Carbon and Phosphorus Dynamics in Restored Minnesota Peatlands

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Abstract

While many peatlands have been drained for anthropogenic purposes across the world, there is currently high interest in restoring peatlands for carbon and nutrient cycling benefits. Peat holds a disproportionate amount of the world's soil carbon, making peatlands promising ecosystems for mitigating greenhouse gas emissions and climate change. Additionally, peatlands can sequester phosphorus (P) and prevent it from causing eutrophication in downstream waters, but they can also act as a P source under high runoff conditions. This study aimed to investigate the factors impacting 1) peat carbon dioxide (CO_2) flux and 2) mobilization of peat P to porewater in a restored bog and fen in Minnesota. Peat CO_2 flux was monitored in-situ throughout the growing season in conjunction with peat type, water table depth, and temperature. Peat columns from each site were saturated and subjected to controlled laboratory incubations to relate porewater ortho-P content to temperature and porewater aluminum (Al), calcium (Ca), and iron (Fe) content.

A higher water table was significantly related to lower peat CO_2 flux in the fen, and peat CO_2 flux across both sites was higher in regions with more decomposed peat. During the peak of the growing season, CO_2 flux was much higher in the fen than the bog, but both sites had similarly low CO_2 flux at the end of the growing season. It is important that restoration ecologists consider a peatland's water table when restoring a site's hydrological, ecological, and biogeochemical functioning in order to achieve the greatest carbon benefit. Higher porewater ortho-P corresponded to higher dissolved porewater Al, Ca, and Fe. Additionally, higher initial peat Ca was significantly related to lower porewater P. These ions play a role in binding and mobilizing P, and their dynamics can help researchers predict and mitigate P release and subsequent export.

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1. Introduction

1.1 Overview

People have historically drained peatlands across the world for row crop agriculture, grazing, forestry, peat mining for fuel, and residential development (Chimner et al., 2017). Over the past several decades, global interest in restoring degraded peatlands has increased due to concern over their carbon dioxide emissions (Leng et al., 2016) and potential to offer climate benefits if restored (Renou-Wilson et al., 2019). While mineral soils can sequester carbon, peatlands do so much more efficiently (Kolka et al., 2016; Leifeld and Manichetti, 2018), currently storing 30% of Earth's soil carbon despite only taking up 3% of its land area (Page and Baird, 2016; Yu et al., 2010). In addition to mitigating global carbon emissions, restored peatlands can also aid in the cycling and stabilization of nutrients (Johnston et al., 1990; Negassa et al., 2020). Peatlands alongside ponds, lakes, rivers, and streams can act as buffers during runoff events. Instead of a large influx of nutrients reaching the adjacent water body, they are stored in the peatland and sequestered in peat over time by microbes, stabilizing them and preventing future transport. Peat is highly absorbent and can store large amounts of water, so it is also helpful in preventing flooding during large precipitation and runoff events.

Minnesota contains 1.4 million ha of peatlands, mainly distributed in the northern part of the state (Minnesota DNR). Peatlands here are defined as containing soils with more than 12% organic matter. Southern, central, and western Minnesota used to have large peatland areas, though much has been drained for agriculture. The state also contains swaths of muck soils, which are peats that have been further decomposed but still contain more than 12% organic matter (SSSA, 2008). Restoring peat and muck lands could mitigate carbon dioxide (CO_2) emissions on the magnitude of hundreds of thousands of metric tons per year in Minnesota alone (TNC, 2020).

Figure 1: Peatland cover in Minnesota in 1920 (Alway, 1920)

Despite the many benefits, restoring peatlands can have some detrimental impacts adjacent or downstream waters. Peatlands drained for agriculture often act as sources of phosphorus (P) when rewetted (Walton et al., 2020), and peat buffer zones have the potential to export heavy loads of P, nitrogen (N), and dissolved organic carbon into adjacent streams. High influxes of nutrients, especially P, enrich aquatic ecosystems and cause eutrophication, reducing biodiversity and causing massive die-offs of biota. Extreme eutrophication can oftentimes be permanent. P is commonly found in a solid state, allowing it to settle in bottom sediments and become buried over time as it is cycled within aquatic systems (Carpenter, 2005). This makes P very difficult to remove once it enters the water bodies, so many remain polluted indefinitely.

Additionally, carbon benefits are uneven across peatlands. Factors such as peatland hydrology, litter quality, moisture content, and climate conditions play a complex role in determining the existence and magnitude of a peatland carbon sink. While CO_2 sinks may become larger after restoration, wet conditions may increase emissions of methane (CH_4), a more potent greenhouse gas that could offset the CO_2 sink (Olsen et al., 2012).

Given the prevalence of peatlands in Minnesota, The Nature Conservancy identified peatland restoration as a potential natural climate solution for mitigating climate change in the state (TNC, 2020). This led to a broader research initiative regarding the feasibility and issues associated with peatland restoration in an effort to maximize benefits. As part of this initiative, this work aims to explore the factors that impact carbon and P dynamics in restored Minnesota peatlands in order to determine their potential for climate change mitigation and risk of P release. Findings can help restoration ecologists decide how and where to prioritize peatland restoration projects that will result in the greatest carbon sink and prevent unwanted eutrophication of downstream and adjacent waters.

1.2 Study Sites

Peatlands can typically be classified as one of two hydrological types: bog or fen. Bogs receive no input from regional groundwater, so almost all of their water comes through direct precipitation input and flow from uplands, while fens receive groundwater contributions in addition to these inputs (Kolka et al., 2011). This groundwater often makes peat in a fen alkaline through mineral transport, while bog peat tends to be acidic and chemically-dependent on the vegetation contained in the bog. These distinct hydrological and chemical characteristics can lead to unique carbon and nutrient dynamics in each type of peatland. We selected a restored bog and fen in Minnesota as study sites in order to evaluate and compare CO_2 and P dynamics in different types of peatlands with similar climates.

1.2-1 Sax-Zim Bog

Sax-Zim bog, a spruce-tamarack bog located in Meadowlands, Minnesota, was originally ditched and drained for grazing and forestry beginning in 1915. These land uses maintained some of the original plant communities, but degraded the area's wetland hydrology. Rewetting of the bog began in 2015, with wetland area now totaling approximately 77,700 ha (Friends of Sax-Zim Bog). The area of the bog selected for this study is located near the Sax-Zim Bog Welcome Center, which is on the fringe of the restored area. This region was passively restored by filling in a ditch with just under a meter of peat to reduce drainage, partially but not fully restoring the hydrology.

Located at 47.15° N, 92.72° W, the site is characterized as southern boreal forest, with canopy comprised of black spruce (*Picea mariana*) and tamarack (*Larix laricinia*). The bog's ground cover is dominated by *Sphagnum* moss and *Carex* sedges, and also contains *Sarracenia* pitcher plants due to the acidic, nutrient-poor peat. No groundwater flowthrough has been detected in the bog, so it is thought to be fed only by precipitation and snowmelt. Mean annual precipitation from 1991-2020 was 28.4 cm ± 3.9 cm, and mean warm season precipitation (May-September) was 18.4 cm ± 3.6 cm (Minnesota DNR). Mean annual temperature from 1991-2020 was 3.6˚C ± 11.4˚C, and normal warm season temperature was 15.0˚C ± 3.3˚C. Temperatures in May through September ranged from 1.3˚C to 28.6˚C for 1991-2020. July had the highest growing season temperatures, with an average high of 25.1˚C ± 1.6˚C (Minnesota DNR).

Figure 2: Spruce, tamarack, and hummocks in Sax-Zim bog

Figure 3: *Sphagnum* ground cover in Sax-Zim bog

1.2-2 Cold Spring Fen

Restoration of the Cold Spring fen, a calcareous fen previously degraded by row-crop agriculture, began in summer 2018 and is ongoing. The Nature Conservancy, Minnesota Land Trust, Sauk River Watershed District, Stearns County Soil and Water Conservation District, and Minnesota DNR collaborated with the landowner on the restoration to replenish the groundwater spring and treat water flowing to the Sauk River. Located at 45.46° N, 94.40° W, the 28.3-ha restored area extends to the Sauk River and contains a hillside fen, as well as a floodplain consisting of wet prairie, savanna, and floodplain forest. To correct negative ecological impacts from a drainage ditch at the top of the hill, a diversion was created in 2020 to redirect water to a flat terrace at the bottom of the hillside fen and restore its functionality. A ditch on the east side of the site is characterized by high baseflow, and caused flooding of the site and the adjacent farm field during stormflow. To prevent this flooding and distribute water more evenly across the wet prairie, a second diversion was constructed in May 2021, simulating a shallow meandering swale that existed on the site prior to ditching. A previous soil mapping of the site found that peat is deeper on the hillside fen than on the floodplain (Ethier, 2019). Staff at The Nature Conservancy and the University of Minnesota have collaborated since 2018 to characterize the groundwater gradient and discharge in order to inform further restoration.

In addition to hydrological restoration, vegetation management has occurred to restore native plants. Current vegetation on the site is not representative of a typical fen. Herbaceous vegetation is dominated by reed canary grass (*Phalaris arundinacea*), ragweed (*Ambrosia trifida*), and bull thistle (*Crosium vulgare*) in the wet prairie, which currently contains no trees but received tamarack plugs in May 2021. The hill contains dense growth of buckthorn (*Rhamnus cathartica*), ragweed and boxelder (*Acer negundo*). Efforts to remove ragweed and buckthorn are still underway, with overgrowth of ragweed presenting a management challenge. Oats and rye from seeding efforts successfully established along the diversions in summer 2021.

The fen receives water from groundwater, and precipitation. Mean annual precipitation from 1991-2020 was 30.1 cm ± 3.9 cm, and mean warm season precipitation (May-September) was 19.2 cm ± 4.3 cm (Minnesota DNR). Mean annual temperature from 1991-2020 was 7.1°C ± 11.6°C, and normal warm season temperature (May-September) was 18.9°C ± 3.2°C. Temperatures from May through September ranged between 4.4°C to 31.4°C from 1991-2020. July had the highest growing season temperatures, with an average high of 28.1°C ± 1.8°C (Minnesota DNR).

Figure 4: The wet prairie region of Cold Spring fen is plentiful in ragweed and grasses

Figure 5: Diversion in Cold Spring fen filled with standing water during high creek flow

Chapter 1: Carbon Dioxide Emissions in Restored Minnesota Peatlands

2.1 Introduction

Peatland restoration is widely viewed as a climate change solution, given the ability of peatlands to accumulate and sequester carbon. Dried peatlands emit large amounts of CO_2 into the atmosphere (Swindles et al., 2019), prompting widespread efforts in boreal and temperate regions to prevent or reduce emissions through rewetting. However, quantifying the carbon benefits of restoration is difficult and highly dependent on environmental conditions. Warm and wet conditions may produce large CO_2 sinks but greater CH_4 sources (Olsen et al., 2012), possibly resulting in an overall unfavorable carbon balance and net greenhouse gas emissions. In addition to the complexity of characterizing multiple fluxes, changing climate factors impact peatland carbon dynamics. The progression of global warming is predicted to result in higher temperatures, higher evapotranspiration, and lower precipitation in boreal and temperate regions (Trettin et al., 2006), altering the behavior of peatlands longitudinally. The need to characterize future peatland carbon dynamics to accurately assess the effectiveness of restoration as a climate change solution is challenging, and current knowledge of soil and hydrometeorological factors can aid in predictions.

The carbon dynamics of peatlands are influenced by peat quality and peatland type. Fibrists are the least decomposed with some of the original plant material still intact, while saprists are highly decomposed and no longer have intact or recognizable plant material, and hemists lie somewhere in the middle. Saprists have the smallest particle size, smallest pore size, and highest bulk density (Zulkifley et al., 2013). CO_2 emissions from peatlands result largely from aerobic respiration of microbes during peat decomposition, and peat's level of humification impacts the rate and extent of this respiration. Bogs tend to contain more intact fibric peat with large pore spaces that allow for aeration (Boelter, 1969), while fens are more likely to contain highly-decomposed sapric peat, which has small pore spaces. Peat volume losses are higher from drained fibrists than saprists due to aeration and availability of undecomposed organic matter (Krause et al., 2021), corresponding to greater respiration (Kechavarzi et al., 2010). CO_2 concentrations in bogs can be greater in deeper aerated peat layers, which are more intact, than at the surface (Clymo et al., 1995). In addition to level of humification, litter quality impacts respiration. Woody litter and *Sphagnum* litter are high in phenolic compounds, which inhibit decomposition under wetted anaerobic conditions, thus reducing respiration rate as compared to other litter types (Freeman et al., 2001). The high C:N ratio of *Sphagnum* litter is also associated with slower peat decomposition (Asif et al., 2021). These decomposition dynamics, as well as vegetation resilience, account for the differing responses of bogs and fens to climate change. The carbon cycle in bogs may be more resilient to warmer and dryer conditions than fens due to sharp decreases in primary production by sedges in fens (Wu & Roulet, 2014). At the initial onset of climate change conditions, bogs act as carbon sinks while fens become carbon sources or do not experience a net change in carbon (Bridgham et al., 2008).

The water table position in a peatland is a primary factor in governing carbon cycling. Because bogs tend to contain fibric peat with a porous bulk structure, they are subject to large water table fluctuations because the adhesive forces which aid in water retention are weak (Kolka et al., 2011). Generally, a higher water table results in slower peat respiration, which can create a greater carbon sink (Trettin et al., 2006; Zhong et al., 2020), but hydrological impacts on vegetation complicate this effect. Drought conditions lower the water table in peatlands, resulting in long-term forest succession and enhanced woody vegetation growth and woody litter fall (Laiho et al., 2003). Due to the phenolic inhibition of litter decomposition (Freeman et al., 2001), an increase in woody and *Sphagnum* litter may reduce peatland respiration rates despite enhanced conditions for rapid peat decomposition. In fens, drought stress can promote vegetative spread, so increased primary production and plant uptake of CO_2 could counteract soil carbon loss over time, resulting in a net sink or reduced source (Koebsch et al., 2020). Drainage impacts on peatland respiration also vary temporally. While dry conditions may generate high carbon emissions in the short-term, an equilibration of hydrological conditions over time can result in a leveling out or reduction in respiration (Bridgham et al., 2008; Carter et al., 2012; Trettin et al., 2006).

Some moisture is required for microbial activity, so slight drainage where soil remains moist but becomes aerated can result in optimal respiration (Kechavarzi et al., 2010). Prolonged drought conditions may result in minimized CO_2 emissions when peat remains completely dry (Carter et al., 2012). Even under water table drawdown, peat capillary action may allow for significant moisture retention so that microbial activity is relatively unaffected (Macrae et al., 2013), with the highest retention occurring in sapric peat under unsaturated conditions (Boelter, 1969). Due to increased methane emissions from bogs with a high water table, the ideal water table height for reducing greenhouse gas emissions overall lies between fully drained and fully saturated conditions (Strack et al., 2014).

Temperature effects on peat respiration are largely dependent on moisture. While aeration causes rapid respiration, a lack of moisture can inhibit microbial activity; thus, CO_2 emissions are sometimes highest in peatlands that experience mild average temperatures where decomposition is not inhibited by extreme low temperatures or low summer moisture (Carter et al., 2012). In aerated peat regions, temperature is the main factor governing decomposition rate (Bridgham et al., 1991). At low moisture, the CO_2 respiration rate is greatest at high temperature (Kechavarzi et al., 2010). Temperature has a lesser impact under saturated conditions (Trettin et al., 2006). Depending on litter type, temperature can have differing effects on decomposition. *Sphagnum* mosses and nutrient-poor litter decompose more slowly at higher temperature, while *Carex* sedges and nutrient-rich litter decompose faster (Thormann et al., 2004).

The purpose of this study was to monitor growing season peat CO_2 flux in a restored bog and fen in Minnesota. We sought to answer the following questions:

1. Does growing season peat CO_2 flux differ between a restored bog and fen?
2. Do water table depth, peat type, temperature, and time in the growing season affect peat CO_2 flux? Which of these factors has the greatest impact?

We hypothesized that water table depth would be the primary factor affecting CO_2 flux in both peatlands, and that flux would be lowest in regions with a high water table. We also hypothesized that the highest CO_2 flux would occur during the peak of the growing season due to higher temperatures and lower water table depth. In the case of a deep water table below 30 cm of the surface, we predicted that less humified peat would release more CO_2 than more humified peat.

2.2 Methods

2.2-1 Site Preparation

We conducted soil sampling and CO_2 flux monitoring from May through October 2021. In May 2021, three 20-cm diameter PVC collars each were installed at three sites at Sax-Zim and Cold Spring. Each collar had a different insertion depth ranging from 6 cm to 13 cm, so the chamber offset, defined as the distance from the peat surface to the top of the collar, was measured at four locations and averaged for each collar prior to flux analysis to ensure an accurate chamber volume.

Monitoring sites at Sax-Zim bog were selected near the Sax-Zim Bog Welcome Center along a transect perpendicular to a trail and drainage ditch (Figure 6). Sites SZA and SZB were situated west of the ditch. SZA was placed furthest from the ditch in an area of sparse tree cover dominated by *Sphagnum* moss, with SZA furthest from the ditch. We installed wells and Solinst Barologgers and Leveloggers at sites SZA and SZC at each site to continuously measure water table, water temperature, and air pressure. After using a soil auger to remove peat for the well, we pounded the well into the hole and sealed it at the ground surface with bentonite clay. A Solinst Barologger was placed above the ground surface in well A to allow for pressure compensation and determination of water table depth from Levelogger data. The Solinst Levelogger at well SZA was placed 26.7 cm below the ground surface, and the Solinst Levelogger at well SZC was placed at 36.2 cm. The well and logger depths were chosen such that the loggers were 10 cm below the water table surface at the time. We experienced some resistance and difficulty installing the wells in the saturated, partially-frozen peat, which is another reason why they were not placed deeper.

Three collars for static chamber flux monitoring were placed in hollows near the installed well at SZA. The hummocks were too spongy for us to insert a collar, and flux measurements likely would have included plant respiration rather than only soil due to the large height of the hummocks of about 30-50 cm. Site SZB was between SZA and the ditch in an area with *Sphagnum* ground cover, as well as black spruce and tamarack. Collars at SZB were placed in hollows, though the hollows here were wider and the hummocks less tall than at SZA. Site SZC lay east of the ditch in a clearing, and collars were placed amongst thick *Carex* sedge cover surrounding the installed well.

Sampling locations at Cold Spring fen were selected based on the positions of two existing wells equipped with Solinst loggers, running down the hill to the floodplain (Figure 7). The Levelogger in well CSA was located at 96.5 cm below the ground surface, and the Levelogger at well CSC was 111.8 cm below. Collars at site CSA were placed around well CSA on a hillside terrace. Ragweed and grasses had to be removed from within and around the collars periodically to complete flux measurements. At site CSB on the bottom of the hillslope, mats of dried cattails were cut away to place collars, and thistles and ragweed were cut away later in the season to allow access for measurements. Past the diversion channels in the wet prairie, collars at site CSC were placed in a less-densely vegetated area near existing well CSC, where bare soil patches allowed for easy installation.

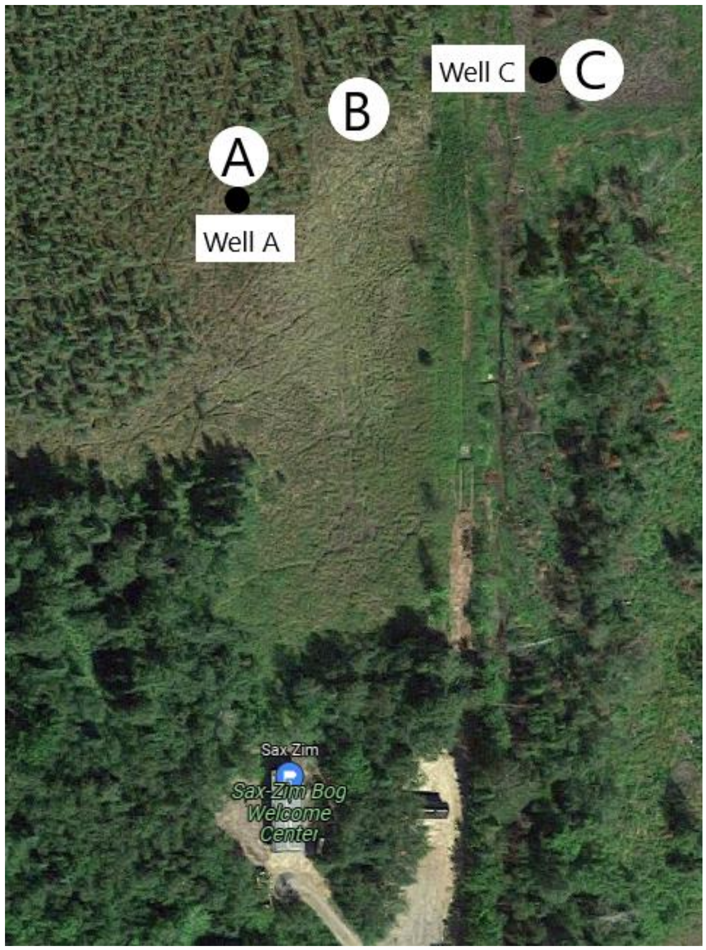

Figure 6: Map of wells and study sites at Sax-Zim bog

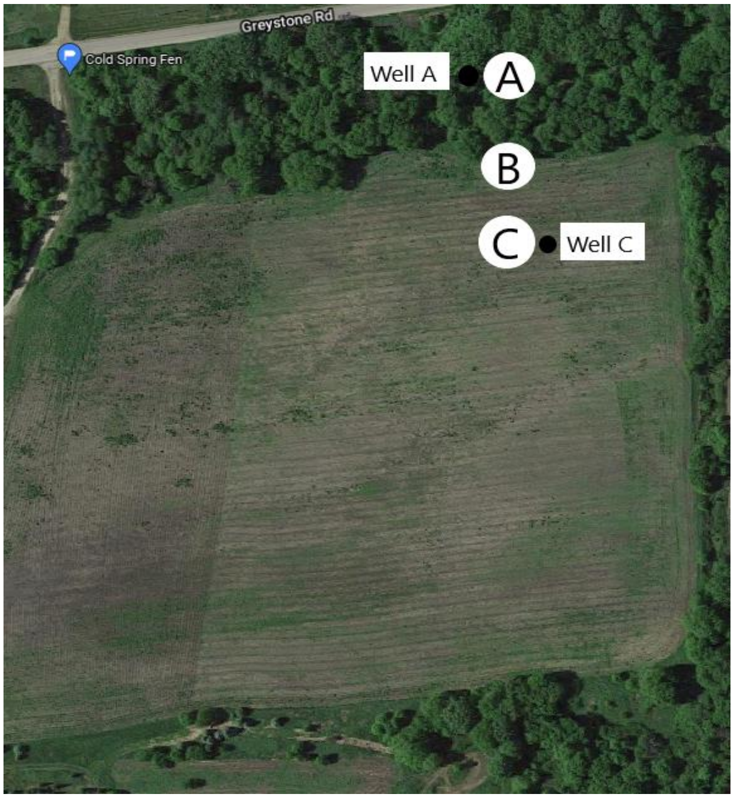

Figure 7: Map of wells and study sites at Cold Spring fen

Figure 8: Collar inserted in hollow at Sax-Zim bog

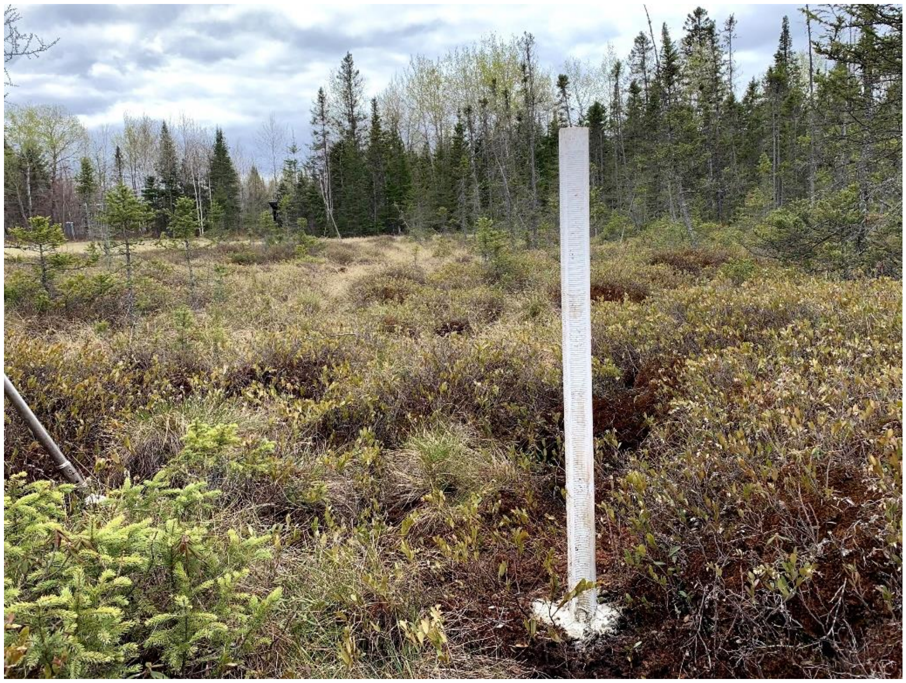

Figure 9: Well SZA at Sax-Zim bog

Figure 10: Well CSC at Cold Spring fen

2.2-2 Peat Sampling

Peat samples were extracted at the bog and fen to characterize peat type and TOC content. We collected soil samples three times throughout the growing season at each site within Sax-Zim and Cold Spring. We used a trowel and soil knife to extract samples at 0 and 15 cm depth, and to reach peat at 30 cm depth, we used a soil auger. We used the von Post humification scale (Table 1) to characterize the peat based on qualitative observations of texture, visual appearance, and squeezing. Then based on the von Post scale, we categorized the peat more broadly as fibric, hemic, or sapric (Table 2). Finally, samples were submitted to the Research Analytical Laboratory at the University of Minnesota, which conducted TOC determination.

Figure 11: Extracting peat sample with soil auger at Sax-Zim bog

Table 1: von Post peat classification scale (Andriesse, 1988)

Symbol	Description
H1	Completely undecomposed peat which, when squeezed, releases almost clear water. Plant remains are easily identifiable. No amorphous material is observed to be present
H2	Almost entirely undecomposed peat which, when squeezed, releases clear or yellowish water. Plant remains are still easily identifiable. No amorphous material present
H3	Very slightly decomposed peat which, when squeezed, releases muddy brown water, but from which no peat passes between the fingers. Plant remains are still identifiable, and no amorphous material present
H4	Slightly decomposed peat which, when squeezed, releases very muddy dark water. No peat is passed between the fingers, but the plant remains are slightly pasty and have lost some of their identifiable features
H5	Moderately decomposed peat which, when squeezed, releases very muddy water with a very small amount of amorphous granular peat escaping between the fingers. The structure of the plant remains is quite indistinct although it is still possible to recognize certain features. The residue is very pasty
H6	Moderately highly decomposed peat with a very indistinct plant structure. When squeezed, about one-third of the peat escapes between the fingers. The residue is very pasty but shows the plant structure more distinctly than before squeezing
H7	Highly decomposed peat. Contains a lot of amorphous material with very faintly recognizable plant structure. When squeezed, about one-half of the peat escapes between the fingers. The water, if any is released, is very dark and almost pasty
H8	Very highly decomposed peat with a large quantity of amorphous material and a very indistinct plant structure. When squeezed, about two-thirds of the peat escapes between the fingers. A small quantity of pasty water may be released. The plant material remaining in the hand consists of residues such as roots and fibers that resist decomposition
H9	Practically fully decomposed peat in which there is hardly any recognizable plant structure. When squeezed it is a fairly uniform paste
H10	Completely decomposed peat with no discernible plant structure. When squeezed, all the wet peat escapes between the fingers

Table 2: Peat categories based on von Post scale (Huat, 2004)

Organic	Von Post scale	Qualifying terms	Symbol	Description and color
Peat			Pt	(>75 % organic content)
	H1–H3	Fibric/fibrous	f	Mostly undecomposed, typically tan to light reddish brown in color
	H4–H6	Hemic/ moderately decomposed	h	Intermediate in degree of decomposition, organic content and bulk density, dark, reddish brown in color
	H7–H10	Sapric/ amorphous	a	Highly decomposed with the highest organic content and bulk density. Darker in color than fibric or hemic peat

2.2-3 Carbon Dioxide Flux

Peat CO_2 flux was measured monthly at the bog and fen throughout the growing season using a static chamber method with the LI-1800A. Before beginning the measurement, we measured the chamber offset, or the distance from the top of the collar to the ground, in order to obtain the proper flux volume. The offset was measured at four locations within the collar using a ruler, and then we averaged the values to obtain the final offset. Internal collar area was 317.8 cm^2. Flux measurements were then conducted using the LI-8100A (LICOR) on a 2-minute sampling interval, followed by a 45-second purge. Flux values were then translated through Soil Flux Pro software from LICOR.

Figure 12: Measuring chamber offset prior to flux measurement at Cold Spring fen

Figure 13: Measuring flux with LICOR LI-8100A at Sax-Zim bog

Figure 14: Measuring flux with LICOR LI-1800A near well CSA at Cold Spring fen

2.3 Results and Analysis

2.3-1 Peat Classification

Based on the von Post humification scale and subsequent grouping, peat samples from each site were divided into two categories: fibric/hemic and sapric/mucky. Based on evaluations at 0 cm, 15, and 30 m depth, peat at sites SZA and SZB were classified as fibric/hemic, while peat at all other sites was designated as sapric/mucky (Table 3).

Table 3: Peat classification of study sites based on von Post scale

	Total Organic C (Mass %, ± 2%)	von Post Class Range	Peat Type
SZA	**42**	**H1-H5**	**Fibric/Hemic**
SZB	**41.4**	**H2-H6**	**Fibric/Hemic**
SZC	**33.7**	**H8-H10**	**Sapric/Mucky**
CSA	**28.8**	**H8-H10**	**Sapric/Mucky**
CSB	**29.6**	**H9-H10**	**Sapric/Mucky**
CSC	**21.7**	**H9-H10**	**Sapric/Mucky**

Figure 15: Fibric peat from Sax Zim bog

Figure 16: Hemic peat from Sax Zim bog

Figure 17: Sapric/mucky peat from Cold Spring fen

2.3-2 Carbon Dioxide Flux

Environmental conditions led to a loss of water table data when it dropped below the bottom of the wells. Minnesota experienced an unexpected drought in 2021 with very infrequent rainfall, creating a deep water table at Sax-Zim bog. The water table remained below the Solinst Leveloggers throughout most of the sampling period at Sax-Zim bog wells SZA and SZC, placed at 26.7 cm and 36.2 cm respectively, so the true water table depth could not be determined (Figure 20). All water table values recorded below logger depth should be assumed to indicate a water table below the logger, but the measured depth is not accurate in these cases. The water table did not drop below the Leveloggers at Cold Spring fen often, but several time periods at Cold Spring well CSA have recorded depths just at or below the logger at 96.5 cm depth (Figure 21). At several times throughout the sampling period, the water table reading at Sax-Zim bog well SZC spikes sharply. This may have occurred due to improper sealing of the well at the ground surface, resulting in water seeping in from the sides of the well during a runoff event. There was also a small increase at well SZA on the same dates as these spikes, and they may reflect faster infiltration at SZA following a rainfall event. After these increases, the water table reading dipped back down to at or below logger depth.

Figure 18: During the severe drought period, the diversions at Cold Spring fen were completely dry

Figure 19: The severe drought caused *Sphagnum* at Sax-Zim bog to dry out and die

2.3-3 Sax-Zim Bog Carbon Dioxide Flux

Measured peat CO_2 flux in Sax-Zim bog remained below 6 µmol/m^2·s throughout the growing season (Figure 20). Flux in the Sphagnum-covered region (SZA and SZB) peaked in August at the peak of the growing season, with the lowest flux occurring in June. In the sedge meadow (SZC), flux was highest from June through August and began to decline in early September. Sedge meadow flux was higher than that of the *Sphagnum* region until this point, at which sedge meadow flux became comparable to that of the *Sphagnum* region through the end of the sampling period.

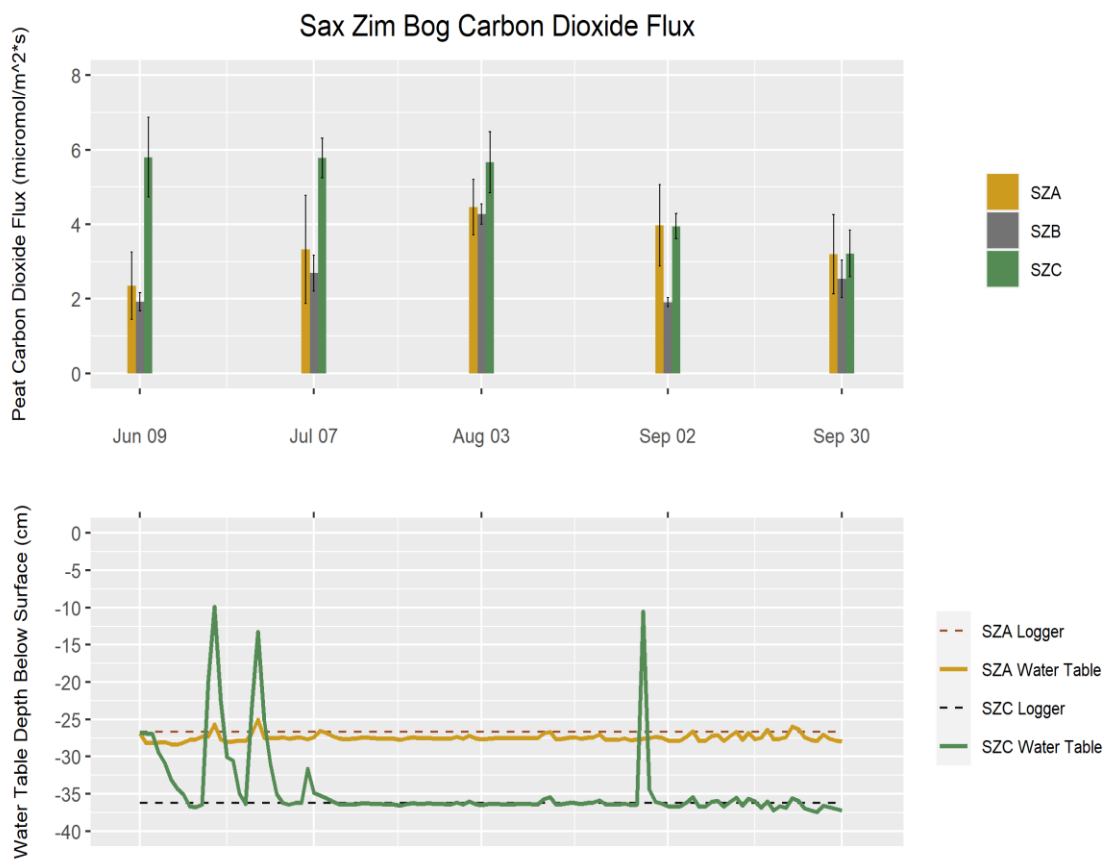

Figure 20: Sax Zim bog carbon dioxide flux and water table depth during 2021 growing season

A two-way ANOVA of data from SZA and SZC reveals a significant correlation between sampling location and CO_2 flux ($F[1,7] = 5.401$, $p = 0.053$), but no significant relationship between water table depth and flux ($F[1,7] = 0.98$, $p = 0.36$), although the loss of water table data complicates the latter relationship. One-way ANOVAs of data from SZA, SZB, and SZC show a more significant relationship between peat type and flux ($F[1,13] = 10.38$, $p = 0.0067$) than between sampling location and flux ($F[2,12] = 6.194$, $p = 0.014$). Lower flux values throughout the growing season are correlated with SZA and SZB, or the fibric/hemic soil, suggesting a correlation between low CO_2 flux and less humified peat. However, with the lack of reliable water table data, we are unable to determine with certainty if peat type is a more important factor than water table depth in affecting peat carbon dioxide respiration.

2.3-4 Cold Spring Fen Carbon Dioxide Flux

Flux in Cold Spring fen varied between the three sampling regions throughout the growing season, with no clear relationship between the regions. The highest CO_2 flux of 17.81 $\mu mol/m^2 \cdot s$ was observed in June at the bottom of the hillslope (site CSB), while the lowest of 0.55 $\mu mol/m^2 \cdot s$ was recorded in the floodplain past the diversions (site CSC) in October (Figure 21). Flux remained above 8 $\mu mol/m^2 \cdot s$ for at least two of the three sampling regions in June, July, and August. The diversions were completely dry these months, indicating the severity of the drought. The diversions contained standing water in September and October, and rising water tables were observed during that time period, corresponding to the lowest flux readings for all sampling locations during the 2021 growing season.

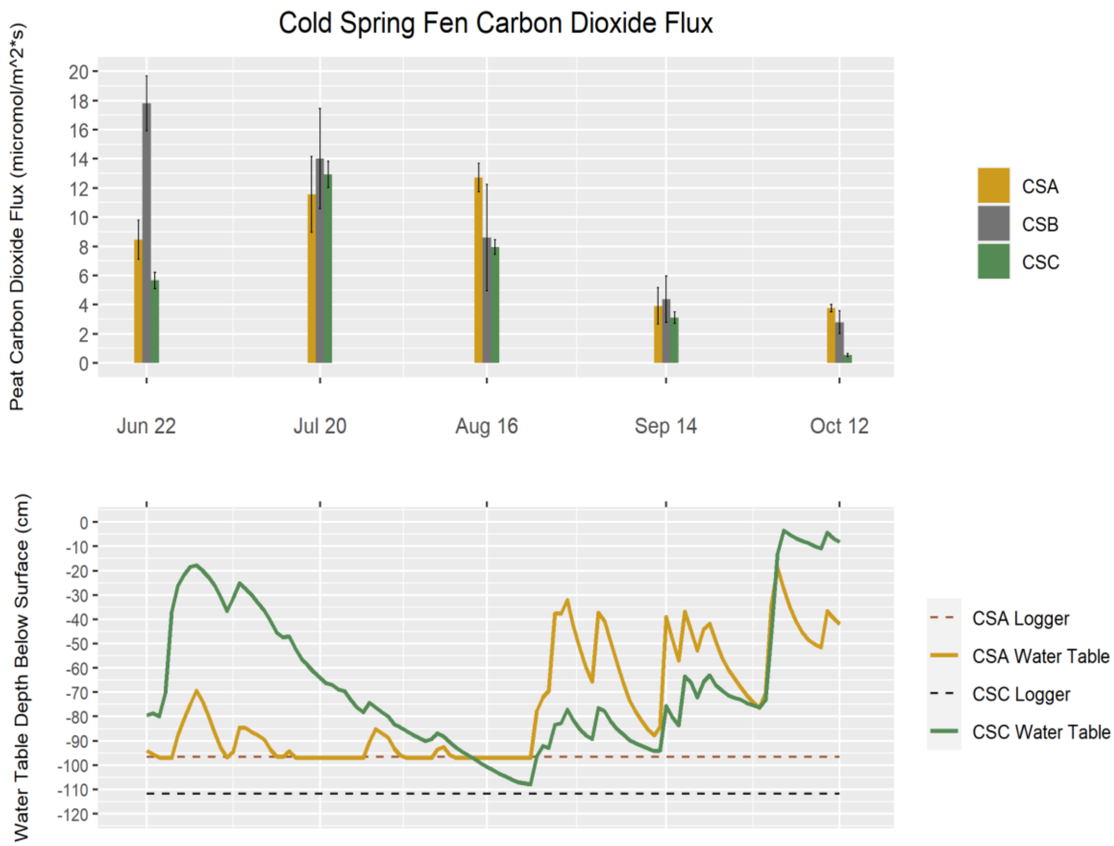

Figure 21: Cold Spring fen carbon dioxide flux and water table depth during 2021 growing season

Based on a three-way ANOVA of CSA and CSC data, there is a significant relationship between CO_2 flux and water table depth in the fen ($F[1,3] = 22.61$, $p = 0.018$), with a water table closer to the ground surface corresponding to lower CO_2 flux. There is not a significant relationship between time and flux ($F[4,3] = 4.31$, $p = 0.13$) or sampling location and flux ($F[1,3] = 2.71$, $p = 0.20$). There is also no significant relationship with regards to sampling location and flux based on two-way ANOVA of data from CSA, CSB, and CSC ($F[2,8] = 1.67$, $p = 0.25$), but there is significance with regards to time ($F[4,8] = 6.77$, $p = 0.041$). Flux may have a significant correlation to time for this full dataset due to CSB flux decreasing consistently through the growing season, or due to the absence of water table depth in the analysis, which is a more significantly correlated factor. Because there is no water table data available for CSB, we are unable to determine if water table depth correlates to flux at that site.

2.3-5 Site Comparison of Carbon Dioxide Flux

We conducted ANOVA analyses of data from the bog and fen together to identify significant factors across both. Three-way analysis of peat type, sampling location, and time for all data reveals significance with regards to peat type ($F[1,20] = 11.35$, $p = 0.0031$) and marginal significance with regards to time ($F[4,20] = 3.96$, $p = 0.016$). Sampling location is not significantly related to flux across all sites ($F[4,20] = 1.75$, $p = 0.18$). Fibric/hemic peat tends to correlate to lower flux values than sapric/mucky peat across both sites throughout the growing season, though it should be noted that four of the six sampling locations are classified as sapric/mucky, including all Cold Spring fen locations. A one-way analysis for SZA, SZC, CSA, and CSC data indicates a significant relationship between flux and water table depth ($F[1,18] = 22.27$, $p = 0.00017$). Given the results of separate bog and fen ANOVAs and inaccuracies in bog water table readings, this significance is likely driven by Cold Spring fen.

Monthly flux data from all three sampling regions at Sax-Zim bog and Cold Spring fen were averaged to produce Figure 22. CO_2 flux in the fen is far greater than that of the bog from June through August, but declines sharply in September, when it becomes comparable to bog flux through the rest of the sampling period. Bog flux does not change dramatically throughout the growing season when compared to fen flux, and remains fairly steady throughout the growing season. These results indicate that peat respiration in the fen may be more sensitive to changes in environmental conditions, such as water table depth and seasonality.

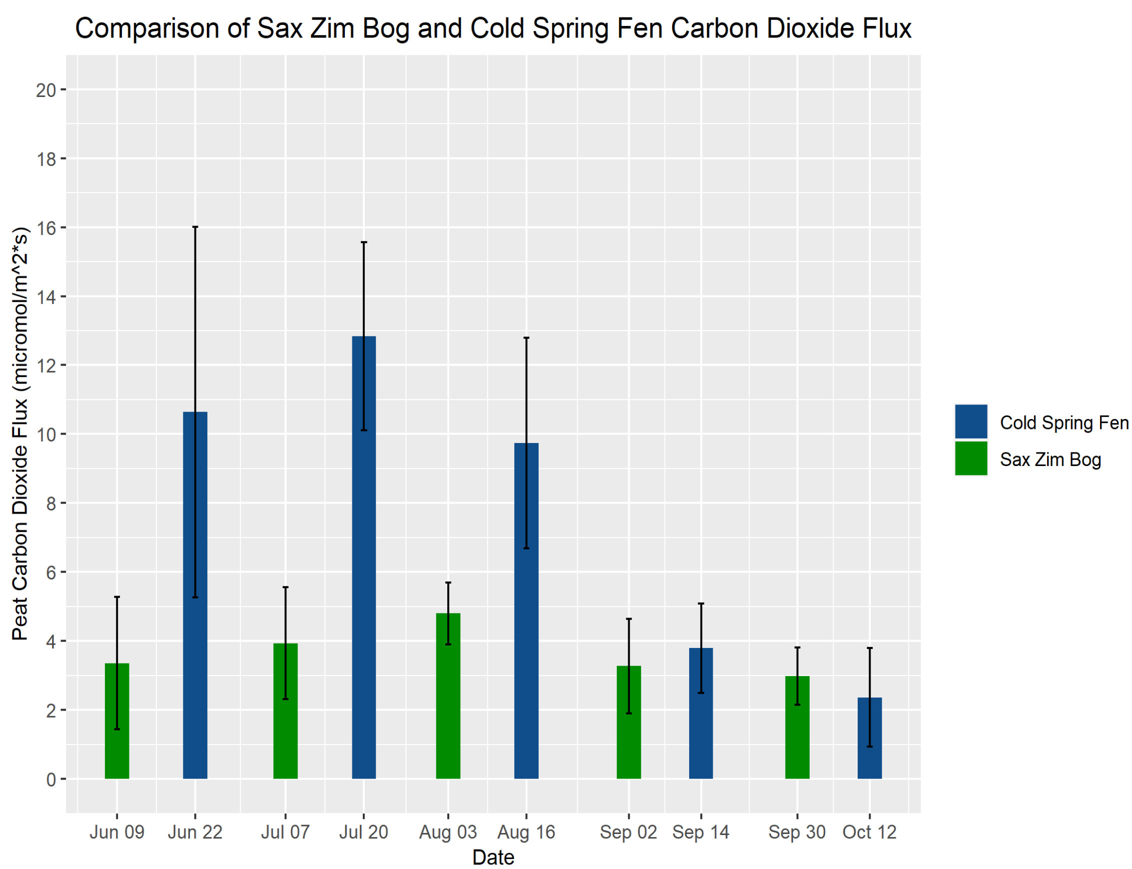

Figure 22: Average carbon dioxide flux in Sax-Zim bog and Cold Spring fen during 2021 growing season

2.4 Discussion

2.4-1 Sax-Zim Bog Carbon Dioxide Flux

CO_2 flux in Sax-Zim bog did not vary greatly throughout the growing season, remaining below 6 μmol/m^2·s throughout the sampling period. The sedge meadow (SZC) had higher flux at the beginning and middle of the growing season, but declined towards the end and became similar to flux in the *Sphagnum*-covered region (SZA and SZB). SZA and SZB contain less humified peat than SZC, suggesting a correlation between lower CO_2 flux and more intact peat. This runs counter to our hypothesis, which predicted higher flux from fibric and hemic peat due to greater volume losses from decomposition under drained conditions (Krause et al., 2021). It is possible that the study period was not long enough to capture these drainage effects in the bog, or that prolonged drought conditions provided aeration in all peat types. It is also possible that a greater presence of *Sphagnum* and woody litter in the peat of SZA and SZB results in the inhibition of decomposition due to the presence of phenolic compounds (Freeman et al., 2001).

Overall, the bog emitted a steady low amount of CO_2 at all points in the growing season, which bodes well for efforts to mitigate climate change through peatland restoration. In a bog in the Marcell Experimental Forest in Minnesota, which has similar climate and latitude to Sax-Zim bog, measured community CO_2 flux during the growing season peak from 2011-2014 was 6-10 $\mu mol/m^2 \cdot s$ (Hanson et al., 2016). This is comparable to other temperate peatlands across the world. Although our study only included respiration from peat and not ground cover vegetation, it is promising that Sax-Zim's peat CO_2 flux remained below this range throughout the growing season.

We are unable to determine the effects of water table depth on peat CO_2 flux in the bog due to shallow placement of the Solinst Leveloggers. Considering negative readings to be below logger depth, the water table at both well locations in Sax-Zim bog remained below the logger depth for much of the sampling period. The passive restoration of the area may have contributed to the low water table during the drought period, and it may have remained higher under fully restored conditions. The ditch that runs through the site is only partially filled in, which may exacerbate water table drawdown during drought by increasing drainage. While we know that the water table remained below a certain depth at both sites, we do not know if the water table at one site was higher than the other, and if this is correlated to the difference in CO_2 flux observed at SZA and SZC. If loggers are installed immediately after the snowmelt period, we recommend they be placed at least a meter below initial water table depth to account for potential drought periods, because the water table tends to be high immediately after the snowmelt period in Minnesota.

2.4-2 Cold Spring Fen Carbon Dioxide Flux

In Cold Spring fen, CO_2 flux varied across a wide range during the study period, from 0.55 μmol/m^2·s to 17.81 μmol/m^2·s. During the early and middle parts of the growing season, including the peak, CO_2 emissions were highest, and may reflect the risk of the fen being a carbon source in its current state. This matches our hypothesis that the highest flux across both peatlands would be observed during the growing season's peak. Flux at the end of the growing season was very low, even less than 1 μmol/m^2·s at site CSC. The sample sites do not have a consistent relationship relative to each other, but there is a significant correlation between water table depth and flux at CSA and CSC. This is most apparent for the last two sample dates, when the water table is increasing and the flux across all three sites declines greatly. It is possible that this decrease is associated with the end of the growing season, with lower productivity, lower evapotranspiration, and cooler temperatures, but there is no significance between peat temperature and flux ($F[1,8] = 3.77$, $p = 0.088$).

Despite initially high flux readings, average flux across the entire fen in October was even lower than that of Sax-Zim bog. Thus, the restored fen's carbon benefits are uneven throughout the growing season, but it has the potential for very low peat respiration under certain conditions. Based on just one season of data, we are unable to conclude if this represents an overall positive or negative impact on carbon emissions. Analysis indicates that the most significant condition correlated to low flux is a high water table. Groundwater flow was not monitored in the fen, but given the high fluxes observed, it does not appear to have had a mediating effect on respiration when the water table was deep. The new diversions placed in May 2021 also altered the hydrology of the fen's floodplain. The diversions were opened and closed to different degrees throughout the sampling period based on storm events, which impacted the amount of surface water reaching the floodplain and ultimately the water table. As the fen progresses in the restoration process, it would be useful to continue this study to monitor how flux changes in response to these alterations over many years. It is possible that the fen will become a better mitigator of carbon emissions after it has been fully restored, or that its seasonal peat respiration dynamics will change.

Even though the Levelogger at well CSA was placed over a meter deep, the water table dipped below the logger for much of July and August, so we do not know how much lower it went. It appears that the groundwater flow is too deep in the fen to impact the water table in the top meter of peat, though it may still have an effect on deeper peat respiration. A future improvement to this research could involve additional groundwater monitoring to better capture the effects of hydrology on flux, and possibly evaluating flux at different depths based on water table and groundwater depths.

2.4-3 Site Comparison of Carbon Dioxide Flux

There is stark disparity in average CO_2 flux between the bog and fen in June, July, and August; fen flux is much higher during this time. In September and October, overall average flux is low and comparable for both sites. These results may indicate that the bog is more reliable than the fen in sequestering peat carbon and mitigating climate change. However, the study only took place over one season, which coincided with an unprecedented severe drought. Further study that includes data over multiple years, including those with more typical precipitation, is needed to draw conclusions about peat CO_2 respiration dynamics in these peatlands over the long term.

2.4-4 Future Research

Across both sites, there are additional factors that could be investigated in future work. Chemically analyzing peat for the presence of phenolic compounds would help indicate possible inhibition of decomposition. While water table depth was the hydrological factor focused on in this study, evaluating peat moisture would elucidate any additional effect on respiration when surface peat is unsaturated. This would also serve as a reliable measure for investigating hydrology in case the water table falls below detectable depth during a drought. Measuring net ecosystem exchange (NEE) would allow us to evaluate the overall performance of these peatland ecosystems as carbon sinks or sources. While NEE estimation would require extensive modeling and involve large uncertainties, the chamber method for flux measurement could be adapted to include the entire ground cover community. The methods detailed in Hanson et al., 2016 involve a permanent collar and chamber installation with periodic flux measurements collected by an LI-7500A. A transparent dome allows for herbaceous vegetation to continue growing, allowing for the combined respiration of peat and plants to be measured. Community respiration gives a better sense of the CO_2 respiration of the ecosystem, instead of just peat, which is better for evaluating impacts on climate change. Collecting CH_4 flux data would also paint a better picture of overall greenhouse gas emissions from the peatland.

This study is a starting point in the evaluation of peatland restoration as a natural climate solution in Minnesota. Monitoring across multiple years and more sites will allow for the creation of peatland gas flux models that scale up and predict carbon benefits across greater spatial and temporal scales. Current peatland restoration guidance in Minnesota emphasizes vegetation establishment and the maintenance of a high water table (Minnesota Board of Water and Soil Resources, 2012). These policies should be updated to comprehensively consider the factors affecting peatland carbon benefits in order to maximize climate change mitigation.

Chapter 2: Phosphorus Mobilization in Restored Minnesota Peatlands

3.1 Introduction

Historic land use heavily impacts the amount of P in drained peat, with the highest levels found in the surface soils of agricultural areas (Hyvarinen et al., 2012; Meissner et al., 2008; Ronkanen and Klove, 2009). Heavy fertilizer use, as well as degradation of soil after intensive farming or drainage, is responsible for this high initial content. Because surface soils in drained peatlands are exposed to the air, they experience rapid rates of microbial mineralization and decomposition under aerobic conditions, giving them high amounts of labile, plant-available P (Hyland et al., 2005). Microbes tend to sequester P when breaking down nutrient-rich plant matter, and mineralize P into plant-available forms when detritus is nutrient-poor (Cheesman et al., 2010). Even when initial total P content is low, the danger of P mobilization could be high due to a higher proportion of extractable P (Kaila et al., 2016).

Peat can be classified by level of decomposition, or humification, as fibric, hemic, or sapric: fibric peat is the least humified and sapric peat is the most humified. Generally, peatlands that have been drained for a longer period of time contain mainly sapric surface peat. Saprists tend to carry a higher P mobilization risk upon rewetting than fibrists and hemists because they often have the highest content of mineral P that is sensitive to release under reduced conditions (Zak et al., 2010).

Over time, rewetting of drained peatlands results in net peat accumulation, leading to long-term P sequestration in organic matter (Richardson and Marshall, 1986). Saturated, anoxic conditions slow down decomposition, resulting in the build-up of fibric peat. Even though P is mobilized on a short-term basis after rewetting, peat accumulation decades after restoration results in the binding of P in organic complexes, increasing the amount of stable P species and reducing the presence of labile forms (Negassa et al., 2020). Metal ions and pH influence P retention in peat. The adsorption of P to peat is one of the most significant processes influencing long-term P sequestration and stabilization (Richardson and Marshall, 1986). Many studies find that mineral P is bound to highly decomposed surface peat by redox-sensitive iron (Fe), aluminum (Al), and calcium (Ca) complexes (Hyvarinen et al., 2012; Kaila et al., 2016; Meissner et al., 2008; Ronkanen and Klove, 2009; Zak et al., 2004, 2010). The oxidized forms of these ions readily form chemical precipitates which bind mineral P, but the precipitates dissolve during water saturation when the ions are reduced, releasing P to porewater (Figure 23). Fe is widely considered the most important metal ion for P binding, but it reduces readily when soils are rewetted, so high Fe is often correlated to high P export (Curtinrich et al,, 2021; Nieminen et al., 2020). However, other studies find that retention of P in peat is greatest when ratios of Fe:P are high (Kaila et al., 2016). One study concludes that a Fe:P molar ratio greater than 3 is sufficient for P retention by Fe(III) oxyhydroxide in degraded eutrophic fen soils (Zak et al., 2004), while another indicates an Fe:P ratio greater than 10 is needed to prevent critical P export from degraded fen soils (Zak et al., 2010). The former of these studies also finds that Fe does not retain P as effectively in poor soils, as it forms Fe-humic complexes rather than Fe(III) oxyhydroxide (Zak et al., 2004). These more organic Fe complexes do not readily bind P, so the speciation of metal ion precipitates can be as important a factor as the content.

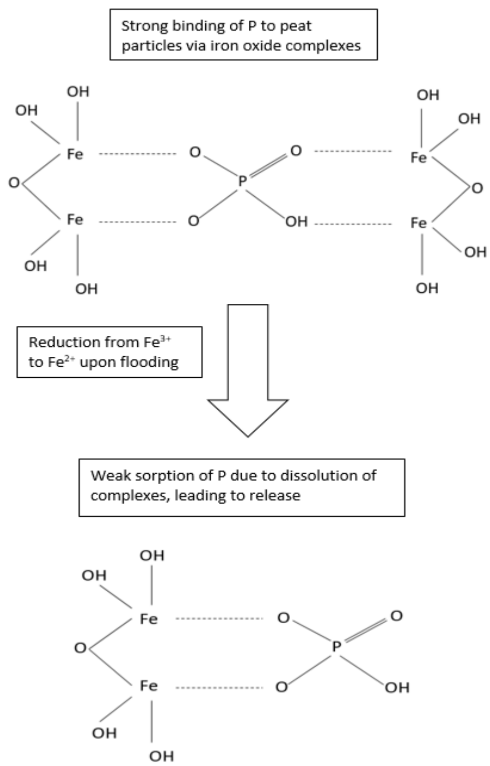

Figure 23: Reductive dissolution of Fe-P binding complexes under saturated conditions

In some cases, high Al content is linked most directly to P retention (Ronkanen and Klove, 2009). Even though mineral P is most commonly Fe-bound, the presence of calcium carbonate enables P retention even under reduced conditions after rewetting (Meissner et al., 2008). Calcium carbonate's low solubility makes it a promising compound for P sorption even under saturated conditions. Ca is often higher in rich fens than in bogs due to groundwater contributions (Griffiths et al., 2019), which could aid in binding P to peat and preventing mobilization (Meissner et al., 2008).

pH is another chemical factor that can impact P mobilization and export risk through speciation and sorption. Most extractable P species exist between a pH of 6 and 7 (Hyland et al., 2005), which is characteristic of some fens (Kolka et al., 2011), though calcareous fens have a more basic pH from 7 to 9. Bogs tend to be more acidic and thus may have a lower proportion of plant-available P as a result (Kolka et al., 2011). Mineral P tends to sorb more readily to Fe and Al compounds at lower pH and to Ca compounds at higher pH, with all sorption species about equal at pH=6.5 (Hyland et al., 2005). Because of speciation, bogs may present less of a risk for extractable P mobilization and downstream eutrophication than fens, depending on upland contributions and other soil factors. The pH range in fens is favorable for mineral P species, but varies with depth. Some agricultural fens have the highest pH at the top of the soil column (Negassa et al., 2019), while groundwater contributions in calcareous fens cause pH to increase with depth due to the presence of alkaline Ca compounds in the aquifer (Griffiths et al., 2019).

Both lateral and vertical flow are important for P movement. Fibrists, more commonly found in bogs, have higher lateral and vertical hydraulic conductivity than saprists due to their large pore spaces (Boelter, 1969; Swenson et al., 2020), though saprists better retain water under unsaturated conditions. P tends to accumulate in areas of preferential flow due to opportunities for sorption and chemical precipitation (Ronkanen and Klove, 2009). The residence time of water flowing through a peatland controls the amount of contact that dissolved and suspended species have with soil, microbes, and plants. In boreal peatlands, peak flows often occur during spring snowmelt, reducing water residence time and preventing significant plant uptake of P (Vaananen et al., 2006). Soil adsorption is the dominant uptake process under high flow conditions, but as discussed previously, rapidly flooding a peatland can release P into soil water if conditions become anaerobic. Greater residence time also increases P retention in peat by adsorption (Koskiaho et al., 2003), especially in peat with a high sorption capacity.

In addition to flow and residence time, water table elevation plays a role in P processes. The water table heavily controls redox potential within the peat column, with the largest fluctuations in potential occurring in the depth range where the water table rises and falls (Meissner et al., 2008). A high water table correlates to high release of extractable P (Meissner et al., 2008; Kaila et al., 2016), as saturation causes reduced conditions that dissolve binding complexes.

As climate change continues, more frequent and severe droughts are expected to lower the water table in peatlands worldwide by reducing precipitation and increasing evapotranspiration losses (Macrae et al., 2013). A high water table is correlated with high P release to porewater due to reductive dissolution of binding complexes (Hyvarinen et al., 2012; Kaila et al., 2016; Meissner et al., 2008; Ronkanen and Klove, 2009; Zak et al., 2004), so drought may actually prevent significant mobilization of extractable P. In terms of drought impacts on microbial activity, dry conditions in a boreal fen result in a more negative P mineralization rate than moist conditions, but temperature impacts on P mineralization rates may be negligible (Morison et al., 2018).

Increased temperatures also influence peat decomposition and nutrient dynamics. In boreal and temperate peat there is a correlation between higher temperature and higher soluble reactive P content in soil porewater (Meissner et al., 2008; Iversen et al., 2019). This may be due to warmer temperatures increasing Fe reduction and prompting greater P release from peat (Curtinrich et al., 2021). Higher temperatures may increase decomposition rates in nutrient-rich *Carex* sedge litter and lower the rate of nutrient-poor *Sphagnum* moss decomposition (Thormann et al., 2004), which could have implications for conversion of P to labile forms in bogs versus fens.

The purpose of this work was to assess the risk of P mobilization in a restored bog and fen in Minnesota. We went about this assessment through in-situ measurement of peat P content and binding metal content, and through controlled incubation experiments to investigate P mobilization under saturated conditions. Our questions were:

1. How do extractable P and metal ion content relate to peat type and location?
2. How do temperature, initial extractable P content, and metal ion content effect P release from peat to porewater?

We hypothesized that initial extractable P content would be highest at the surface of more humified peat, and that it would be higher overall at Cold Spring fen than Sax-Zim bog due to runoff from adjacent farmland. For the incubation experiment, we predicted that greater P release into porewater would occur in peat at a higher incubation temperature, and that high initial Ca concentration would correspond to lower P release. We also predicted that greater P release would correspond to greater Al and Fe release.

3.2 Methods

3.2-1 Site Description

Our sample sites at Sax-Zim bog were near the Sax-Zim Bog Welcome Center along a transect perpendicular to a trail and drainage ditch. Selected points reflect a gradient of drainage impact based on distance from the ditch. Sites SZA and SZB were situated west of the trail and ditch in an area dominated by *Sphagnum* moss cover, with A furthest from the ditch. The terrain is heterogeneous, with a network of 30-50 cm tall hummocks and narrow hollows. Site SZA was in an area sparsely populated by black spruce and tamarack, while site SZB was surrounded by denser tree cover. Site SZC lay east of the ditch and just north of an upland forest containing mineral soil. Thick *Carex* sedge cover overlays this area, with small segments of *Sphagnum* interspersed, and it is clear of trees. Sandy loam underlies sapric peat just below 30 cm at SZC.

At Cold Spring fen, we selected sampling locations based on the positions of two existing wells, with points running north to south from the hill to the floodplain. Site CSA was placed on a terrace on the hillside fen next to a well, site CSB lay just at the bottom of the hillslope, and site CSC was situated next to a well deeper in the wet prairie, separated from the hill by two diversion channels. The soil in the fen at A contains muck at the surface and sapric peat below 20 cm, while CSB and CSC were characterized by muck from the surface to 30 cm. During the peak of the growing season, 2-2.5 m high ragweed covers much of the site, with knotweed growing in the diversions. CSC has smaller herbaceous vegetation such as mint and rye, and is a few yards away from the new tamarack plugs.

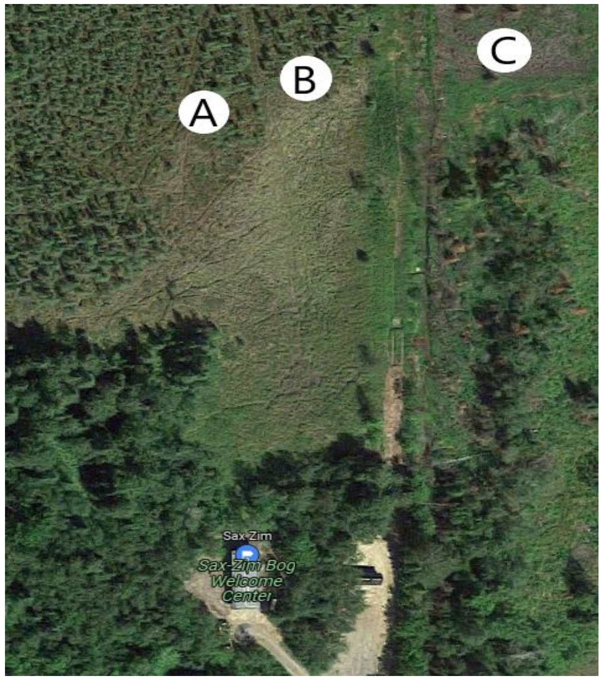

Figure 24: Map of peat sampling sites at Sax-Zim bog

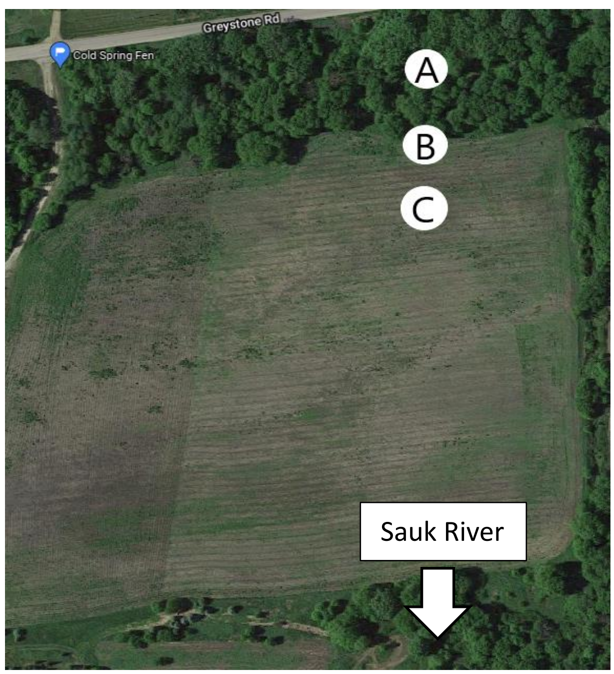

Figure 25: Map of peat sampling sites at Cold Spring fen

3.2-2 Peat Sampling

Peat samples were extracted throughout the growing season at Sax-Zim and Cold Spring to characterize soil P content. We collected soil samples three times throughout the growing season at each site from sites A, B, and C at 0 cm, 15 cm, and 30 cm depth. A trowel and soil knife were used to extract samples at lower depth, while a soil auger was required to reach the deepest peat. Samples were submitted to the Research Analytical Laboratory at the University of Minnesota, which conducted Olsen and Bray extractions for soluble reactive P, as well as Inductively Coupled Plasma (ICP) analysis for metal cations. Bray P extraction was conducted on Sax-Zim peat due to bogs being acidic, and Olsen P extraction was conducted on Cold Spring peat due to the site containing a calcareous fen and alkaline peat (USDA NRCS).

Figure 26: Extracting peat samples using a trowel at Sax-Zim bog

3.2-3 Incubation Experiments

To study the effect of temperature on P mobilization from peat, we performed controlled incubations on peat columns (30 cm tall, 10 cm diameter). In May 2021, we extracted polyvinyl chloride (PVC) tubes of peat at sites A and C at both Sax-Zim and Cold Spring. PVC tubes were inserted into the peat and then pounded with a mallet until the top was even with the peat surface. Columns were then immediately pried out of the ground by digging out the surrounding area. A 10 cm diameter PVC cap was affixed to the bottom of each column with electrical tape and then transported to the University of Minnesota for incubation. We extracted two columns per site for a total of eight columns, providing one column from each site per incubation location (Figure 27).

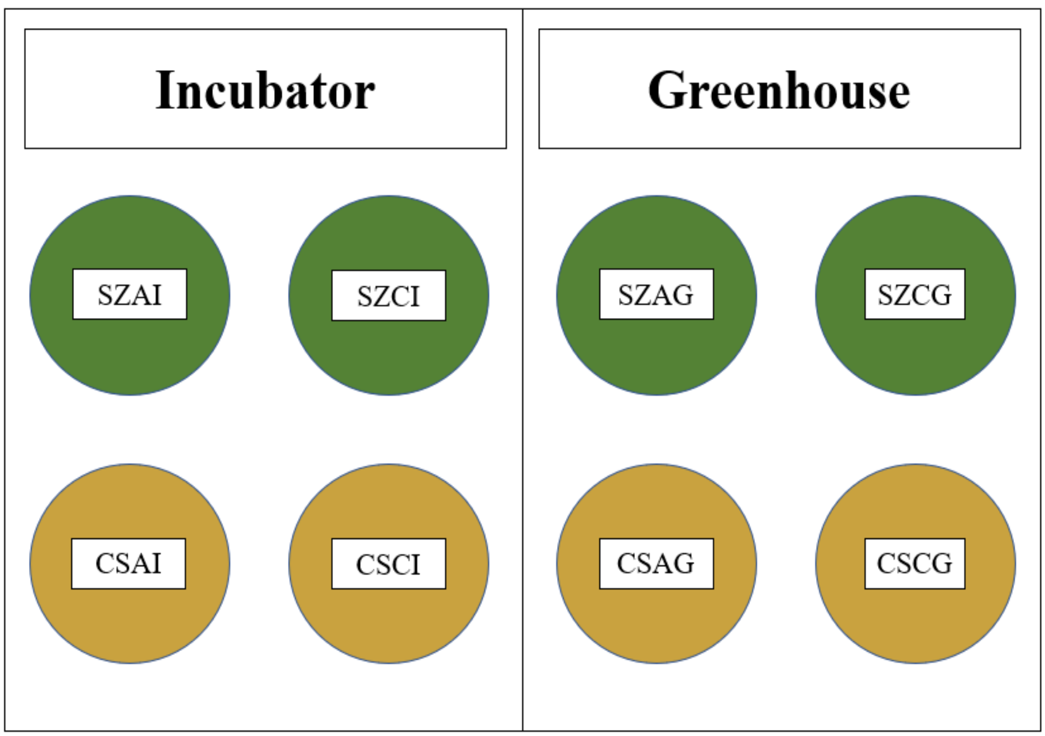

Figure 27: Set-up of peat columns in incubation experiment

Figure 28: Peat columns in greenhouse

Figure 29: Peat columns in incubator

HOBO Tidbit continuous temperature loggers were inserted several centimeters into each column and tied to a length of twine for easy removal. We filled the columns from the top with deionized (DI) water to several centimeters above the peat surface and left the top open throughout experimentation (Sirota et al., 2020; Zak and Gelbrecht, 2007). Half of the columns were placed in an enclosed incubator set to 30˚C, while the other half were placed in a greenhouse set to a diurnal temperature cycle between 21.67 and 24.44 ˚C. Evaporation and percolation losses required us to add DI water to the top of each column every 3-4 days to maintain saturation. Small weeds sprouted in the greenhouse bog columns, and these were removed each time water was added. Because peat takes several weeks to reach anoxic conditions after saturation (Kaila et al., 2016; Zak and Gelbrecht, 2007), the columns were allowed to sit for 11 weeks after consistent saturation was achieved before extracting the first sample. We used MacroRhizon samplers, which have a membrane pore size of 15 µm, to sample porewater (Figure 30). To create a space for the MacroRhizons, we inserted a 4.5 mm steel knitting needle into the column at 90 degrees to depths of 10, 15, and 20 cm. MacroRhizons were attached to a syringe via luerlock, and 25-30 mL of porewater were extracted at each depth. Collecting this volume took 30-45 minutes in less dense peat, while denser peat columns required 2-3 hours. Samples were then submitted to the Research Analytical Laboratory for orthophosphate and ICP analysis.

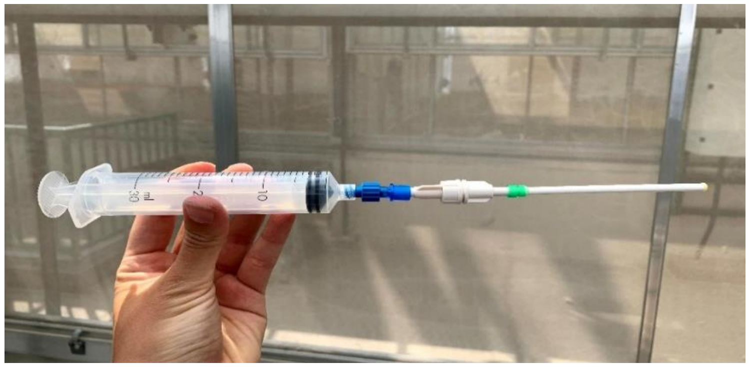

Figure 30: MacroRhizon porewater sampler fixed to syringe

Figure 31: Syringes filling with peat porewater during sampling

3.3 Results and Analysis

3.3-1 Peat P and Metal Cation Content

Initial surface peat P content was highest at sites CSA and SZC, with concentrations of 41 mg/kg and 43 mg/kg, respectively (Figure 32). We found the lowest surface peat P content at SZA (18 mg/kg) and SZB (17 mg/kg). P concentration decreased from the surface downward at all sites, but the magnitude of the decrease varied from site to site. Bray P concentration below the surface at Sax-Zim was mostly the same for all sites (Figure 33). At Cold Spring, CSA had the largest decrease and lowest concentration in Olsen P at 30 cm. CSC had the smallest change in Olsen P across depth, and also had the highest concentration at 30 cm.

Table 4: Peat type and extractable surface P concentration for each site

	Extractable Surface Bray P (mg/kg)	**Peat Type**
SZA	**18**	**Fibric/Hemic**
SZB	**17**	**Fibric/Hemic**
SZC	**43**	**Sapric/Mucky**
	Extractable Surface Olsen P (mg/kg)	**Peat Type**
CSA	**41**	**Sapric/Mucky**
CSB	**27**	**Sapric/Mucky**
CSC	**29**	**Sapric/Mucky**

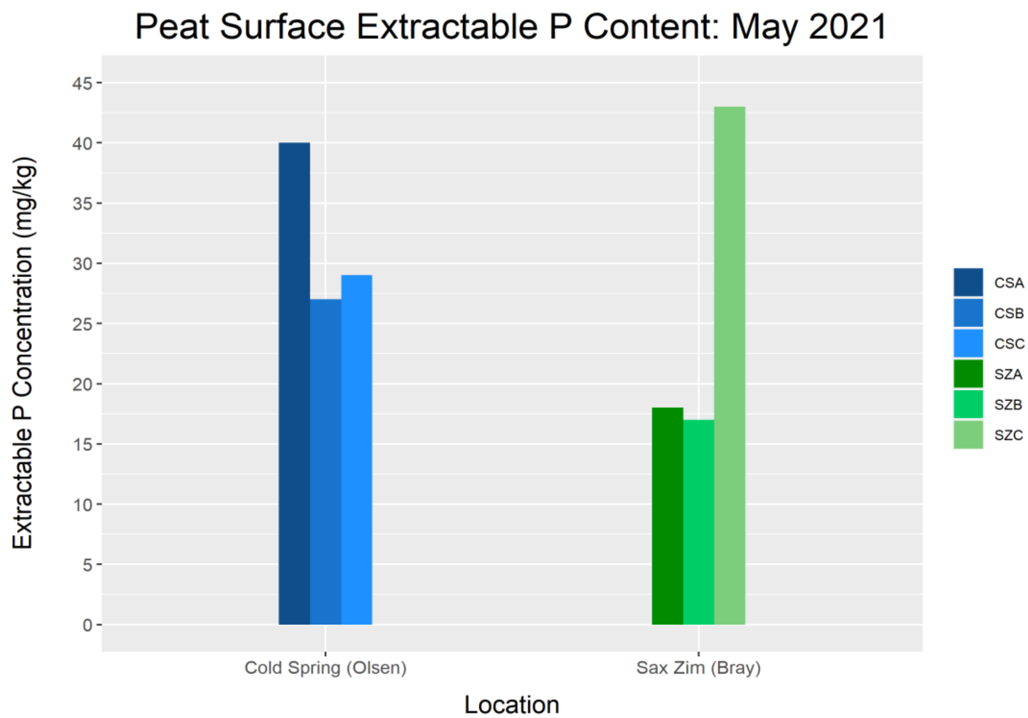

Figure 33: Extractable P at peat surface by study site

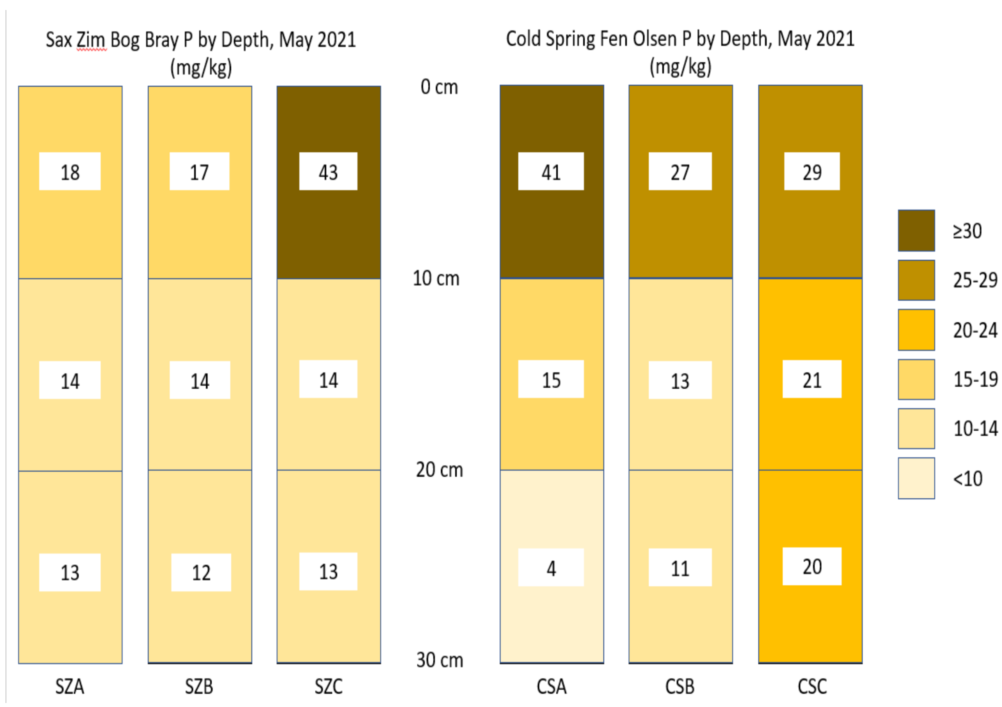

Figure 32: Initial peat extractable P by depth

Average Al for the top 30 cm depth was highest at SZC and lowest at SZA and SZB (Figure 34). Average Ca was very low for all sites in Sax-Zim bog (Figure 35). At Cold Spring fen, Ca was highest in the fen region (CSA) but still high at the other sites. Sax-Zim bog also had low Fe content at all sites. Fe at Cold Spring fen was highest at CSA and relatively low at CSC compared to the rest of Cold Spring (Figure 36).

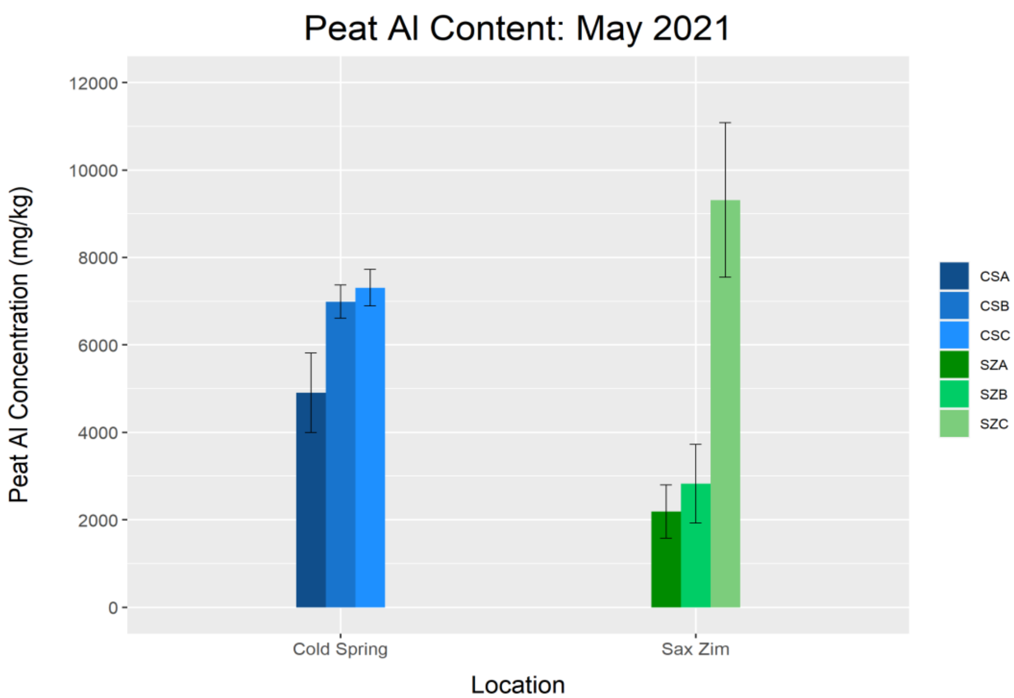

Figure 34: Average peat Al content across top 30 cm depth

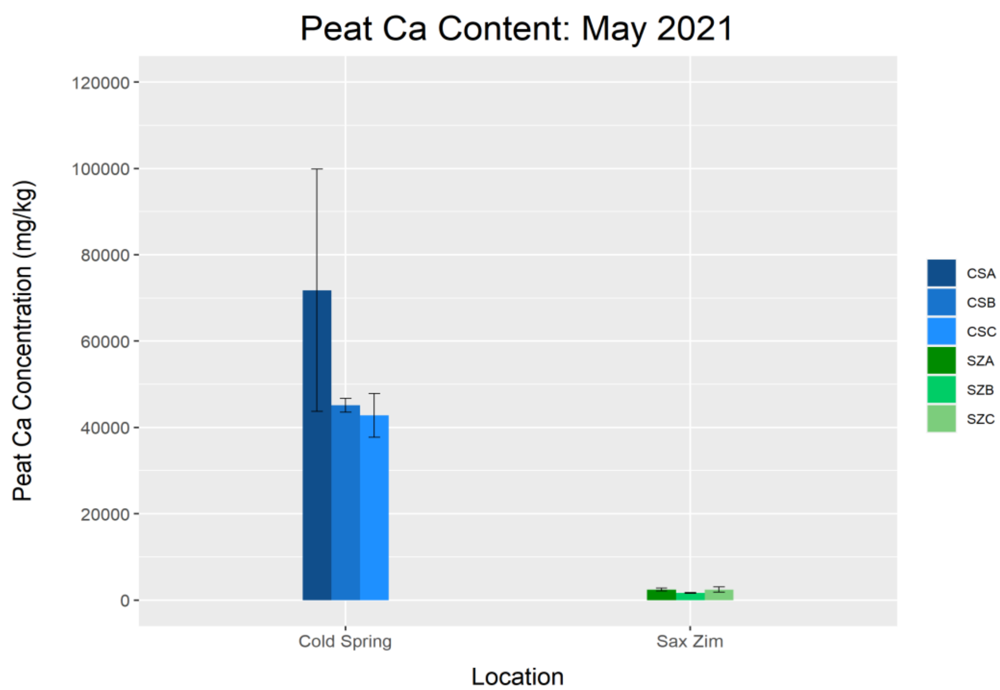

Figure 36: Average peat Ca content across top 30 cm depth

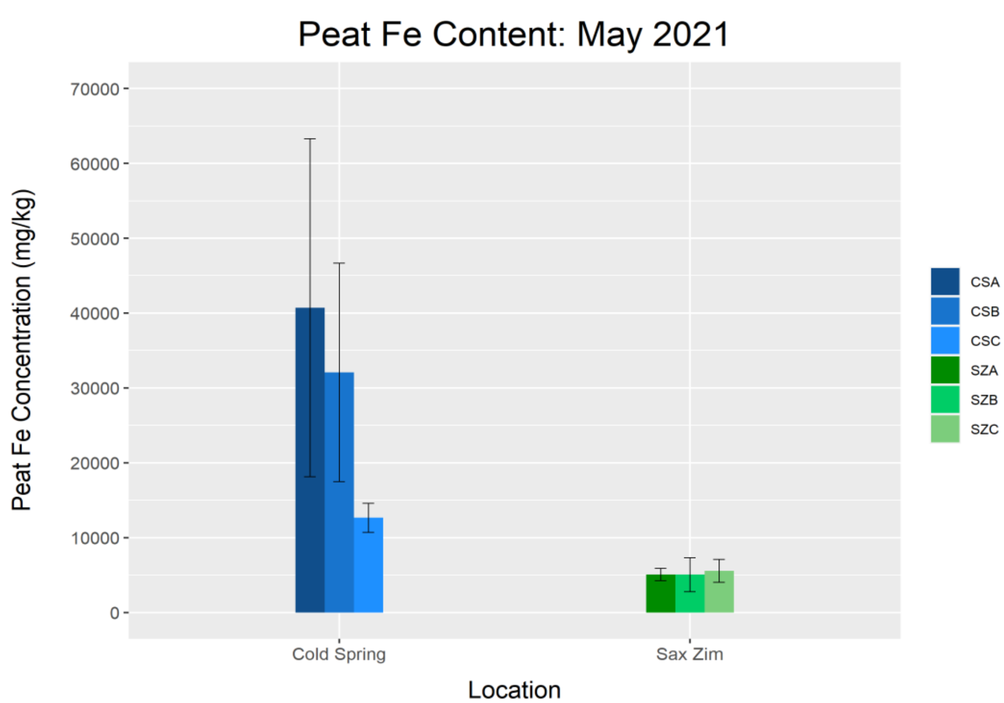

Figure 35: Average peat Fe content across top 30 cm depth

3.3-2 Incubation Experiment

The highest porewater ortho-P concentrations were recorded in SZCI, the incubator column containing peat from site SZC (Figure 37). Porewater ortho-P concentrations from SZCI were higher than from SZCG throughout the incubation period, and the difference between each increased over time. The smallest overall porewater ortho-P concentrations came from CSAI and CSAG, though the relationship between the two was not consistent throughout the incubation period.

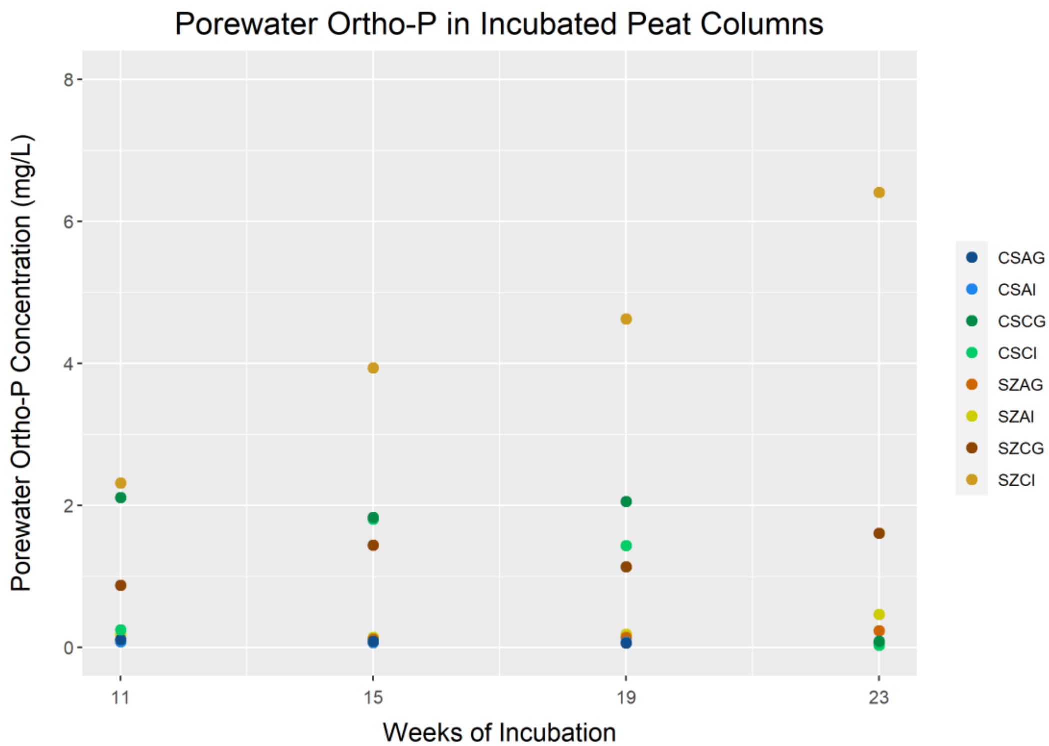

Figure 37: Porewater ortho-P content in peat columns throughout incubation experiment

Temperature fluctuated greatly in columns located in both the incubator and greenhouse (see Appendix II for full temperature data). While the temperature of columns in the incubator remained near 26°C for much of the sampling period, large increases and decreases occurred as a result of incubator malfunctioning and periods of shut down. The diurnal cycle of the greenhouse is somewhat reflected in the temperature data, but the magnitude of temperature change decreases throughout the growing season, and the temperature declines overall with time. Sunlight and outdoor temperature may have caused these changes. As such, incubation temperature was less consistent than desired for all columns. Based on a one-way ANOVA for all porewater ortho-P data, there is no significant relationship between temperature and porewater ortho-P concentration ($F[1,30] = 0.25$, $p = 0.62$). This is also true when individually analyzing data for Sax-Zim bog ($F[1,14] = 0.20$, $p = 0.66$) and Cold Spring fen ($F[]=0.017$, $p = 0.90$). There is also no significant relationship between elapsed incubation time and porewater ortho-P concentration across all data ($F[1,14] = 0.22$, $p = 0.65$).

There is not a significant relationship between initial peat extractable P concentration and porewater ortho-P concentration for all columns ($F[1,30] = 3.94$, $p = 0.056$). Two- and three-way ANOVAs were conducted for all data to relate porewater P concentration to the concentrations of three P-binding metal ions: Al, Ca, and Fe. A three-way ANOVA of initial peat cation concentrations shows a significant relationship between porewater ortho-P and initial peat Al ($F[1,28] = 22.80$, $p = 0.00024$) and initial peat Ca ($F[1,28] = 7.57$, $p = 0.010$), but not initial Fe ($F[1,28] = 1.21$, $p = 0.28$). The highest initial peat Ca concentration was found at site CSA, corresponding to the columns with the overall lowest porewater ortho-P concentrations throughout the incubation period (CSAI and CSAG). Porewater metal ion concentrations are also related to porewater P concentration. Based on three-way ANOVA analysis, porewater Fe and Al concentrations are significantly related to porewater ortho-P concentration ($F[1,28] = 39.837$, $p < 0.0001$ and $F[1,28] = 17.78$, $p = 0.00024$ respectively), but porewater Ca concentration is not ($F[1,28] = 0.25$, $p = 0.62$). For columns from Sax-Zim bog, porewater Ca and Fe are significantly related to porewater P ($F[1,12] = 41.54$, $p < 0.0001$ and $F[1,12] = 10.98$, $p = 0.00062$ respectively). For Cold Spring fen peat columns, only porewater Ca is significantly related to porewater ortho-P ($F[1,12] =79.07$, $p < 0.0001$).

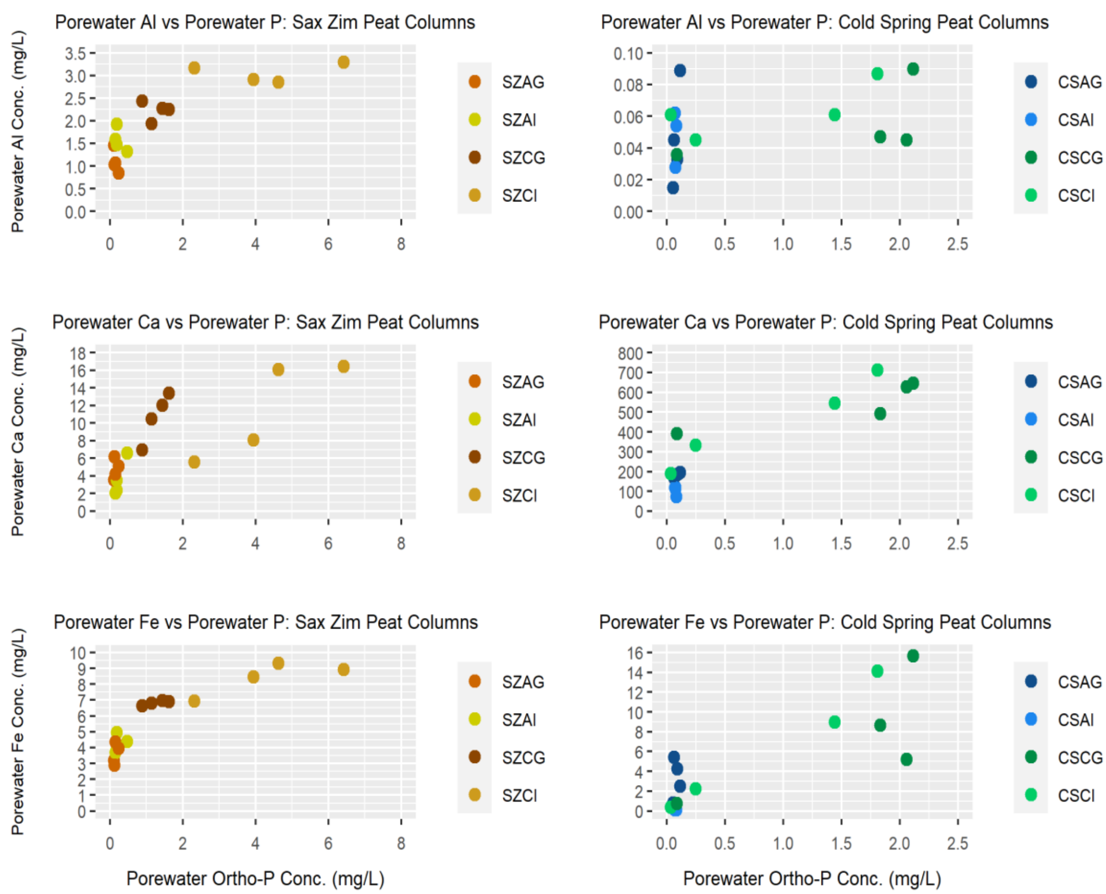

Figure 38: Porewater metal cation concentration versus porewater ortho-P concentration in incubated peat columns

3.4 Discussion

3.4-1 Peat P and Metal Cation Content

The highest surface P concentration was found in peat classified as sapric/mucky, and the lowest in peat classified as fibric/hemic (Table 4). These findings are consistent with our hypothesis and with the literature (Zak et al., 2010). We predicted that surface P would be greatest at Cold Spring fen because it receives runoff from adjacent agricultural fields. While Sax-Zim bog is close to farmland, it is not situated down a steep slope relative to agricultural land use like Cold Spring is. Even though SZC had the highest surface P content overall, every site at Cold Spring had relatively high amounts of P at the surface. The high extractable P content at SZC may be the result of greater peat decomposition and P mineralization, rather than P transport from fertilizer runoff.

Sax-Zim bog is mostly poor in metal ions compared to Cold Spring fen, with the exception of high Al at SZC (Figure 34). The two sites have the greatest difference in Ca content, which we expected due to Cold Spring containing a calcareous fen. The greater presence of metal binding ions suggests a higher P adsorption capacity at Cold Spring than Sax-Zim, but Cold Spring also has higher surface extractable P overall. High Ca content may decrease the risk of P mobilization at Cold Spring because P-calcium carbonate complexes do not as readily dissolve under saturated conditions (Meissner et al., 2008), but it is unknown if this Ca content is sufficient to sorb the high amount of P. Similarly, the P sorption capacity at SZC may be high due to high Al (Ronkanen and Klove, 2009), but saturated conditions and reductive dissolution of Al compounds may pose a risk of P mobilization. In-situ P mobilization dynamics are outside the scope of this study, but knowing the concentrations of P-binding cations can help restoration managers predict and mitigate P mobilization risk.

3.4-2 Incubation Experiment

We found the greatest porewater ortho-P concentrations in column SZCI, indicating the greatest P release under saturated conditions (Figure 37). Both peat columns from site CSA had the lowest porewater ortho-P concentrations throughout the experiment. There is not a significant relationship between extractable peat P and porewater ortho-P ($F[1,30] = 3.94$, $p = 0.056$), indicating that peat P content may not be the most reliable factor in assessing P mobilization risk.

Due to inconsistences in incubation temperatures, we cannot draw conclusions about the relationship between temperature and P release. However, there are some significant relationships between metal content and porewater ortho-P content. SZCI had the highest porewater ortho-P overall, and also higher porewater Al and Fe than other columns from Sax-Zim (Figure 38), possibly indicating dissolution of Al-P and Fe-P binding complexes. We do not know for certain why SZCG had lower porewater Al and Fe than SZCI, but this may account for the difference in their porewater ortho-P concentrations. Temperature fluctuations in the greenhouse make it difficult to ascertain a temperature effect for individual measurements, as it oscillated above and below incubator temperature and there is no significant relationship from ANOVA analysis. Additionally, average temperature throughout the incubation period between SZCI and SZCG was not significantly different ($p = 0.076$ and $p = 1.86$, respectively) so it cannot be ascertained if this is a result of higher temperature increasing Fe reduction and release (Curtinrich et al., 2021). Both columns from SZC largely had higher porewater ortho-P, Ca and Fe than the columns from SZA, and ANOVA analysis reveals a significant relationship between these metal ions and ortho-P ($F[1,12] = 41.54$, $p < 0.0001$ and $F[1,12] = 10.98$, $p = 0.00062$ respectively). Thus, greater loss of Al, Ca, and Fe to porewater may correspond to greater ortho-P mobilization in Sax-Zim bog, but in-situ confirmation is required.

While CSAI and CSAG had the lowest overall porewater ortho-P, they also had the lowest porewater Ca of Cold Spring columns. Peat from site CSA also had the highest initial Ca concentration across all sites. ANOVA analysis confirms the significance of the direct relationship between porewater Ca and porewater ortho-P at Cold Spring (($F[1,12] =79.07$, $p < 0.0001$), indicating that Ca may play an important role in keeping P bound to peat at the site. High peat-Ca content and lower release of Ca from peat to porewater may result in better P retention.

Across both Sax-Zim and Cold Spring, porewater Al and Fe are significantly related to porewater ortho-P ($F[1,28] = 17.78$, $p = 0.00024$ and $F[1,28] = 39.837$, $p < 0.0001$ respectively). This is suggestive of reductive dissolution of P-binding complexes under saturated conditions, resulting in P release to porewater. While these findings would need to be validated in-situ, this relationship is consistent with literature showing that Al and Fe release are correlated to P release (Hyvarinen et al., 2012; Kaila et al., 2016; Meissner et al., 2008; Ronkanen and Klove, 2009; Zak et al., 2004). Peatland managers should consider and monitor these dynamics under saturated conditions, as extended wet periods and large runoff events could cause high P export and downstream eutrophication. Managers should be wary of P release risk if peatlands have high P, Al, and Fe concentrations and export high amounts of runoff due to their topography and hydrology. Peat cation content is one important factor to assess, but it is vital to also investigate porewater cation content to understand the potential for release. Initial peat Ca is also significantly related to porewater P ($F[1,28] = 7.57$, $p = 0.010$), and the columns with the highest initial Ca had the lowest porewater P concentrations. A higher Ca concentration in a peatland may suggest it is at lower risk for P mobilization, because Ca is not as readily reduced as Al and Fe (Meissner et al., 2008).

3.4-3 Future Work

This work could be built upon by confirming porewater P's relationships to temperature and metal ions through in-situ monitoring. These experiments were conducted with stationary columns in which the water either evaporated or drained to the bottom of the column, and did not represent lateral transport dynamics or capture environmental factors such as weather and plant productivity. In-situ experiments would provide a more accurate picture of actual P mobilization in peatlands. Work being conducted on the SPRUCE project at Marcell Experimental Forest to investigate temperature effects on peat nutrient release to porewater provides a model for how these in-situ experiments could be set up (Iversen et al., 2019). Expanding on this, we could track ortho-P movement laterally through peatlands using radioisotope tracing (Frossard et al., 2011).

Another drawback to our experimental set-up was the inconsistency in temperature in the incubation locations. Because the temperatures across both the greenhouse and incubator did not end up being significantly different, we could not determine a relationship between temperature and porewater P. A set-up similar to the one at SPRUCE would also improve temperature consistency and allow for us to investigate temperature effects in-situ.

We did not begin porewater sampling until 11 weeks after the beginning of incubation because we wanted to investigate porewater P release only under fully saturated, anoxic conditions. Collecting porewater throughout the early phase on incubation would allow us to look at P release during the transition to anoxic conditions, and see how it differs from P release under fully anoxic conditions. We could also draw from a study conducted by Kaila et al. (2016) and compare P release at different water table depths. Expanding on water table manipulation, we could also fluctuate the water table over time to analyze temporal responses in P dynamics.

4. Conclusion

Restored peatlands have the potential to mitigate climate change through carbon sequestration (Renou-Wilson et al., 2019) and regulate nutrient cycling (Johnston et al., 1990; Negassa et al., 2020). As interest grows in prioritizing peatland restoration across the world, it is important that land managers assess carbon and nutrient dynamics in restored sites to determine benefits, risks, and best management practices on a site-by-site basis. Peatlands sequester carbon much more efficiently than ecosystems with mineral soil (Kolka et al., 2016; Leifeld and Manichetti, 2018), but prolonged drought conditions and high temperatures can accelerate peatland CO_2 emissions (Bridgham et al., 1991; Kechavarzi et al., 2010; Trettin et al., 2006; Zhong et al., 2020). While restored peatlands may cycle and sequester imported P and prevent it from being exported to waters downstream, they may also be large P sources depending on environmental conditions, hydrology, and peat characteristics (Nieminen et al., 2020). To best mitigate the risks of CO_2 emissions and P export from restored peatlands, managers should consider peat type and chemistry, peatland hydrology, temperature, and climate trends.

We selected Sax-Zim bog and Cold Spring fen, restored peatland sites in Minnesota, to investigate the effect of these factors on C and P dynamics in the temperate-boreal region. We monitored peat CO_2 flux and environmental conditions throughout the growing season. CO_2 flux from Sax-Zim bog remained low and steady throughout the growing season, around 2-6 $\mu mol/m^2 \cdot s$, which is comparable to community CO_2 flux in other temperate and boreal bogs across the world (Hanson et al., 2016). Cold Spring fen had high CO_2 emissions during the peak of the growing season, but flux sharply decreased late in the season when precipitation and water table depth increased. Lower CO_2 flux corresponded to sites with less decomposed peat and a high water table. Managers should consider these conditions when deciding where and how to restore peatlands for the greatest carbon sink potential.

We performed laboratory incubation experiments on peat columns from each site to assess ortho-P release to porewater. The results are inconclusive with regards to temperature effects, but the release of P-binding metal cations to porewater, especially Al and Fe, is related to greater ortho-P release. Additionally, there is a significant relationship between higher peat Ca content and lower porewater ortho-P. Monitoring peat P content alone is not sufficient for making predictions about P mobilization in restored peatlands, as peats with similarly high peat P concentrations can experience different rates of P release under wetted conditions. In order to more comprehensively assess P mobilization and export risk, managers should also consider the content and dynamics of Al, Ca, and Fe. Through continuous monitoring and frequent reassessment of environmental conditions and management practices on a site-by-site basis, drained peatlands can be restored into thriving ecosystems which function as carbon sinks to mitigate climate change and prevent downstream eutrophication by reducing P export.

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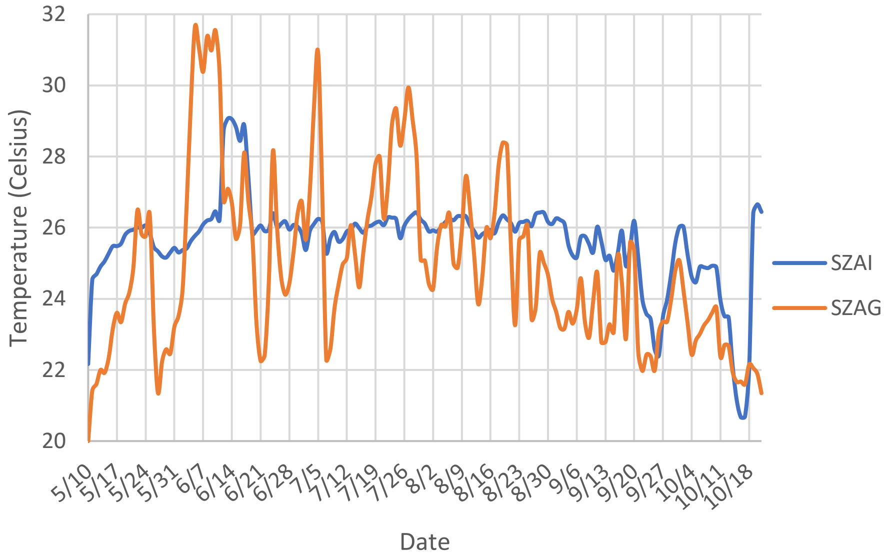
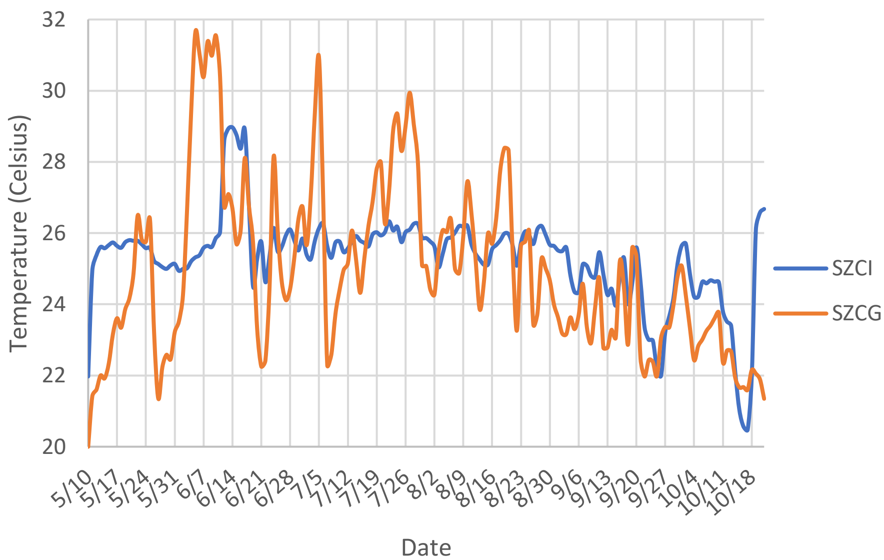
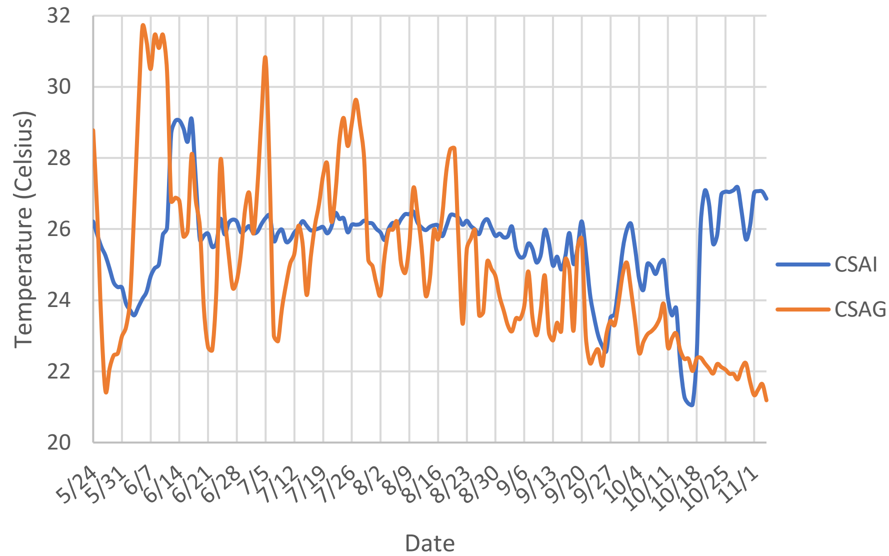
Appendix I: Full Soil Phosphorus Data

Peat Sampling Site and Depth (cm)	Bray P (mg/kg): May 2021	Bray P (mg/kg): July 2021	Bray P (mg/kg): September 2021
SZA0	18	8	8
SZA15	14	5	11
SZA30	13	18	11
SZB0	17	24	13
SZB15	14	10	16
SZB30	12	11	10
SZC0	43	46	45
SZC15	14	29	24
SZC30	13	20	13
Peat Sampling Site and Depth (cm)	**Olsen P (mg/kg): May 2021**	**Olsen P (mg/kg): July 2021**	**Olsen P (mg/kg): September 2021**
CSA0	41	19	32
CSA15	15	19	21
CSA30	4	13	12
CSB0	27	53	20
CSB15	13	17	17
CSB30	11	18	11
CSC0	29	27	14
CSC15	21	13	12
CSC30	20	5	12

Appendix II: Incubation Temperature Data



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Temperature (Celsius)
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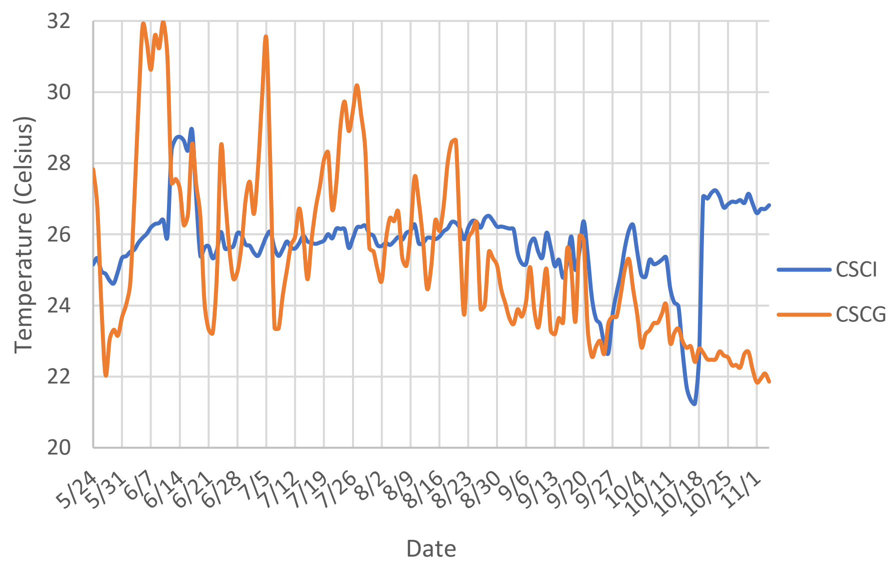
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