal contribution of different predictors on FCH4.

# 3. Results

## 3.1 Meteorology and hydrological conditions

Figure [1](#fig-met_ts).

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| Figure 1: met\_ts. |

Given the proximity of the sites, Hogg and Young experienced similar meteorological conditions; there were no significant differences in mean growing season daily average incoming photosynthetically active radiation (PPFD\_IN), air temperature (TA), vapor pressure deficit (VPD), and precipitation (P) between sites. Though, water levels (WTD) at Young were significantly higher than at Hogg, and WTD was significantly higher in 2022 relative to 2021 (Table **?@tbl-MET**; Figure [1](#fig-met_ts)). Mean growing season temperatures did not differ significantly between years at the 5% significance level, but TA was significantly higher in the 2021 than 2022 growing season at the 10% significance level (Table **?@tbl-MET**). Other meteorological variables did differ significantly between years at the 5% level, with higher daily precipitation and VPD observed in 2021 relative to 2022 (Table **?@tbl-MET**).

| site | year | TA | VPD | PPFD\_IN | P | WTD |
| --- | --- | --- | --- | --- | --- | --- |
| Hogg | 2021 | 17.3 | 8.5 | 440 | 246.2 | 235.8 |
| Hogg | 2022 | 16.4 | 6.9 | 449 | 178.2 | 438.4 |
| Hogg | 2023 | -4.3 | 2.7 | 346 | 53.3 | NaN |
| Young | 2021 | 17.1 | 8.3 | 438 | 254.9 | 481.8 |
| Young | 2022 | 16.2 | 6.3 | 447 | 225.2 | 573.8 |
| Young | 2023 | -4.7 | 2.7 | 334 | 61.8 | NaN |

## 3.2 Water quality observations

Significant differences were observed in water quality parameters across sites (Table [1](#tbl-WQ), Figure [3](#fig-PCA)). Averaged across years, Hogg had significantly higher , specific conductivity, dissolved organic carbon (DOC), total dissolved nitrogen (TDN), and Specific ultraviolet absorbance at 280 nm (ABS 280) than Young (Table [1](#tbl-WQ)). Conversely, dissolved reactive phosphorus (DRP), total dissolved phosphorus (TDP) concentrations than Young, total phosphorus (TP) was significantly lower at Hogg than Young. No significant differences in pH, NO3 or NO2, or NH4 were observed between sites.

Table 1: Annual GHG budgets.

| site | year | pH | SO4 | Specific\_cond | DOC | TDN | NO3\_NO2\_N | NH4\_N | DRP | TDP | TP | ABS\_280nm |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Hogg | 2021 | 9 | 1211 | 3848 | 95 | 5 | 15 | 116 | 19 | 94 | 181 | 2 |
| Hogg | 2022 | 9 | 2101 | 1522 | 52 | 3 | NaN | NaN | 6 | 63 | 155 | 1 |
| Hogg | 2023 | NaN | NaN | NaN | NaN | NaN | NaN | NaN | NaN | NaN | NaN | NaN |
| Young | 2021 | 9 | 340 | 1017 | 30 | 2 | 4 | 44 | 289 | 387 | 505 | 0 |
| Young | 2022 | 9 | 251 | 822 | 22 | 2 | NaN | NaN | 394 | 490 | 506 | 0 |
| Young | 2023 | NaN | NaN | NaN | NaN | NaN | NaN | NaN | NaN | NaN | NaN | NaN |

Figure out best figure(s) to use. ALL WQ variables?

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| --- |
| Figure 2: SO4. |

|  |
| --- |
| Figure 3: PCA. CHANGE VAR NAMES |

## 3.3 GHG budgets - REVISE WHEN WE GET FULL YEAR OF DATA!

Both wetland sites were net sinks over the course of the growing season, although net uptake was lower at Young relative to Hogg in both 2021 and 2022 due to lower GPP at Young (Figure [4](#fig-fluxes)). Annually, this resulted in in Hogg being a weak net sink in 2021 and a strong sink in 2022, taking up 34 and 151 gC , respectively. Conversely, Young was a net source of 57 gC in 2021, and a weak sink of 31 gC in 2022. Annual GPP at Hogg was 23-32% greater than Young depending on the year, while differences in annual Reco were smaller between sites (on average ~12%) (Table [2](#tbl-fluxes)).

Large differences in fluxes were also observed between sites (Figure [4](#fig-fluxes); Table [2](#tbl-fluxes)). While Young showed a strong seasonal cycle in FCH4 in both years of observation, emissions at Hogg hovered near zero across the measurement period. However, there were significant differences in fluxes at Young between years with higher annual emissions in 2021 relative to 2022 (6.8 versus 4.4 gC , respectively). Hogg also exhibited differences in fluxes between years (1.9 and 2.4 gC in 2021 and 2022, respectively), although differences were not significant [CONFIRM] (Table [2](#tbl-fluxes)).

Combining CO2 and CH4 fluxes, on a 100-year time scale Hogg was GHG neutral in 2021, but a notable GHG sink in 2022 driven by higher net uptake that year. Conversely, Young was always a net GHG source (168 and 616 gC-eq in 2021 and 2022, respectively) due to both higher fluxes and lower net uptake (or even net emissions) at Young relative to Hogg.

Add 20 & 500 year time scale??

ALSO PLOT OF CUMULATIVE FLUXES???

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| Figure 4: Fluxes. |

(Table [2](#tbl-fluxes))

Table 2: Differences in fluxes across sites.

|  | NEE | FCH4 | GPP\_DT | GPP\_NT | Reco\_DT | Reco\_NT | GHG |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Hogg | -35 ± 20 | 1.9 ± TBD | 838 ± 4 | 869 ± TBD | 677 ± 835 | 834 ± TBD | -4 ± TBD |
| Young | 49 ± 21 | 6.8 ± TBD | 641 ± 18 | 658 ± TBD | 621 ± 707 | 707 ± TBD | 616 ± TBD |

# 4. Controls on net CO2 exchange

RF first (get % vegetation cover from Darian), then Light response curves for veg vs open water.

## 4.1 Predictors of FCH4 - ADD Cond or salinity?

Across sites, the RF model explained 83% [insert code for this] of observed variance () when evaluated against out-of-bag (OOB) data. Based on the variable importance rankings, concentration was the dominant predictor of FCH4 (Figure [5](#fig-VarImp)a), indicating that the significant difference in concentration across sites (Table [1](#tbl-WQ)) was the dominant factor explaining the differences in FCH4 across sites. The partial dependence plot for the RF model indicates that FCH4 is strongly inhibited below concentrations greater than ~500 UNITS when the effects of other factors were excluded Figure [6](#fig-pdp)a). In addition , other water quality variables, including DOC, pH and NO3/NO2 along with WTD were also among the top predictors of FCH4 across sites.

When trained with data within sites, the RF model explained 71% of observed variance at Young when evaluated against OOB data, although the RF model was unable to explain the variance at Hogg ( = 0). The poor performance at Hogg is likely due to the low FCH4 observed at this site, which are close to the detection limit of the system [REF]. As such, we only consider the variable importance rankings for Young (Figure [5](#fig-VarImp)b). While water quality parameters were also dominant predictors of FCH4 at Young, with TP ranked first and ranked 4th, TA and GPP were also among the top predictors at Young. Based on the partial dependency plots for the Young RF model, TP appeared to limit FCH4 at concentrations greater than 500 UNITS, while FCH4 followed roughly logistic growth with TA and GPP.

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| Figure 5: Variable importance. |

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| Figure 6: Partial dependence plots showing the effects of SO4 used in the random forest models computed across sites & ADD HERE. |

# 5. Discussion

In this study, we conducted the first eddy covariance observations of GHG fluxes from PPR wetlands. Observations were conducted at two wetland sites that differ both in terms of vegetation cover and water quality; Young is a heterogeneous wetland composed of a mix of open water and vegetation and characterized by low sulfate concentrations and higher phosphorus concentrations, while Hogg is a more homogeneous site dominated by emergent vegetation and characterized by high sulfate concentrations.

While Hogg was a C sink, as reported in previous studies that estimated C sequestration rates using soil cores, C uptake (-35 ± 20 gC m-2 yr-1) was on the low end of values reported in the literature which range from 35 to 610 g C m-2 yr-1 (REFS). Furthermore, we observed that Young was a net C source in over the observation period.

CH4 flux - can look at drivers and functional relationships….

Wetlands in the PPR are generally observed to have high C sequestration rates and the potential for high CH4 emissions [refs].

While there have been a growing number of studies focused on C cycling in the PPR wetlands, to date observations of greenhouse gas (GHG) fluxes in the region have only been conducted using chamber-based methods (e.g., Bansal et al., 2016, more refs).

Several studies have shown that restored wetlands in the Prairie Pothole Region of North America are particularly proficient at sequestering C

Wetlands in the PPR have been

Notes:

Also, waters of the permanentwetlands in the PPR tend to contain relatively high sulfateconcentrations (Phillips and Beeri2008;Pennocketal.2010 ), which suppresses methane production. Thus, chemicalvariation among PPR wetlands may play a key role in moder-ating greenhouse gas emissions from wetlands, especiallyfrom those with longer periods of ponding

Badiou et al., 2011 Additionally, thedilution effect resulting from this increase in waterlevel greatly reduced concentrations of nutrients andmajor anions and cations. This is important as sulfatereduction is known to at least partially inhibit CH4

production (Gauci et al.2004). A recent studyconducted in ephemeral prairie pothole wetlands inSK by Pennock et al. (2010) has demonstrated thatCH4emissions decrease as sulfate (SO42-) concen-trations increase. Rapid increases in CH4emissionsassociated with increased spring runoff leading to

depletion in SO42-concentrations has also beendocumented by Phipps (2006) for a permanentwetland located in the St. Denis National WildlifeArea in Saskatchewan, Canada

Read about P, DOC & pH on FCH4

Sheel’s paper…

# 6. P

https://www.sciencedirect.com/science/article/pii/S135223101200533X?casa\_token=-80RBudOMqgAAAAA:J4kAMkLyyqSO-VlVz-xWAeFYBfC5TJV9SZfs9\_Vb3mkzRNITLDtclb0bewoGwe2oqRMUdRiLOw#fig3

Our results indicated that the effect of P enrichment on CH4 emission was time-dependent. Increased P availability did not affect CH4 emission in 2007 and 2008, but decreased in 2009 and 2010. Notably, four years of P addition decreased cumulative CH4 emission during the growing season in the freshwater marsh, and the effect did not change with fertilization rates. From 2007 to 2010, P additions of 1.2, 4.8 and 9.6 g P m−2 year−1 caused a decline in growing-season CH4 emissions by averages of 23%, 38% and 26%, respectively. Our results suggest that long-term P enrichment driven by agricultural activities would reduce CH4 emission from temperate freshwater wetlands.

Similar to other natural ecosystems, wetlands are currently experiencing increased P loading as a result of human activities (Keller et al., 2005; Song et al., 2011). In wetland ecosystems, P enrichment is assumed to stimulate plant growth and increase plant production, enhancing substrate availability for methanogens through root exudates and litter turnover, which increases CH4 fluxes to the atmosphere. However, previous studies have found that the response of plant productivity to P addition is often species-specific and that this response varies by wetland type (Verhoeven and Schmitz, 1991; Chapin et al., 2004; Keller et al., 2006).

Moreover, increased P loading to wetlands may change soil microbial community and activity (Keller et al., 2006) and alter plant-mediated transport of CH4 (Lu et al., 1999).

See 4. Discussions

This finding implies that elevated P loading would exert a consistent suppression of CH4 emission in temperate freshwater wetlands.

Matt’s paper Salinity can also interact with other key CH4 controls, with organic C availability modulating the SO42- inhibition of methanogenesis12,19,25,26, and nutrient availability changing with salt content due to sorption to sediments19,27.

We show that salinity restricts CH4 emissions in small lentic waterbodies, especially through ebullition, leading existing freshwater models to overpredict emissions

We show that salinity is a key driver of CH4, interacting with organic matter (OM) content to shape surface CH4 partial pressure (pCH4).

As salinity increases, individual ions (not necessarily SO42-) with greater binding capacities can replace N bound in sediment complexes, and liberate NH4+ which is a precursor to important terminal electron acceptors (NO32- and NO2-) that fuel AOM (detailed above).

As such, salinity is a useful empirical predictor of CH4 content in part because it reflects the geochemical limitations that can be imposed on primary producer growth and organic matter supply to methanogens.

the DOC (mg L-1) to salinity (ppt) ratio -> DOC modulates the influence of salinity

suggests that organic-rich systems (with elevated DOC concentrations) can compensate for the inhibitory effect of salinity on methanogenesis. Similarly, pCH4 correlated with ratios of TN and TP to salinity (Fig. S3b,c), indicating that DOC was a proxy for OM content and ecosystem productivity

In line with previous research, the correlation with DOC likely reflects the absence of competition for organic substrate between methanogenesis and other reduction pathways when OM is abundant or when the low concentration of other electron acceptors limits alternative redox processes12,19,25.

Most sampled sites (78%) in the Prairie landscape exhibited moderate salinity < 1 ppt (Fig. S1, Table S1), a range within which even modest salinity changes from year to year45,49 could have a substantial effect on CH4 dynamics (Fig. 1c). For example, at the same DOC concentration (10 mg L), a 0.5 ppt increase in salinity at low salinity conditions (0.5 ppt) results in a 35% reduction of pCH4, (710 to 458 ppm) while a 0.5 ppt increase in salinity from 3.5 to 4 ppt only decreased pCH4 by 8% (207 to 190 ppm) (Fig. 1c). -> Compare salinity response at our sites!

Past work has emphasized the need for detailed spatio-temporal sampling to constrain uncertainties in flux budgets for single-system research51.

Were salinity not a controlling factor, we would have anticipated consistently high rates of CH4 emissions from both wetland ecosystems, given the hypereutrophic status of both sites, and the DOC-rich surface water environments (Table S4).

Overall, our eddy-covariance measurements provide independent support for the Prairies-wide inverse relationship that we observed between salinity and CH4 emissions.

In the Canadian Prairies, SO42- concentrations have increased in 64 % of the 14 monitored lakes for which data are available in Saskatchewan over the past 30 years (Fig. S8). This is consistent with previous findings that, despite high-local variability, many Prairie waters are becoming more saline42,68. This may in part be linked to rapid increases in the application of S-based fertilizers in agricultural landscapes69, which may in turn lead to enhanced SO42- content and salinity in receiving waters (though such a mechanistic link remains unconfirmed).

# References

Badiou, P., Mcdougal, R., Pennock, D., and Clark, B.: Greenhouse gas emissions and carbon sequestration potential in restored wetlands of the canadian prairie pothole region, <https://doi.org/10.1007/s11273-011-9214-6>, 2011.

# Tables