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Sara Helen Knox

Department of Geography, University of British Columbia

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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.

## 2.2 Eddy covariance measurements

## 2.3 Gap-filling, NEE partitioning, and annual budget computation

## 2.4 Supporting measurements

### 2.4.1 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?

## 2.5 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 [1](#tbl-MET); Figure [1](#fig-met_ts)). Mean growing season temperatures did not differ significantly between years (Table [1](#tbl-MET)). However, the other meteorological variables did differ significantly between years, with higher daily precipitation and VPD observed in 2021 relative to 2022 (Table [1](#tbl-MET)).

Table 1: Growing season mean air temperature (TA) and vapour pressure deficit (VPD), photosynthentically active radiation (PPFD\_IN), and water table dept (WTD), and cumulative precipitation at Hogg and Young during 2021 and 2022.

| site | year | TA | VPD | PPFD\_IN | P | WTD |
| --- | --- | --- | --- | --- | --- | --- |
| Hogg | 2021 | 16.5 | 8.3 | 418 | 267.2 | 230.5 |
| Hogg | 2022 | 15.4 | 6.6 | 429 | 180.1 | 438.4 |
| Young | 2021 | 16.4 | 8.0 | 415 | 281.0 | 462.3 |
| Young | 2022 | 15.5 | 6.1 | 427 | 225.2 | 573.8 |

## 3.2 Water quality observations

Significant differences were observed in water quality parameters across sites (Table [2](#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 [2](#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 2: 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 | NaN | NaN | NaN | NaN | 6 | 63 | 155 | NaN |
| Young | 2021 | 9 | 340 | 1017 | 30 | 2 | 4 | 44 | 289 | 387 | 505 | 0 |
| Young | 2022 | 9 | 251 | 822 | NaN | NaN | NaN | NaN | 394 | 490 | 506 | NaN |

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

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| Figure 2: SO4. |

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| Figure 3: PCA. CHANGE VAR NAMES |

## 3.3 GHG fluxes

Both wetland sites were net sources over the course of the growing season, although net update was lower at Young relative to Hogg due to lower GPP at Young (Figure [4](#fig-fluxes)). Annually, this resulted in in Hogg being a net sink in 2021-2022, taking up 34 gC , while Young was a net source of 57 gC . Cumulative annual GPP at Hogg was 31% greater than Young, while differences in annual Reco were smaller between sites (~10%) (Table [3](#tbl-fluxes)).

Relative difference in fluxes were even larger between sites (Figure [4](#fig-fluxes); Table [3](#tbl-fluxes)). While Young showed a strong seasonal cycle in FCH4 over the course of the year, with daily emissions exceeding >100 mgC during the growing season, emissions at Hogg hovered near zero across the measurement period. As such, cumulative annual FCH4 at Young was >6 time larger at Young relative to Hogg (7.6 versus 1.12 gC , respectively) (Table [3](#tbl-fluxes)).

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| Figure 4: Fluxes. |

(Table [3](#tbl-fluxes))

Table 3: 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 |

## 3.4 Predictors of FCH4

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 [2](#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. |

# 4. Discussion

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

# 5. 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.

# 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