

Wetlands as filters of heavy metals: A study in Temperate Fens of Central Ontario

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Abstract

Heavy metal concentrations (As, Cd, Cr, Cu, Ni, Pb, and Zn) were investigated in water, peat, and macrophytes across three fens in Central Ontario in relation to the water parameters and peat properties to elucidate the interactions between plant sequestration and heavy metal concentrations in the overlying water systems. The water parameters monitored include pH, dissolved oxygen, conductivity, total dissolved solids, salinity, nutrients, chlorophyll *a*, and dissolved organic matter. The peat properties studied included bulk density, volumetric porosity, and humification, and the plant properties studied included root length and the development of root plaques. In addition, all samples were analyzed for heavy metals. The fens were categorized from poor to rich depending on their water chemistry and plant community. Surface water samples were collected from the inlet, outlet and midpoint of the fens in the spring, summer, and fall of 2023. Porewater samples were collected from the midpoints of the fens using *in situ* pore water sampling device. In situ pore water sampling devices were deployed in the peat, and the porewater samples were collected from 10, 20 and 30 cm below the peat surface. Peat cores were also collected in fall 2023 from the inlet and the midpoints of the fens to analyze the peat properties and heavy metal concentrations at three different depths (10, 20, and 30 cm below the peat surface). Additionally, 13 plant species were collected in fall 2023 from the fens' midpoints and divided into upper and lower biomass for heavy metal analysis.

Analysis of the samples revealed that the peats were enriched with several anthropogenic pollutants, particularly lead. The porewater and plant analysis showed enrichment of several heavy metals. Porewater heavy metal concentrations varied with depth, with a lower concentration in the water column compared to peat, suggesting that the fens function as sinks for many heavy metals. Generally, fens reduced the heavy metal concentrations in the surface water as water traversed through the wetland; however, the richer fen became a source of heavy metals in the fall, whereas the poorer fen became a source in the summer. Macrophytes demonstrated the capacity to sequester Zn, Cr, and Cu while frequently acting as non-accumulators of Cd, Pb, Ni, and As. The highest transfer coefficients from peat to plants were observed in plant species from the moderately-rich to rich site (MW). In plants, heavy metals were predominantly sequestered in the lower biomass, with only Zn, Cu, and Cr being translocated to the upper biomass. The poor fen site (SS) exhibited the highest number of plants capable of translocating heavy metals to the upper biomass. The processes of heavy metal sequestration and translocation were found to be largely dependent on site-specific biogeochemical factors within the fens, which influenced the speciation and mobility of these metals. Additionally, the uptake and translocation processes were affected by the interactions among various metals and competition for transporter pathways. Overall, macrophytes played a significant role in sequestering heavy metals within the peats and water of fens, thereby reducing the heavy metal load in the outflowing water from the fens.

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Layperson Summary

This research studied levels of heavy metals (arsenic, cadmium, chromium, copper, nickel, lead, and zinc) in water, peat (peat at the bottom of the wetland), and plants in three different fens (a type of wetland) in Central Ontario, to determine how plants help interact with the peat and water to sequester heavy metals. These fens differed in terms of nutrient levels and acidity and were graded from poor to rich.

In order to understand these interactions, water entering and leaving the fens, water from various depths and locations within the fens, and water during different seasons—spring, summer, and fall—were collected. Special tubes inserted into the peat were used to gather water from different depths (10,20 and 30 below the peat surface). All water samples were analyzed for heavy metals. In addition, various water quality parameters such as pH, dissolved oxygen, conductivity, and levels of nutrients and organic matter were monitored. Peat samples were collected in the fall from the inlet and the midpoint of the fens using a core sampler. The core was divided into four equal sections, dried and analyzed for heavy metals. The properties of the peats, such as porosity and bulk density, were also measured. Lastly, 13 species of plants were collected and washed to remove any peat and were divided into upper (the part above ground) and lower biomass (the roots and below-ground parts). These were also dried and analyzed for heavy metals.

The results showed that the amount of heavy metals in the water was lower than in the peat, which suggests that the peat can trap these metals. However, the concentration of metals varied with peat depth, indicating that different environmental processes influenced their distribution. As water flowed through the fens, the concentration of heavy metals in the water also varied with depth, influenced by seasonal changes, the physical properties of the peat, and biological processes. For example, in summer, some metals were more concentrated, likely due to changes caused by plant activity, but this shifted in the fall when plants started to decompose and release nutrients and metals back into the water.

The results also showed that the peats, water and plants showed high levels of some heavy metals. The research also found that the amount of heavy metals in the fens was higher than what is usually found in the area, with metal levels being greater at the points where water entered the fen than in the middle of the fens. These results indicate that fens acted as filters to reduce the metal concentration in water as the water flowed through them.

The study found that plants in these acidic wetlands greatly influence how heavy metals are stored in the peat. Most heavy metals were found in the lower parts of the plants, with only a few like zinc, copper, and chromium moving to the upper parts. The ability of plants to take up and transfer heavy metals depended on specific conditions in each fen, including how different metals interacted with each other and competed for absorption sites in the roots. The fen plants help to reduce the movement of heavy metals from the peat to the water. They do this through processes called rhizofiltration and phytostabilization, which use the roots to hold the heavy metals in the plants.

Overall, these wetlands were effective in lowering the concentration of heavy metals in the water flowing out. The plants in these areas were particularly good at absorbing zinc, chromium, and copper, while they usually did not absorb cadmium, lead, nickel, and arsenic as effectively. Interestingly, plants at richer fens absorbed more metals than those at poorer fens, and the plants at the poor fen moved more metals to the above-ground portion of the plant.

In summary, the plants played an important role in capturing heavy metals from the peat and water of the fens, which helped to decrease the amount of these harmful metals in the water that eventually leaves the wetlands. While it is generally thought that how much heavy metal plants absorb is related to the metal levels in the peat and water, this study found little connection except for copper and lead.

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Abbreviations

As	Arsenic
BAF	Bioaccumulation Factor
BD	Bulk Density
Cd	Cadmium
Cond.	Conductivity
Cr	Chromium
Cu	Copper
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
EF	Enrichment Factor
Fe	Iron
Igeo	Geoaccumulation Index
Mn	Manganese
Ni	Nickel
P	Phosphorus
Pb	Lead
Plqs	Root Plaques
Sal.	Salinity
TDS	Total Dissolved Solids
TF	Translocation factor
VP	Volumetric Porosity
Zn	Zinc

Chapter 1: Introduction and Literature Review

Peatlands are important sinks for carbon and pollutants and often serve as archives for temporal records of heavy metal pollution (Nieminen et al., 2002; Shuttleworth et al., 2017). Peatlands cover about 3% of the Earth and are characteristically low in oxygen and potential of hydrogen (pH). This results in a slow decomposition of plant material, which accumulates over time (Borgulat et al., 2018). The majority of heavy metals accumulate in the upper 30 cm of the peat (Smieja-Król et al., 2010; Ukonmaanaho et al., 2004). Heavy metal accumulation studies on the bog peatlands are more prevalent due to the ability of *Sphagnum*, the primary life forms in bog peatlands, to accumulate heavy metals. Fens, compared to bogs, have an extensive diversity of bryophytes and vascular plants, influencing the biogeochemical cycles of heavy metals in peatland systems (Sahar et al., 2022). Like other wetlands, fen plants aid in water purification as they pass through, enabling them to act as sinks for heavy metals and other contaminants. However, the efficacy of this function varies due to differences in hydrology, anthropogenic inputs, weather, vegetation, and peat composition (Wiken et al., 2003).

1.1 Fen ecosystems

Fens are peatlands characterized by low nutrients, rich biodiversity, and slightly lower pH than marshes and swamps but higher than bogs. Fens range from poor to rich based on nutrient status and pH (Bourbonniere, 2009). Fens support a range of wildlife and rare and endangered plant species. Fens have continuous or intermittent input of both surface and groundwater with a fluctuating water table. The water moves through channels, pools or open waters in the fens before being released at the outlets. The peat layers consist of a poorly decomposed organic matter surface layer and a highly decomposed organic matter deeper layer. Like other wetlands,

fens risk destruction due to land conversion/drainage for various reasons (urbanization, industrial, and agricultural). They are also exposed to transformation from rapid climate change (Diggelen et al., 2006).

1.1.2 Environmental and ecological functions of wetlands

Wetlands are critical ecosystems for all living organisms, yet throughout history and in many countries, wetlands have been regarded as wastelands, resulting in their destruction for land conversion (Woodward & Wui, 2001). Wetlands play a pivotal role in water resource management and have more value than their goods and services, which are typically aesthetic or economical (LePage, 2013). However, they continue to be impacted by pollution and destruction due to urban expansion and agricultural activities (J. Yang et al., 2017). The processes within a wetland are defined by their functions (Fretwell et al., 1996), consisting of water quality control through ground recharge and discharge, nutrient cycling, and carbon storage (Salimi & Scholz, 2021). Acting as natural filters, they help to purify water through various physical, chemical, and biological processes. The peat and vegetation remove pollutants from the water column by filtering or trapping them. Adsorption and chemical reactions bind contaminants to peat and plants; other processes, such as denitrification and phosphorous uptake, break down pollutants through microorganisms and vegetation uptake (Lepage, 2011). These actions increase productivity and reduce drinking water purification costs. Lastly, wetlands stabilize peats and protect them from floods and storm surges. Like other ecosystems, not all wetlands perform the same functions or perform them at the same level. Factors such as location, wetland type, climate, disturbances and abundance, landscape patterns, and water quality entering the system can influence the system (Chou et al., 2018; Kang et al., 2019; Fretwell et al., 1996).

1.1.3 The value of peatlands

Peatlands are transitional environments between terrestrial and aquatic ecosystems that serve various ecosystem services such as water quality protection, flood mitigation, biodiversity conservation, and climate change regulation through their hydrological, ecological and biogeochemical functions (Rezanezhad et al., 2016; Shuttleworth et al., 2017; Vitt et al., 2020). Using photosynthesis, wetland plants accumulate and sequester the carbon in their biomass (Salimi & Scholz, 2021). Over time, permanent water saturation and low oxygen content trap the carbon, which accumulates in the peat over time, producing peat. The accumulating carbon in the peatlands makes it a vast carbon sink and one of the most productive ecosystems (Salimi & Scholz, 2021). Peatlands are often used as a historical record of pollution and carbon sequestration, acting as sinks and sources of carbon, heavy metals, and other contaminants (Qin et al., 2022).

The role of peatlands in climate change

The World Bank (2008) identified that one of the greatest threats to biodiversity is urbanization and climate change. These threats have led to wetland degradation, habitat loss, fragmentation, and drainage, which affect pollution and peatation. Wetlands are imperative in reducing the vulnerability and survival of urban areas in the eminent face of climate change and extreme weather events (Dinsa & Gameda, 2019). It is believed that climate change will have the greatest impact on peatlands (Tarnocai, 2009).

Global warming, caused by an increase in greenhouse gases (GHG) such as methane, nitrous oxide, and carbon dioxide, is partially mitigated through the capacity of wetlands to balance atmospheric concentrations (Salimi & Scholz, 2021). Climate change influences the productivity of wetlands through variations in temperature and precipitation, which alter the biogeochemistry

of peatland ecosystems (Tarnocai, 2009). Weather changes and their patterns affect wetlands through rising temperatures, rainfall intensity, and frequency. These weather changes result in drought and flooding, which modify the hydrology and biogeochemical functions within the wetland, leading to the release of nutrients to surface water, resulting in eutrophication (Corman et al., 2018; Salimi & Scholz, 2021).

Research has revealed that peatlands are greatly impacted by temperature and water availability. When faced with droughts and floods, peatlands undergo mineralization and carbon release, which can have a harmful effect on water quality and gas emissions (Waddington et al., 2015). Heavy metals may also be mobilized to surface water, increasing toxicity levels (Watmough & Orlovskaya, 2015). Droughts can cause a drop in gross primary production (Chivers et al., 2009) and a rise in gas emissions (Lund et al., 2012; Salimi & Scholz, 2021). Conversely, flooding can lead to an increase in gross primary production (Chivers et al., 2009; Salimi & Scholz, 2021). However, the effects of droughts and floods can vary depending on the initial state of the peatland (Laine et al., 2013). Additionally, temperature increases have been found to influence the biogeochemical processes in peatlands.

Peatlands in Canada are unique in that they store approximately one-third of the world's terrestrial organic carbon (Ervin, 2023). They attract attention because northern areas are warming faster than the world average (McLaughlin & Webster, 2014). The low boreal peatlands have large human populations (Warner & Asada, 2006), making them more susceptible to anthropogenic impacts such as fires and urbanization (Ervin, 2023).

1.1.4 The contamination of wetlands

Water is an essential part of the wetland system, and its quality dictates its potential for supporting biodiversity and ecosystem function; therefore, the imbalance of organic and inorganic materials can lead to ecosystem degradation (Hong et al., 2020). Both point sources and non-point sources influence the quality of freshwater. However, the quality of surface waters is more vulnerable than groundwater due to runoff and waste disposal (Saalidong et al., 2022).

Heavy metals are ubiquitous in low natural quantities in water, peats, and plants. Due to their inability to degrade in the environment, heavy metals can serve as human historical archives and monitor anthropogenic changes in activities (Newman et al., 2023; Yu et al., 2014). Natural processes cannot remove or transform trace elements from water, leading to toxic metals accumulating in peats (Forstner et al., 2012).

Anthropogenic activities release large quantities of heavy metals (Jiang et al., 2017), threatening humans, aquatic life, and the environment. (Jiang et al., 2017). This knowledge generates a growing concern due to its ability to bioaccumulate in the food chain and affect aquatic organisms and human life, altering trophic structure, biodiversity, microbes and communities (Algül & Beyhan, 2020; Hong et al., 2020; Saalidong et al., 2022; Wuana & Okieimen, 2011; Y. Zhang et al., 2018; Z. Zhang et al., 2022).

Heavy metals in wetlands

Wetlands are considered the "kidneys" of the environment and are crucial sinks for heavy metals due to their physicochemical properties (Zhang et al., 2022). Peats aid in storing and releasing heavy metals, making them both a source and a sink (Gao et al., 2014; Pradit et al., 2022; Zhang et al., 2022). Heavy metals that have entered the wetland through air deposition and runoff can be impacted by flooding and sudden influxes of water and peat, which influence post-

depositional mobilization (Bai et al., 2016). Heavy metals can bond to peat and accumulate in considerable quantities depending on their input and sources (Zhang et al., 2016).

In aquatic systems, peats are sinks for heavy metals and are usually elevated compared to water (Algül & Beyhan, 2020; Forstner et al., 2012; Varoll & Şen, 2012). When biogeochemical processes change, the heavy metals in the peat can be released into the surrounding water, becoming a non-point source of water contamination (Algül & Beyhan, 2020; Forstner et al., 2012; Varol & Şen, 2012). In surface waters, contaminants are dissolved or sorbed into the suspended matter and settle into peats. However, contaminants are not easily degraded in anoxic conditions and become preserved; they quickly transform, accumulate, or transfer to water or organisms (Chiaia-Hernández et al., 2022; Lara-Martín et al., 2015). Heavy metals exceeding acceptable levels result in decreased biodiversity and irreversible damage to animals and plants. (Bai et al., 2016; Schipper et al., 2011; Yan et al., 2022).

1.1.5 Various mitigation techniques

Various techniques have been employed to clean up pollutants in ecosystems. These include, but are not limited to, methods such as evacuation, precipitation, heat treatment, electro-remediation, chemical leaching, peat washing, excavation, solidification, nitrification, etc. (Dada et al., 2015; Sharma et al., 2023). All these methods are costly and are limited to small areas (Delgado-González et al., 2021; El-Liethy et al., 2022; Sharma et al., 2023; Sundarakumar et al., 2022). Other issues affecting their use are electricity requirements and toxic sludge production (Sharma et al., 2023). Phytoremediation is an environmentally friendly and successful means to immobilize and sequester pollutants.

1.1.6 Phytoremediation

Heavy metals are ubiquitous in our environment and pose a global environmental threat to ecosystems and human health. Many techniques have been implored to mitigate the mobility of heavy metals and other pollutants from entering our aquatic ecosystem, but they are time-consuming and very costly. Phytoremediation is "the efficient use of plants to remove, detoxify, or immobilize environmental contaminants" (UNEP, 2019); they aid in the removal of excess contaminants and improve water quality (Lu et al., 2010). Phytoremediation offers a cost-effective and low-maintenance means of mitigating heavy metals in the water and peats (Aziz et al., 2020; Yan et al., 2022). Phytoremediation uses plants to sequester, degrade, stabilize, or transfer pollutants in peats and water. Plants can remediate the system through various methods (Kafle et al., 2022). Plants that remediate are classified as either tolerant of pollutants or hyperaccumulators, meaning that they show no signs of toxicity and can accumulate high amounts of pollutants in the roots and shoots (Nedjimi, 2021). Wetlands have long been considered sinks for contaminants, and plants remediate them through sequestration or immobilization in the lower or upper biomass. Removal of upper biomass will help to remove the contaminants from the system (Weis & Weis, 2004).

Plants exhibit several means of coping with heavy metal pollution. Excluder species prevent and restrict the accumulation of heavy metals (Nedjimi, 2021), and microorganisms in the rhizosphere release metal-chelating agents to prevent heavy metal absorption (Nedjimi, 2021). Hyperaccumulator plants uptake heavy metals and use biochemical pathways to maintain metal concentrations in the cytoplasm and to protect the organelles from toxins. Plants with no prevention strategy accumulate large amounts of heavy metals, which become sequestered or compartmentalized in their vacuoles to keep toxins away from the cytosol, thereby limiting or

reducing damage (Nedjimi, 2021). Organic solutes and amino acids reduce and translocate heavy metals to other parts of the plant. Indicator plants uptake more heavy metals than are in the peats (Kafle et al., 2022).

The ability of a plant to remediate heavy metals depends on the combination of the species, the metal, and its solubility. The solute passes through the epidermis, endodermis, and xylem, where it is translocated from the roots to the shoots through hydraulic conductivity and transpiration in the leaf (Nedjimi, 2021). Heavy metal availability decreases in peats with higher pH, clay, and organic matter; however, the bioavailability increases in low-pH peats, such as peatlands (Kafle et al., 2022).

Phytoextraction is the most sought-after type of phytoremediation in terrestrial cleanup. It involves a high accumulation of heavy metal in the upper biomass of the plant (Nedjimi, 2021). Hyperaccumulators can uptake large amounts of heavy metals from the substrate, translocate heavy metals fast and effectively, and sequester large amounts in the plant body (Rascio & Navari-Izzo, 2011). Plants with large biomass and deep roots are best suited for phytoextraction (Cronk & Fennessy, 2016). This type of remediation is highly beneficial in areas where the upper biomass can be harvested and removed from the site; plants that remain become ineffective in remediating when leaf and stem litter decompose and release the pollutant back into the environment.

Phytodegradation breaks down the pollutants into less toxic forms and redistributing them through the plant tissues. Rhizodegradation is similar but involves the rhizosphere; contaminants are broken down and released into the peat with the aid of microbes (El-Liethy et al., 2022; Kafle et al., 2022).

Phytovolatilization occurs when a plant takes a pollutant, transforms it into a less harmful form, and releases it as gas through the stomata of the leaves, lenticels, or in a peat-root interaction zone (Kafle et al., 2022). Few natural plants can transform heavy metals, such as selenium and arsenic, into gaseous states and release them into the environment (Sharma et al., 2023).

Rhizofiltration precipitates pollutants into the roots through ground or surface water. The metals are absorbed, concentrated, and precipitated in the roots and other organs (Kafle et al., 2022).

Aquatic plants typically provide this type of phytoremediation, which is recommended in highly eutrophic waters. Fibrous roots, which have large surface areas, are best suited for this type of phytoremediation; the roots act as a pump and draw water (Sharma et al., 2023).

Phytostabilization stores the pollutants in the root or rhizosphere and reduces the mobility of the pollutants through the water and substrates, thereby reducing their bioavailability (Kafle et al., 2022; Rascio & Navari-Izzo, 2011). This process occurs in the vadose zone of the root (Sharma et al., 2023); pollutants bind to the roots through transpiration, establishing aerobic conditions in the root zone and preventing contaminants' leaching into the environment (Sharma et al., 2023). Some plants can prevent further poisoning or remobilization by forming bound residues with the help of transport proteins and phytochemical exudates (Sharma et al., 2023).

Water quality and phytoremediation

Many pollutants cannot be easily destroyed; however, they can be transformed into less harmful forms using plants (Jiang et al., 2017; Sharma et al., 2023). The literature demonstrates that various species of macrophytes have been verified and recognized for their efficiency in accumulating inorganic and organic contaminants from waters through hydroponic or field applications (Jiang et al., 2017). Numerous macrophytes genera, such as *Lemnaceae*, *Cyperaceae*, *Haloragaceae*, *Juncaceae*, and *Zosterophyllaceae*, demonstrate the ability to reduce

eutrophication and remove heavy metals in water. Those capable of water cleanup through rhizofiltration are the most studied plants. Each plant's capabilities are different and related to its biomass, oxygen transportation, root capacity, and root development (Sharma et al., 2023).

Many studies demonstrate the ability of phytoremediation to remove contaminants in constructed wetlands (Nattress et al., 2019), wastewater (Jones et al., 2006; Singh et al., 2023), industrial effluent (Hemamalini et al., 2019; Sundarakumar et al., 2022; Ugya et al., 2016), and in *ex-situ* experimentation which examines the potential of a plant for remediation. Phytoremediation has been used *in-situ* to reduce eutrophic waters, reduce pollution in acid mine drainage (AMD), reduce textile dyes in wastewater (Chandanshive et al., 2018), and perform oil cleanup (Panchenko et al., 2023). Nevertheless, *in-situ* studies examining the ability of a natural aquatic system to remediate water are limited. Of those studied, Hanafiah et al. (2021) found a significant decrease in the contamination of the Klang River through the ability of *Pistia stratiotes* and *Lemna minor* to reduce chemical contaminants in the water. Similarly, Dean et al. (2013) studied a wetland as a long-term remediation system and demonstrated that it significantly reduced contaminants and improved water quality. Knox et al. (2008) found that 50 years after inputs of acid mine drainage (AMD) into a stream, the wetland still retained uranium in the upper 19–25 cm of the core (Knox et al., 2008).

1.1.7 The Role of Water Chemistry in Phytoremediation

Multiple processes result in the behaviour of heavy metals in the environment, such as the physical, chemical, and biological interactions between plants and water and peat processes (Pinto et al., 2014). The ability of a plant to remediate depends not only on the plant's morphological structure and characteristics but also on the properties of the environmental conditions (El-Liethy et al., 2022).

The cation exchange capacity (ECE) is the ability of peat to hold and exchange cations; it is a function of organic matter concentration and pH. pH strongly influences a plant's ability to remediate; when pH is reduced, cations' availability increases as cations in the peat are replaced with H⁺ ions (Pinto et al., 2014). pH also influences oxygen and a plant's remediation abilities and therefore controls the metal release into the water (El-Liethy et al., 2022). pH and heavy metal mobility are inversely related; a lower pH increases metal mobility (Rosenfeld et al., 2018; Watmough & Orlovskaya, 2015). Peats that hold more water have more binding sites for ions. Thus, the biogeochemistry of fen water and peat, coupled with the unique characteristics of fen plants, may assist in sequestering heavy metals and provide a long-term sink compared to other wetland systems, provided the ecosystem remains undisturbed.

1.2 Importance of research

Although many studies have focused on heavy metals in peatland bogs, few examine heavy metal accumulation and mobility in fens (Krumins & Robalds, 2014), particularly in relation to water, peat, and vegetation. In general, studies on heavy metals in wetlands have found varying results. For example, studies demonstrate that wetlands are sinks of heavy metals over a long term (Jacob & Otte, 2003). Similarly, Ury et al. (2023) analyzed 139 wetlands and their ability to retain phosphorous and concluded that although wetlands can act as both sources and sinks, the majority acted as sinks. The degree of difference between a wetland being a source or a sink could depend on the role of plant species in the wetlands. Dean et al. (2013) found a long-term reduction in contaminants in wetlands which they attributed to wetland plants. Plant community variations have been found to play roles in many biogeochemical cycles. Rezanezhad et al. (2012) found that fen plants are more likely to grow in oil-sands-contaminated waters than bog plants. The microbial community under fens is more active than in bogs but responds to seasonal

variation. Paul et al. (2006) evaluated upland and lowland forested fens and determined that the long-term storage of sulphur was different at both sites, which was explained by the role of vascular plants.

Moreover, Weis & Weis (2004) suggest that studies need to examine the release of metals from roots to make a sufficient determination of whether a wetland is a source or a sink. Qin et al. (2022) determined that seasonal changes alter the ability of the wetland to act as a sink or source of heavy metals, which could result from perennial cycles. A recent study by Kharanzhevskaya et al. (2023) concluded that the metal concentration of pore water in bogs is related to the vegetation and the upper peat metal concentration and is strongly influenced by temperature. Consequently, inconsistencies remain in the literature regarding seasonal variation and the role of vegetation in heavy metal storage. It should be considered that climate change and urbanization can affect diversity and plant communities (Tyler et al., 2021), creating a shift in biochemistry and resulting in vegetation that could alter the sink and source capacity of the peatland.

By increasing our understanding of the functions and the relationship between heavy metals in the peat, plants, and water, we can better assess and address the management of fens in south-central Ontario and other temperate fens worldwide. The information gained through this research will assist site managers in determining fen sites that may release higher levels of contaminants when disturbed, and which vegetation may enhance uptake in contaminated fens during the mitigation process. This study aims to examine the changes in water quality and contaminate load before and after entering three fen systems and to determine if variations and distribution of flora within each fen system play a role in the reduction of heavy metal contaminants in the water.

1.3 Gaps in the research

While there has been substantial research on the availability and accumulation of heavy metals in bogs, there is still a significant dearth of knowledge on these ecosystems (Krumins & Robalds, 2014). Earlier studies indicate that some heavy metals are retained temporarily in fen ecosystems (Leendertse et al., 1996), while others consider them as long-term sinks (Dean et al., 2013; Jacob & Otte, 2003; Knox et al., 2008). This variation suggests that wetlands can be either a source or a sink of heavy metals. This also depends on the composition of plant communities (Borgulat et al., 2018; Dean et al., 2013; Rezanezhad, Price, et al., 2012) and environmental factors (Yu. A. Kharanzhevskaya et al., 2011; Qin et al., 2022; Tyler et al., 2020). Furthermore, Borgulat et al. (2018) highlighted a significant gap in knowledge regarding the accumulation of heavy metals in peatland vascular plants. The type and structure of peat were found to influence the heavy metal accumulation, with moderately rich fens exhibiting the greatest accumulation (Osborne et al., 2024). This variation may be attributed to differences in plant communities. If this is the case, then if shifts in climate and biogeochemistry (Wikens, 2003) occur, it could shift the vegetation and, therefore, the role of peatland, i.e. as sink or source of these metals.

The review of literature showed a limited number of studies on peatland systems from south-central Ontario where fens are at risk of degradation through anthropogenic activities. While the role of vegetation in remediation has been well-studied in constructed wetlands, the mechanisms by which fen plants mitigate heavy metal contamination and filter surface water remain poorly understood.

Furthermore, information on whether fens function as short-term sinks and sources is limited. Also, the influence of plant communities in the fens and their senescence on the absorption and release of heavy metals is not well understood. Therefore, this study aims to broaden our knowledge of the roles of fen ecosystems, including its plant community, on the water quality by filtering and or retaining heavy metals from the water body. The following are the major objectives of the study.

1.4 Major objectives of the study:

1. To characterize three fen ecosystems in south-central Ontario with respect to their water quality, peat properties and plant communities
2. To monitor heavy metal composition in water (both surface and porewater), peat and major plant species in the fens
3. To assess the roles of fens as heavy metal sources or sinks
4. To assess the potential of macrophytes as agents of phytoremediation of heavy metals and
5. To assess the roles of peat properties in the heavy metal retention in the fens

Chapter 2 - Site Selection and Data Analysis

2.1 Sites Overview

Three fens (study sites) were selected for the present study. They are Langman Sanctuary (N44.59.949 W79.492914) and Minesing Wetland (N45.107486 W79.769358), located near urban centers, and the Muskoka wetland (N44.381411 W79.840314) located near small communities with an increased highway traffic (Fig. 1.1, Table 2.1). The sites were selected based on location and accessibility, i.e. fens with a water flow inlet and outlet. Peat depth was not determined for this study. The following vascular plants characterize all three sites: pitcher plants *Sarracenia purpurea*, bog rosemary *Andromeda polifolia*, sweet gale *Myrica gale*, leatherleaf *Chamaedaphne calyculata*, sundew plants *Drosera spp.*, and white-beaked sedge *Rhynchospora alba*, with varying degrees of *Sphagnum spp.* and brown mosses (*Drepanocladus sp.*, *Scorpidium sp.*, *Aulacomnium sp.*) populations.

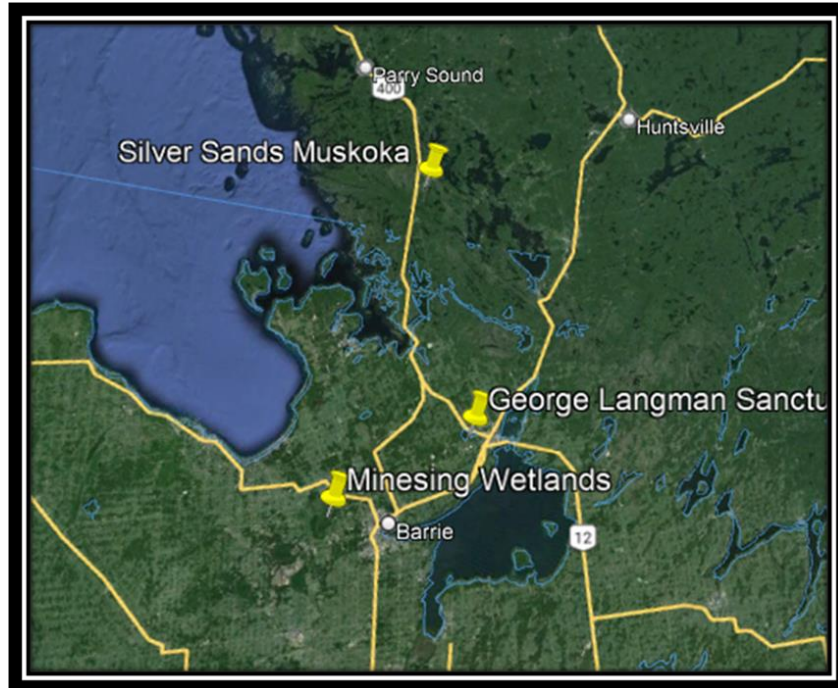


Figure 2.1. Location of the three study sites in Central Ontario (Google Maps, 2024)

2.1.1 Site descriptions

The Langman Sanctuary and Minesing Wetland are located in Ontario within the 6E-6 eco-region (M.N.R., 2021), which is part of the Mixed Woods Plains Eco Zone in Ontario (*The Ecosystems of Ontario – Part 1*, n.d.). The study area is part of the Oro-Medonte region (Fig. 2.1), which contains high-quality deciduous forest. The moraine drains into the headwaters that drain into Georgian Bay (Simcoe County, 2021). The climate here is considered mild and moist, with a mean annual temperature range from 4.9 to 7.8 and a mean precipitation range from 759 mm to 1087 mm. This ecozone is located predominantly on limestone and dolostone rock formations from the Precambrian Shield. It is bound by the water bodies Lake Huron, Lake Erie, Lake Ontario and the St. Lawrence River (*The Ecosystems of Ontario – Part 1*, n.d.). The topography in the region varies from flat to rolling. The peat substrates are typically well-developed fertile luvisol and gleysol (*The Ecosystems of Ontario – Part 1*, n.d.). The vegetation in the ecozone is mixed deciduous-evergreen forest, with hardwood forest including sugar maple (*Acer sacrum*), American beech (*Fraxinus americana*), oak (*Quercus spp.*) and trembling aspen

(*Populus tremuloides*). Many wetlands remain in the area close to Georgian Bay. Flora and fauna in the area are very diverse and contain several at-risk species. Disturbance in the area was once dominated by the clear-cut forest for urbanization (*The Ecosystems of Ontario – Part 1*, n.d.).

Much of the area within this ecozone is fragmented and altered into areas for infrastructure and agriculture (57%). This region is the most densely populated ecozone in Canada, and it is predicted that these activities will make the area susceptible to drought and favour those species which prefer drought conditions (*The Ecosystems of Ontario – Part 1*, n.d.). Many of the natural ecosystems in this area have been converted to human use for agriculture and infrastructure. Seasonal changes are somewhat influenced by the Great Lakes, which can bring lake-effect snow to the area. Winters are cool, and summers are warm, with daily average temperature between -3° in the winter and 22° in the summer. The area receives about 880 mm of precipitation per year.

Langman Sanctuary and Minesing Wetlands are on the traditional territory of the Anishnaabeg, specifically the Chippewas of Rama First Nation, a member of the Chippewa Tri-Council and Three Fires Confederacy, and it continues to be home to many diverse First Nation, Metis and Inuit Peoples.

2.1.2 George Langman Sanctuary (LM)

The George Langman Sanctuary is located in the township of Oro-Medonte, just southwest of the City of Orillia, Ontario. It is owned and maintained by the Orillia Fish and Conservation Club (OFGCC). The sanctuary, which sits on a 61-acre parcel of land, can be accessed from the Bass Lake sideroad, Oro-Medonte (Fig. 2.2. Table 2.1). The study site makes up 34.72 acres and is 183 m long. Within 100 m of wetlands, 26% of the land has been developed or altered, and 74% is relatively natural. The George Langman Sanctuary is situated near the southwest corner of Bass Lake at the 14th Line of Oro-Medonte, just west of Bass Lake Provincial Park. South of the sanctuary is a wooded poor fen, an agricultural field, and a quarry. The sanctuary has two main inlets: one from the forest and another from the 14th Line, which drains through a wooded area, agricultural fields, and a residential zone.

Water flows through LM to a private pond that connects to Bass Lake, forming part of the Bass Lake watershed. The sanctuary is privately owned by the Orillia Hunters and Anglers Club and features a complex wetland system surrounded by various upland landscape features. A wooded fen surrounds the southern portion of LM which is dominated by black spruce and a variety of vascular plants such as Labrador tea (*Ledum groenlandicum*), balsam fir, (*Abies balsamea*), bunchberry (*Cornus canadensis*), within a small section of pitcher plants (*Sarracenia purpurea*), royal fern (*Osmunda regalis*) and pink ladies slipper orchid (*Cypripedium acaule*). As this forest extends west and east, the vegetation changes to include pine (*Pinus spp*), *A. balsamea*, and colts foot (*Tussilago farfara*), among others. Along the west side, the upland forest transitions into a small cedar reforestation plot before merging with the main entrance area of the sanctuary. Shrubs and sumac dominate the east side and follow the 14th line.

The interior wetland complex consists of a small area near the forested inlet with a few cattails (*Typha spp.*) and water lilies (*Nymphaeaceae spp*). The watercourse has created several pathways through the wetland, the middle portion consists of an outer ring of ericaceous shrubs such as (*Sarracenia purpurea*), bog rosemary (*Andromeda polifolia*), sweet gale (*Myrica. Gale*), leatherleaf (*Chamaedaphne calyculata*), non-native phragmites (*Phragmites australis*), and some vascular plants such as ferns and sundew plants (*Drosera spp*). The inner area consists of sedges and mosses, with some bog golden rod (*Solidago uliginosa*), grass of Parnassus (*Parnassus spp.*), pitcher plants (*Sarracenia purpurea*), bog cranberry (*Vaccinium oxycoccos*), leatherleaf (*Chamaedaphne calyculata*) and sundew plants (*Drosera spp.*). The water surrounding this middle portion has water lilies and a few other aquatic plants.

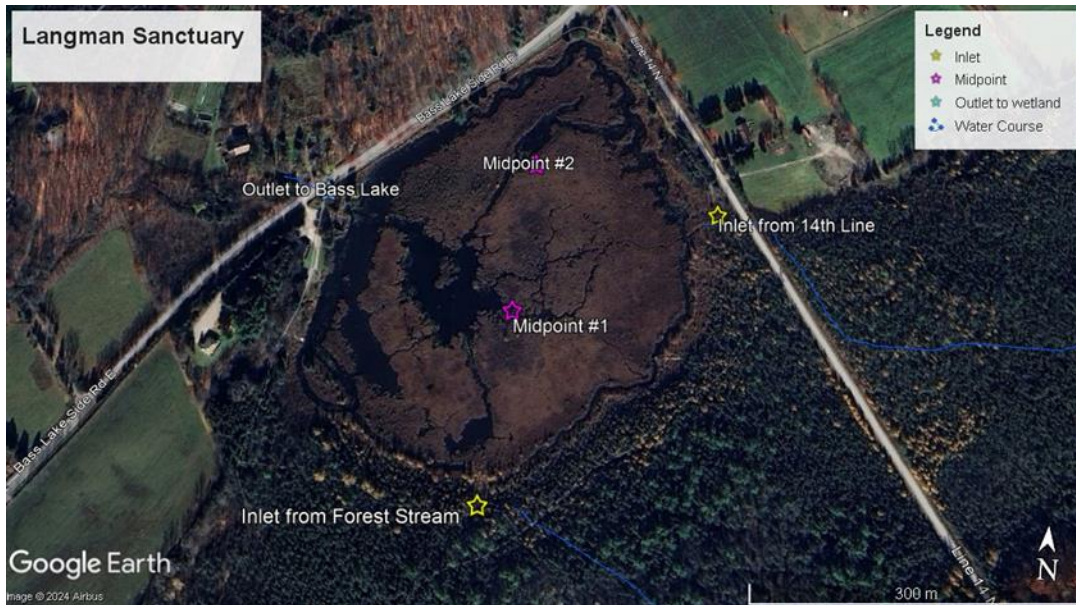


Figure 2.2. Site map of Langman Sanctuary, including testing locations (Google Maps, 2024)

2.1.3 Minesing Wetlands – Tom Wilcox Nature Preserve (MW)

Minesing Wetlands (Fig. 2.3, Table 2.1) consists of a 70km² (6000 hectares) wetland complex of international significance (Becker, 2001) by the RAMSAR Convention on Wetlands (Post et al, 2009) located in Simcoe County. The wetlands are home to many rare plants and endangered species (Becker, 2001; Mitsch & Gosselink, 2000). Minesing is surrounded by several large towns and cities, namely Barrie to the east and Angus to the southwest. Less than 5 km to the east lies the Barrie landfill site. The MW lies in the basin between the Innisfil and Snow Valley uplands, with Willow Creek being the largest of the three main creeks. The open fen complex constitutes 12.42 ha of the wetland area. The land use surrounding the eastern portion of the MW consists of agriculture fields (210.45 ha), industrial and (102.65 ha) residential areas (86 ha) and transportation facilities (50.45 ha).

Water flows to the northwest within the fen system, with a slight gradient lateral flow (Bradford, 1999). Small tributaries join together and open into graminoid string fens outlined by the boreal forest complex. The Snow Valley upland recharge area results in small spring-fed creeks along the eastern portion of the wetland. Several small surficial water courses extending from agriculture areas flow from the eastern

edges of the wetland flow through the fens into the Nottawasaga River. These water courses are both perennial and intermittent (Post et al., 2009)

The study area consists of 5.42 acres and is 583 m in length. The upland forest surrounding the fen consists mainly of black spruce (*Picea mariana*) and tamarack (*Larix laricina*). The dominant vascular vegetation in the fen consists of pitcher plants (*Sarracenia purpurea*), bog rosemary (*Andromeda polifolia*), horned bladderwort (*Utricularia cornuta*), sweet gale (*Myrica gale*), leatherleaf (*Chamaedaphne calyculata*), native phragmites, (*Phragmites americanus*), sundew plants (*Drosera spp.*) and sedges (*Cyperaceae spp.*).



Figure 2.3. Map of Minesing Wetland site, which denotes the test locations (Google Maps, 2024)

2.1.4 Muskoka wetland (SS)

Muskoka River watershed lies within the Georgian Bay eco-region E5 on the south edge of the Precambrian Shield. The climate here is cool, temperate, and humid. The substrate in the area includes humo-ferric podzols, acid bedrock and marisol. Land cover is dominated by mixed forest and deciduous forest. Situated in the heart of the Great Lakes-St Lawrence forest region, the area is representative of

elements from both north and south. The fen in the quaternary sub-catchment - Moon River Bay watershed includes calcareous, luvisolic, and brunsollic substrates. Like other watersheds, population growth and development threaten the Muskoka River watershed (Sale et al., 2020). In the Muskoka River watershed, 18% is protected through a land trust or reserves, 31% is crown land, and 14% of municipal land is protected by provincial law. Wetlands in the Muskoka River watershed face anthropogenic pressures such as graywater dumping, septic spills, removal of shoreline vegetation, climate change etc.

The Muskoka study site lies on the traditional territory of the Anishnaabeg, specifically the Ojibway/Chippewa Odawa and Potawatomi Nations, collectively known as the Three Fires Confederacy. The Huron-Wendat and the Haudenosaunee Nations have also walked on this territory.

In Muskoka, peatlands are dominated by open graminid fens (sedge) (Monenco, 1984). The study area is part of the Precambrian Shield or Grenville province. The area comprises granitized peaty gneiss with crystalline limestone and lava (Monenco, 1984). Faulting and glaciation transformed the area, leaving several large freshwater lakes and a flat landscape with rugged terrain and small depressions. This results in fragmented drainage, small lakes, and ponds, leading to the development of peatlands. The peatlands in the area tend to be eutrophic (Monenco, 1984).

The climate in this area of the Muskoka is slightly different from the other sites. The mean annual temperature for the area (Mactier, Ontario) is 6.6°C (Climate Data, 2024) and varies from 2.8 to 6.2 from May to Sept. The mean annual precipitation in Muskoka is 1091 mm, with 150 mm falling in summer. It receives about 115 hours of sunshine.

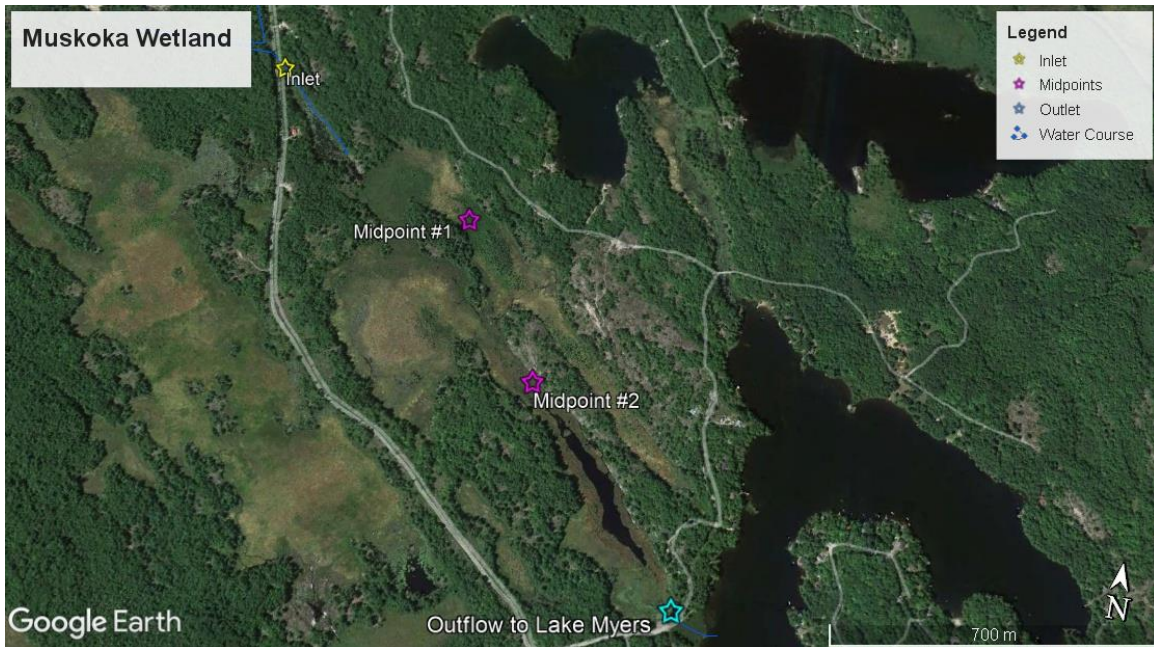


Figure 2.4. Map of the Muskoka location, showing the testing locations within the study site (Google Maps, 2024)

The peatland, a complex wetland selected for this study, is situated in Georgian Bay township in the district of Parry Sound, about 5 km east of Highway 11 and 1 km south of Highway 69 (Fig. 2.4). It is approximately 4.5 km from Foots Bay, 5 km from MacTier and 20 km from Port Carling. An upland spruce mixed forest and steep rockface surround the eastern side of the fen, while a cottage road borders the west side. There is a First Nations reserve to the south. The inlet water enters the fens from the north through a culvert under the Silver Sand road, originating from a forested area and the highway corridor. Several residences and commercial buildings exist along this section of the highway. There are several cattails (*Typha spp.*) in this area of the wetland, which then lead the way to a sedge-dominated fen to the west and a mixed *Sphagnum spp.* and *Cyperaceae spp.* dominated fen to the east, separated by a small island. The wetland continues past the island, dominated by a sedge fen with *Sphagnum spp.*, sedges (*Cyperaceae spp.*), pitcher plants (*Sarracenia purpurea*), bog rosemary (*Andromeda polifolia*), horned bladderwort (*Utricularia cornuta*), sweet gale (*Myrica gale*), leatherleaf (*Chamaedaphne calyculata*), sundew plants (*Drosera spp.*). The peatland drains southward into Lake Myers, surrounded by cottages and full-time residences. The Muskoka site is 83 acres with a length of 1766 m.

Table 2.1 GPS coordinates of sites and sampling locations

	Langman (LM)	Silver Sands (SS)	Minesing (MW)
Inlet 14 th Line	N44.594866 W79.489139	N/A	N/A
Inlet	N44.59.949 W79.492914	N45.107486 W79.769358	N44.381411 W79.840314
Mid Point 1	N44.593640 W79.492180	N45.103893 W79.761768	N44.382014 W79.841499
Mid Point 2	N44.595388 W79.491550	N45.099909 W79.757715	N44.382966 W79.843615
Outlet	N44.594756 W79.494392	N45.096154 W79.752484	N44.383344 W79.845248

2.2 Statistical Analysis

Several statistical and multivariate analyses were conducted to assess the variation of heavy metals and other parameters in water, plants, and peats. Before performing these analyses, the concentration of the first and second midpoints were combined and averaged for ease of calculation and explanation. BDL Analytes were represented using the value of the lowest detectable limit. The normality of the distribution was tested using the Shapiro-Wilk test alongside calculations of skewness and kurtosis. The Levene test was also performed to check for homoscedasticity among the samples. All tests for normality indicated a non-normal distribution of the data, and the Levene test revealed heteroscedasticity. As a result, the Kendall rank correlation coefficient was used to explore the relationships between the variables, followed by a post-hoc Dunn test and Bonferroni correction. To evaluate the significance of seasonal and spatial variations of heavy metals within the fen water and peats and to determine which heavy metals differ seasonally and spatially, the Kruskal-Wallis non-parametric test was used, followed by Dunn's test or the Wilcoxon test for two variables. These analyses were performed using R Studio 4.3.3 (R Core Team, 2021), assuring that assumptions were met. A Principal Component Analysis (PCA) was conducted using the R package "vegan" to visualize the dataset and identify patterns and relationships of heavy metals in water and peats. Seasonal, site, and location differences were distinguished through this PCA. A forward

selection Canonical Correspondence Analysis (CCA) with a Hellinger transformation was also performed using the "vegan" package to determine which water parameters and properties were most significant in relation to heavy metals found in water, peats, and plants. An additional CCA was conducted using PAST 4.07 (Hammer et al., 2001) to assess the influence of water and peat attributes on the sequestration of heavy metals in fen plants. Pearson correlation coefficients between heavy metals and the properties of water, peats, and plants were calculated using the "corrplot" package in R.

Chapter 3 - Water Parameters and Heavy Metals

Water is essential for all forms of life and serves as a fundamental resource that supports ecological balance and diverse ecosystems (Gorde & Jadhav, 2013). Water quality includes not only the chemical composition of water but also its physical and biological characteristics, which together determine its suitability for sustaining life (Omer, 2019). Key parameters such as temperature, pH, dissolved oxygen levels, turbidity, and the concentration of nutrients and contaminants significantly influence water quality.

Anthropogenic activities, including industrial discharges, agricultural runoff, urbanization, and deforestation, have detrimental effects on water quality, resulting in issues like nutrient loading, chemical contamination, and habitat loss.

This chapter examines the water quality entering and leaving the fens and attempts to determine if fens are sinks or sources of heavy metals.

The following heavy metals were assessed in the surface and porewaters collected from three different depths: nitrogen (N), phosphorous (P), arsenic (As), beryllium (Be), boron (Bo), barium (Ba), calcium (Ca), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), lead (Pb), selenium (Se), strontium (St), sulphur (S), silicon (Si), titanium (Ti), vanadium (V) and zinc (Zn).

However, for this chapter, only arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn) will be discussed because these heavy metals are considered to have the greatest environmental concern due to their persistence and danger to humans and aquatic ecosystems (Jaishankar et al., 2014).

3.1 Water Chemistry and Parameters - Introduction

3.1.1 Water Quality and Canadian Guidelines

Good-quality drinking water availability is a global issue (Delgado-González et al., 2021), and water pollution is a serious and dangerous issue that remains uncontrolled because of the lack of information, awareness, and strict implementation of eco-friendly policies, legislation, and financial resources. In light of this, the World Health Organization (2008) has identified various heavy metals and other contaminants that are of special consideration. Due to their persistence in the environment, the heavy metals of most significant concern are mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), and lead (Pb) (Delgado-González et al., 2021). Aluminum (Al) is high in Canadian peats, and its solubility is affected by pH and temperature. Aluminum can act as a sink for contaminants such as As, Cr, manganese (Mn), and nickel (Ni) and can alter the concentrations of Pb and copper (Cu). Another example is cadmium (Cd). It is found in the environment in elemental form or salts and is associated with Pb, Cu, and zinc (Zn) ores. Cadmium in source water is typically very low, but its removal from drinking water is inefficient.

3.1.2 Water Parameters

Water is needed for all life (Gorde & Jadhav, 2013). Water quality is a measure of the quality of water required for organisms to survive (Omer, 2019). Anthropogenic activities and disturbances negatively impact water quality; therefore, water quality is monitored to ensure it is safe for drinking and other ecosystem services. Water quality is monitored using a variety of parameters that describe its chemical, physical, and biological characteristics (Gorde & Jadhav, 2013; Omer, 2019).

Potential of Hydrogen: pH

The potential of hydrogen (pH) is a measure of hydrogen ion concentration, and it influences the chemical processes occurring in water (Saalidong et al., 2022). The pH of peat and water is a strong indicator of the availability of nutrients and heavy metals for organisms and plants to uptake. As one of the most influential physicochemical parameters, pH can affect other water quality parameters, microorganisms, and the bioavailability of heavy metals by affecting oxidation-reduction, sorption-adsorption, and precipitation-solubility through Al, calcium (Ca), and Fe availability (Peng et al., 2021; Saalidong et al., 2022; Zhang et al., 2018). The solubility of heavy metals in acidic conditions tends to increase, thereby increasing the toxicity of some chemicals. In contrast, higher pH causes the precipitation of metals and leads to other chemicals becoming toxic (Saalidong et al., 2022). The desorption of oxyanion from peat occurs as pH increases and the positive charges of the peat surface decrease (Wei et al., 2021). In acidic peats, nutrients and heavy metals are immobilized, minimizing plant uptake (Naz et al., 2022). For example, the release of Cd and Ni from peat decreases as pH increases, and Cu is stable at a neutral pH (Huang et al., 2017) but will mobilize at both high and low pH (Zhang et al., 2018).

Dissolved oxygen (DO)

Oxygen is one of the most important environmental parameters of all life; without it, life on earth would be affected; therefore, low oxygen is one of the critical stressor factors for aquatic life (Butler & Burrows, 2007). Oxygen gas is incorporated into the water as a by-product of photosynthesis, abiotic processes (aeration), or chemical reactions. Since many freshwater systems are small, aeration by wind or flow is limited, and small water bodies must rely on submerged photosynthetic organisms to produce enough DO (Viet et al., 2008).

Dissolved oxygen is a crucial factor in peatlands; if increased, the oxidation rate of organic compounds also increases, allowing them to release CO₂ from the peat (Peng et al., 2021). For example, the release of Cu and Cd during anoxic conditions is limited but increases during oxic conditions (Liu et al., 2022; Willow & Cohen, 2003).

Dissolved Organic Matter (DOM) or Dissolved Organic Carbon (DOC)

Browning or brownification is a term used to refer to the changing of watercolour to a yellow or brown hue arising from increased dissolved organic matter (DOM) or dissolved organic carbon (DOC) particles of less than 0.45µm, resulting from the decomposition of organic matter (Blanchet et al., 2022). The particles affect water biogeochemistry and prevent light attenuation, resulting in changes in thermal stratification, DO, and chemical oxidation (Härkönen et al., 2023). Browning in lakes can assist in productivity up to a DOC of 5 mg/L; on the contrary, higher DOC decreases productivity, and 10 mg/L is considered browning and can be linked to increased Fe in the water (Blanchet et al., 2022). Increased browning affects food webs and ecosystem services, making some contaminants more bioavailable. Global warming causes DOM (dissolved organic matter) to leach into water systems, reducing oxygen availability to other organisms (McLaughlin & Webster, 2014).

3.1.3 Elements of wetland stocks and losses

Landscapes and their processes can result in sources and sinks of heavy metals, with sources promoting the development of ecological processes and sinks delaying or preventing ecological processes (Chen et al., 2008). Heavy metals in wetlands are poorly water-soluble and tend to sorb to suspended particles and peat, becoming a sink for heavy metals (Algül & Beyhan, 2020). However, many factors can affect the remobilization of heavy metals, thus changing wetlands

from a sink of heavy metals to a source. Changes in biogeochemical factors, such as pH (Zhong et al., 2020) and organic matter (Zeng et al., 2011), influence the availability of heavy metals. Lower pH and higher water temperatures affect the release of heavy metals from peats, and higher dissolved oxygen rates increase the oxidation rate and enhance release, which is found to be enhanced as flow increases (Li et al., 2013).

Plants have been observed to release heavy metals from the leaf tissue to the leaf surface to cope with metal accumulation; this release increases the bioavailability of heavy metals in the environment (Weis & Weis, 2004). Contaminates are released and re-enter the ecosystem from the upper biomass through detritus as portions fall off, through senescent plant tissue, or herbivore feeding (Weis & Weis, 2004). Detritus can be transported through wind and water and is affected by climate, bacteria, and peat, with concentrations that can increase during decomposition (Weis & Weis, 2004). Undisturbed wetlands produce more plant biomass than is decomposing, resulting in a sink (McCarter et al., 2020).

3. 2 Methodology

3.2.1 Water Samples

All water samples were collected in spring (the first week of June 2023, after the last heavy frost), summer (the last week of July and the first week of August 2023), and fall (after the first heavy frost, mid-November 2023).

Surface water sampling: Water samples were collected in duplicate in acid-washed bottles at the water inlet and outlet of the fens.

Porewater sampling: Samples were collected in duplicate using a P.V.C. in situ pore water sampling device deployed at three depths. The in situ pore water sampling devices were placed at

two locations within each fen. Porewater samples were siphoned out using acid-washed syringes and tubes into acid-washed bottles.

3.2.2 Water parameters

Water parameters, conductivity (uS/cm), salinity (ppt), water temperature (C°), total dissolved solids (T.D.S.) (mg/l), dissolved oxygen (DO) (ppm), percent saturation and atmospheric pressure in hPa were taken at all sampling locations. The porewater parameters were taken by placing the meter probes inside the P.V.C. tubes to the depth corresponding to the collection depth. Surface water parameters were taken by placing the probes about 5cm below the water surface. Conductivity (uS/cm), salinity (ppt), water temperature (C°) and T.D.S. (mg/l) were taken using an **Ecosense EC300M**. The water pH was measured using **2 Ecosense pH100A** probes, and the dissolved oxygen (ppm), percent saturation and atmospheric pressure in hPa were measured using a **Hach HQ40d** probe. All probes were calibrated before use at each location.

3.2.3 Porewater sample collection

Water samples were collected using an **in situ** pore water sampling device, modified from Casagrande standpipe piezometers and a device developed by Fiedler et al. (2008). The *in situ* pore water sampling devices were prepared with P.V.C. pipe (2 cm diameter and 65 cm long with a cap attached at the bottom with the help of marine-grade silicon) (Fig. 2.5). The length permitted the accumulation of an adequate volume of water to be collected. A marker was placed at 30cm to ensure proper placement of the *in situ* pore water sampling device at the desired depth in the peat. Below this mark, incisions were cut using a table saw to allow water to flow into and through the pipe. The incisions were about 2 cm long. *In situ* pore water sampling devices were

constructed to permit water collection from three depths, one allowing water to flow into the pipe at 0 – 10 cm below the peat surface, the next to collect water from 10– 20 cm depth, and the third to collect water from 20 to 30 cm depth. Nylon mesh (125 μm mesh size) was attached to the slits by using marine-grade silicon on the outside of the pipe. This was allowed to dry and cure before the pore water sampling device was installed in the peat. Twelve (12) pore water sampling devices were installed at each site. In each fen, these pore water sampling devices were deployed at 1/3 and 2/3 distance from the inlet to the outlet, respectively. The pore water sampling devices were washed with 3% HCl before installation. The first set of six pore water sampling devices were installed approximately 1/3 of the distance from the water inlet to the outlet in the fen, while the second set was installed about 2/3 from the water inlet to the outlet of the fen. Duplicate pore water sampling devices were installed to collect porewater from the three depths described above.

Porewater was collected in polyethylene bottles using 200 ml syringes, both were acid-washed prior to collection. In spring and summer, one 150 ml bottle of water was collected for heavy metal analysis and another 100 ml for nutrient analysis. In the fall, an additional 50 ml was collected for dissolved organic carbon (D.O.C.) analysis.



Figure 3.1 A In situ pore water sampling device, B. Example of Piezometer placement in the sampling area

3.2.4 Surface water sample collection and Heavy metal analysis

Surface water samples for phytoplankton and chlorophyll analyses were collected in 1-litre sample bottles from the inlet, outlet and midpoint locations where the *in situ* pore water sampling devices were deployed. After collection, the water samples were placed in a cooler box and transported to the lab, where they were either frozen (nutrient samples) or stabilized with HNO₃ to a pH of 2 or lower for the heavy metal analysis. All water samples were analyzed at the Lakehead University Environmental Laboratory (LUEL) for analysis using the LUEL SOP#WICP1 Metals in Water based on the following references:

- Standard Methods for the Examination of Water and Wastewater, 18th edition, 1992
- EPA 3051
- CEM Mars XPress Manuals
- Protocol for the Sampling and Analysis of Industrial/Municipal Wastewater, MOEE Aug 1994.

3.2.5 Chlorophyll *a*

One litre of water was filtered through a Whitman 45 mm fibreglass filter fitted on a vacuum pump filtration system. The filters with retained materials were placed in 50 ml centrifuge tubes filled with 12 ml 90% acetone and mashed until disintegration. The centrifuge tubes with the samples were covered in aluminum foil, capped, and placed in the refrigerator at 4°C for approximately 16 hrs before centrifuging in a Thermo Scientific Sorvall ST 8 Centrifuge at 4200 RPM for 15 minutes. 3ml of the supernatant was transferred to a cuvette, and absorbance was measured in a spectrophotometer (Beckman Coulter DU730 UV/Vis) at 750, 664, 647, and 630 nm. Blanks with only 90% acetone and only filter paper were run similarly. The concentration of chlorophyll was calculated using the following equation.

$$(11.85*(E664-E750)-1.54*(E647-E750)-0.08(E630-E750))*V_e/L*V_f$$

Where:

L= Cuvette light path in centimetres

V_e=Extraction volume in millilitres

V_f= filtered volume in litre

Concentrations are in unit mg m⁻³ (Aminot, Rey 2001)

3.2.6 Nutrients

Phosphorous

Water samples sent to LUEL in Thunder Bay, Ontario, were analyzed for total phosphorus, while orthophosphate measurements were completed in the Orillia campus by using Hach Permachem Reagents PhosVer 3 phosphate reagent for 10 mls samples (Method 4500-P E) adapted from APHA (1992). The water samples collected in 100 ml bottles were brought to room

temperature. After mixing correctly, 10 ml samples were pipetted into small flasks cleaned with 3% HCl. Hach PhosVer 3 pillows were added and mixed for 15 seconds. 3 mls were transferred to acid-washed (3%HCl) cuvettes and absorbance at 880 nm was measured in a spectrophotometer (Beckman Coulter DU730 UV/Vis). Blanks were run similarly with deionized water.

Nitrogen

Nitrate nitrogen (NO₃-N) was analyzed using Hach Permachem Reagents pillows, adapted from APHA (1992). Samples were brought to room temperature and mixed thoroughly. 15 ml of the sample was transferred into 25 ml acid-washed test tubes. Deionized water was run as blanks. Contents of 1 Hach NitraVer 6 Nitrate reagent were added to each sample and blanks. The samples were mixed uniformly for 3 minutes and then set to rest for two minutes. After two minutes, 10 mls were transferred to another set of acid-washed test tubes, where a Hach NitraVer 3 nitrite reagent pillow was added. The test tube was shaken for 30 seconds and set to rest for 15 minutes. From this, 3 mls was transferred to a washed (3% HCl) cuvette in the spectrophotometer (Beckman Coulter DU730 UV/Vis). Absorbance was measured at wavelength 507nm. Blanks were run similarly with deionized water.

3.2.7 Dissolved Organic Matter/Carbon

Porewater and surface water were collected in acid-washed 50ml conical centrifuge tubes. Samples were transported in a cooler and placed in the freezer until their analysis in LUEL, Thunder Bay.

The DOC was analyzed using LUEL method "Determination of Dissolved Organic and Inorganic Carbon Using the Skalar Autoanalyzer" which is based on the following references:

- Standard Methods for the Examination of Water and Wastewater, 18th edition, 1992
- Automated Determination of Carbon in Natural Waters, P.D. Goulden, rec. Dec 5, 1976. Water Research Vol 10, pp 487-490, Pergamon Press, 1996
- Automated Determinations of Dissolved Organic Carbon in Lake Water, P.D. Goulden and Peter Brooksbank, rec Mar 31, 1975. Analytical Chemistry, Vol 47, No 12 pp 1943-1946, October 1975
- Methods for Chemical Analysis of Water and Wastes. U.S. Environmental Monitoring and Support Lab. Cincinnati, OH. March 1983.

3.3 Results

3.3.1 Overall Site Comparisons

The comparison of the three fens showed a significant decrease in the heavy metals and nutrient contents in the water between the inlet and outlet of the fen systems. This would lead to the assumption that the fens are sinks for all heavy metals and nutrients. Further comparisons using the Kruskal Wallis and Pairwise Dunn tests demonstrated differences in the above trend for individual heavy metals. These trends and distinctions will be described in detail in this chapter.

The chart below illustrates the concentrations of the metals of concern at the fen inlets, in order from the highest to the lowest, observed during summer and fall.

Site Muskoka (SS)

Inlet Summer: As>Ni>Pb>Zn>Cu>Cr>Cd to outlet Zn>Pb>As>Ni>Cu>Cr>Cd

Inlet Fall: Zn>As>Ni>Pb>Cu>Cd>Cr to outlet Cd>Cr>Zn>Cu>Ni>As>Pb

Site Minesing (MW)

Inlet Summer: Zn>As>Ni>Pb>Cu>Cd>Cr to Outlet Zn>Ni>Pb>Cu>Cd>Cr>As

Inlet Fall: Zn>As>Ni>Pb>Cu>Cd>Cr to Outlet Zn>Pb>As>Ni>Cu>Cd>Cr

Site Langman (LM)

Inlet Summer: As>Ni>Pb>Zn>Cu>Cd>Cr to Outlet Cr>Cd>Cu>As>Ni>Pb>Zn

Inlet Fall: As>Ni>Pb>Cd>Zn>Cu>Cr to Outlet As>Ni>Pb>Zn>Cu>Cd>Cr

3.3.2 Water parameters

3.3.2.1 Surface Water:

The variations in surface water pH, dissolved oxygen (DO), salinity, dissolved organic carbon (DOC) and temperature for each fen during the three sampling periods are shown in Table 3.1. The fens significantly differed in pH ($F=24.7$, $p,0.001$). Site SS recorded the lowest pH, while site LM recorded the highest. All three sites followed similar patterns of variations in pH as the water moved through the fen, with pH higher at the inlet, dropping significantly by the midpoint and the outlet showing lower pH than at the inlet. The greatest difference in pH was detected between the inlet and the surface water at the midpoint ($p=0.04$). Differences in the outlet pH varied with the site and season. However, the differences in pH readings at the inlets and the outlets were not found to be significantly different.

The dissolved oxygen (DO) concentration (Table 3.1) varied between fens, with only LM displaying a similar pattern in all the seasons. Dissolved oxygen and percent saturation were not significantly different between the sites. Site SS had the lowest DO, and MW had the highest DO levels.

Water temperature (Table 3.1) did not differ between sites. As expected, the water was warmest during summer, often exceeding 25°C at the inlet. In spring and summer, the water temperature dipped after entering the fen and rose by the time it reached the outlet. In fall, the temperatures were close to 5°C. The temperature was slightly higher within the fen than at the inlet and outlet.

Chlorophyll *a* levels measured in the surface waters were not found to be significantly different within the fens. Nevertheless, the three fens differed in the chlorophyll *a* concentrations ($F=15.4$, $p<0.001$). However, only sites LM and MW were found to be significantly different from one another ($z=-3.89$, $p<0.001$). MW had the highest concentration of chlorophyll *a*, and LM had the lowest.

The DOC (Table 3.1) was only measured in the fall season. DOC concentrations differed significantly among the fens ($F=17.2$, $p<0.001$). Significant differences were observed between sites SS and MW ($Z= -3.76$, $p<0.001$) and SS and LM ($Z= -3.38$, $p<0.001$). At SS, DOC increased from the inlet to the outlet. However, at the other sites, DOC at the outlet was similar to the DOC at the inlet.

The conductivity and TDS of the three fens differed significantly ($F=22.2$, $p<0.001$) (Table 3.1). The highest conductivity was found at MW, and the lowest was found at SS. Examination of the conductivity of the surface water showed variation from just below 400 uS/cm to 550 uS/cm at the inlet, which was decreased to below 400 uS/cm at the outlet ($p=0.0179$), with SS exhibiting the greatest decrease.

Table 3.1. The surface water parameters at the inlet and outlet of the fens in each season, consisting of mean value and standard deviation. “*” denotes a significant statistical difference was found between sites ($p < 0.05$)

Season	Site	Loc.	pH*	SD +/-	Cond.	SD +/-	TDS	SD +/-	Sal*	SD +/-	Temp	SD +/-	DO*	SD +/-	Sat	SD +/-
Spring	SS	Inlet	6.55	0.06	514.50	0.71	334.50	0.71	0.25	0.07	21.10	0.14	3.18	0.10	36.70	0.85
		Outlet	6.01	0.07	91.15	0.92	59.90	0.00	0.00	0.00	23.75	0.07	2.69	0.64	32.85	8.13
	MW	Inlet	6.96	0.12	370.50	47.38	266.85	3.32	0.20	0.00	25.45	0.21	1.03	1.20	13.20	14.42
		Outlet	6.95	0.03	283.50	4.95	186.05	2.90	0.10	0.00	21.70	0.00	0.18	0.10	2.05	1.20
	LM	Inlet	8.01	0.02	502.25	18.03	341.50	33.23	0.20	0.00	10.55	0.35	8.83	0.11	80.95	0.35
		Outlet	7.79	0.00	307.15	8.27	209.75	18.74	0.20	0.00	19.55	0.21	7.59	0.06	84.50	0.28
Summer	SS	Inlet	6.71	0.04	394.60	0.00	255.50	0.71	0.20	0.00	19.75	0.07	0.74	0.18	8.40	2.12
		Outlet	5.43	0.10	74.90	0.57	48.25	0.49	0.00	0.00	24.40	0.00	2.79	0.04	34.40	0.42
	MW	Inlet	7.02	0.09	416.25	1.63	270.60	0.99	0.20	0.00	21.85	2.33	2.66	0.05	30.65	0.35
		Outlet	7.04	0.04	347.55	1.34	226.45	0.07	0.20	0.00	22.80	0.00	1.35	0.78	5.85	5.16
	LM	Inlet	7.86	0.03	500.30	12.30	324.60	6.22	0.20	0.00	14.00	0.57	8.80	0.09	86.70	4.53
		Outlet	7.72	0.04	397.25	0.21	258.20	0.14	0.20	0.00	26.95	0.07	7.46	0.05	95.90	0.28
Fall	SS	Inlet	6.40	0.02	298.30	0.00	193.65	0.35	0.10	0.00	4.85	0.07	8.38	0.02	67.15	0.21
		Outlet	5.16	0.01	73.65	0.35	47.95	0.07	0.00	0.00	5.93	0.18	6.00	0.12	46.85	4.17
	MW	Inlet	7.30	0.13	371.80	1.70	241.80	1.27	0.20	0.00	4.15	0.07	10.01	0.47	77.00	3.68
		Outlet	7.45	0.33	328.80	19.37	213.70	12.16	0.15	0.07	2.10	0.00	7.55	0.23	54.25	1.48
	LM	Inlet	7.65	0.30	386.48	115.75	251.30	75.18	0.15	0.06	5.50	0.69	9.51	0.76	77.08	8.12
		Outlet	7.59	0.01	333.95	0.07	217.05	0.07	0.20	0.00	5.80	0.00	10.32	0.01	83.30	0.00

The salinity (Table 3.1) of the three fens differed significantly ($F=21.9$, $p < 0.001$), specifically between MW and SS ($Z=4.01$, $p < 0.001$). These results corresponded to those found for conductivity and TDS. Salinity was highest at the SS inlet in spring. This is likely due to the road salt runoff (Radosavljevic. At SS, the salinity was reduced to below detection level by the time the water reached the outlet. In spring, the most elevated salinity was recorded at the SS inlet, which was reduced at the midpoint.

3.3.2.2 Porewater:

The pH of the porewater did not vary significantly with depth; however, each fen showed a variation in pH with depth, although there is no discernible pattern (Fig. 3.2 A).

The porewater conductivity indicated minor variations with depth, either increasing or decreasing, but the variations were insignificant. The porewater conductivity at MW ranged between 400 uS/cm and 500 uS/cm, unlike SS, where it was often lower than 100 uS/cm (Fig. 3.3 A).

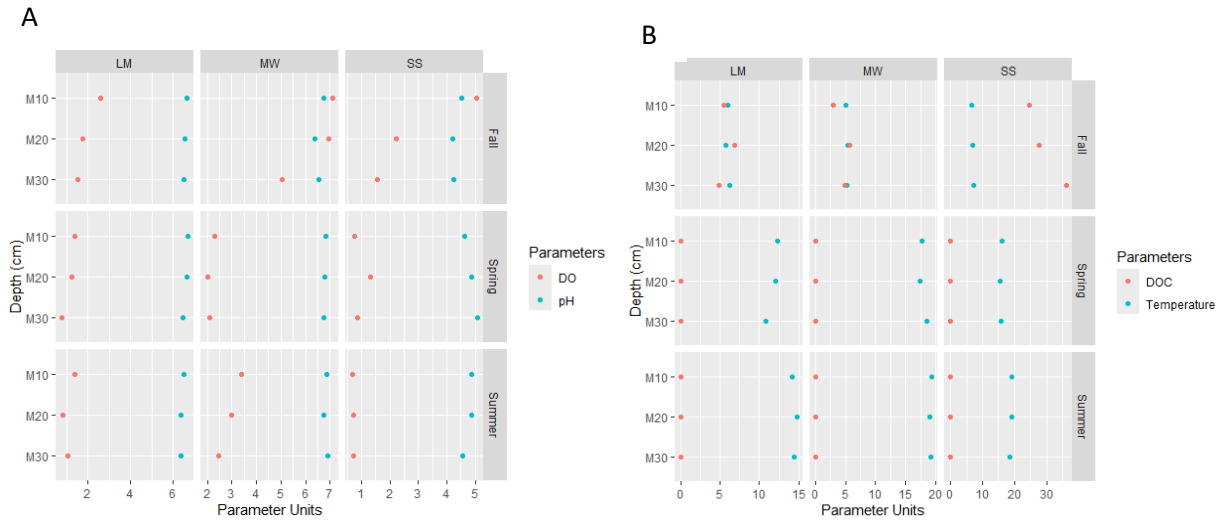


Figure 3.2 A & B. Water Parameters (DO, pH, Temperature and DOC) by depth and location at each fen and season (Spring, Summer and Fall, 2023). “M10” represents porewater depths 0-10 cm, “M20” represents porewater depths 10-20 cm, and “M30” represents porewater depths 20-30 cm. Fig. 3.2A illustrates the dissolved oxygen and pH values, and Fig. 3.2 B illustrates the dissolved organic carbon and water temperature

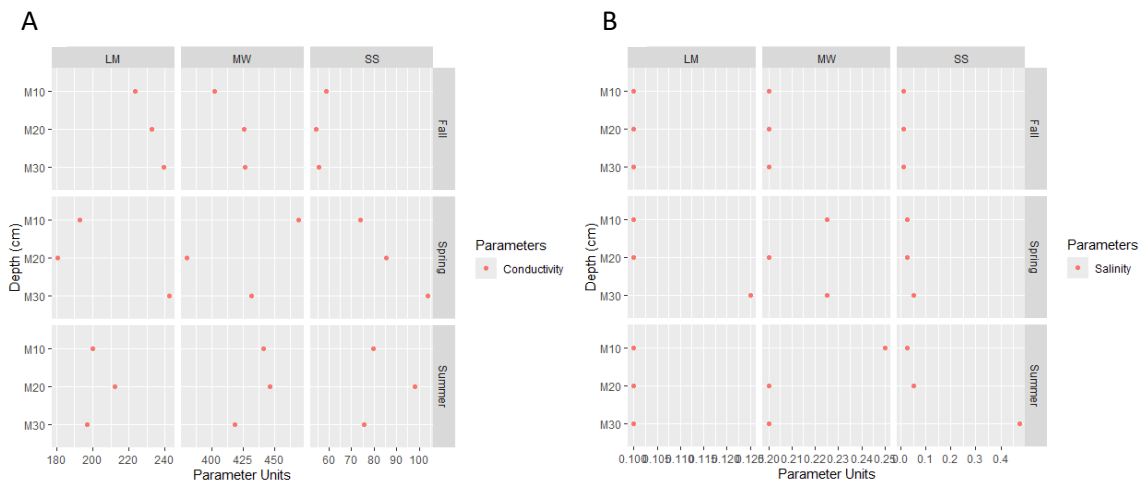


Figure 3.3 A & B. The conductivity of the porewater (a) and salinity of the porewater (b). “M10” represents porewater depths 0-10 cm, “M20” represents porewater depths 10-20 cm, and “M30” represents porewater depths 20-30 cm.

The salinity levels of the porewater were either changed or remained stable with the depth in the fens, which appears to be a function of season. In spring and summer, there was an increase in salinity with depth. However, in the fall, the salinity levels remained constant with the depth. Upon entering the fens, the salinity was reduced and remained lower than the inlet at sites MW and SS. At LM, the salinity showed a higher reading at the outlet than the inlet and within the fen (Fig. 3.3 B).

Porewater temperature did not indicate any clear patterns in variation with depth. In spring and summer, the water temperature in the porewater was much lower than that of the outlet water. This pattern was not observed in the fall sampling period (Fig. 3.2 B).

A significant difference in dissolved oxygen was found from the inlet to M30 cm depth ($p < 0.001$). An increase in DO from M30 cm depth at the midpoint to the outlet occurred, except at MW, which may be due to the slow movement of water through the fen. Oxygen was low at all sites in the spring and high in the fall. The percent saturation significantly differed between the inlet and M20 cm and M30 cm depths at the midpoint ($p < 0.05$) (Fig. 3.2 B).

The DOC of the porewater was found to increase with depth at all sites. DOC significantly differed between M20 and M30 cm at SS ($z = -2.91$, $p = 0.035$). Differences were also noted between M20 and the outlet; however, they were insignificant. The DOC was highest at SS, reaching almost 30 mg/L. At LM, the DOC of the 0-10cm porewater was the lowest of the three fens, which then exceeded the DOC of MW by 20-30cm depth (Fig. 3.2 B).

3.3.3 Seasonal variations

The water parameters did not vary significantly with the seasons except for differences in pH between spring and fall and salinity between summer and fall (Fig. 3.2 A & Fig. 3.3 B)

As expected, the water temperatures significantly differed with seasons ($F=30.3$, $p<0.001$)(Fig. 3.2 B). The greatest difference was observed between summer and fall. The dissolved oxygen concentration was significantly different between seasons ($F=11.4$, $p<0.001$), with summer and fall showing a high degree of variation ($Z=2.9$, $p<0.001$).

Chlorophyll *a* concentration and pH did not differ significantly between seasons. However, dissolved oxygen varied significantly among seasons ($Z= 4.6$, $p<0.001$), with spring to fall demonstrating the greatest difference ($Z=4.7$, $p<.001$). Percent saturation differed significantly between spring and summer and spring and fall ($Z=3.6$, $p<0.001$)

Conductivity significantly varied among seasons ($F= 13.3$, $p=0.001$) and between summer and fall ($Z= -3.61$, $p=0.0009$) (Fig 3.3 A). Similarly, seasonal variations were noted in salinity between the fens ($F=5.94$, $p=0.05$), with summer to fall exhibiting the greatest variation ($Z= -2.4.8$, $p=0.04$).

3.3.4 Heavy metals in Surface water

Heavy metals in the surface water varied between and within the fens. Certain samples exhibit seasonal variations in the concentration of heavy metals, as depicted in Figure 3.4. Notably, chromium was the only heavy metal demonstrating significant seasonal differences ($F = 6.61$, $p = 0.03$). Specifically, the levels of chromium during the summer and fall seasons were found to be significantly different, with a statistical comparison yielding $Z = 2.54$ and $p = 0.001$.

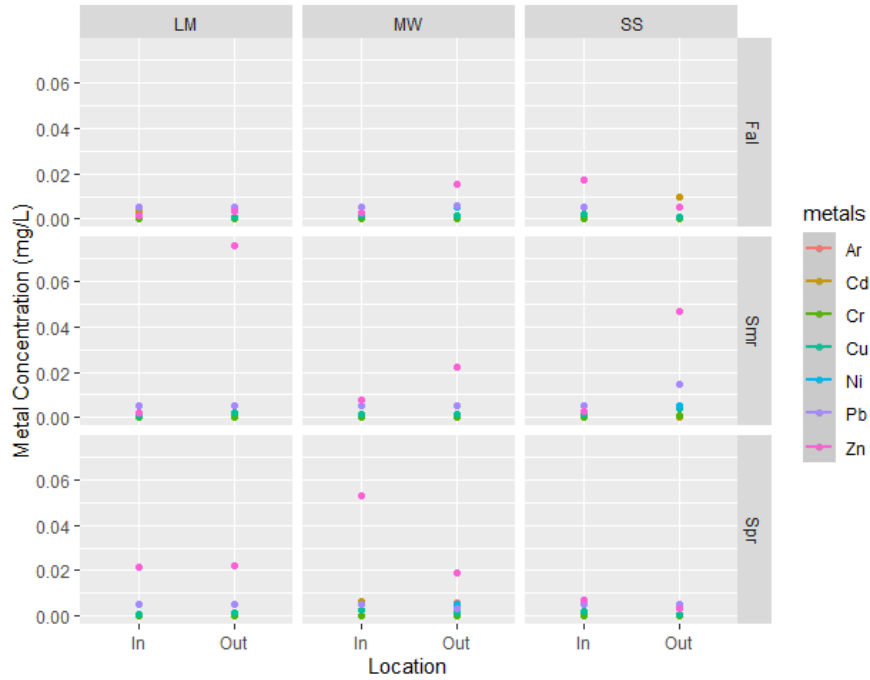


Figure 3.4 Heavy metal concentrations in the surface water at the inlet and outlet of the three fens in the spring, summer, and fall 2023

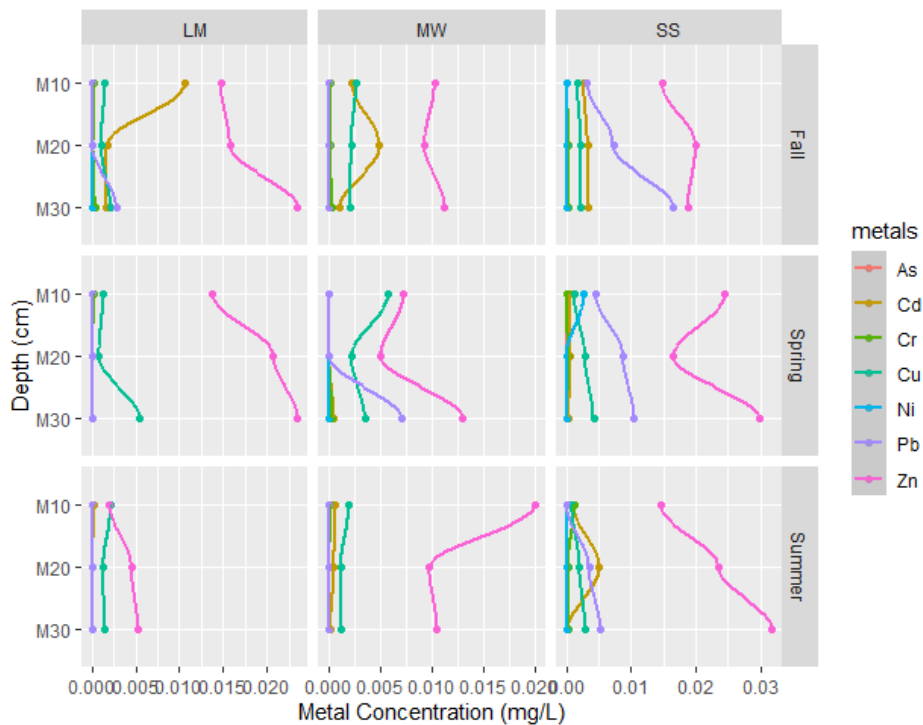


Figure 3.5 Variations of heavy metals between fens and seasons in porewater from different depths. M10 represents the porewater from a depth of 0-10 cm, M20 represents the porewater from a depth of 10-20 cm, and M30 represents the porewater from depths of 20-30 cm below the peat surface of the fen.

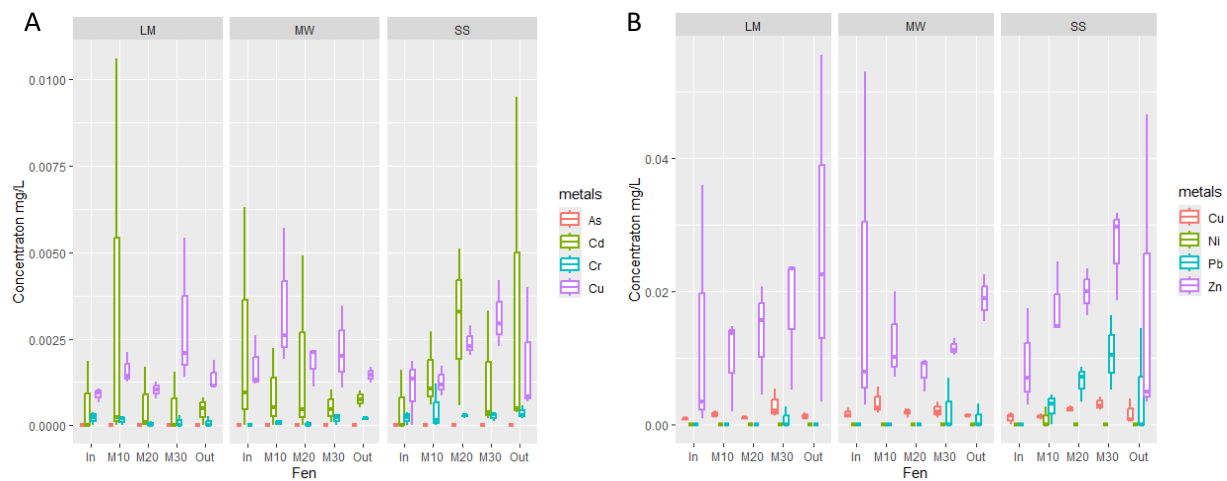


Figure 3.6 A & 3.4B. Boxplots of the average heavy metal concentration (mg/L) within the fens in surface water (“In”, and “Out”) and porewater (“M10”, “M20”, “M30”). The figure on the left includes Arsenic, Cadmium, Chromium, and Copper. The figure on the right includes Copper, Lead and Zinc. M10 represents the porewater from a depth of 0-10 cm, M20 represents the porewater from a depth of 10-20 cm, and M30 represents the porewater from depths of 20-30 cm below the surface of the fen. The box represents the 25th and 75th percentile, the line represents the median value. The whiskers represent the minimum and maximum.

Arsenic

The arsenic concentration was below the detection level (BDL) at sites LM and SS and was only detected slightly above BDL in the outlet water in MW. However, there were no significant differences between the inlet and the outlet locations (Fig. 3.4 & Fig 3.6 A).

Cadmium

The cadmium level was highest in the 0-10cm porewater at MW in spring. The second highest concentration was found at the outlet of SS in fall. The cadmium concentration at the midpoint and the outlet of SS was high in fall. The MW site also had an elevated cadmium concentration at the outlet in spring and summer. However, no significant differences in cadmium concentration were found between fens (Fig. 3.4 & Fig. 3.6 A).

Chromium

The chromium concentrations were also often at BDL. Chromium was detected at the inlet and outlet of SS in spring. Generally, the highest level of chromium was detected in summer while the lowest was in fall, in the porewater at the midpoints of the fens. Chromium concentration in the water at MW was generally at BDL except in the fall. Here, too, the concentrations at the outlet were lower than those at the midpoint of the fen. At LM in the spring, increased chromium concentrations were found at the inlet and at the midpoint, which was reduced to BDL by the outlet. In summer, the concentration of chromium at site LM was BDL. This changed in the fall when chromium was detected in the inlet water and in the midpoint of the fen. The concentration was then reduced at the outlet. Generally, the chromium concentration was found to be significantly different among sites within a fen ($F= 17.1$, $p=0.0001$) with significant differences between SS and LM ($Z= -2.72$, $p<0.013$) and SS and MW ($Z= -3.67$, $p=<.001$). The highest concentration of chromium was found at SS (Fig. 3.4 & Fig. 3.5 6).

Copper

The copper concentration did not vary significantly throughout the fen. The highest (0.00571 mg/L) and lowest levels of copper were found in spring and summer at LM midpoint. In the spring, copper did not differ significantly between fens (Fig. 3.4 & Fig. 3.6 A).

Nickel

The nickel concentration in surface water was generally in BDL at all sites except for the midpoint at SS in spring. The nickel concentrations in the fens were not significantly different from those in the inlet and the outlet. No significant differences were found within the fens or from the inlet to the outlet (Fig. 3.4 & Fig. 3.6 B).

Lead

The lead concentration in the water was at BDL. However, it was detected in the midpoint of all the fens, often at elevated levels (Fig. 3.4 & Fig. 3.6 B). In the summer, the lead was at BDL at LM, and MW it was at BDL at LM in the spring. Lead was found at SS in spring at the midpoint during all three seasons but was found to be reduced at the outlet. Lead was detected at MW in spring, only slightly above the detection limit, and the concentration was reduced at the outlet. At LM, lead was detected only at the midpoint in the fall. The concentration of lead in water differed between sites ($F=25.4$, $p<0.001$), with significant differences between LM and SS ($Z= -3.31$, $p=0.002$) and between MW and SS ($Z= -3.19$, $p=0.002$). The highest concentration was detected at SS. Site MW also showed some variability. No significant difference was found between the inlet and the outlet.

Zinc

The zinc concentrations did not differ significantly between sites and varied from 0.0755 mg/L to 0.001 mg/L (Fig. 3.4 & Fig. 3.6 B). At SS during spring, the concentrations were higher at the midpoint than at the inlet but decreased by the outlet. At MW, zinc was higher at the inlet and decreased by the outlet in spring and summer except in fall, when the outlet recorded higher zinc concentration than at the inlet. At LM, zinc was at its highest level in spring. The level was found to be reduced by the outlet. In summer, zinc concentration increased from the inlet to the outlet.

3.3.5 Heavy Metals in Porewater

Arsenic (As) concentrations in the porewaters were below the detection limit (BDL) in all fens (Fig. 3.5 & Fig. 3.6 A).

Cadmium (Cd) concentration changed with porewater depth. The concentration increased at M20cm depth of the porewater but then decreased by M30cm depth. This pattern was observed at SS and MW. At LM, Cd was only detected at M10cm depth in spring and summer. In the fall, Cd was found at all depths at LM. The maximum porewater concentration of Cd was 0.0105 mg/L, also at M10 cm depth. Cd concentration was reduced at all the sites from the surface to the M30 cm depth. However, no significant differences in the concentration of Cd were found between fens or porewater from different depths (Fig. 3.5 & Fig. 3.6 A).

Chromium (Cr) was detected in the porewater of all fens. The concentration showed an increase initially but decreased at M30 cm depth. The most notable difference was noted at SS in the fall. Cr was at BDL in the pore water at LM during spring and summer. BDL concentrations of Cr were also found at several depths at MW in spring and summer. The fall concentration of Cr was elevated in the porewater of all the sites (Fig. 3.5 & Fig 3.6 A).

The copper (Cu) concentrations significantly differed in the porewater between M20cm and M30cm depths ($Z=-3.305$, $p=0.02$). In all seasons, copper increased with depth at SS. At LM and MW, the copper concentration decreased at M20 cm depth and then increased by M30 cm depth. This was consistent across all seasons (Fig. 3.5 & Fig.3.6 A).

The nickel (Ni) concentrations were BDL in fens' porewater except at the M10 cm depth of SS in spring (Fig. 3.5 & Fig. 3.6 B).

Lead (Pb) was generally at BDL at LM and MW. When Pb was detected, it was in the M30 cm depth of the porewater. At SS, Pb was occasionally at BDL but typically increased with depth. The lead concentration in the surface water at midpoint and at M20 cm and M30 cm depths was significantly different ($Z= -3.34$, $p=0.02$) (Fig. 3.5 & Fig. 3.6 B).

Zinc (Zn) was detected in all porewater depths; however, the pattern of distribution in each fen varied with the depth of the porewater. Most sites and seasons showed an increase in concentration with depth. However, at site MW, the concentration of Zn showed a reduction with the depth of the porewater. Site SS had the highest Zn concentration in the porewater, while site MW recorded the lowest concentration (Fig. 3.5 & Fig. 3.6 B).

3.3.6 Fen Characterization

Nutrient and pH composition are often used as the critical components in determining the peatland type and can aid in characterizing the fen ecosystems into “poor,” “moderately rich,” or “rich” subcategories (Bourbonniere, 2009). A summary of research on differentiating bogs and poor fens using pH suggests that fens have pH range between 4.0 and 6.7 while bogs have pH <4.0. Thus, this includes two pH modes, bogs with a pH around four and fens with a mode of six, with few peatlands maintaining a pH of 5 (Gorham et al., 1984). Moreover, poor fens have been noted with a pH range of 4.3-5.5, while moderate fens have a pH of 5.5-6.2 and rich fens of 6.2-7 (Bourbonniere, 2009). In rich fens, the base cation concentrations are three to five times higher than that in poor fens (up to 425 mg/L of Ca and just under 175 mg/L of Mg, Na and K). Moderate fens are about half of those values, and poor fens fall below 25 mg/L of Ca and less than 10 mg/L of the other major cations. In the study by Bourbonniere (2009) the water chemistry of fens was used to classify fens (Table 3.2). According to Bourbonniere (2009), site MW would be considered a moderately rich to rich fen, site LM would be identified as a moderately rich fen, and site SS would be closer to a poor fen (Table 3.3).

Table 3.2. Chemistry of bogs and fens in Canada and the Northern United States. Revised from Bourbonniere (2009).

Cation	Bog	Poor Fen	Mod. Rich Fen	Rich Fen
Ca ²⁺	0.06-6.8	0.10-16	0.80-179	1.4-428
Mg ²⁺	.04-2.8	0.16-4.6	0.10-29	0.27-47
Na ⁺	0.03-16.5	0.03-4.9	0.05-76	0.80-36
K ⁺	0.02-1.4	0.02-3.4	0.05-11	0.40-23

Table 3.3. Water chemistry of the three fens during this study and the fen type* based on the cation concentration as suggested by Bourbonniere (2009) (Table 1).

pH and Cation	Muskoka-SS	Minesing-MW	Langman-LM
pH	4.4-5.4	6.2-6.9	6.2-6.5
Ca	2.6-7.9	62-65	20-40
Mg	.7-.8	1.0-10.6	3.2-5.4
K	1.2-5.3	1.0-11.2	.2-5.4
Na	2-8.6	4.9-5.3	1.7-2.9
Fen type*	Poor fen	Moderately Rich to Rich Fen	Moderate Rich Fen

3.3.7 Seasonal variations

Arsenic, Copper, Chromium, Nickel, Lead, and Zinc concentrations in surface water did not differ significantly with seasons (Fig. 3.3). Fall and spring displayed the highest fluctuations of heavy metals in the porewater. Cadmium concentrations fluctuated significantly with seasons, with the highest concentration in spring. Cadmium concentrations were significantly different among all the seasons ($Z=22.4$, $p<0.001$).

3.3.8 Ordination

Principal Component Analysis (PCA)

A PCA using all the results from the water analysis was completed to identify the trends in the fluctuation of heavy metals within each fen (Fig. 3.7). When all the data were combined into a matrix, the results showed prominent trends and variations within the dataset. When the sites were examined individually, the results showed the correlations of the parameters within a site.

The PCA was performed using the “vegan” package in R (RStudio Team, 2020). For the PCA, the data was analyzed without any transformation; however, it was scaled and centred. The scree plot suggested that the first three components explained most of the variance in the data set, and therefore, these three principal components will be further analyzed. The first principal component (PC1), which explained 23.7% of the variance in the data, was strongly positively associated with the water parameters, including Conductivity (10.2%), pH (10.5%), DO (9.16) and moderately by Chlorophyll a (8.4) and negatively with Zn (-7.4%), and Pb (-5.7%). The second principal component (PC2), which explained 14.7% of the variance, was strongly associated with Temperature (11%) and negatively associated with Cd (-8.5%), and DO (-8.1%). The third principal component, PC3, explained 11.6% of the variance and was associated with Cu (10.1%), Zn (-7.2%), and Pb (7%).

The loadings plot (Fig. 3.8) shows the correlation between the variables and each principal component in a two-dimensional visualization. It reveals the relationships between heavy metals, water parameters, and other environmental variables such as fens, locations within fens, and seasons. The results indicate that Zn, Ni, and Cu have a negative relationship with DO and Pb, P, and Al have a positive relationship with pH. Cr and Cd are weakly and positively correlated to DOC and negatively correlated with conductivity and salinity.

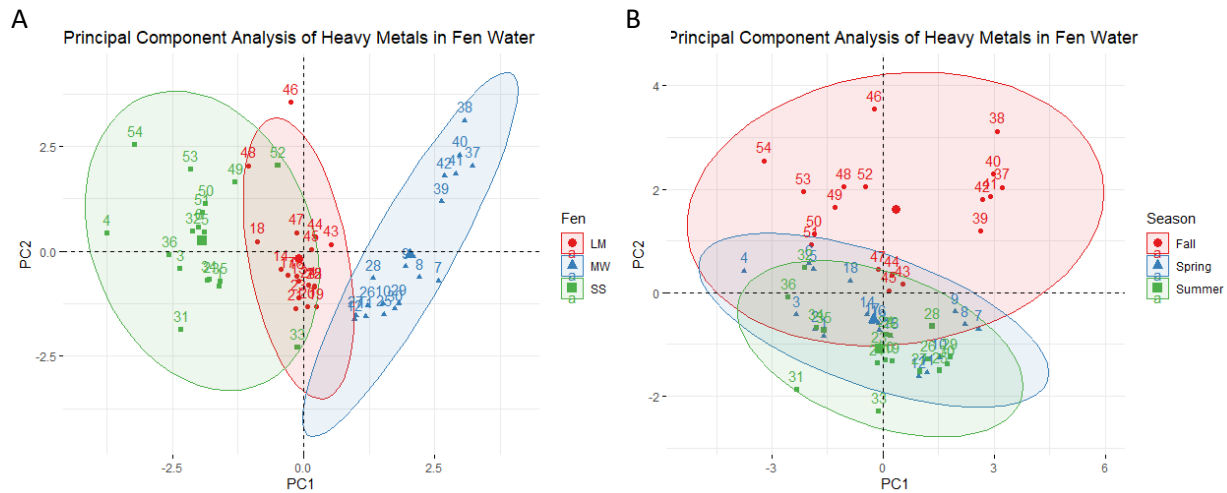


Figure 3.7. A & B The PCA of the seven heavy metals of concern in the porewater. Elliptical PCAs examine the variability and associations of heavy metals between the fens (on the left, Fig. 9A) and the seasonal variations of the heavy metals in the water (on the right, Fig. 9B). The coloured numbered points represent the water samples from each fen and season

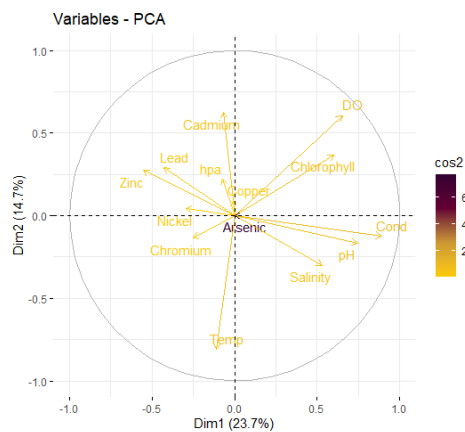


Figure 3.8. The principal component analysis (PCA) loading plot displays the relationship between the heavy metals in the porewater and the water parameters.

The PCAs indicate that the porewater in all three fens are unique (Fig. 3.7 A & B). The biplot scores indicate the distribution of water parameters in the first two principal components. We can see that there is a clear separation between the three fens. Site SS has the greatest variability in water parameters and is positively associated with PC2 and negatively associated with PC1. Site MW is associated positively with PC1, and site LM is associated with PC1 and PC2. It can also

be seen that LM has the least variability in water parameters compared to other sites, even though it overlaps with other sites. In the PCA with the 95% ellipse around the seasons, we can see the variability between the seasons, with fall having the greatest variability. The comparison of the PCA plot for the seven heavy metals of concern with the plot that includes all tested metals highlights distinct differences. While the fens appear unique when analyzed alongside all nutrients and metals, they show greater similarity when focusing solely on the seven specific metals of concern.

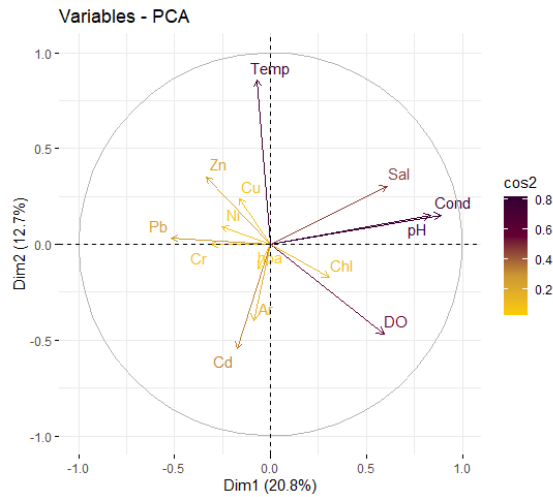
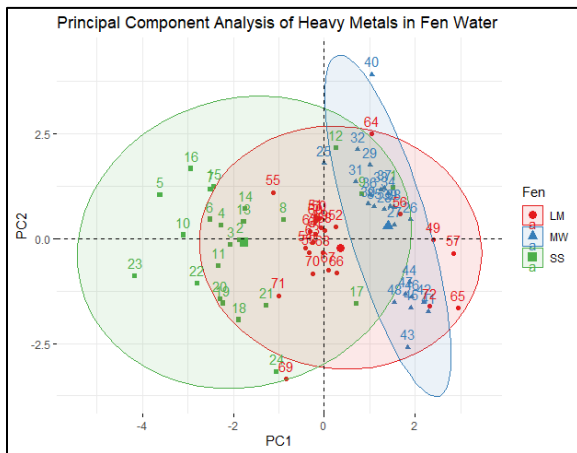


Figure 3.9 The loading plot from the PCA, including the surface and porewater heavy metals and water parameters.

A



B

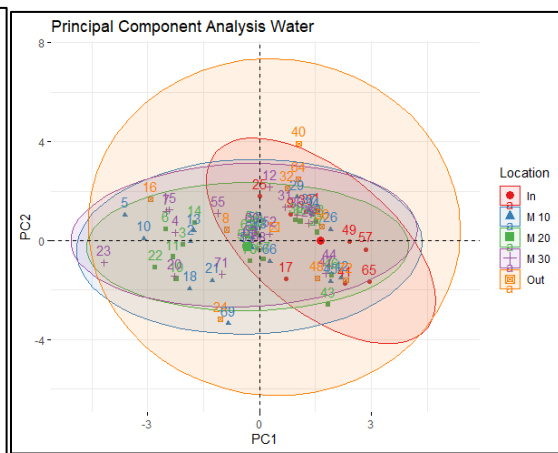


Figure 3.10. Elliptical PCAs examine the variability and associations of surface and porewater heavy metals and parameters in the water between the fens (on the left, Fig. 3.7 A) and the locations (on the right, Fig. 3.7 B). The coloured numbered points represent the water samples from the three fens.

A second PCA using surface and porewater as shown in Figure 3.10. The PCA indicates the changes in heavy metals and water parameters between the inlet and the outlet. PC1 explains 20.8% of the variability and is associated mainly and negatively with the water parameters, while PC2 explains 12.7% of the variability and is associated with Cd, As, and Zn.

Canonical Correlation Analysis (CCA)

A multivariate analysis with forward selection constrained Canonical Correlation Analysis (CCA) was performed to examine the physicochemical attributes most influential on heavy metal distribution in surface and porewater within the fens (Fig. 3.11). Figure 3.11 illustrates the correlation and variation of various water parameters, nutrients, and metals, including the seven heavy metals of concern. A Hellinger transformation was performed to standardize the data prior to performing the CCA analysis. Constraint inertia was found to be 80.1%. The ANOVA result indicated that the model was significant ($F=8.12$, $p<0.001$). CCA1 explained 62.6%, while CCA2 explained 19.8% of the variations. Using the forward selection, including fen, conductivity, and seasons, the constraint inertia was 70.6%. An ANOVA found the following attributes to be the most influential on the model: fen ($r^2=0.58$, $F=31.73$, $p<0.001$), conductivity ($r^2=0.64$, $F=7.45$, $p<0.001$) and season ($r^2=0.67$, $F=2.82$, $p=0.015$).

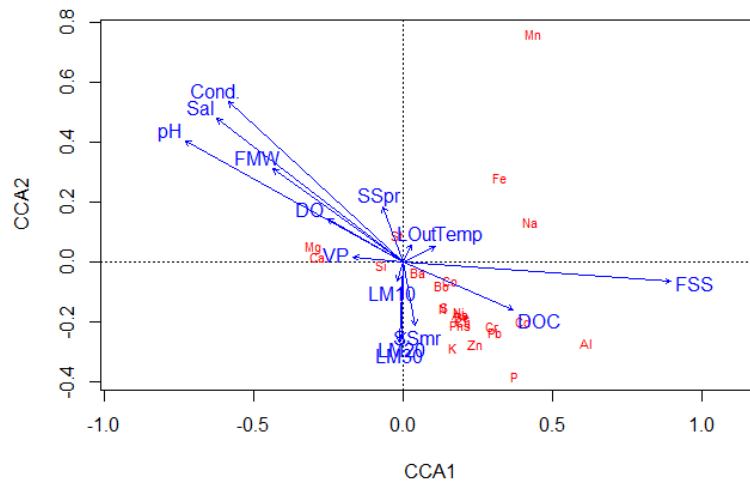


Figure 3.11. The CAA shows the relationship of water parameters and environmental variables with the heavy metals in the water. The red font denotes the heavy metals, and the blue represents the fens, locations, seasons, and water parameters. The following abbreviations were used in the CCA: DO=dissolved oxygen, Cond = conductivity, FMW, FLM and FSS denotes the fens, Sal = salinity, and DOC = dissolved organic carbon.

CCA1 explained (62.6%) of the variance. The biplot scores suggest that site SS (98.6%), DOC (41%), pH (-79.8%), salinity (-68%) and conductivity (-64%) strongly affected Al (61%), Cd (40%), Pb (31%), and Cr (31%) distribution. CCA2 explained (19.8%) of the variance. The biplot scores explained that conductivity (58.8%), salinity (52%), and pH (45%) were positively associated with Mn (76%) and negatively with Zn (-27%), Al (-20%), Fe (28%), and K (-28%). Cu, As, and Ni were weakly associated with CCA1 and CCA2.

A correlation coefficient (bivariate analysis) examined the relationships between heavy metals and water parameters, including the seven heavy metals of concern (Fig. 3.12). The results indicated that several heavy metals positively correlated with water parameters. Strong, positively significant correlations were found between lead and DOC ($r=0.71$, $p<0.001$), Al ($r=0.87$, $p<0.001$), and phosphorus ($r=0.71$, $p<0.001$), while a moderate positive relationship

was between pH and lead ($r = -0.64$, $p < 0.001$). Moreover, arsenic and beryllium also had a strong positive correlation ($r = 0.82$, $p < 0.001$) and arsenic and nickel ($r = -0.89$, $p = 0.004$) were strongly negatively correlated. Finally, Pb was strongly and positively correlated with P ($r = 0.87$, $p < 0.001$).

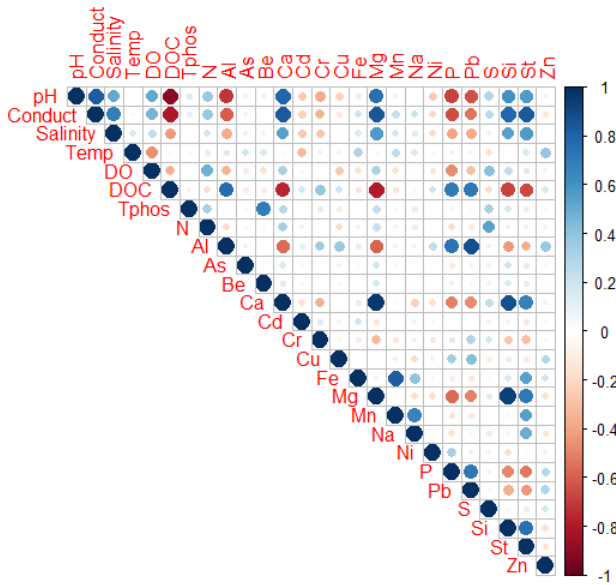


Figure 3.12. The above correlogram indicates the correlation coefficients between heavy metals and water parameters. Blue boxes indicate positive correlations, and red boxes indicate negative correlations. The white boxes indicate no significant difference ($p > 0.05$). The size of the circle indicated the strength of the relationship.

3.3.9 Sink or Source Calculations

The calculation of sink-source ratio can also be applied to the wetland system by using the metal concentration in the Inlet water Metal(In) and the metal concentration in the outlet water, to calculate the Metal(In)/Metal(Out) ratio. The resulting ratio with a value lower than 1 would be a sink, and a ratio greater than 1 would be a source.

Applying similar calculations for sink and source (magnification ratio) as outlined by Qin et al. (2022) and Ury et al., (2023) suggests that the productivity of the three fens varies based on their

classification as either a sink or a source. Additionally, this productivity is influenced by temporal changes, as shown in Table 3.4.

Table 3.4. The table shows the ratio of Metal (Out)/Metal (In) of heavy metals of concern during the study. Values lower than 1 suggest the fen is a sink, whereas values greater than 1 suggest the fen is a source.

Fen	Season	As	Cd	Cr	Cu	Ni	Pb	Zn
SS	Spring	0	2.4	0.8	0.4	0	0	0.5
SS	Summer	0	1.9	2.3	2.9	0	2.9	15.5
SS	Fall	0	5.8	0.7	0.3	0	0	0.2
MW	Spring	0.5	0.1	1.01	0.5	0	0.6	0.3
MW	Summer	0.01	2.6	0.8	1.01	0	0	2.8
MW	Fall	0	1.01	1.2	1.2	0	1.2	5.1
LM	Spring	0	0.7	0.8	1.2	0	0	1.01
LM	Summer	0	2.2	0.5	2	0	0	33.5
LM	Fall	0	0.2	0.9	0.8	0	0	2.3

3.3.10 Summary of results

The study revealed significant spatial and seasonal water and porewater chemistry variations across the three wetland ecosystems. Heavy metal concentrations and distributions in surface and porewater revealed various patterns influenced by environmental factors, with some metals exhibiting notable differences among the wetland sites and with the seasons.

3.4 Discussion

In recent years, the study of heavy metals in porewater has gained significant importance, given their overwhelming implications on the environment and the health of ecosystems. Porewater, the water found in the small spaces between peat or peat particles, plays a crucial role in the transport and bioavailability of heavy metals. Understanding the behaviour of heavy metals in peatland porewater will help us to evaluate the potential risks associated with them to these ecosystems. This discussion aims to characterize the presence and distribution of seven heavy

metals of concern: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn) across the three fen ecosystems studied in this research.

3.4.1 Water Parameters

Potential of Hydrogen (pH)

It is well documented that low pH promotes the release of heavy metals from the peat into the water column. This is due to the increase of hydrogen ions and their affinity to displace the negatively charged heavy metal ions (Miranda et al., 2021).

Changes in pH by depth varied between fens and between locations within fens (Fig.3.1

A). Generally, the pH was lowest in the fall and highest in the spring, and there were differences in pH between the fen midpoint and the outlet. Wider changes in pH in the fall at SS may have been caused by the abundance of sphagnum moss, which contributes to the pH reduction through cation exchange (Gagnon & Glime, 1992). At MW, the pH remained somewhat stable, and in LM, the pH showed a reduction from the midpoint to the outlet. The pH variation alters speciation and the mobility of heavy metals in porewater. However, Novak (2008) reported that pH between 2.5 and 5 had little influence on metal mobility. Other studies have revealed that pH <7 releases heavy metals into the water column, whereas pH >7 magnifies the adsorption and precipitation of heavy metals into the peats (Chou et al., 2018; Kang et al., 2019; Wang et al., 2018b).

Dissolved Oxygen

Dissolved oxygen (DO) was high at the inlet and outlet and low at the midpoint. It also decreased with the porewater depth (Fig 3.1 A). This is consistent with other research, indicating a gradual descent to anoxic conditions (Pezdir et al., 2022 ; Dou et al., 2018). DO was highest at MW and

lowest at SS. This can be partly explained by the plant's radial oxygen loss (ROL) by rhizosphere oxygenation (the passing of oxygen to the roots from the shoots) which is performed by various macrophytes. This results in increased oxygen concentration at the rhizosphere thus altering the rhizosphere redox potential (J. Yang et al., 2010). ROL is expected to be lower in poor fen systems with sphagnum dominance and fewer macrophytes that perform ROL. The dissolved oxygen content was higher in fall compared to spring and summer.

Earlier studies confirmed that DO affects the precipitation and solubility of some heavy metals in the water column. For example, Kang et al. (2019) demonstrated that in aerobic conditions, the high nutrient content promotes the adsorption of Pb and Zn to the peat, but neither has any effect on Ni adsorption. They also noted that anoxic conditions reduce the mobility of Pb, Zn, and Cu. Conversely, anoxic conditions (those with DO less than 0.5 mg/L) in a controlled experiment were found to release Pb, Cd, Cu and Cr into the water column (J.-J. Liu et al., 2019).

Dissolved Organic Carbon (DOC)

DOC concentrations at SS were significantly higher than at LM and MW (Fig. 3.1 A). Similar elevated DOC concentrations (30-60 mg/C/L) were found at Mer Bleue, the largest bog in Ontario (Fraser et al., 2001). These concentrations were deemed a result of natural leaching and low microbial decomposition of the anoxic peat. The current research demonstrated that an increase in pH decreased DOC, and an increase in depth increased DOC.

The DOC concentrations observed to be highly related to the levels of certain metals such as Cr, Ni, and As in porewater (Raudian et al., 2017). This suggests that a higher DOC concentration would explain higher Cr, Ni, and As levels in the porewater which was not supported in this research. Heavy metals in the peat and water combine with the DOC with the help of chelating agents, which cause the mobilization of heavy metals in the water, often referred to as “water

browning”, often is the result of environmental changes and anthropogenic activities (Sherene, 2009). In the current study, site SS had the highest DOC concentrations and the highest Pb, Cd, and Zn concentrations in the water, which is contrary to the finding by Raudian et al. (2017). Moreover, DOC/DOM in sphagnum-dominated fens may differ from that of sedge-dominated fens (D'Andrilli et al., 2010). Other studies support a relationship between DOC and conductivity (Fraser et al., 2001); however, this research found no such significant relationship between DOC conductivity.

Electrical Conductivity (EC)

Reduction in conductivity and total dissolved solids from the inlet to the outlet occurred in all fens. Similarly, all fens showed slight variations in conductivity with depth (Senal et al., 2020), but the greatest occurred in the fall. Significant differences in EC were observed in fens. This may be due to the variation in fen types, from a poor to rich fen (Walter et al., 2019; Heidel et al., 2017).

3.4.2 Fens as Sources of Heavy Metals

The heavy metal concentrations in the water varied as the water passed through the fens. In spring, in all three fens, an overall reduction of heavy metals was observed as the water passed through. However, a significant increase in several heavy metals (Zn and Cu) is seen at the outlet in summer and fall. Thus, the concentration of heavy metals varied between sites within fens and with seasons.

The increased concentrations at the inlet of MW and LM may be due to spring runoff from adjacent areas. Both these fens are located near large urban centers and agricultural land. Site SS is located at a distance from smaller urban centers, and the water to this fen travels alongside a

well-used two-line highway. In all sites, zinc showed the highest concentration among the heavy metals studied. Porewater samples indicated that heavy metals increased with depth.

The water residence time, the time for water to travel from inlet to outlet, can influence wetlands' ability to act as sinks or sources (Ghosh & Gopal, 2010). Longer retention in the wetland and the reduction of flow can greatly enhance the retention of heavy metals (Knox et al., 2008). Longer water residence time permits nutrient speciation and microbial processes to occur (Knox et al., 2008), the increased residence time in a fen could increase the concentration of metals in the peat. In channelled wetlands, such as LM, there are areas where residence time is greater and areas where it is shorter, such as in the channel.

Sulphate-reducing bacteria play a crucial role in the sulphur cycle in peatlands. These bacteria thrive in oxygen-deprived environments, where they convert sulphate into sulphide. This process occurs in the waterlogged areas with anoxic conditions typically found in peatlands. As a result, sulphate-reducing bacteria significantly influence the chemistry and ecology of these unique ecosystems.

3.4.3 Heavy Metal Concentrations and Distributions in Porewater

Our findings indicate substantial variations in heavy metal concentrations between the three wetland sites and across different seasons. Arsenic, Cd, Cr, Cu, Pb, Ni, and Zn concentrations varied significantly between the fens' inlet and outlet, suggesting differential retention and mobilization of these metals within the wetland systems. Porewater concentrations also varied with depth, indicating that distribution is potentially influenced by chemical, physical and biological processes.

Griffiths et al. (2019) found differences in porewater chemistry between poor fens and rich fens, which were not dependent on temporal and spatial variations. Conversely, this study found seasonal differences between Cd and Cr, particularly in the fall, where concentrations of the metals at the outlet were increased; this suggests that some metals may be remobilized in the fall, which may be due to changes in temperature, oxygen or plant bio cycling (Páez-Bimos et al., 2023).

Arsenic

Mikutta and Rothwell (2016) reported that arsenic concentrations in pore water of bogs in England ranged from 1.5 µg/L to 129 µg/L, which are substantially higher than our study. Arsenic concentrations were found to be below detectable levels at all sites, except for MW during the spring, summer, and fall seasons. At the MW site, a significant difference in As concentration was observed at the outlet ($p < 0.001$). These findings contradict those of Weigand (2010), who suggested that seasonal variations in the water table and the presence of Fe oxides significantly influenced the release of arsenic from peats. Investigations into the impact of pH on arsenic levels indicated adsorption into organic peats within a pH range of 5.5 to 8. Typically, the release of arsenic from peats occurs under reducing conditions. The increased rainfall observed in 2023 may have hindered water table fluxes in our study areas, thus preventing the establishment of aerobic or reducing conditions that would otherwise modify arsenic concentrations in the water. Furthermore, correlation coefficient analyses indicated a linear relationship between total phosphorus and arsenic concentrations (Fig. 3.12). It is essential to recognize that the solubility of As III is often regulated by the presence of sulfide precipitates. Additionally, microbial mechanisms may play a role in altering arsenic speciation in the water, contributing to its detoxification (Fendorf et al., 2010).

Cadmium

Cadmium is one of the more soluble metals which do not form strong bonds with other metals and particulates (Miranda et al., 2021), thus it is considered to be highly mobile even in acidic conditions (Kicińska et al., 2022). DOC can decrease the bioavailability of Cd through binding and complexing (Wright & Welbourn, 1994). Cadmium levels were high at the SS outlet and LM midpoint during the fall. There was a significant decrease in Cd concentration from the midpoint to the outlet across all fens ($F = 8.71$, $p = 0.0128$), indicating a potential retention or transformation process occurring within the fens. These results are similar to those found in European bog porewaters (Novak & Pacherova, 2008). In the acrotelm, the living layer, Cd, may bind with living organic matter, whereas in the mesotelm, the decomposition of the organic matter and changes in the water table change redox conditions, resulting in the release of Cd. Site LM and MW exhibited a reduction in Cd with depth is similar to the finding by Koretsky et al. (2006).

Chromium

Chromium (Cr) is present in the environment in two oxidation states: Cr (III) and Cr (VI). While Cr (VI) is mobile and toxic, Cr (III) is relatively immobile in slightly acidic water (Palmer & Puls, 1994). pH significantly influences Cr solubility;(Ju et al. 2022). Cr leaching from peat in freshwater systems was notably higher at lower pH, particularly around pH 3. Under aerobic conditions, Cr (III) becomes fairly immobile due to sorption and precipitation in peat. Additionally, Cr (III) is less soluble in slightly acidic conditions and tends to immobilize. Conversely, oxic environments enhance Cr release in freshwater, indicating that certain wetlands serve as essential sinks for chromium.

In this study, the highest chromium concentrations were detected in the surface water of site SS, a poor fen (Fig. 3.4 & Fig. 3.5). Although chromium concentrations were generally below detectable levels, significant differences were observed in porewater at depths of 20 cm and 30 cm ($Z = -3.39$, $p = 0.024$). Site SS exhibited the highest chromium levels, especially during spring and summer, with notable decreases by the outlet. Mean concentrations increased slightly with depth and distance from the inlet, while similar concentrations were recorded at both the outlet and inlet. Koretsky et al. (2006) reported that Cr concentrations in porewater are usually low and decrease with depth, contradicting our findings at SS. However, Sricharoenvech et al. (2024) indicated that Cr is primarily bound to particles in the water column, which could account for increased Cr with depth at SS, where dissolved organic carbon (DOC) also increased.

Copper

In aqueous environments, copper primarily exists as Cu^+ and Cu^{2+} , with Cu^{2+} forming from Cu^+ under oxic conditions. In natural freshwater systems, copper tends to be complex with dissolved organic matter (DOM). Copper toxicity may increase in acidic waters with low complexation capacity (soft water) (Sylva, 1976). Most copper in natural waters is found as copper-DOM complexes (Xue & Sigg, 1993), and the sorption of Cu(II) rises with pH (Dzombak & Morel, 1990). Consequently, Cu adsorption increases with pH, while desorption occurs at pH levels below 6, which may be influenced by other elements.

In the current study, the lower pH and higher dissolved organic carbon (DOC) at site SS led to elevated copper concentrations in outlet water and increased concentrations with depth in porewater (Fig. 3.3 & Fig. 3.5). In the fens, copper concentrations were relatively stable, with a significant change observed at depths between 20cm and 30cm ($Z = -3.305$, $p = 0.02$). Site SS had the highest mean copper concentration, with significant differences noted between LM and

MW ($F = 7.64$, $p = 0.0219$). While no seasonal variations of copper were significant in the studied peatlands, Sudbury, Ontario's peatlands showed higher Cu concentrations in spring and a decrease in fall. Additionally, Koretsky (2006) reported a strong trend of decreasing concentration with depth, similar to the patterns observed in this study, although no consistent trend was determined.

Nickel

In natural aquatic systems, nickel primarily exists as Ni (II), the most harmful form of nickel. Nickel forms complex with DOM and, therefore, is less bioavailable in suspended materials. Nickel precipitates with iron and manganese or is adsorbed to suspended organic matter at $\text{pH} > 6$ (Richter & Theis, 1980), which decreases its bioavailability (Klerks & Fraleigh 1997). When pH is < 6 , nickel is highly mobile. Its mobility is further increased in aerobic waters by microorganisms (Stokes & Szokalo, 1977). This asserts that the nickel concentration in the fen waters at our sites should be highly mobile, and this is what appears to be the case. In spring, the levels of nickel were mostly undetectable, except at SS (Fig. 3.4 & Fig 3.5). There were no significant differences in nickel concentrations between the inlet and outlet. However, there was a significant decrease between the inlet and the midpoint of the fen ($Z = -2.04$ and $p = 0.04$). Interestingly, a study on peatlands in Sudbury found that nickel concentrations were low in spring but increased as the season progressed, reaching the highest level in fall (Pennington & Watmough, 2015). This was not observed in this study.

Lead

Lead concentrations in water and peat can reflect its concentration in the atmosphere. For example, Ontario peatlands exhibit an enrichment of lead in the peat compared to the peatlands in Alberta (Shotyk et al., 2023). It is suggested that this is due to increased industrialization and

anthropogenic atmospheric deposition of Pb in Ontario. Leaching of lead from peat is more likely to occur at pH below 6.5. Lead concentrations in the porewater were often below detectable levels but were detected at all sites, at the midpoints (Fig 3.4 & Fig. 3.5). A significant increase in lead concentrations was observed from the inlet to the mid-fen, with site SS showing the highest variability ($F = 25.4$, $p < 0.001$). At site SS, Pb displayed a tendency towards vertical stratification, similar to the results of less compacted and less decomposed peat noted in a study by Novak & Pach (2008). Lead and DOC were found to be significantly positively correlated in the fen porewater, which was contrary to results found in a study on the relationship of geochemical parameters to heavy metals by Jiann et al. (2013).

Zinc

Zinc most often occurs in the oxidation state of Zn^{2+} , considered the most toxic, and less often in the metallic form of Zn, usually seen in highly reduced environments (Lindsay, 1979). Redox potential does not play a role in Zn mobility. However, mobility may occur from releasing other redox-sensitive metals, such as Mn and Fe (Dewey et al., 2023). In low pH, zinc occurs dominantly in the form of free zinc, which becomes more available and mobile (Reddy et al., 1995). This suggests that zinc observed in this study is likely in free form and is highly mobile and bioavailable.

Zinc concentrations showed statistically significant variation between LM and SS ($Z = -3.04$, $p < 0.001$), with distinctive seasonal fluctuations. At site SS, zinc levels increased from the inlet to the midpoint during summer. Conversely, site MW showed higher zinc concentrations at the inlet during the spring and summer, gradually decreasing towards the outlet. Furthermore, the mean concentrations of zinc demonstrated a minor increase with depth. These findings suggest complex seasonal and spatial dynamics within the study area.

3.4.4 Vertical Migration of Heavy Metals in Porewater

Novak and Pach (2008) suggest that the vertical stratification of porewaters may be attributed to compaction and decomposition. Novak and Pach (2008) also suggested that bog water metals Zn, Cu and Cd are mainly present in small-sized colloidal particles, while Pb tends towards large colloids. Some movements of Cu, Cd and Zn through the fens in this study can be explained by this and will be discussed further in the next chapter. Thus, it can be deduced that the vertical mobility of metals attached to large particles may have been reduced in areas with more compaction. In addition, Korksky (2006) concluded that the increased metal concentrations in the shallower portion of porewater in fall and winter are likely due to the reduced redox potential.

3.4.5 Fens as Sinks or Sources of Heavy Metals of Concern

Wetlands can act as either a sink or source of heavy metals, which can be altered through changes in environmental conditions (Qin et al., 2022). It is suggested that the difference in metal concentration between porewater and overlaying water determines if a wetland is a sink or a source. In a study of constructed wetlands, Qin et al. (2022) suggested that the wetlands act as a source of Zn in summer and winter and as a sink in spring and fall. However, the wetlands always act as a sink of Cu (Qin et al., 2022). In the present study, the fens typically act as a sink in spring and as a source in the summer and fall. These results may be due to the differences in biogeochemical processes between constructed wetlands and fen peatlands.

All three fens were identified as sinks for arsenic (As) and nickel (Ni) across all seasons.

However, their behaviour concerning cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), and zinc (Zn) varied, with the fens acting as either sinks or sources depending on the season (see

Table 3.4). Cadmium and zinc were the most frequently observed metals acting as sources, followed by copper, chromium, and lead. The fluctuations in metal release during summer may result from redox changes in the rhizosphere caused by radial oxygen loss (Koretsky et al., 2006; Weis & Weis, 2004). In spring, the release of metals in the outlet water may occur due to conditions that impede adsorption to the peat (Lepage, 2011). The PCA results also identified the variability in the range of heavy metals between seasons, with spring and summer reporting a broader range of heavy metals than the fall. Interestingly, LM was the greatest sink, and MW was the greatest source of the heavy metals of concern. Three source metals at SS, MW and LM were the same in the summer and may suggest a similar response to metal speciation from radial oxygen loss and the release of metals from the peat. The increase in source metals at site SS may be due to pollutant inputs from underground hydrology or the differences in pH and DO between sites, altering speciation and mobility. Sites SS and LM were the sources of numerous metals in the summer but were sinks in the fall. At site MW, the fall period was the source of heavy metals, while spring was a sink for most. This may, in part, be explained by plant desiccation. Fens often transition from sinks to sources in the fall due to plant senescence, leading to decomposition that releases heavy metals and nutrients back into the water (Weis & Weis, 2004).

Interestingly, As and Ni were not identified as sources of contamination, and correlational analyses indicated a strong relationship between the concentrations of As and Ni in the water (Fig. 3.12). Furthermore, these metals did not show a strong correlation with other metals and nutrients, as indicated by the Principal Component Analysis (PCA) and Canonical Correspondence Analysis (CCA) (Fig. 3.8-3.12). During spring, the sink and source ratios varied without a consistent pattern across all three fens. Site SS was identified as a source of Cd, site MW as a source of Cr, and site LM as a source of Cu and Zn. The PCA (Fig. 3.10) also indicated

a strong relationship between Cu and Zn, suggesting that the release of one metal is likely to correspond with the release of the other. This may be due to their similar reactions to changes in environmental conditions, such as redox potential or pH, which can stimulate dissolution from the peat. All fens were sources of Cd, Cu, and Zn during the summer sampling periods.

Additionally, site SS was a source of Cr and Pb in the summer and Zn in the fall. The PCA and CCA analyses indicated a relationship between the concentrations of Pb and Cr in the water, suggesting they may respond similarly to environmental changes. Moreover, the CCA highlighted a meaningful association between dissolved organic carbon (DOC) and the concentrations of Pb and Cr. The PCA also suggested that environmental factors such as salinity, pH, and conductivity may have less influence during the summer compared to spring. In the fall, site MW was identified as a source of all heavy metals except As and Ni. During this season, site LM was also found to be a source of zinc. Notably, high zinc ratios were observed in the summer at both SS and LM. The PCA illustrates significant dynamics in metal release throughout the seasonal sampling periods.

The distinct patterns of heavy metal concentrations and their correlation with environmental and anthropogenic factors emphasize the complexity of heavy metal contamination in wetland environments and the influence of environmental parameters in the bioavailability of heavy metals. The findings suggest that these wetlands act as both sinks and sources for various heavy metals, and this depends on the site and seasons.

The results emphasize the need for targeted strategies to mitigate potential ecological impacts. These strategies should focus on anthropogenic activities that lead to heavy metal and other nutrient input into the ecosystems and not cause alterations of other important water parameters. Regular monitoring and assessment of heavy metal concentrations, combined with management

practices such as controlled water flow and vegetation management, could help maintain these wetland ecosystems' ecological balance and health.

Chapter 4 - Peat Chemistry and Properties

Peat chemistry plays a crucial role in immobilizing heavy metals within peat. Many heavy metals can sorb to suspended particles in the water column, depending on their speciation, and subsequently settle onto the peat. However, changes in pH, water flow, and oxidation may alter the biogeochemistry, potentially leading to the release of these heavy metals. This section presents the results regarding the concentrations and distributions of heavy metals in the peat from three wetland ecosystems. The heavy metals assessed include nitrogen (N), phosphorus (P), arsenic (As), beryllium (Be), boron (B), barium (Ba), calcium (Ca), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), sulfur (S), silicon (Si), nickel (Ni), lead (Pb), selenium (Se), strontium (Sr), titanium (Ti), vanadium (V), and zinc (Zn). However, for this chapter, we will only discuss arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn), as these heavy metals pose the greatest environmental concern due to their persistence and the dangers they present to human health and aquatic ecosystems.

4.1 Peat Chemistry and Properties - Introduction

4.1 Distribution of heavy metals in peat

Peatlands accumulate large quantities of contaminants (Miszczak et al., 2020). Many studies have used trace metals to construct vertical profiles reflecting temporal accumulation but do not consider the mobility of metals after deposition (Newman et al., 2023). In general, the movement, storage, and reactivity of solutes in water are strongly linked to the biogeochemistry of peat peats, which is contingent on water chemistry, microbes, organic matter, and porosity (Rezanezhad et al., 2016; Todorova et al., 2005; Wei et al., 2021). The vertical translocation and

redistribution of heavy metals in peat have been linked to hydrology and deviations in peat density (Miszczak et al., 2020; Rezanezhad et al., 2016), with the highest concentrations usually found in the top 28–40 cm (Ukonmaanaho et al., 2004), which then decreased rapidly. Vakovley et al. (2021) found significant fluctuations in heavy metal concentrations at different peat horizons. It has been established that the porosity of the peat aids in the transportation of water and metals through its open, dead-ended, and connected pore system, which can shrink, alter, and expand in response to hydration and compression, altering mobility (Rezanezhad et al., 2016).

Structure and composition of peat

The peatland substrate is comprised of two horizons: the upper horizon, known as the acrotelm, contains the living plants, is high in organic matter, receives some oxidation, and is <0.3 m in depth, while the lower horizon, the catotelm, is the deeper anaerobic layer (Malmer & Wallen, 2004).

Peatlands are dominated by organic peats, which are highly structured and complex porous mediums with distinctive physical, chemical, thermal, and hydraulic properties (McCarter et al., 2020). The decomposition and compaction of *Sphagnum* moss, graminoids, and other vascular plants enable their unique properties and complex pore structures (McCarter et al., 2020; Paivanen, 1973). Peat accumulates on top of slowly decomposing plant litter, resulting in various pore configurations and flow-through variations (McCarter et al., 2020). Furthermore, porosity changes with depth due to the parent material and geochemical and hydroclimatic conditions that result in peat formation (Xia et al., 2021; Yang et al., 2016). Comparatively, peat peats have higher organic mineral content, lower bulk density, and up to 100% more pore space than mineral peats (Hoag & Price, 1997; Liu & Lennartz, 2019).

Peat has a unique dual porosity structure (Rezanezhad et al., 2012, 2016), which influences the transportation of water and solutes through advection in open and connected pores and molecule diffusion into closed and dead-end pores, leading to either mobile or immobile porosity (Hoag & Price, 1997; McCarter et al., 2020; Rezanezhad et al., 2012, 2016). Dual porosity controls water flow and solute migration and regulates transport processes and biogeochemical functions (Rezanezhad et al., 2016). Active porosity is the movement of water through large pores and comprises about 60% of the pore space (Hoag & Price, 1997); the small, closed, and dead-ended pores that are formed through the partially decomposed plant remains reduce mobility and are referred to as inactive porosity (Rezanezhad et al., 2012). The complex dual porosity of peat is a critical factor in the reduction of solute transportation when inactive porosity is present (Rezanezhad et al., 2012).

There are three dominant peat types: *Sphagnum*, sedge, and woody (Paivanen, 1973), which vary in pore structure. Macropores (> 250 μm) are typically in the inter-plant spaces (Holden et al., 2012) and decrease in abundance with depth in *Sphagnum* peat due to the hyaline cells in the living peat, which collapse during compression (Hoag & Price, 1997; Rezanezhad et al., 2012). The smaller pores increase with depth, as does advection; however, there is a decrease in pore connectivity (Liu & Lennartz, 2019; Rezanezhad et al., 2012). In sedge-dominated peats, the surface has an increased proportion of tiny pores compared to *Sphagnum* peat. Despite increased immobilized pores, the macropores still provide flow pathways for water and solutes. Dying sedges, often lying horizontal, create bedding planes as pathways for water flow (Baird & Gaffney, 2000; McCarter et al., 2020). Decomposed materials in sedge peats are closer to the surface than in *Sphagnum* peats (Liu et al., 2016) because they are more likely to decay (Broder et al., 2017; Hajek et al., 2019). These factors result in a more uniform pore size distribution as

depths increase. Woody peat detritus orientation creates macropores, permits greater hydrological connectivity and rapid horizontal movement of water and solutes (Holden, 2009; Paivinen, 1973), and may cause anisotropy (Ong & Yogeswaran, 1991).

Hydrology in Peatlands

Hydraulic conductivity, the ease of water flow through peat pores, is vital in regulating drainage and evapotranspiration (Morris et al., 2022). Saturated hydraulic properties of peat peats are affected by peat decomposition, botanical composition (Letts et al., 2000; Liu & Lennartz, 2019; Rezanezhad et al., 2016), and pore structure, including porosity, distribution, and continuity (Liu & Lennartz, 2019).

4.1.2 Transport of solutes

Solute transportation through peat occurs with water transportation as it travels through the pore system of the peat. Surficial undecomposed *Sphagnum* peat consists of large, connected pores that provide solute transportation in the upper centimetres of the peat. Hyaline cells collapse as decomposition increases, limiting solute transportation in the catotelm (Hoag & Price, 1997; McCarter et al., 2020; Weber et al., 2017). Non-*sphagnum* peat has increased uniformity with depth, which allows for less variation in solute transportation, but compared to *sphagnum* peat, research in solute transportation of non-*sphagnum* peat is limited.

Peat colloids and dissolved organic matter assist in the movement of trace metals through peat and depend on pore water velocity and the shape of colloids and grains (McCarter et al., 2020). Due to the pore construction and size, colloid transportation in the upper peat may be rapid, with movement decreasing with depth and decomposition; however, this also needs to be better understood (McCarter et al., 2020).

Sediments can contain high concentrations of heavy metals which are readily bioavailable in oxidized terrestrial soil. In wetlands, the anoxic zone can be a sink and accumulate heavy metals in reduced states (Weis & Weis, 2004). The oxygen in peatlands drops with depth and is therefore vertically redox stratified; thus, the limited oxygen in the oxic zone is quickly consumed through respiration and oxidization (Hamilton-Taylor et al., 1999; Koretsky et al., 2007; Weis & Weis, 2004). In the suboxic zone, chemical reactions occur through the oxidization of H₂S, or microbially, and in the sulphide zone, organic matter is mainly due to sulphide reduction (Hamilton-Taylor et al., 1999; Koretsky et al., 2007). Metal distribution through changes in redox stratification can alter mobility and bioavailability through varying aqueous and solid states (Hamilton-Taylor et al., 1999; Koretsky et al., 2007).

4.2 Methodology

4.2.1 Peat Samples collection and Heavy metal analysis

During the summer data collection, core peat samples and peat monoliths were collected at the inlet and midpoint locations. Due to the hiking distance to most sites, peat samples (peat) could not be collected using a peat corer. Therefore, to maintain consistency, a core sampling method was used, as described by Newman (2023). A 2" round P.V.C. pipe was cut length-wise, and ½ P.V.C. pipe 45 cm long was placed on the surface of the peat. A plastic lettuce knife was used to cut into the acrotelm around the proposed outline of the P.V.C. pipe. The ½ was pushed into the peat, following the outline. A second matching ½ piece of P.V.C. pipe was installed similarly to create a core. Next, a hole was dug beside the P.V.C. core so that underneath the P.V.C. could be reached, and the P.V.C. pipe with the peat inside was removed. This was wrapped in cellophane and placed in a cooler immediately. The core was frozen until further

processing. The core was removed and cut into sections in the lab, including the top 2 cm, 2cm – 10 cm, 10 – 20 cm and 20 – 30 cm. The sections were weighed and placed in an incubator at 50°C until a constant weight. The peat was ground using a mortar and pestle, and larger pieces of organic debris were removed; the peat was then sieved through 2 mm mesh and placed in polyethylene bags until analysis. Samples were sent to the LUEL laboratory in Thunder Bay for analysis using LUEL SOP#EL110, Total Metals in Biota Samples, which is based on the following references:

- E.P.A. method 1631b, Guide to total mercury analysis in sludge, peat and biota samples. Mars XPress Operation Manual. CEM Corp. Rev. 3, 2009.
- E.P.A. Method 3051A total metals in peat, peat and biota samples
- LUEL-ICP Operator Guide

4.2.2 Humification

Humification tests were performed on-site during the fall sampling using the Von Post (1922) method. A humification test on peat was performed at all locations at the inlet and midpoints and at depths 0 cm, 10 cm, 20 cm, and 30 cm. This was done by removing a small portion of the peat from the depths mentioned above and squeezing it by hand to release water, then assessing the water colour and remaining peat for its consistency and the amount of plant debris. The tests were duplicated.

4.2.3 Bulk Density

Additional core samples were taken as monoliths at the inlet and midpoint locations during the fall sampling period. Monoliths approximately 10 cm wide and 30 cm deep were wrapped in cellophane and placed in the cooler as soon as possible. Each peat core was cut into

three depths (0-10, 10-20, 20-30 cm), measured in volume, fully saturated with deionized water, and then weighed. The samples were dried in the incubator at 50 °C until they reached a constant weight. The bulk density of the samples was calculated using the following equation (Whittington et al., 2021).

$$\text{Bulk Density } \left(\frac{\text{g}}{\text{cm}^3} \right) = \frac{\text{Dry soil weight (g) Soil Mass}}{\text{Soil Volume cm}^3}$$

4.2.4 Volumetric Porosity

Volumetric porosity refers to the total peat volume that is made up of pore spaces, which aids in the movement of water, solutes and air within the peat (Ramesh et al., 2019). After monoliths were initially divided into 10 cm sections and weighed, they were completely saturated with deionized water until the sample would not hold any more water. Any water which was not absorbed during the saturation was removed before weighting. Samples were dried to the touch within the lab and placed in an incubator at 50 °C until they reached constant weight. These weights were recorded. Volumetric porosity was calculated using the following equation (Whittington et al., 2021);

$$n_{vol} = \frac{(Mass_{saturated} - Mass_{Dry}) / Density_{water}}{Volume_{total}}$$

Whereas the density of water is 0.9982 g /cm³

4.2.5 Enrichment Factor (EF)

The Enrichment Factor (EF) is used to indicate the presence and intensity of heavy metal contamination from anthropogenic causes (Akoto & Anning, 2021). Reference levels from shale samples by (Turekian & Wedepohl, 1961) are used as a standard for comparison. Due to their

limited mobility in peats, aluminum (Al), iron (Fe) or titanium (Ti) are often used as the reference background. In this study, titanium was used as the reference background due to the potential of the reaction of Al and Fe with pH (Osborne et al., 2024).

$$EF = \frac{C_n / C_{ref} (Sample)}{B_n / B_{ref} (Background)}$$

Where C_n is the concentration of metal in the peat sample; C_{ref} is the concentration of reference element in the peat sample; B_n is the background concentration of reference study metal taken from Turekian & Wedepohl (1961) and B_{ref} is the background concentration of reference elements from Turekian & Wedepohl (1961) and (Akoto & Anning, 2021). The EF is classified 5 categories $EF \leq 1$ – no enrichment; $2 < EF < 5$ – minimal enrichment; $5 < EF < 20$ – significant enrichment; $20 < EF < 40$ – very high enrichment; $EF > 40$ – extremely high enrichment.

4.2.6 Geoaccumulation Index (Igeo)

The geoaccumulation index (Igeo) was developed by Muller (1969) to assess the level of heavy metal and metalloid elements in the peat by comparing the status of the current concentration with the pre-industrial level.

The Geoaccumulation Index (Igeo) is a measure of the extent of heavy metal accumulation relative to background concentrations (Muller, 1979), which is classified by the degree of contamination as follows: $I_{geo} < 0$ – not contaminated; $0 < I_{geo} \leq 1$ – light to moderate contamination; $1 < I_{geo} \leq 2$ – moderate contamination; $2 < I_{geo} \leq 3$ – moderate to strong contamination; $3 < I_{geo} \leq 4$ – strong contamination; $4 < I_{geo} \leq 5$ – strong to extreme contamination; $5 < I_{geo} \leq 10$ – extreme contamination.

Igeo is calculated using the following (Z. Zhang et al., 2022):

$$I_{geo} = \log_2 \frac{C_n}{1.5 \times B_n}$$

Where C_n is the mean concentration in the sample, and B_n is the concentration in the background sample.

4.3 Results

4.3.1 Peat Properties

4.3.2 Geo accumulation Index (Igeo) and Enrichment Factor (EF)

The geo accumulation index (Igeo) and Enrichment Factor (EF), indicators of the increased concentration of heavy metals in peat compared to pre-industrial levels (Igeo), were calculated using background values from Walford (2011) (Cr, Cu, Ni, Pb, Zn, Arsenic and cadmium values were not available from the aforementioned study; they were taken from The Interim Sediment Quality Guidelines (2011) for sediment and the Canadian Council of Ministers of the Environment (1999).

Enrichment factor calculations indicated that most sites in this study varied from low to very highly enriched with several of the above-mentioned heavy metals (Fig. 4.1). Lead and zinc were found to be “extremely highly enriched.” In sites MW and SS, arsenic was significantly to extremely highly enriched within the fen and minimally to moderately at the Inlet. In contrast, at site LM, the inlet, midpoint and outlet were very highly to extremely highly enriched by arsenic. Cadmium was minimally enriched at all fens, and chromium was moderately enriched. Copper was “highly” to “extremely high” enriched in all three fens other than the inlet of site SS, where it was slightly lower. Nickel was significantly enriched at all fens.

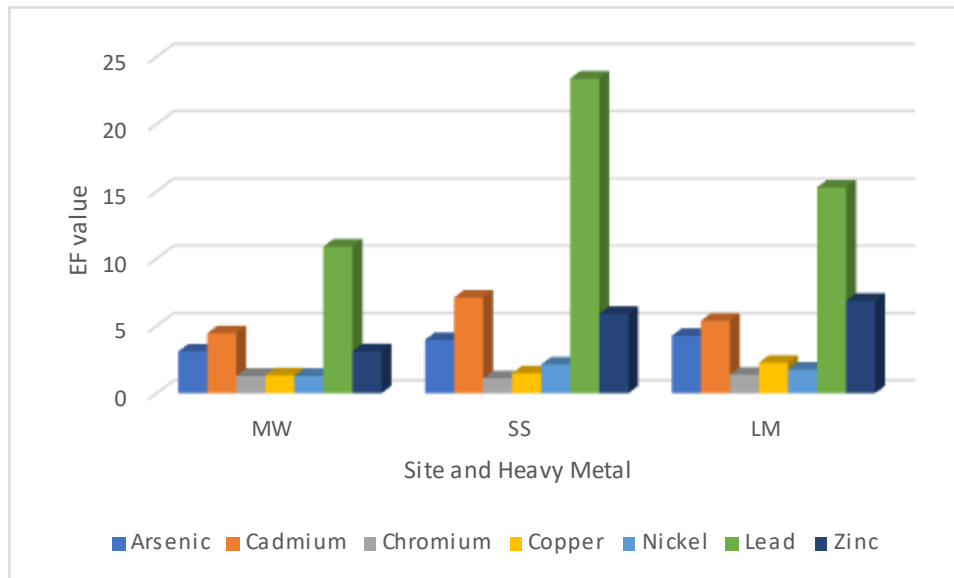


Figure 4.1. The Enrichment Factor values at the midpoint of the fens are calculated using the averages from the 30cm core profiles. Arsenic is indicated by dark blue, cadmium by orange, chromium by grey, copper by yellow, nickel by light blue, lead by green and zinc by purple. Values above 5 are significantly enriched.

Igeo scores indicated that many sites were moderately to strongly contaminated with lead. (Fig.

4.2). Additionally, the sediment in the inlet of site SS was moderately contaminated with Zinc.

All other metals were below the levels of contamination as suggested by the Igeo index (Muller 1969). Arsenic and other metals were below one, suggesting that the sites were not contaminated with these heavy metals. Lead was most elevated at the inlet of site SS, and the midpoint at site LM. Although several peat samples indicated moderate contamination at site MW, this site was the least contaminated with lead.

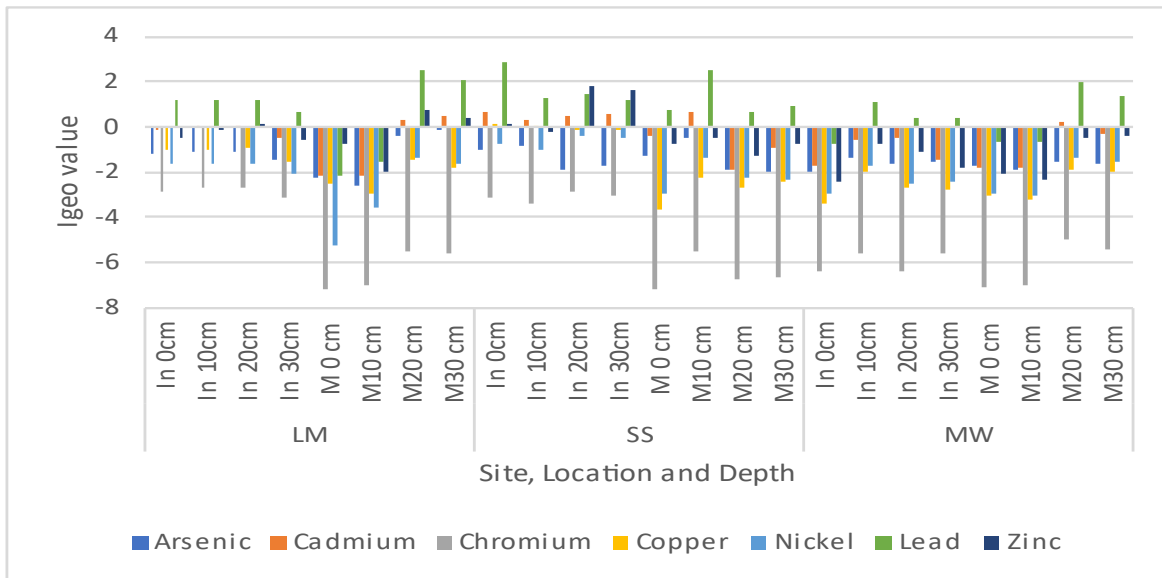


Figure 4.2. The Igeo scores for the inlet and midpoints of the three fens. Note that Cadmium, lead and zinc are often enriched in site SS.

Nutrients and heavy metals in the peat largely influence the plant's uptake. Peat nutrient and heavy metal analysis from the inlet and the midpoints showed variations in the concentrations of heavy metals and nutrients within wetlands, between wetlands, and with depth within wetlands. The variations in heavy metals and nutrient concentrations in peats between the inlet and the midpoint at SS were the most extreme. The high variations in concentrations were detected for aluminum, calcium, magnesium, iron, and titanium. However, some heavy metals and nutrient concentrations at LM and MW showed a reduction from the inlet to the midpoints e.g. calcium, sulphur and iron.

4.3.3 Between Site Comparison

The surface peat's bulk density (BD) and volumetric porosity (VP) did not differ significantly between fens. However, they exhibited similar patterns of decrease from the inlet to the midpoint fen (Fig.4.3 A, B, C).

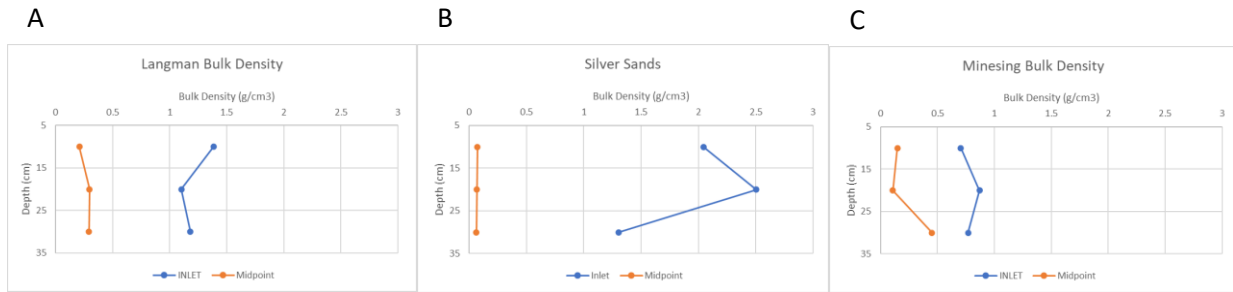


Figure 4.3 A, B, and C The surface peat bulk density at the inlet and fen midpoint at the three fens.

The surface peat bulk density of all sites decreased from the inlet to the midpoint fens and ranged from 0.1835 to 0.08888 at the inlet to 0.01769 to 0.001178 at the midpoint fen, indicating that the peat structure at the midpoint fens is more porous and less compact than at the inlet. Bulk density at the inlets did not increase with depth, but it did with depth at the fen midpoint, thus indicating a reduced porosity and compaction of deeper peats at the midpoint (Fig. 4.3 A, B, C).

Each fen was found to have a unique volumetric porosity, which was negatively related to the bulk density. Although all fens had higher volumetric porosity in the inlet than at the midpoint, no distinct pattern was observed with depth (Fig. 4.4). Interestingly, the peats reached peak porosity at different depths. For example, the volumetric porosity at MW was found to be highest at the 10 cm depth of the peat, while, at site SS, the peak was observed at the 30 cm depth. Site SS had the lowest porosity variation with depth. The volumetric porosity with depth demonstrated a limited variation between the fens.

A

B

C

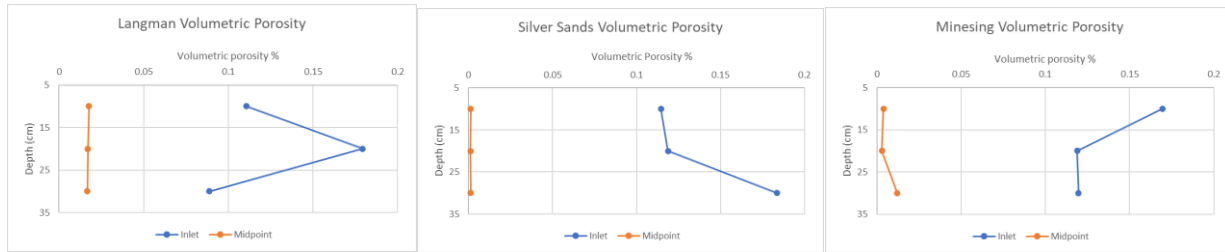


Figure 4.4 A, B & C. Volumetric porosity in peats with depth at the three fens.

The humification, or degree of decomposition, data of the peat, which was determined by using Von Post scoring and analyzed using Kruskal Wallis, indicated a significant difference between fens ($F=7.36$, $p=0.025$). Further analysis with the Dunn test showed that sites LM and MW differed significantly ($Z= -2.63$, $p=0.025$). The Von post score at SS inlet was higher compared to the other sites, while the midpoint score was lower when compared to other sites (Fig. 4.5). The least variability of humification observed within the fen was at LM. All sites demonstrated an increased humification with depth.

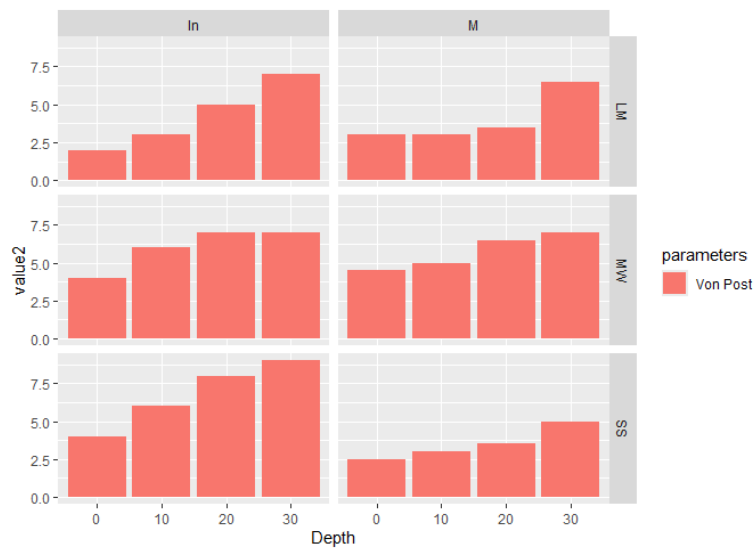


Figure 4.5. The humification scores of peats at different depths of the three fens.

4.3.4 Within Site Comparison

Bulk density and volumetric porosity significantly differed within fens between the inlet and the midpoint (BD $F=27.1$, $p<0.001$, VP $F=25.1$, $p<0.001$). Neither bulk density nor volumetric porosity differed significantly with depth. The bulk density of the surface peat was greater at the inlet of the fens than at the midpoint. The bulk density at the inlet was higher at SS than the other sites and followed a similar pattern as site LM.

Although Kruskal-Wallis analysis determined that there were no significant differences in humification values from the inlet to the midpoint fens, a significant difference was found between different depths ($F=11.4$, $p=0.009$), particularly between the surface and 30 cm ($Z=-3.26$, $p<0.001$). The surface peats at the inlet of all sites were slightly more humified than those at the midpoint fens. Interestingly, the humification variation with depth at the inlets was much more defined than that observed at the midpoint fen.

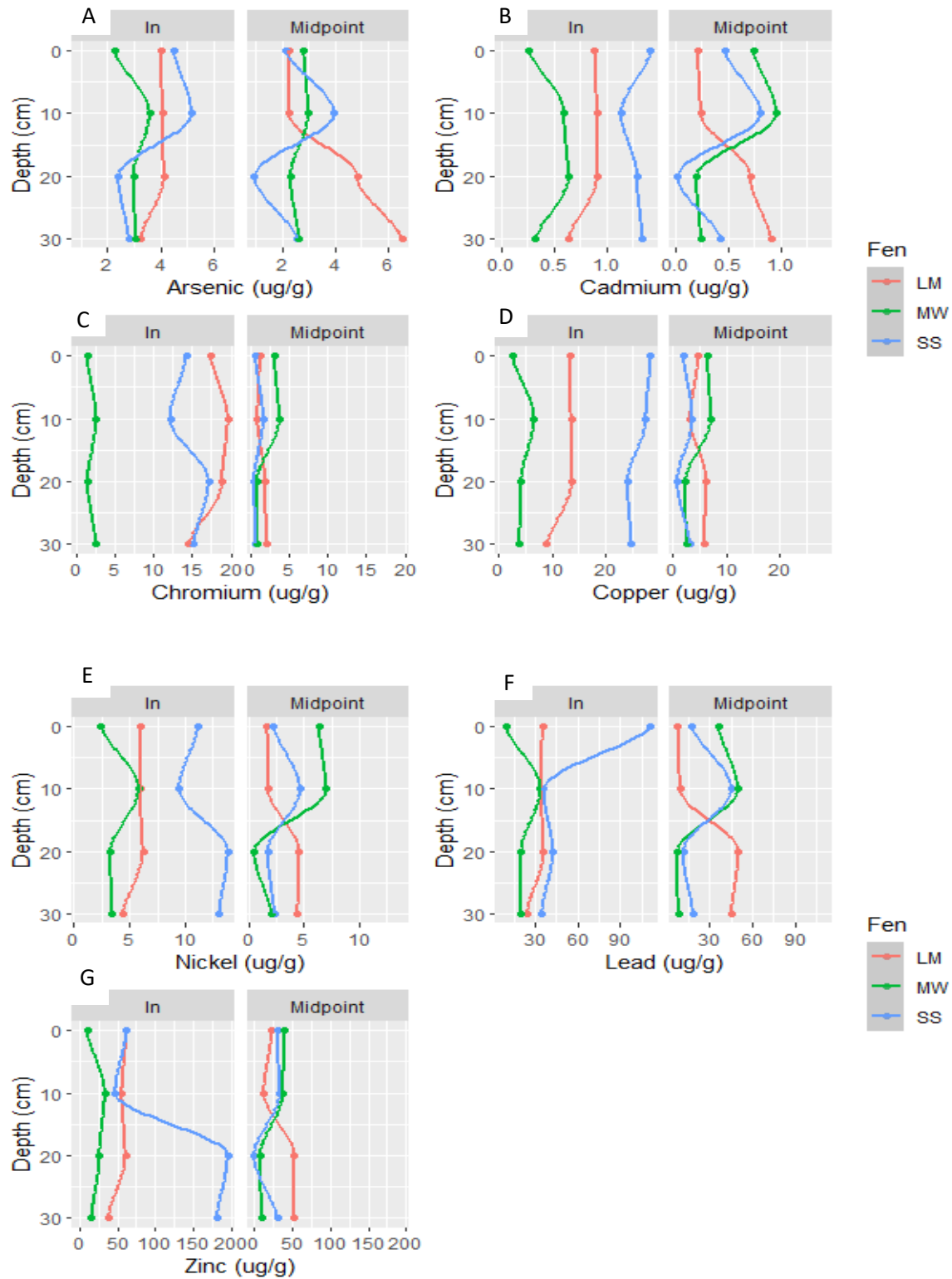


Figure 4.6 A, B, C, D, E, F, G. Heavy metal concentrations in the core profile at depths “0”, “10 cm”, “20 cm”, and ” 30 cm” in the inlet and midpoint core samples from sites LM, MW and SS. Note the different scales.

4.3.5 Heavy Metals

4.3.6 Variation with depth

The distribution of heavy metals varied with peat depth, as illustrated in Figure 4.6. Chromium and copper exhibited the least variation across different depths, while other metals showed greater fluctuation. Sites MW and SS displayed similar trends in the midpoint core samples, whereas site LM often exhibited an opposing trend. However, the inlet samples revealed some variations. The inlet core samples at sites MW and SS demonstrated diverse trends, while site LM showed a more linear pattern. Site SS showed the greatest variation in its distribution. Notably, the concentration of metals at the midpoints often exhibited the most significant changes between the depths of 20 cm and 30 cm. However, no heavy metals were found to change significantly with depth overall. The inlet of SS had higher concentrations of most metals

A throughout the depths, while MW had higher B concentrations in the midpoint.

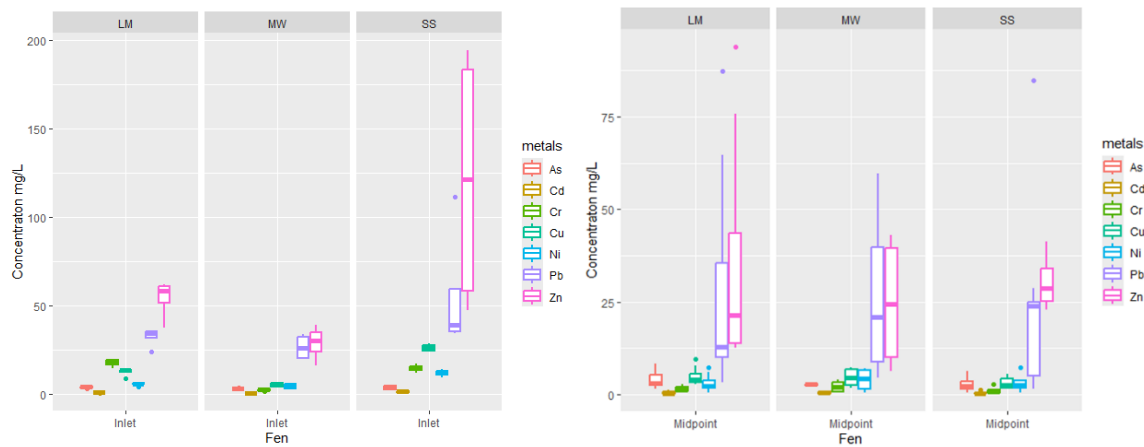


Figure 4.7 A & B. Boxplot showing the mean concentrations of seven heavy metals of concern at the inlet and midpoint of the three fens. The boxes represent the 25th and 75th percentile, and the line represents the median value. The whiskers represent the minimum and maximum.

4.3.7 Between-Site Comparison

Arsenic (As) was observed in the peat at all the sites (Fig. 4.6 A & Fig 4.7). Background arsenic in Ontario soil is typically 6 ug/g (Ministry of the Environment Ontario, 2011) and The Interim

Sediment Quality Guidelines (ISQG) sets the limit below which adverse biological reactions can occur in freshwater sediment at 5.9 mg/kg (), making some of the peat sample readings at the fens studied here are in the above the acceptable threshold. Arsenic in the peat changed significantly between the inlet and the midpoint (Wilcoxon, $p < 0.001$). The highest concentration of As was at the LM midpoint, at 30cm depth (8.25 ug/g). The lowest concentration of As was also found at the LM midpoint at 10 cm depth (1.5 ug/g). At SS, the As concentration decreased by more than 50% between 10 cm (5.16 ug/g) depth and 30 cm depth. At MW, the concentration remained most stable, site SS had variation, and site LM As increased drastically with depth.

According to McKeague and Desjardins (1979), cadmium in Canadian soils ranges from 1.7 ppm to BDL with a mean of 0.06 ppm. The recommended limit for Cd in soils suggests 0.6 mg/kg (Ministry of the Environment Ontario, 2011). The current study observed concentrations from 1.42 ug/g to 0.2ug/g with a mean value of 0.58 ug/g. The lowest Cd concentration was found at MW at 20 cm depth (0.2 ug/g), and the highest concentration was at SS at 10cm depth (1.41ug/g), all of which exceeded the mean concentration recommended for Canadian soils (McKeague & Desjardins, 1979) (Fig. 4.6 B & Fig. 4.7). Cadmium concentrations differed significantly between the inlet and the midpoint fen (Wilcoxon=118, $p=0.007$) but not between fens. Cadmium displayed similar variations to arsenic in that the concentration at the 10 cm depth was often greater than that of the surface and depth below 10cm. However, the pattern at site LM was the opposite. Site LM was the only site to show an increase in concentration with depth. At MW and SS, the distribution patterns were similar, Cd increased slightly from the surface to 10cm and then decreased with depth.

Chromium concentrations in Canada range from 10-100 ppm (McKeague & Desjardins, 1979). The CCME (1999) interim guidelines for sediment quality for freshwater peat suggest a

concentration limit of 37.3 ug/g for peats. The peats at the three studied fens were lower than the above limit (Fig. 4.6 C & Fig. 4.7). There was a pronounced reduction in Cr from the inlet to the midpoint fen. The highest concentration was at LM inlet (18.89 ug/g), and the lowest was at SS at 20cm depth (0.2ug/g). Chromium differed significantly between the inlet and the midpoint fen (Wilcoxon, $p < 0.001$). The inlets had higher concentrations than the midpoint, which were generally linear, although some variation was observed at the inlet of site SS. Chromium varied from 0.95-2.14ug/g at LM, where it decreased in depth. The overall concentration at the inlet MW was lower than the other fens but higher in the shallower depths at the midpoint. At the MW midpoint, Cr concentrations decreased slightly with depth but had the highest overall concentrations among the fens. At site SS, Chromium was higher at the inlet than at the midpoint of the fen. In LM, chromium concentration was high in the inlet peat, and there was a slight increase with depth. The concentration was lower at the midpoint of the fen, where the concentration slightly increased with depth.

The range of copper in Canadian soils varies from 5-50 ppm with a mean concentration of 22 ppm (McKeague & Desjardins, 1979). The ISQG sets the limits of copper to 16 ug/g (CCME, 1999), which is the threshold for adverse biological reactions. Copper in the wetlands in this study was often lower than the range found by McKeague and Desjardins (1979) (Fig. 4.6 D & Fig. 4.7). Copper varied significantly between the inlet and the midpoint (Wilcoxon, $p < 0.001$) and was lower in concentration at the midpoint than at the inlet. In this study, both the highest and lowest values of copper were found at SS in the midpoint surface peat (28.57ug/g) and at 10 cm depth (1.66 ug/g), respectively. Among all sites, the highest concentration was recorded at site SS. The copper variation was found to be different within each fen. Copper fluxes followed a similar pattern as chromium's, increasing at 10cm and then decreasing with the depth. Site SS

had the most elevated level of copper at the inlet. Site MW had the highest copper concentration in the midpoint.

Nickel in Canadian soils ranges from 5-50 ppm with a mean value of 22 ppm (McKeague & Desjardins, 1979). The ISQG limit of Ni in freshwater sediment is 16 ug/g (CMEE, 1999). The sites in this study were observed to have nickel concentrations well within this range (Fig 4.6 E & Fig 4.7). Site SS inlet at 20 cm depth peat has the highest concentration at 13.84 ug/g. The lowest concentration was at the midpoint of LM at 10cm depth (1.76 ug/g). Significant differences in Ni concentrations were observed between locations (Wilcoxon, $p=0.003$) within each fen, with no significant differences between fens. Nickel at the midpoint of MW and SS sites decreased with depth. However, the concentrations at the LM inlet increased with depth. The pattern nickel followed MW was unique in all fens compared to the other metals. Nickel at the surface peat was lower than at the 10 cm depth. At 20cm depth, nickel decreased but increased by the 30 cm depth. Nickel in SS displayed an opposite distribution pattern. Nickel at the midpoint surface peat was higher than at 10 cm depth. Nickel concentrations at SS and LM were higher at the inlet than at the midpoint. At site LM, a similar pattern to site SS was noted; however, concentration at 30 cm increased more dramatically. The pattern nickel followed in MW was unique compared to the other metals. Nickel at the surface peat was lower than at the 10 cm depth. At 20cm depth, nickel decreased but increased by the 30 cm depth. Nickel at the surface peat was higher than at 10 cm depth. Nickel concentrations at all sites were higher in the inlet than at the midpoint. At site LM, a similar but opposite pattern to site SS and MW was noted; however, concentration at 30 cm increased more dramatically.

Lead concentrations were higher than those of the other heavy metals studied; however, unlike the other heavy metals in this study, no significant differences were found between the fens or

the locations within the fens (Fig. 4.6 F & Fig. 4.7). The background level of Pb for Canadian soil is between 5 ppm to 50 ppm with a mean value of 22 ppm (McKeague & Desjardins, 1979). In soil in Ontario, it is 31ug/g (MOE, 2011). The ISQG limit for Pb is 35.0 mg/kg (CMEE, 1999). Lead concentrations in the fens range from 3.34 to 111.55 ug/g, with many samples showing concentrations above the ISQG limit for freshwater peats. At LM, the inlet had a higher concentration than midpoint sites; the concentration remained relatively stable, while at the midpoint, the concentration increased between 10 and 20 cm, then reduced at 30 cm compared to the surface. Within the fen, the surface concentrations were at their lowest. The highest lead concentration was at the surface of SS (111.55 ug/g), which was reduced by more than 3.2 times at 30cm. There was a pronounced reduction in Pb from the inlet to the midpoint in the upper profile. Site MW had the lowest inlet concentration. Here, the concentration increased from the surface to the deeper peats. Also, lead concentrations at the midpoint were higher than those of the other heavy metals studied. Lead at the surface of site SS was more than double that of the other inlets, dropping considerably by 10 cm depth. Peak concentrations were at the 10cm depth at Site MW and SS. The lowest concentrations were at 20 and 30 cm.

In Canadian peats, Zinc background is found between 10 – 200 ppm with a mean concentration of 77 ppm (McKeague & Desjardins, 1979), and the acceptable level for soil in Ontario is 120 ug/g (OME, 2011). Peat concentration within fens in this study was found to be within the acceptable range recommended by the OME; however, peat at the inlet of SS exceeded the limit with a reading over 190 ug/g, while at MW (20 cm depth) showed a lower background value (6.33 and 7.99 ug/g & 10.95 ug/g) (Fig 4.6 G & Fig. 4.7). The Pb concentrations increased with depth at LM, while at MW and SS zinc decreased with depth. Similar to other metals examined in this study, zinc was significantly reduced from the inlet to the midpoint fens, with a more

pronounced variation observed at site SS. At the midpoint, the trend for zinc was less pronounced but followed a pattern similar to that of lead. In contrast, at the inlet, zinc exhibited a completely different trend; the concentrations of lead increased to almost 200 $\mu\text{g/g}$ at depths of 20 and 30 cm. At sites LM and MW, the concentration of zinc decreased with depth.

4.3.8 Ordinations

Principle Component Analysis (PCA)

In order to further examine the relationships between the heavy metals in the peat, a PCA was carried out using the Vegan R package (2017). The initial PCA, which examines the seven heavy metals of concern in the midpoint of the fens, along with peat properties and water parameters, indicated that PC1 explained almost 50% of the variance in the data and contains all the metals of concern, all of them weakly associated with each other, as seen in the loadings plot in Figure 4.8. PC2 explained almost 18% of the data variation and was associated positively and moderately with peat properties, water parameters, and Cr. PC2 was associated negatively with As, Cd, Pb, Zn, and porosity. Cu and Ni were positively and negatively associated with PC2. Using the Kaiser criterion, the eigenvalues observed are PC1 5.94, PC2 2.18, PC3 1.5, and PC4 1.01, accounting for 88.4% of the variance. The loadings plot (Fig 4.8) shows that pH, Pb, Cd and As strongly influence PC1 and capture the majority of the variance. Bulk density and D.O. contribute more towards PC2. Peat porosity and pH are negatively correlated, while Pb, Zn, As, and Cd are positively correlated, and humification and bulk density are also closely correlated. The biplot (Fig 4.8) with the ellipse indicates the confidence intervals of each fen and suggests the spread of each variation. Site LM (red) is more spread out and extends to both positive and negative PC1 axes and has greater variability than sites MW (blue) and SS (green). Site MW is centred mainly on the positive PC1 axis and extends into the positive PC2. Meanwhile, site SS is

primarily located in the lower left quadrant, indicating similarities in the characteristics represented by PC1 and PC2. This analysis reveals significant differences in peat properties and heavy metal concentrations among the fens, with Site SS being the most distinct and Site LM exhibiting the greatest variability. In contrast, site MW is positioned somewhat in the middle of these variations.

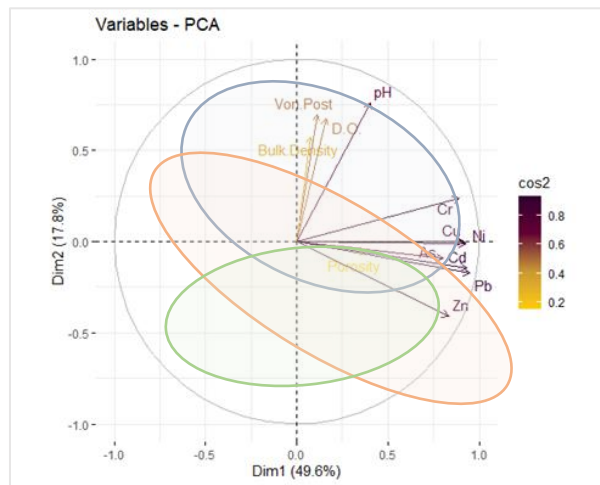


Figure 4.8. The PCA (Principal Component Analysis) was conducted on seven heavy metals of concern, examining their associations and variations with factors such as pH, dissolved oxygen, and peat properties including porosity, humification, and bulk density at three different fens. The first principal component (PC1) accounts for 49.6% of the variation in the data, while the second principal component (PC2) accounts for 17.8%. The red ellipse represents the LM site, the blue ellipse represents the MW site, and the green ellipse represents the SS site.

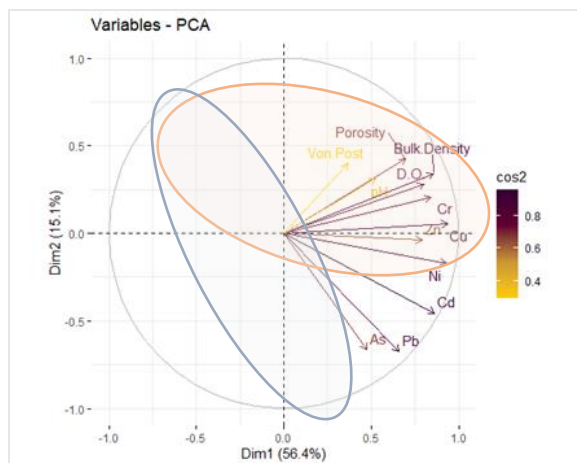


Figure 4.9. The PCA on the left illustrates the relationships between the heavy metals of concern in the peats of the three fens, specifically between the midpoint and the inlets. The first principal component (PC1) accounts for 56.4% of the total variation in the data, while the second principal component (PC2) accounts for 15.1%. In the graphic, the red ellipse represents the inlet peat, and the blue ellipse indicates the midpoint peat.

The differences between the inlets and midpoints of the fens are highlighted in Figure 4.9, which presents another PCA analyzing data from seven heavy metals of concern, along with peat properties, water pH, and dissolved oxygen levels. In this figure, we observe changes in the proportion of variance explained by PC1. The loading plot indicates that the first principal component explains a larger proportion of the variance (56.4%), while the second component accounts for 15.1%. Together, these two components capture a significant amount of data variation. The PCA reveals that three principal components explain 80% of the variance, with eigenvalues of 14.8, 4.2, and 2.5, respectively. The variables pH, Pb, As, Cd and Ni strongly influence PC1. In contrast, for PC2, bulk density, DO, and porosity have a more significant effect. Humification and porosity are closely aligned with PC2, contributing to more variance along this axis. The biplot shows that Pb, Cd, and As are positively correlated, whereas pH and porosity are negatively correlated. However, it is worth noting that pH positively correlates with heavy metals such as Pb, Cd, and As, indicating a complex relationship. Furthermore, bulk density, humification, and porosity are also positively related. In the biplot, the ellipse illustrates

greater variation at the inlet compared to the midpoint for the fens. The inlet is primarily centred on the positive axes, while the midpoint is situated on the negative axis, showing a stronger tendency towards PC1, with similarities in PC2 as well.

These findings are supported by previously presented results, which indicate that pH, dissolved oxygen, bulk density, humification, and porosity are higher at the inlet than at the midpoint of the fen. Additionally, As, Pb, Ni, and Cd concentrations are strongly positively correlated with PC1 and negatively correlated with PC2, further substantiated by correlation coefficient analysis (Table 4.2).

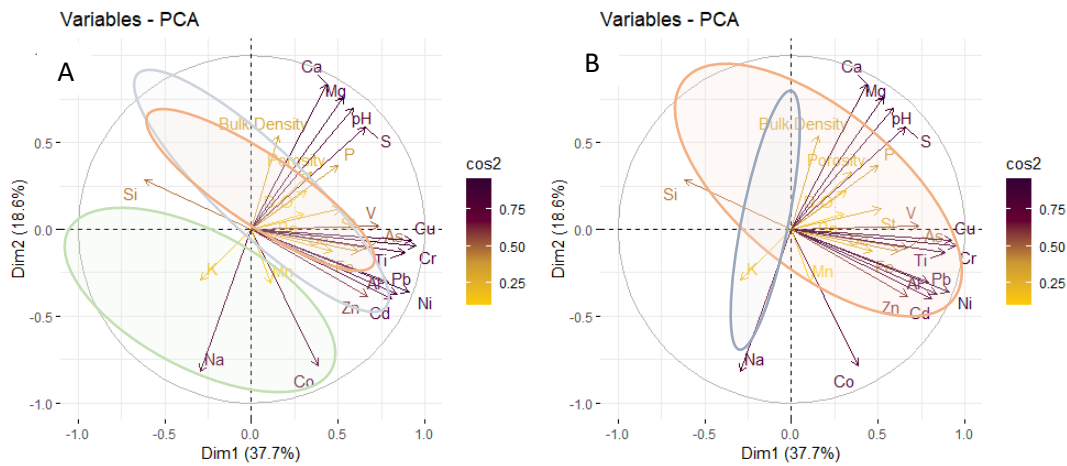


Figure 4.10 A & B. The PCA on the left compares the concentrations of various heavy metals found in the peats of three fens, with each fen represented by a different colour: red for LM, blue for MW, and green for SS. Meanwhile, the PCA on the right (B) highlights the associations and variations in heavy metal concentrations between the Inlet and midpoint of the fens, with the red ellipse denoting the Inlet and the blue ellipse representing the midpoint.

A final Principal Component Analysis (PCA) of 28 metals, nutrients, water parameters, and peat properties provides more in-depth data interpretation (Fig. 4.10 A & B). The analysis reveals that PC1 explains 37.7% of the variance, PC2 explains 18.6%, and PC3 explains 15.1%. PC1 primarily explains the seven heavy metals of concern, although the bulk density and porosity influences are weaker than in previous analyses. Most metals and nutrients are positively

influenced by PC1, except for silicon, potassium, and sodium. Notably, pH has a stronger influence on the metals compared to earlier PCAs. Metals such as vanadium, copper, and arsenic significantly contribute to PC1, while iron plays a lesser role. In PC2, bulk density, calcium, and sodium positively affect the data, whereas cobalt has a negative influence. In the biplot of the fens, site SS has the greatest variation, remaining distinct compared to the overlapping layout of sites MW and LM.

The Principal Component Analyses revealed distinct differences in the relationships between peat properties and heavy metals within the fens and between the inlet and outlet. The PCAs of the seven heavy metals, when compared to all the metals and nutrients, indicate that although the geochemistry in each fen varies significantly, the behaviour of these seven metals of concern is less influenced by those peat properties.

Canonical Correlation Analysis (CCA)

A second multivariate analysis (CCA)(Fig. 4.11) with forward selection constraint was used to identify the influence of peat properties such as location, bulk density, porosity, fen and water pH on heavy metal distribution in peat in the three fens. The CCA model was significant ($p < 0.001$) and explained 76.5% of the variance within the CCA1 (Eigenvalues = 0.0133), which explains 42.4% variation, while the CCA2 (Eigenvalues = 0.006) explains 19.3% variation. A subsequent ANOVA analysis revealed significant variations in heavy metals concentration related to fens ($r^2=47.6, p < 0.001$), bulk density ($r^2=0.70, p < 0.001$) and location within fens ($r^2=71.7, p=.049$). CCA1 associations were identified using the following species scores: negative with the following species scores: Se (-0.213), Ti (0.209), Ca (-0.182), and positive with Co (0.187) and Al (0.177). CCA2 was associated positively with Na (0.189) and Si (0.125), while negatively with Mn 9-0.143) and Cr (-0.1309). The biplot demonstrated a strong influence of SS (0.766)

and bulk density (0.7105) on heavy metal distribution, with the fen midpoints having a weaker negative influence (-0.502). In terms of CCA2, heavy metals in the midpoint of the fens were negatively influenced by porosity (-0.738), bulk density (-0.7105) and pH (-0.707).

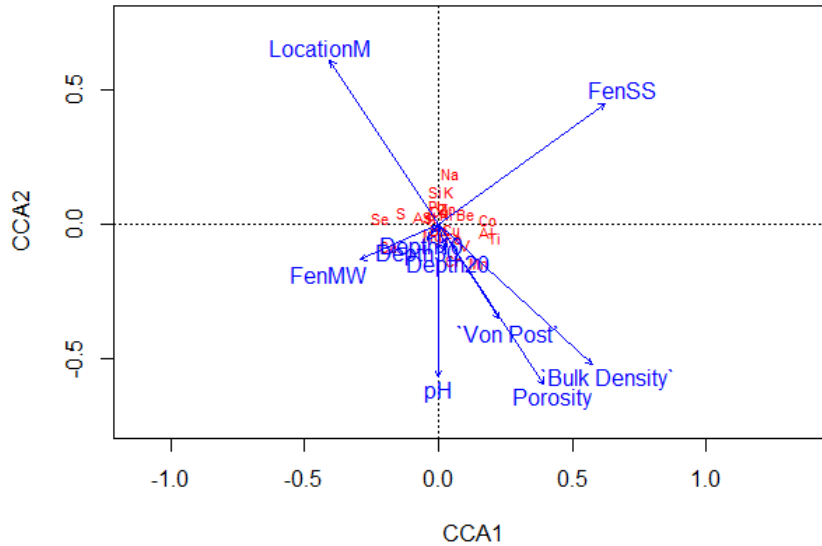


Figure 4.11 CCA of heavy metals in the peat and the impact of the studied peat properties, locations and sites.

The CCA indicated an association of bulk density with heavy metals V, Cr, Mn, Ti, Al, and Fe. Midpoint locations were associated with S, Se, and Si. Site MW and LM are associated with Se and Ca, while site SS is associated with Na, K, and Co. Depth appeared to have the least significant role in the variations of heavy metals within the fens.

4.3.9 Correlation Coefficient

A correlation coefficient (bivariate analysis) analysis examined the relationships between heavy metals and peat properties. The results, shown in Table 4.1, indicated significant correlations among many heavy metals. Copper and nickel had a strong and significant correlation with many

other heavy metals. Arsenic had the fewest significant correlations, while Pb showed limited relations with other metals. Cadmium was most strongly influenced by Cu and Cr by Barium (Ba). Copper had the highest correlation with vanadium (V) and Ni by iron (Fe). The heavy metals with strong correlations were Pb with cobalt ($r^2=0.95$) and Zn with titanium ($r^2=0.95$). Additionally, the bulk density and volumetric porosity were significantly and positively related to several heavy metals in the peat. At the same time, the pH of the water was not significantly correlated with the peat concentration of the heavy metals.

Table 4.1. The table shows the r^2 value indicating the strength of the relationship of the associated heavy metals and peat properties ($p<0.05$).

	As	Cd	Cr	Cu	Ni	Pb	Zn
Bulk density		R ² 0.74 p=0.012	R ² 0.83 p<0.001	R ² 0.88 p<0.001	R ² 0.75 p<0.008		
Porosity			R ² 0.71 P=0.028				
Al			R ² 0.90 p<0.001		R ² 0.88 p= 0.001		
As	1	R ² 0.82 p<0.001				R ² 0.81 p<0.001	0.71, p=0.012
Ba		R ² 0.74, p=0.011	R ² 0.93 p<0.001	R ² 0.87 p<0.001	R ² 0.72 p=0.023		R ² 0.69 p=0.046
Cd	R ² 0.71 p<0.001	1	R ² 0.80 p<0.001	R ² 0.84, p<0.001	R ² 0.93 p<0.001	R ² 0.96 p<0.001	R ² 0.77, p=0.003
Co		R ² 0.72, p=0.022		R ² 0.85, p<0.001	R ² 0.87, p<0.001	R ² 0.95, p<0.001	
Cr		R ² 0.80 p<0.001	1	R ² 0.84, p<0.001	R ² 0.93 P<0.001	0.79 P<0.001	0.77, p<0.001
Cu		R ² 0.84, p<0.001	R ² 0.72 p=0.022	1	R ² 0.89, p<0.001	0.78, p<0.001	R ² 0.79, p<0.002
Fe		R ² 0.77 p=0.003	R ² 0.76, p=0.005	R ² 0.86, P<0.001	R ² 0.91, p<.001		R ² 0.93 p<0.001
Ni				R ² 0.89, p<0.001	1	R ² 0.71, p=0.034	R ² 0.89, p<0.001
Pb	R ² 0.70 p<0.001	R ² 0.96 p<0.001	0.79 p<0.001	0.78, p<0.001	R ² 0.90, p<0.001	1	0.82, p<0.001
St			R ² .60 p=0.009	R ² 0.74 p<0.001	R ² 0.62 p=0.005		
Ti		R ² =0.73, p=0.004	R ² =0.96, p<0.001	R ² 0.81 p<0.001	R ² 0.84, p<0.001	0.71 p=0.009	R ² 0.95, p<0.001
V	R ² .68, p=0.029	R ² 0.80, 0.001	R ² 0.81 p<0.001	R ² 0.94, p<0.001	R ² 0.88, p<0.001		R ² 0.89, p<0.001
Mg				R ² 0.75, p=0.0006	R ² 0.83, p<0.001		R ² 0.90, P<0.001
Zn	R ² =0.71, p=0.012	R ² =0.79, p<0.001	R ² =0.77, p<0.001			R ² =0.82, p<0.001	

4.4 Discussion

4.4.1 Peat Properties

4.4.1.1 Igeo and EF

Geo accumulation Index (Igeo) (Fig. 4.1) and Enrichment Factor (EF) (Fig. 4.2) assessments of the three fens determined that some heavy metal pollution was elevated compared to the background levels. Similar results were reported for Cd, Cr, Cu, Ni, Pb and Zn concentrations in the sediment of the Lake Simcoe watershed (Landre et al., 2011). The study by Landre et al., (2011) indicated that tributaries draining forested and agricultural lands were lower in Al and Zn than those draining from urban areas. Similar results were found at MW, which received water that drains through a forest before entering the fen. Historically, tanneries and metal finishing factories have caused chromium pollution in the Simcoe and Muskoka areas, providing insight into Cr sources for LM and MW. Other possible sources of metals include air deposition, wastewater treatment plants, septic systems in Muskoka, highway run-off, and quarries. The most prevalent metals from urban run-off include Cu, Pb, and Zn, which comprise the highest concentrations of heavy metals entering the fen ecosystems. A study by Krumins & Robalds (2014) comparing the heavy metals in peatland also found extreme enrichment of Pb, which they interpreted as the result of atmospheric deposition.

Cadmium and Pb enrichment in surface peats can occur due to atmospheric deposition in southern Ontario (Whitby et al., 1978). Cadmium can originate from various sources, such as P fertilizers (Sheppard et al., 2009), urbanization, and agricultural activities (Sojka & Jaskuła, 2022). Lead is a common metal found in the surface peats, usually contributed by leaded gasoline and atmospheric deposition. Zinc can come from tire wear and is often found near

roadways (Lofts et al., 2007). Sojka & Jaskuła (2022) suggest that heavy metals in peat mainly originate from agriculture and natural sources and that Cr, Cu, Ni, Pb and Zn come from point and non-point sources.

4.4.1.2 Bulk Density, Volumetric Porosity and Humification

Bulk density can affect filtration, root depth, water storage capacity and thus nutrient availability. In natural systems, bulk density increases with peat depth, resulting in reduced root penetration (I. Ali et al., 2022). Ali et al. (2022) reported a negative relationship between heavy metals, peat porosity, and bulk density; however, other studies indicate the opposite (Khudhur & Khudhur, 2015). Our study agrees with the later finding (Table 4.1), the volumetric porosity (Fig 4.4) was found to correlate positively with Cr (0.71, $p=0.028$), and Bulk density (Fig.4.3) was strongly related to Cu (0.88), Cr (0.83), Ni, (0.75) and Cd (0.74).

Nuralykyzk et al. (2021) found that bulk density was negatively correlated with pH. The present study did not support these findings (Fig. 4.3, Table 4.1). In our study, an association between humification and pH was noted in the PCA results. Overall, the inlets with slightly higher pH had the highest bulk density and concentrations of heavy metals, and the midpoint with lower pH had the lowest bulk density and the lowest overall concentration of heavy metals.

Humification, the degree of peat decomposition of the three fens, ranged from 3 to 7 (Fig. 4.5), with more than half the samples scoring four or less. Schafer (2002) and Johnston et al. (2012) found similar results in their research of 146 fens in Colorado. They suggest that the scores indicate that the peat had relatively low decomposition and are indicators of good health.

4.4.2 Peat Chemistry

4.4.2.1 Heavy metals of fen peat

Increased concentrations of heavy metals were found at the inlets compared to the midpoint of the fens (Fig. 4.6 & Fig 4.7). This is consistent with the wetlands' continuous inflow of water from streams (J. Phillips, 2007). Water flow reduces as the water moves through the wetland, enabling the suspended particles to settle before the water leaves (Phillips, 2007). Changes in pH, water flow, and organic matter oxidation result in wetland peat remobilization (de Souza Machado et al., 2016; Morais et al., 2021). Likewise, heavy metal mobility is affected by temperatures, particularly above 30°C, when the metals become most mobile. A comparison of mean metal concentrations in peat worldwide suggests that the peat metal load in the temperate fens in Ontario are most similar to those in Russia (Haojie et al.,2016)

Streams and other aquatic ecosystems may be extensively contaminated by heavy metals such as As, Cd, Cu, Ni, Pb, and Zn (Barbieri, 2016). These heavy metals accumulated in the streams from anthropogenic activities are transported into the wetland through fluvial processes (Sojka & Jaskuła, 2022). The accumulation of these metals in the peat can cause environmental concern as the concentration above the threshold results in ecosystem damage. The heavy metal concentrations differ between the inlet (Fig 4.6 & Fig. 4.7 A) and the fen midpoint (Fig. 4.6 & Fig. 4.7 B) and with the peat depth.

Peat pH and dissolved oxygen may also increase heavy metal concentrations in the peat. Some studies have found that small changes in pH can affect metal retention in peats (Król et al., 2020). However, Huang et al.'s (2017) study did not support these results. Kicińska et al., (2022) found increased mobility of heavy metals in the order of Cd, Zn, and Pb with a drop in pH

caused by oxidation (Calmano et al., 1993; Huang et al., 2017). Under anoxic conditions, metal retention is enhanced due to metal sulphide formation in porewater, except for Mn and other redox-sensitive metals (Guo et al., 1997). The above descriptions provide insight into the lower concentrations of heavy metals in the peat in SS fen, where pH and dissolved oxygen are the lowest. Zamri et al. (2022) reported that pH was correlated to the concentration of Zn, Cu, Pb, Cr and Ni in peat. However, the results of the current study found collinearity only between water pH and Cr and Cu ($p < 0.001$) (Table 4.1).

Under oxidizing conditions, the behaviour of As, Zn, and Cr is influenced by the chemical reactions involving Fe and Mn and their oxides and carbonates. Humic materials regulate Zinc and chromium in reducing conditions, while sulphides and carbonates control cadmium. When peat's redox potential increases, the environment becomes more oxygen-rich. Fe and Mn form stronger bonds with As, Cd, Cr, and Zn in this condition. Similarly, these metals form stronger bonds with insoluble sulphides and large molecular humic matter in anoxic conditions. These findings suggest that if the peat is in a reducing state, it will lead to higher levels of soluble cadmium and Zinc and thus be in a more bioavailable and toxic form (Guo et al., 1997). This supports the findings that the peat's dissolved oxygen and Cr are positively related (0.83, $p = 0.013$). In addition, Fe was very strongly correlated to Zn (0.093, $p < 0.001$), Ni (0.91, $p < 0.001$), Cu (0.86, $p < 0.001$), Cr (0.76, $p = 0.005$), and Cd (0.77, $p = 0.003$). Both As and Pb were not significantly correlated to Fe, and Mn did not correlate with any of the seven metals focused on in this study.

4.4.3 Behaviour of Heavy Metals in Peat

Heavy metal concentrations by depth varied between the three fens.; While the overall concentrations of As, Ni, and Zn increased with depth, those of Cd, Cr, Cu, and Pb decreased with depth (Fig. 4.6 & Fig. 4.12). Higher concentrations in the upper portion of the peat could be from the decaying plant biomass (Gregorauskiene & Kadunas, 2006), plant biocycling (Zhang et al., 2016; Zhao et al., 2021), and atmospheric deposition (Whitby, 1979). The increased concentrations in the lower-depth peats might have resulted from the peat remobilization and the vertical leaching from the upper layers (Nuralykyzy et al., 2021). The PCA analysis showed a stronger positive association of PC1 with heavy metals and peat properties at MW and SS, while LM was strongly associated with As, dissolved oxygen, pH and peat properties. Site SS was negatively associated with PC2, peat properties, pH and As, while it was positively associated with most heavy metals. This shows that the peat properties and pH play a weakly negative role in accumulating heavy metals in site SS, resulting in lower heavy metal retention. Metal retention at MW shows a similar pattern with more variation and is the only site showing the influence of peat porosity. Conversely, LM is influenced by less metal accumulation and stronger influences of pH and bulk density, As and Cd, and a lesser influence of DO, which results in less heavy metal retention.

The concentration of As in peat was similar in each fen (Fig. 4.6 A, 4.7 B). Accumulation of As in the peat can occur from aerosols resulting from anthropogenic processes, and its distribution with depth can be similar to those of Pb (Yakovlev et al., 2021a). In this study, the correlation coefficient between As and Pb was strongly and positively related (Table 4.1). Similar to Yakovlev et al.(2021) and Zaccone et al.(2008), this study also found a significant correlation between As and Pb, which they suggest confirms a common source of anthropogenic pollution.

Concentrations of As at LM were greater than at the other sites, and this may be due to the agriculture run-off in the area, which began to phase out in the 1970s (Mucci, 2013) along with the decaying and leaching of buried chromate copper arsenic-treated wood use in trail construction within the wetland (Morais et al., 2021). The vertical transportation of As may depend on the chemical form of As, i.e. arsenite or arsenate (Ukonmaanaho et al., 2004); however, it must be considered that only total As was determined in this study. Rewetted peat, following drying, shows increased As mobility due to redox changes that increase mobility (Nuralykyzy et al., 2021). While metals excluding Fe and Mn oxides are assumed to be relatively immobile, the presence of phosphate can decrease As mobility in low pH and suboxic conditions. However, in anoxic conditions with phosphate-deficient peats, P may mobilize As (Deng et al., 2020). Although a strong relationship between Pb and As was established, As was not found to be mobile in the fens' water column.

Cadmium concentrations in all fens were low (Fig. 4.6 B & Fig. 4.7 B) compared to the other heavy metals and compared to those found in other peatlands worldwide. Still, they were similar to those in Sudbury, Ontario (Krumins & Robalds, 2014). However, contrary to results in Sudbury, where enrichment was in the top profile, this research found greater concentrations beneath the surface, often increasing with depth. In contrast to As, Cd has higher mobility under anaerobic conditions when DO is low (Haiyan et al., 2013). This may explain the mobility observed in this study, particularly at SS, where the lowest DO was observed. At a slightly acidic pH, solubility increases but is more soluble when the pH is 3.3. In general, lower pH and reducing conditions create situations for mobilization (Chuan et al., 1996). The mid-core Cd peaks can be attributed to coal burning around 1850-1880 (Krumins & Robalds, 2014).

According to Krumins and Robalds (2014), Cr is a lithophile that forms compounds with oxygen and does not migrate through the peat (Martello et al., 2007). In the peatlands, Cr accumulates mainly from natural weathering and anthropogenic emissions (Yakovlev et al., 2021a). In studies of wood peat, Cr showed a slight decrease at 25 cm from the surface and then another increase. This is similar to the current findings at LM but not the observations at MW and SS (Fig.4.6 C, Fig. 4.7). However, other studies have demonstrated that Cr distribution can vary with depth. For instance, Cr showed higher concentrations near the surface, with a decrease in the middle and occasional increase at greater depths (Zaccone et al., 2008), and others find variations of Cr with depth (Arkhipov et al., 2000). These findings agree with the trends at SS and MW. Wetlands are effective at immobilizing Cr by reducing it to a less soluble form (Mattuck & Nikolaidis, 1996). Copper is considered mobile due to leaching caused by pH and redox variations (Yakovlev et al., 2021a). A study by Krumins and Robalds (2014) observed that Cu levels in peat decreased with depth in the upper 30 cm of the core, with a slight increase at about 10 cm depth. This is consistent with the data found in other research (Dumontet et al., 1990; Smieja-Król et al., 2010a) and this research at site SS. In LM and MW, the Cu increased at a depth of 20cm (Fig. 4.6 D, 4.7). A study of 37 ombrotrophic peatlands showed a low concentration of Cu in the upper portion of the peat with an increase at the depths of 20-30cm (Kettles, 2005). This supports findings in Site SS.

Mucci (2013) found Ni concentrations to be highly variable. In contrast, this study found Ni to peak at 10-20cm and decrease at 30cm (Fig. 4.6 E), similar to a pattern reported by Evgeny et al.(2021) and Mucci (2013). Ni is a siderophile without oxygen affinity (Krumins & Robalds, 2014). It readily forms strong bonds with sulphur. Therefore, it prefers to migrate downwards through the peat profile and can be influenced by changes in redox and pH (Evgeny et al., 2021).

Aside from the increase at 20cm, this research found that nickel decreased with depth, which may indicate a temporal pattern (Fig.4.6 E & Fig 4.7).

Ukonmaanaho et al.(2004) reported that the highest concentrations of Pb were observed between 10 to 50cm depth of peats. Similar conclusions were drawn by Yakovlev et al.(2021). These findings supported a study examining lead in the Great Lakes, which showed that ~64% of the lead in Lake Ontario was accumulated via industrial air deposition (Flegal et al., 1989). Lead in gasoline was the primary source of Pb before the 1970s. In the present study at LM, the highest concentration of Pb was observed at 20 cm depth of the core (Fig. 4.6 E). However, SS and MW showed the highest concentrations at 10 cm depth, suggesting the sources are either atmospheric deposition or bio-cycling processes (Talbot et al., 2017).

Increased Zinc concentrations on the surface layers suggest the influence of smelters and industries. In a study by Ukonmaanaho et al. (2004), Zinc decreased with depth within bogs in Finland. Similar results were obtained by Dumontet et al.(1990) in Sudbury peatlands and by Espi et al. (1997), who found that levels substantially decreased after 40cm depth. They attributed the results to plant bio-cycling, which is similar to the conclusions drawn by Rausch et al. (2005) and Livvett et al. (1979). According to Yakovlev et al. (2021), the immobility of Zn is related to the concentration of Pb in peats; higher correlation coefficients suggest immobility and higher levels of Zn in the upper layers suggest accumulation from human activity and biogenic accumulation by plants. This research also found Pb to be highly correlated to Zinc (0.82, $p<0.001$) but with less variation with depth (Fig 4.6 F & Fig 4.7).

Thus, the vertical distribution of heavy metals in peat often shows variations due to different ecological and anthropogenic factors. Environmental parameters such as redox potential, total organic carbon, and peat grain size influence metal distribution along the depth profile, causing

variations in metal concentrations at specific depths and distances from the source (Lin et al., 2020).

5.1 Chapter: 5 Macrophytes

Peatland flora, which includes a diverse range of macrophytes and bryophytes, plays a crucial role in maintaining the ecological stability of these environments and serves as important indicators of ecosystem health. This chapter explores the varying abilities of fen plants to sequester heavy metals and the mechanisms that help immobilize these metals. Key processes such as radial oxygen loss and root plaque formation in macrophytes enhance phytoremediation and contribute to peatland health. By investigating the interactions between plant communities and their peatland environments, this chapter aims to identify the complex biological and chemical drivers at play in heavy metal sequestration in peatland ecosystems.

Macrophytes Literature Review

5.1.1 Characteristics of fen flora

Fens are wetlands that can be ombrogenous (rain-fed) or geogenous (ground-fed). Nitrogen and phosphorous are limited, which determines the productivity of the peatland (Vitt et al., 2020). Poor-rich gradients in fens are an indication of the number of species within the peatland, with *Sphagnum* fens having lower characteristic species than rich, brown moss-dominated fens (Vitt et al., 2020); however, these communities can change through eutrophication (Bootsma & Wassen, 1996). Vegetation communities in fens are primarily due to local environmental conditions; the unique wetland creates challenges for many wetland species, which leads to azonal communities (similar despite being geographically very distant) despite conditions varying across the peatland (Hinze et al., 2022).

Wetland-rooted plants differ from upland plants in their ability to survive and thrive in saturated peats. Wetland plants have adapted to the low oxygen through several mechanisms, including the exchange of gas through channels called aerenchyma tissue (Armstrong, 1978; Cronk & Fennessy, 2001; Ervin, 2023). In emergent plants such as those found in fens, oxygen enters the plant through the stomata in the leaves and lenticel in the stem and travels to the roots with limited resistance (Rydin & Jeglum, 2006; Vartapetian & Jackson, 1997). Aerenchyma provides oxygen to the roots and rhizomes of wetland plants, and large amounts of gas stored within the leaves sustain the plant in times of stress (Ervin, 2023). Most peatland plants have roots in the top 10 cm of the acrotelm, and the upper biomass is larger than the lower biomass; however, there are many deep-rooted plants, such as *Phragmites (americanus)*, which reach depths of 100 cm (Rydin & Jeglum, 2006). Other adaptations to increase oxygen include the development of adventitious roots, which grow up to the surface and assist with water and nutrient uptake (Cronk & Fennessy, 2016).

Nutrients in peatland may be limited; they enter wetlands through precipitation, air deposition, and weathering but bind to organic matter rather than be mineralized; thus, plants obtain nutrients through association with mycorrhizal fungi, nitrogen fixation, and carnivory (Cronk & Fennessy, 2001). Mycorrhizal fungi form a symbiotic association with the plant roots; the roots provide carbohydrates for the fungi, which assist the plants in obtaining phosphorous and other nutrients. Plants with mycorrhizal associations exhibit enhanced growth in phosphorous-deficient peats (Cronk & Fennessy, 2016). Some mycorrhizal fungi are unique to peatlands and form on the roots of *Ericaceous* plants, breaking down the organic compounds and making the nitrogen available. In *Orchidaceae*, the fungi help with the germination of seeds. Plants lacking fine root hairs are more dependent on the fungi than species such as *Poaceous*, which only depend on

mycorrhizal fungi in phosphorous-deficient conditions (Cronk & Fennessy, 2001; Claton & Bagyaraj, 1984).

Nitrogen fixation is another symbiotic relationship between plant roots and bacteria, in which the gaseous form of nitrogen (N_2) is available for uptake by plants and organisms (Cronk & Fennessy, 2016). The bacteria develop in the root nodules of the plants and use their energy, which, in return, provides nitrogen (Ervin, 2023). Few wetland plants have this association, but it is a function of several peatland shrub species such as *Alnus* and *Myrica* (Cronk & Fennessy, 2016).

5.1.2 Vascular and nonvascular plants

Plants are either vascular or nonvascular. Nonvascular plants are bryophytes, which are small compared to vascular plants; they lack supporting structures, true roots, and cuticle layers (Kempter et al., 2017; Wojtuń et al., 2013). Bryophytes have a large surface-to-weight ratio (Stanković et al., 2018), which allows them to quickly absorb large amounts of water and heavy metals without any detrimental effects (Wendel et al., 2011). The leaves contain two types of cells: hyaline cells and chlorophyllase cells used for photosynthesis (Bengtsson et al., 2020; Sharma et al., 2023). In *Sphagnum* mosses, hyaline cells hold water received from capillary forces in the pendant branches; their tiny pores help prevent drying out (Bengtsson et al., 2020; Goetz & Price, 2015; Rezanezhad et al., 2010). This moisture is shared with neighbouring *Sphagnum* species to prevent desiccation (Sharma et al., 2023). Nonvascular plants do not have root systems and instead have rhizoids that provide support to the plant.

Vascular plants differ from nonvascular plants in that they have a vascular structure containing xylem and phloem, which transport water and nutrients through the plant to and from the roots

(Cronk & Fennessy, 2016). The vascular tissue is a layered system that wraps around the xylem, phloem, and parenchyma in unique, well-organized patterns (Ervin, 2023). The leaves of vascular plants transport nutrients to other parts of the plant and are more complex than in nonvascular plants (Cronk & Fennessy, 2016). Water is transported from the roots through the plant's xylem via water's transpiration from the stomata. Roots of wetland plants can be fibrous, consisting of a biomass of small, delicate roots with larger root surface areas, or they can be rhizomatic, which consists of a rhizome or thick root and grows slower but with enhanced distribution (Cheng et al., 2009). Fibrous roots have an increased root abundance and larger surface area and are thought to be more successful at contaminant removal (Breen & Chick, 1995; Cheng et al., 2009; Kyambadde et al., 2004). Conversely, other studies have not found a significant difference in root morphology and contaminate uptake (Cheng et al., 2009).

Plants contain many cells, which serve various responsibilities and pathways throughout the plant. The apoplastic path moves water and dissolved minerals through extracellular spaces along cell walls. In contrast, the symplastic pathways move water and solutes along the cell walls. Finally, the transmembrane path moves dissolved minerals and water to other cells through the cell wall (Cronk & Fennessy, 2016).

5.1.3 The impact of flora on the chemistry of peatlands

Plants play an integral role in maintaining peatland ecosystem processes. However, communities can easily alter in response to climate change (Robroek et al., 2016). Plants provide many services that help maintain wildlife and biodiversity in the peatlands (Koretsky et al., 2007). Plant communities also change in response to ecosystem changes, which makes them as ecosystem monitors (Brown et al., 2009).

Macrophytes provide sinks for excess nutrients and carbon (Koretsky et al., 2007; Tarnocai, 2009) and play an essential role in the mobility and/or immobility of heavy metals (Vodyanitskii & Shoba, 2015) and nutrient cycle (Fennessy, 2001; Koretsky et al., 2007; Weis & Weis, 2004). The roots of macrophytes play an important role in a plant's ability to contain heavy metals (Schück & Greger, 2020). Vegetation growing on contaminated peat reduces erosion, which aids in protecting the contaminated peat below (Shuttleworth et al., 2017).

Macrophytes can alter peat oxidation with vertical redox stratification and the distribution of metals through several processes. Some macrophytes can release O₂ into the rhizosphere of plants, known as radial oxygen loss, which creates microclimates with altered chemistry, leading to the formation of iron plaques (Koretsky et al., 2007; Weis & Weis, 2004). Macrophytes also create a more compressed redox zone through respiration, which reduces electron receptors by producing primary productivity (Koretsky et al., 2007). Lastly, macrophytes influence chemistry through heavy metal uptake and release (Koretsky et al., 2007; Weis & Weis, 2004).

Plant communities in peatlands have been known to change in response to water levels (Zhong et al., 2020), nutrient cycles (Macrae et al., 2013), and heavy metals (Barrett & Watmough, 2015). Woody plants are generally more productive in unflooded peats; *Sphagnum* moss is more productive in wet conditions; and sedges are site-specific.

5.1.4 Root plaque, radial oxygen loss, and phytoremediation

In macrophytes, oxygen travels through the aerenchyma to the roots (Doležal et al., 2021; Davis, 2016), where it is depleted to the substrate surrounding the roots through diffusion; this is termed radial oxygen loss (ROL), which results in an increase of oxygen in the rhizosphere surrounding the substrate (Cronk & Fennessy, 2001). The rhizosphere includes an area of about 1mm

surrounding the roots (Pinto et al., 2014). The result is the oxygenation of the area surrounding the roots and rhizosphere, which increases the peat redox potential, and it varies depending on the root's oxygen levels, the permeability of roots, and the size of root mass (Cronk & Fennessy, 2001; Koncalova, 1990). Radial oxygen loss varies among species and is linked to morphological differences such as root-to-shoot ratio. It seems contradictory that a plant that may not receive sufficient oxygen is oxygenating the surrounding substrate of its roots, but plants benefit from this behaviour. Radial oxygen loss oxidizes the potentially toxic compounds in the rhizosphere (Art, 1983; Cronk & Fennessy, 2016; Yan et al., 2022; Yang et al., 2017). Root oxygenation also permits nitrifying bacteria to transform ammonia into nitrate (Cronk & Fennessy, 2001; Tolley et al., 1986). Radial oxygen loss prevents the uptake of heavy metals to the upper biomass by precipitating them as hydroxides on the root surface as plaques. The root plaque is positively correlated with tolerance to heavy metals and salinity (Yan et al., 2022). ROL plants have larger biomasses and metal accumulation abilities (Yang et al., 2017). Root plaques have been found with 5–10 times of the heavy metal concentration of the peats surrounding the roots (Weis & Weis, 2004). Sedges in peatlands, pod grass, and bogbean are fen species known to have aerenchyma (Davis, 2016).

5.2 Methodology

Vegetation density counts and plant sample collection occurred during summer.

5.2.1 Macrophyte and bryophyte density

Macrophytes and bryophyte densities were determined in replicates using 30 x 30 cm P.V.C. quadrants placed at the outer corner of 4 in situ pore water sampling devices and one in the center of the piezometer cluster. Macrophytes (plants) were identified and individually

counted in each quadrat—the bryophyte densities/percentage was determined within each quadrat using percent cover. A sample of bryophytes and sedges was brought to the laboratory for confirmed identification.

Population density of vascular plants, the number of individuals per unit area, was determined through the following calculation;

$$\text{Population Density} = \frac{\text{\# of individuals in each plot}}{\text{area sampled}}$$

Population size (in the fen studied) of vascular plants, the total number of plants, was determined using the following equation;

$$\text{Population Size} = \text{Population Density} \times \text{Total Area}$$

5.2.2 Heavy Metal content in plants

The five most abundant plant species, determined by the number of plants in the quadrat at each piezometer location, were chosen for heavy metal study. A minimum of three plants/species samples were chosen during the summer data collection. Both upper and lower biomass were collected at all sites for each plant. The collected plant samples were placed in plastic bags and stored in a cooler. Plants with inflorescences or seed heads were chosen to ensure they were mature. One species which grew at all three fens was collected from the three locations. Upon return, plants were placed in the refrigerator until processing. While processing, plants were washed with deionized water and separated into upper and lower biomass. The roots of one plant from each location were not washed with deionized water, and the peat was gently removed by hand. This was done to find out the root surface and rhizosphere influence on the heavy metal composition of the plant's lower biomass. Plants were dried to a constant weight in an incubator

at 50°C, ground, and sieved with 2 mm. mesh. They were stored in polyethene bags until they were sent to the LUEL laboratory in Thunder Bay. The plant material was analyzed using LUEL SOP#EL110 Total Metals in Biota Samples, which is based on the following references:

- E.P.A. method 1631b, Guide to total mercury analysis in sludge, peat and biota samples. Mars XPress Operation Manual. CEM Corp. Rev. 3, 2009.
- E.P.A. Method 3051A total metals in peat, peat and biota samples
- LUEL-ICP Operator Guide

5.2.3 Root Plaques

The presence and absence of root plaques were determined by visual confirmation through a Fisher dissection microscope and/or an Olympus compound microscope of an orange-brown coating on the root surface. Root plaques were given a score of 0-5 (no colour to dark brown/black) based on the colour of the plaques (Batty et al., 2000; Fan et al., 2023; Siqueira-Silva et al., 2012). For this study, elemental determination of plaques was considered but not used.

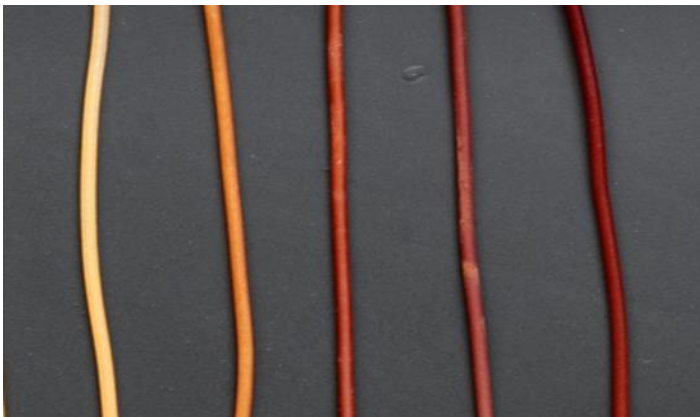


Figure 5.1. The figure above illustrates the scoring key. Roots were assigned scores based on their colour. Scores ranged from 0 to 5, as depicted in the image from left to right. Roots with no plaque received a score of 0, and very dark roots received a score of 5.

5.2.4 Bioconcentration Factors (BCF)

Bioconcentration Factor (BCF) estimates the heavy metal uptake capacity of plants. The BCF is the ratio of mean heavy metal concentration in the plant's upper and lower biomass compared to the peat's heavy metal concentration. A BCF of ≤ 1.00 means a plant can absorb but not accumulate heavy metals. A BCF of > 1.00 suggests that the plant may be able to accumulate heavy metals in its biomass (Chitimus et al., 2023; Liu et al., 2009). The BCF is calculated using the following equation.

$$BCF = C_{\text{Plant (mg/kg)}} / C_{\text{Peat (mg/kg)}}$$

Where $C_{\text{Plant (mg/kg)}}$ is the heavy metal concentration in the plant, and $C_{\text{Peat (mg/kg)}}$ is the heavy metal (X. Chen et al., 2023).

5.2.5 Translocation Factor

The translocation Factor (TF) is the ratio of heavy metal between the aerial parts of the plant (upper biomass) and the roots (lower biomass) of the plant. A translocation Factor ≥ 1 means the plant may be a hyperaccumulator and perform phytoextraction. The translocation factor was calculated to estimate the transfer of heavy metals from roots to shoots of $TF=(C_{\text{shoot}}/C_{\text{root}})$ (Islam et al., 2020).

$$TF = \frac{\text{Plant Upper Biomass}}{\text{Plant Lower Biomass}}$$

Where $C_{\text{Upper Biomass}}$ is the concentration in the upper biomass of the plant and $C_{\text{Lower Biomass}}$ is the concentration in the lower biomass of the plant. A translocation factor greater than 1 indicates that the plant can translocate the heavy metal from the roots to the shoots (Islam et al., 2020).

5.3. Results

5.3.1 Plant Sequestration of Heavy Metals

This chapter investigates the accumulation and distribution of heavy metals in plants growing in three different fens. Bioconcentration factors (BCF) were calculated to understand the plants' capacity to accumulate heavy metals from peat and water, revealing notable differences across sites and species. Additionally, the study examined the translocation of metals within the plant biomass and the influence of rhizosphere processes and the formation of root plaques on metal retention, thus providing insights into the mechanisms of phytoremediation in fen wetland environments.

5.3.2 Macrophyte Density and Richness

Macrophyte density was measured at the midpoints of the fens at the two sampling locations and five 30cm x 30cm quadrats. The findings suggest that the density varied significantly among the fens ($F=36$, $p<0.001$). The plant density was lowest at LM (50/ft²), and the species richness was 15. Site SS had the greatest density at 116/ft², with the lowest species richness of 11. In contrast, the density at MW was 63/ft² and species richness averaged 15.

5.3.3 Root Plaques

Root plaques were scored on a scale of 0-5 (Fig. 5.1), with 0 being absent and 5 being very dark, almost black; this was done to indicate the strength of the formation of iron plaques on the roots (Batty et al., 2000; Fan et al., 2023; Kjellberg, 1998; Sand-Jensen, 2008; Siqueira-Silva et al., 2012). Plants growing in SS accumulated fewer plaques ($F=20.5$, $P<0.001$, $Z=4.419$, $P<0.001$) than those growing in LM and MW ($Z=3.11$, $P<0.001$). The root plaques on plants in MW varied

scores from 2 to 5, while the plants growing in LM had root plaques scores of 4 or 5. Kruskal Wallis and Dunn's tests were used to determine the significance of the root plaques to the uptake of the heavy metals of concern. The presence of plaques was significant in the uptake of several metals ($F=10.4$, $P=0.0155$), including inhibiting the uptake of As ($F=11$, $P=0.011$, $Z=-2.9$, $P=0.02238$) and enhancing the uptake of Ni ($F=11$, $P=0.009$, $Z=2.705$, $P=0.0341$) and Zn ($F=11.0$, $P=0.011$, $Z=3.09$, $P=0.0718$).

5.3.4 Heavy metal uptake by plants

5.3.4.1 Plants studied for heavy metals:

The following plants from the three fens were studied for their potential to sequester heavy metals (Table 5.1). The plants were selected based on their prevalence in the wetlands (from the density measurements in the fens). Heavy metal concentrations were measured from the upper and lower biomass of all plants and the rhizosphere of three plants. The lower biomass (roots) was analyzed both with and without washing to study the role of the rhizosphere in sequestering heavy metals.

Table 5.1. Plants studied for heavy metals and the properties assessed in each of the three study locations

Site	Plant	Upper & Lower Biomass	Washed	Unwashed/ Rhizosphere	Plaques
Langman (LM)	<i>T. palustris</i>	Both	Yes	No	Yes
	<i>A. polifolia</i>	Both	Yes	Yes	Yes
	<i>C. calyculata</i>	Both	Yes	No	Yes
	<i>M. gale</i>	Both	Yes	No	Yes
	<i>C. canadensis</i>	Both	Yes	No	Yes
Minesing (MW)	<i>P. americanus</i>	Both	Yes	No	Yes
	<i>M. gale</i>	Both	Yes	No	Yes
	<i>C. mariscoides</i>	Both	Yes	Yes	Yes
	<i>E. quinqueflora</i>	Both	Yes	No	Yes
	<i>M. trifoliata</i>	Both	Yes	No	Yes
Muskoka (SS)	<i>E. virginicum</i>	Both	Yes	Yes	Yes
	<i>C. calyculata</i>	Both	Yes	No	Yes
	<i>M. gale</i>	Both	Yes	No	Yes
	<i>C. trisperma</i>	Both	Yes	No	Yes
	<i>R. alba</i>	Both	Yes	No	Yes
	<i>Sphagnum spp.</i>	Upper	Yes	No	No

The maximum concentration of arsenic in plants before it becomes harmful is 20 mg/ kg, and 5 mg/kg is the normal concentration in plants (Hajar et al., 2014). Although arsenic concentrations in plants in this study were often BDL (below the detectable limit), arsenic was found in four plants (Fig. 5.2 A, B, C). Arsenic was only found in the lower biomass of plants, and the highest concentration was in *Eleocharis quinqueflora*. (1.66 ug/g) from MW. Also, from MW, *Cladium mariscoides* was found to have a concentration of 0.71 ug/g in the lower biomass, and *Myrica gale* had 0.69 ug/g in the lower biomass. Only one plant at LM was found to have a concentration of As above BDL, which was *Calamagrostis canadensis* (0.69 ug/g).

Cadmium is harmful to plants between 5-30 mg/kg (Hajar et al., 2014), with 0.02 mg/kg being the harmless concentration (Osmani et al., 2015). Cadmium was accumulated in several studied plants (Fig. 5.2 A, B, C). The highest concentration of Cd was found in the lower biomass of *M.*

gale from SS (0.231 ug/g), *M. gale* in MW had the lowest concentration at 0.077 ug/g, whereas in *M. gale* at LM, it was at BDL. Cadmium was not found at levels above the detectable limit in the upper biomass of any plant. However, it was found in the *Sphagnum* moss (0.106 ug/g).

The range of Chromium in plants is 0.006-18 mg/kg, with a harmless concentration at 1.3 mg/kg (Hajar et al., 2014; Osmani et al., 2015). Chromium was found in the upper and lower biomass of all plants in the study. *Phragmites americanus*, found in MW, had the highest concentration, with 2.7 ug/g in the lower biomass and 0.93 ug/g in the upper biomass (Fig. 5.2 a, b, c). *C. mariscoides*, also found at MW, accumulated the second-highest chromium concentration with 1.4 ug/g in the lower and 0.25 ug/g in the upper biomass. The lowest chromium concentration was found in *Menyanthes trifoliata* upper biomass (0.071 ug/g), also from site MW.

The harmless level of copper in plants is 10 mg/kg, with severe toxicity occurring at 60 mg/kg (Hajar et al., 2014). Copper was accumulated by the plants and was translocated to the upper biomass by all plants in the study (Fig. 5.2 A, B, C). The plants with the highest concentration were *Chamaedaphne calyculata* in SS, with 12.18 ug/g of copper distributed between the upper and lower biomass, and *C. mariscoides* from MW, with 9.17 ug/g concentration. The lowest concentration of copper was in *C. calyculata* at LM and *P. americanus* at site MW.

A nickel concentration of 10 mg/kg is the average concentration in plants (Osmani et al., 2015). Nickel was often found at BDL in the studied plants (Fig. 5.2 A, B, C). High nickel concentrations were found in the lower biomass of plants from MW, *C. mariscoides* (1.67 ug/g) and *P. americanus* (1.56 ug/g). Nickel was not found in plants from LM.

The critical limit for lead in plants is 2 mg/kg (Osmani et al., 2015). In the present study, *Eleocharis* sp. (site MW) had the highest concentration of Pb (5.54 ug/g). In fact, all plants at

MW were found to sequester lead (Fig. 5.2 A, B, C). Three of the plants in SS sequestered Pb in their lower biomass. The lowest value of Pb was recorded in *C. canadensis* (1.03 ug/g), the only plant at LM to sequester lead above BDL. Detectable levels of lead were always found in the lower biomass of plants in this study.

Table 5.2 The heavy metal concentrations within the upper and lower biomass of each plant (ug/g) and the mean concentration in the peat (ug/g). Also listed are the calculated BCF and TF values for each plant

Plant & Site	Component	Arsenic ug/g	Cadmium ug/g	Chromium ug/g	Copper ug/g	Nickel ug/g	Lead ug/g	Zinc ug/g
<i>T. palustris</i> LM	Upper Biomass	0	0	0.17	2.49	0	0	11.12
	Lower Biomass	0	0.11	0.18	1.93	0	0	19.4
	Peat	4.57	0.7	1.8	6.43	4.12	40.17	54.25
	BCF	0	0.16	0.2	0.69	0	0	0.56
	TF	0	0	0.92	1.28	0	0	0.57
<i>A. polifolia</i> LM	Upper Biomass	0	0	0.28	2.01	0	0	16.71
	Lower Biomass	0	0.09	0.55	3.51	0	0	10.25
	Peat	4.57	0.7	1.8	6.43	4.12	40.17	54.25
	BCF	0	0.12	0.46	0.86	0	0	0.5
	TF	0	0	0.51	0.59	0	0	1.63
<i>C. calyculata</i> LM	Upper Biomass	0	0	0.18	1.37	0	0	17.82
	Lower Biomass	0	0	0.34	1.06	0	0	11.09
	Peat	2.3	0.23	1.07	4.04	2.14	8.06	18.37
	BCF	0	0	0.48	0.6	0	0	1.57
	TF	0	0	0.51	1.3	0	0	1.61
<i>M. gale</i>	Upper Biomass	0	0	0.27	1.22	0	0	35.31
	Lower Biomass	0	0	0.27	2.66	0	0	18.41
	Peat	4.57	0.7	1.8	6.43	4.12	40.17	54.25
	BCF	0	0	0.3	0.6	0	0	0.99
	TF	0	0	0.99	0.46	0	0	1.92
<i>C. canadensis</i>	Upper Biomass	0	0	0.25	1.48	0	0	11.34
	Lower Biomass	0.69	0	0.33	1.84	0	0	17.72
	Peat	2.3	0.23	1.07	4.04	2.14	8.06	18.37
	BCF	0.3	0	0.55	0.82	0	0	1.58
	TF	0	0	0.75	0.81	0	0	0.64
<i>P. americanus</i> MW	Upper Biomass	0	0	0.99	1.09	0	0	15.94
	Lower Biomass	0	0	0.93	1.31	0.96	2.94	19.25
	Peat	2.5	0.43	1.57	3.8	3.47	19.75	21.1

	BCF	0	0	1.22	0.63	0.28	0.15	1.67
	TF	0	0	1.07	0.83	0	0	0.83
<i>M. gale</i>	Upper Biomass	0	0	0.09	1.31	0	0	21.26
MW	Lower Biomass	0.69	0.08	0.19	1.66	0	1.16	16.52
	Peat	2.5	0.43	1.57	3.8	3.47	19.75	21.1
	BCF	0.28	0.18	0.18	0.78	0	0.06	1.79
	TF	0	0	0.48	0.79	0	0	1.29
<i>C. mariscoides</i>	Upper Biomass	0	0	0.14	1.97	0	0	12.61
MW	Lower Biomass	0.71	0.13	0.24	7.2	0	4.07	25.27
	Peat	2.5	0.43	1.57	3.8	3.47	19.75	21.1
	BCF	0.28	0.3	0.25	2.41	0	0.21	1.8
	TF	0	0	0.58	0.27	0	0	0.5
<i>E. quinqueflora</i>	Upper Biomass	0	0	1	1.22	0	0	30.09
MW	Lower Biomass	1.66	0.14	0.8	2.03	0.87	5.54	25.75
	Peat	2.43	0.45	1.73	4.26	3.36	21.12	19.96
	BCF	0.68	0.31	1.04	0.76	0.26	0.26	2.8
	TF	0	0	0.75	0.36	0	0	0.95
<i>M. trifoliata</i>	Upper Biomass	0	0	1	2.07	0	0	39.6
MW	Lower Biomass	0	0	0.1	5.82	0	2.29	41.64
	Peat	2.43	0.45	1.73	4.26	3.36	21.12	19.96
	BCF	0	0	0.63	1.85	0	0.11	4.07
	TF	0	0	1.26	0.6	0	0	1.17
<i>E. virginicum</i>	Upper Biomass	0	0	0.1	2.51	0	0	30.39
SS	Lower Biomass	0	0	0.29	3.31	0	0	29.44
	Peat	1.95	0.24	0.64	2.51	2.02	7.93	23.84
	BCF	0	0	0.61	2.32	0	0	2.51
	TF	0	0	0.35	0.76	0	0	1.03
<i>C. calyculata</i>	Upper Biomass	0	0.07	0.17	2.35	0	0	32.92
SS	Lower Biomass	0	0.21	0.4	4.92	1.32	2.12	38.17
	Peat	1.95	0.24	0.64	2.51	2.02	7.93	23.84
	BCF	0	1.15	0.89	2.89	0.65	0.27	2.98
	TF	0	0.35	0.41	1.47	0	0	0.86
<i>M. gale</i>	Upper Biomass	0	0.08	0.16	2.62	0	0	60.78
SS	Lower Biomass	0	0.23	0.08	1.66	0	1.83	47.6
	Peat	3.81	0.77	1.95	4.71	5.03	43.59	35.41
	BCF	0	0.41	0.12	0.91	0	0.04	3.06
	TF	0	0.35	2.01	1.58	0	0	1.28
<i>C. trisperma</i>	Upper Biomass	0	0	0.21	2.25	0	0	38.11
SS	Lower Biomass	0	0	0.21	3.8	0	0	31.96
	Peat	3.81	0.77	1.95	4.71	5.03	43.59	35.41
	BCF	0	0	0.21	1.28	0	0	1.98

	TF	0	0	1.01	0.59	0	0	1.19
<i>R. alba</i>	Upper Biomass	0	0	0.21	2.25	0	0	27.89
SS	Lower Biomass	0	0.13	0.48	3.48	0.87	1.54	33.5
	Peat	3.81	0.77	1.95	4.71	5.03	43.59	35.41
	BCF	0	0.17	0.35	1.21	0.17	0.04	1.73
	TF	0	0	0.43	0.65	0	0	0.83
<i>Sphagnum</i>	Upper Biomass	0	0.11	0.38	2.79	0	0	19.05
SS	Lower Biomass	0	0.11	0.38	2.79	0	0	19.05
	Peat	1.95	0.24	0.64	2.51	2.02	7.93	23.84
	BCF	0	0.03	0.24	0.65	0	0	0.49

All plants in the study accumulated zinc in the upper and lower biomass (Table 5.2). Zinc concentration in plants is generally between 1 and 160 mg/kg (Hajar et al., 2014). A high zinc concentration was found in *M. gale* at SS (60.78 ug/g upper & 47.6 ug/g lower biomass). *M. trifoliata* at MW also had high concentrations (44.61 ug/g in the upper and 39.6 ug/g in the lower biomass). Plants from LM had less concentration overall, while those at SS had the highest concentrations.

5.3.5 Bioconcentration Factor (BCF)

The Bioconcentration factor was calculated for each heavy metal and plant, using the total concentration in the upper biomass and the gently washed lower biomass, divided by the total concentration in the peat and water. This was done to determine which plants have a greater tendency to accumulate the heavy metals of concern focused on in this study. In addition to the washed upper and lower biomass portions of plants, samples of the lower biomass of three unwashed plants were also analyzed for the heavy metals. The unwashed lower biomass of plants was prepared by gently cleaning the roots by hand but not with water. This was done to determine the concentration of the heavy metals in the rhizosphere root zone that might have been adsorbed to the outside surface of the roots through rhizostabilization processes. In addition

to analyzing the washed upper and lower biomass portions of plants, samples of the unwashed lower biomass from three plants were also examined for heavy metals. Thus, BCF was calculated for both the washed and unwashed roots of *Andromeda polifolia*, *C. mariscoides* and *Eriophorum virginicum*.

The BCF calculations highlighted that all plants in the study were moderate to high accumulators of the studied heavy metals. Plants at LM had the lowest BCF values of the heavy metals among the three sites ($F=8.18, p=0.0167$, Fig. 5.3). Plants at MW had the highest BCF value when compared to plants from LM and SS. The plant with the lowest total BCF value was *Thelypteris palustris* at LM. In contrast, the plant with the highest BCF value was *C. calyculata* at site SS, which accumulated almost double the copper concentration compared to other plants.

Figures 5.2 & 5.3 show that plants have different accumulation factors based on locations. *C. calyculata* was studied in two sites. In site SS, *C. calyculata* had higher BCF values than at LM. Similarly, *M. gale*, examined at all three sites, had a higher BCF in MW and SS than at LM. MW had the largest number of plants with high Bioconcentration factors (Fig.5.4). *Eleocharis quinqueflora* (site MW) was the only plant to accumulate all the studied heavy metals. However, it did not have the highest BCF value. *C. calyculata* from SS had the highest BCF values and accumulated all the studied heavy metals except arsenic (Fig.26). *M. gale* at LM accumulated the least heavy metals (copper, chromium and zinc) and had the second-lowest BCF value.

In this study, arsenic was the heavy metal which plants sequestered the least (Fig. 5.2 & Fig. 5.3). It was present in peats from all sites but not sequestered by any plants at SS. Only *C. canadensis* sequestered arsenic at LM, while at MW, *M. gale*, *C. mariscoides*, and *Eriophorum* spp. were found to sequester arsenic moderately. The Bioconcentration factor (BCF) of arsenic in

C. mariscoides increased from 0.28 to 0.37 when the heavy metals in the root rhizosphere zone were included.

Cadmium was found sequestered in low to moderate levels in several plants at all sites (Fig. 5.2 & Fig 5.3). Site LM had the fewest plants which sequester cadmium. *T. palustris* moderately sequestered cadmium, and both unwashed and washed samples of *A. polifolia* sequestered cadmium at a low level (Fig.5.5). At MW, *Eriophorum* spp. and *C. mariscoides* moderately sequestered cadmium, while *M. gale* was a low accumulator. Many plants except *Carex trisperma* and *E. virginicum* at site SS were found to be low to moderate accumulators of cadmium. *C. calyculata* from site SS was the only high accumulator of Cadmium (BAF 1.15).

All plants in the study sequestered chromium (Fig. 5.2 & Fig. 5.3). Two plants, *M. trifoliata* and *E. virginicum*, were found to be low chromium accumulators. In contrast, all other plants were found to be moderate chromium accumulators except *P. americanus* (BCF 1.22) and *E. quinqueflora* (BAF 1.04), which were found to be high chromium accumulators.

Copper was accumulated either moderately or highly in all plants in this study (Fig. 5.2 & Fig 5.3). *C. calyculata* (BCF 2.89) in SS recorded the highest BCF. In contrast, *C. calyculata* and *A. polifolia* in LM had the lowest BCF (BCF 0.6). The difference in copper BCF between washed and unwashed roots in *E. virginicum* was quite notable (Fig.5.3). Washed roots had a moderate BCF of 0.42. In contrast, the copper BCF for the unwashed roots was 1.36, making *E. virginicum* a high accumulator. All plants from LM were moderate accumulators. A rank sum test using Kruskal Wallis followed by a Dunn test suggested that there is a significant difference in the BCF values of copper between fens ($F=6.65$, $p=0.0359$), specifically between LM and SS ($Z=-2.57$, $p=0.0297$). In addition, a significant difference was found between the uptake of copper by the upper biomass in each fen ($F=9.85$, $p=0.007$), particularly between LM and SS ($Z= -2.39$,

p=0.033) and MW and SS ($Z = -2.89$, $p = 0.112$). No significant difference in copper was found in the unwashed lower biomass of plants from different sites. A rank sum test using Kruskal Wallis followed by a Dunn test suggested that there is a significant difference in the BCF values of copper between fens ($F = 6.88$, $p = 0.032$), specifically at LM and MW ($Z = -2.55$, $p = 0.0286$)

Nickel was not accumulated by any plants collected from LM (Fig 5.2 & Fig. 5.3). However, the unwashed roots of *A. polifolia* showed a low accumulation, suggesting the possibility that rhizofiltration processes are occurring in this plant (BCF 0.02) (Fig.28). At MW, two plants were found as moderate accumulators of Nickel. However, like *A. polifolia*, *C. mariscoides* at MW did not accumulate nickel within the roots but showed a moderate concentration in the rhizosphere, which suggests that the plant may be using rhizofiltration processes. Two SS were moderate accumulators, including *C. calyculata* (BCF 0.65), which accumulated the highest nickel concentration.

Similar to nickel, no plant from LM accumulated lead. However, *A. polifolia* was a low accumulator when the concentration in the rhizosphere was included (Fig. 5.2). All plants at MW accumulated lead. The highest BCF at MW was found in *E. quinqueflora*. (BCF 0.26). Lead accumulation by plants at SS was either absent or low, except by Leatherleaf (BCF 0.27). A rank sum test using Kruskal Wallis followed by a Dunn test suggested that there is a significant difference in the BCF values of copper between fens ($F = 8.68$, $p = 0.013$), specifically between LM and MW ($Z = -2.94$, $p = 0.009$). In addition, a significant difference was found between the fens when comparing the concentration sequestered by the lower biomass ($F = 11.7$, $p = 0.002$). Further investigation using the Dunn test indicated MW differed most significantly from other sites (LM-MW $Z = -3.04$, $p < .001$, MW-SS, $Z = 2.77$, $p = 0.01$).

Zinc was highly accumulated in all plants at MW. At LM and SS, the BCF of Zinc varied among the plants, with the highest BCF in *M. trifolia* at MW (BCF 4.07) and the lowest in *Sphagnum* and *A. polifolia* (BCF 0.50) (Fig. 5.2 & Fig. 5.3), indicating that this plant did not accumulate enough zinc to be considered an accumulator. Further investigation indicated a significant difference between the uptake by the lower biomass of plants at LM versus the other sites (MW; $Z=-2.33, p=0.03, SS; Z=-3.97, p<0.001$)

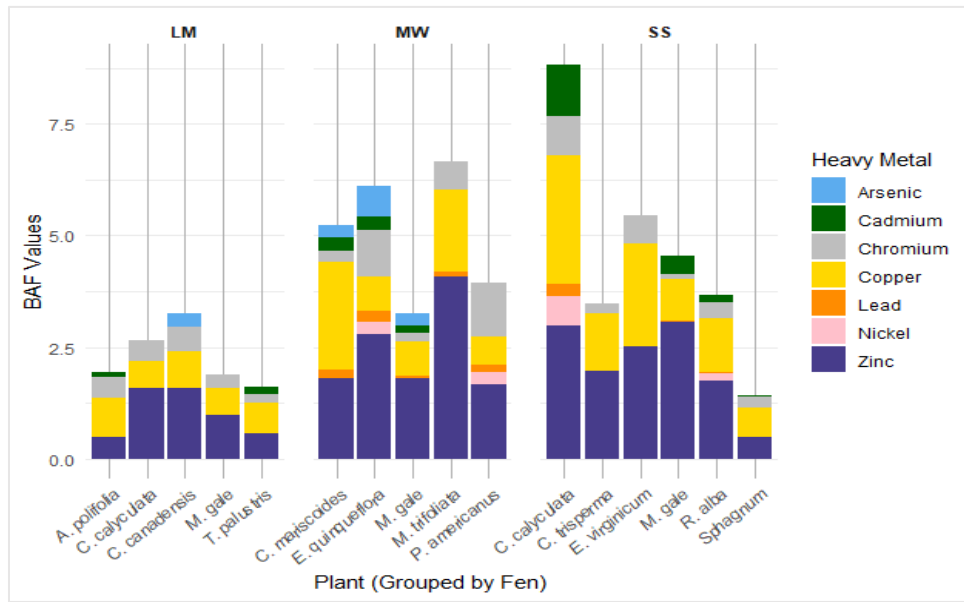


Figure 5.2. The BCF values of seven heavy metals in plants at three sites. Site LM's total BCF values are significantly lower than the plants at MW and SS ($p<0.001$).

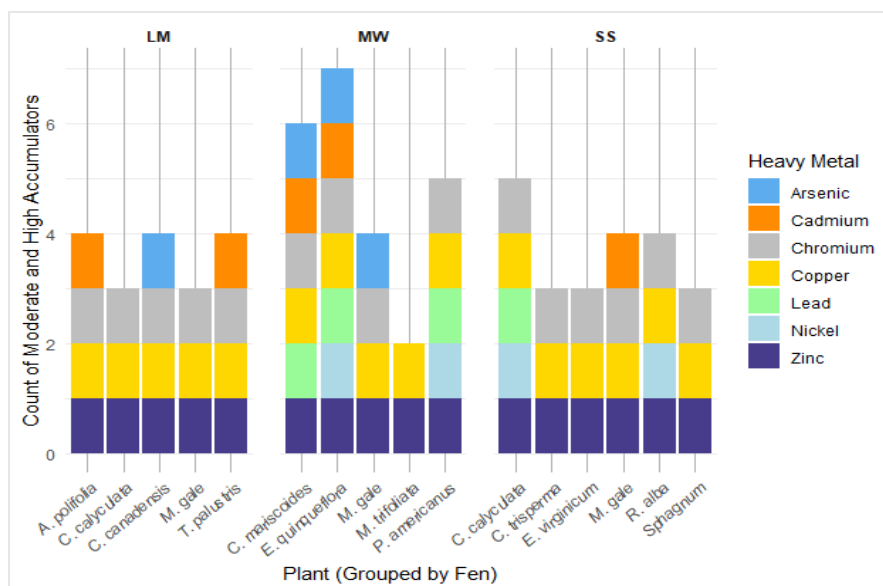


Figure 5.3. The figure above depicts the number of moderate and high accumulator BCF values for each plant. Site MW has the greatest number of plants with moderate and high accumulations of the heavy metals of concern. In contrast, site SS has the lowest number of moderate and high accumulators. It can be seen that plants at site MW accumulate a great variety of heavy metals, while plants at site LM accumulate the least.

5.3.6 Plant Rhizosphere

The rhizosphere of plant roots, the interface between plant and peat, is only a few microns in thickness (Wen et al., 2018) but plays a crucial role in immobilizing heavy metals and other pollutants through a process known as rhizostabilization. Although heavy metals are not sequestered in the plant biomass, this phytoremediation mechanism retains them via adsorption in the rhizosphere root zone. Washed and unwashed roots were analyzed for heavy metal concentrations, and the comparison can be seen in Fig. 5.4; the comparison of the washed and unwashed roots of *C. mariscoides* (site MW) and *E. virginicum* (site SS) indicates a distinct difference in the concentration of heavy metals. Whereas there was very little difference between the concentration of heavy metals on the roots of the washed and unwashed *A. polifolia* at LM. These results suggest that *E. virginicum* and *C. mariscoides* use rhizostabilization as a

mechanism to sequester heavy metals. However, a Wilcoxon rank sum test indicated no significant difference between heavy metal accumulation of washed and unwashed roots. The insignificance in results may be due to the smaller number of unwashed roots used in the study.

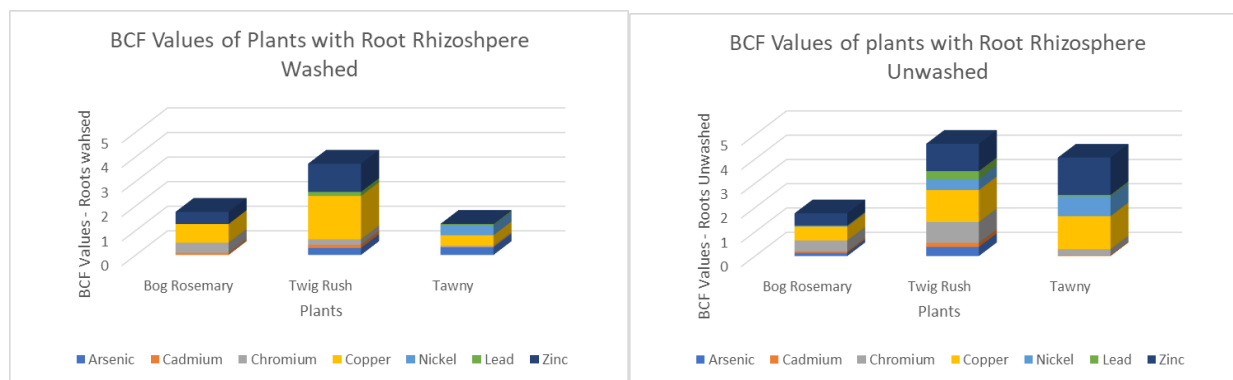


Figure 5.4. The BCF values for plants with roots washed in deionized water vs. those unwashed. When concentrations within the rhizosphere were included, a greater number of heavy metals were found with higher concentrations.

5.3.7 Translocation Factor

The translocation factor (TF) measures the concentration ratios of heavy metals in the upper biomass (above ground) compared to the lower biomass (below ground) portions of the plant. Translocation factors with values above one indicate that the plant primarily sequesters heavy metals in the upper biomass, categorizing it as an extractor. The heavy metals chromium, copper, and zinc were translocated to the upper biomass of several plants with a translocation factor greater than 1 (Fig. 5.5). Additionally, a Wilcoxon rank test found Cd and Cr to significantly differ in the concentrations between the upper and lower biomass of plants (Cd, $p=0.003$ & Cr, $p=0.015$). The translocation of heavy metals to the upper biomass was more prevalent in plants at SS, with a value of >1 for several heavy metals (7 TFs >1). MW had the lowest number of heavy metals with a translocation factor >1 (4 TFs >1). This trend was also observed when other heavy

metals were included (Fig. 5.7). Zinc was the most frequently translocated heavy metal, with nearly half of the plants studied exhibiting TFs greater than 1. Copper was also commonly translocated; interestingly, copper was detected in *C. calyculata* at SS and LM, *M. gale* at SS and *T. Palustris* at LM, but not in plants from MW.

Arsenic, nickel and lead were not found to have TF's>1 in any plants in the study. A Wilcon rank test found a significant difference in the concentrations of heavy metals between the upper and lower biomass with Ni ($p=0.024$) and Pb ($p<0.001$). Chromium was translocated in minimal amounts in two plants from SS (*C. mariscoides* & *Carex trisperm*) and two from MW (*P. americanus* & *E. quinqueflora*).

The plant with the greatest number of heavy metals with TF>1 was *M. gale* in SS (Fig.5.5), which translocated three heavy metals, chromium, copper, and zinc. However, *M. gale* growing in LM and MW had only one heavy metal (Zinc) with a TF>1. In MW, the *M. gale* had a combined TF value of 5 for several heavy metals, while the combined TF value of heavy metals in *M. gale* at LM was 3.5. Thus, various plants uptake and translocate heavy metals differently through their biomass.

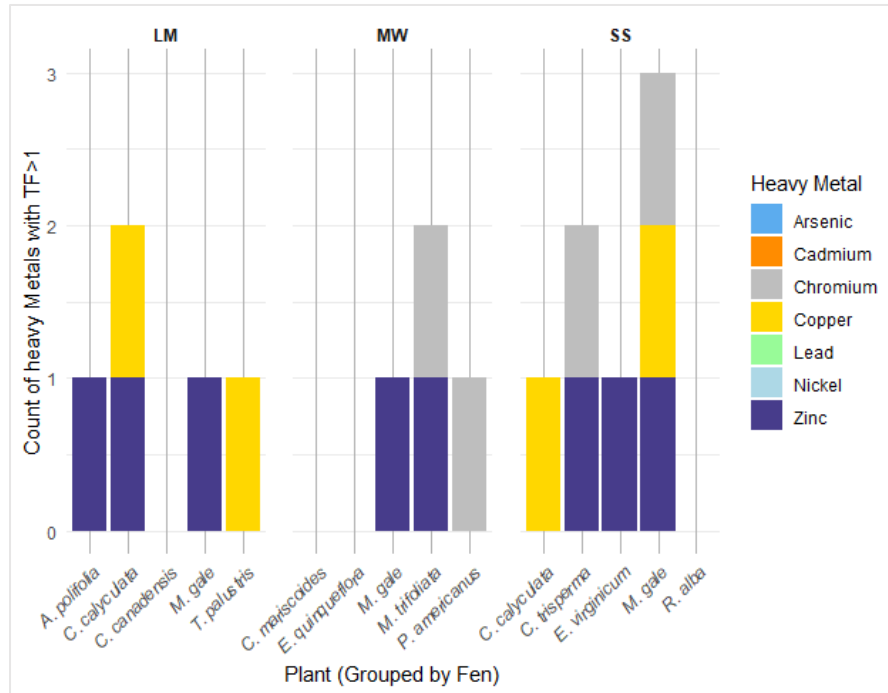


Figure 5.5. The heavy metals in plants with translocation factor >1.

The translocation patterns observed in the heavy metals of concern were consistent across all heavy metals tested (see Fig. 5.6). In Muskoka, plants were found to translocate 11 of the 18 metals analyzed, while plants in MW translocated only seven. Specifically, in addition to chromium, copper, and zinc, the plants did not translocate aluminum, cobalt, titanium, or vanadium to the upper biomass, with a translocation factor of less than 1.

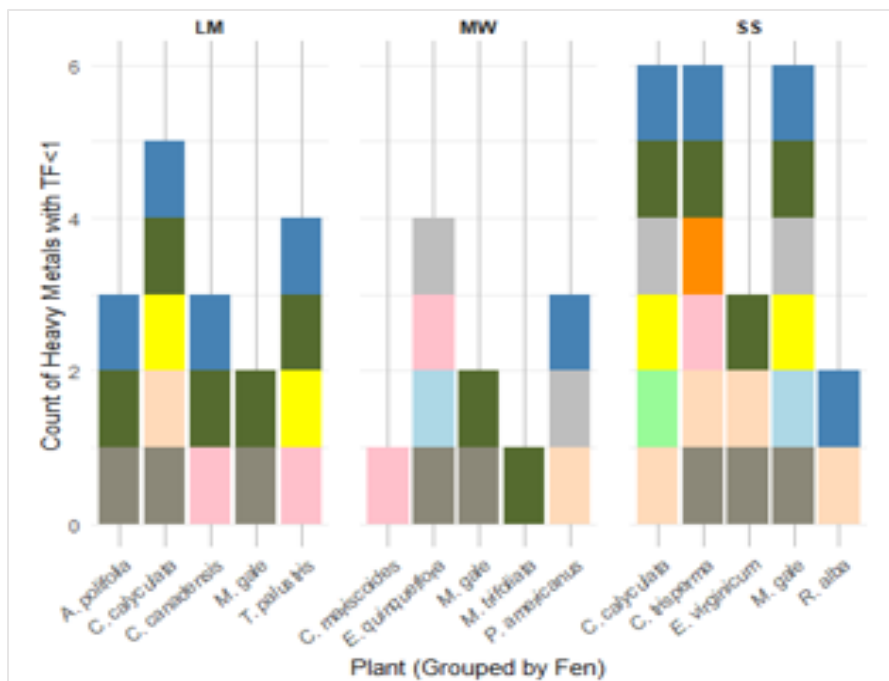


Figure 5.6. Translocation factors > 1 for 18 metals. Plants in site MW translocated the least number of heavy metals to the upper biomass, while plants in site SS transferred the greatest number of heavy metals to the upper biomass.

5.3.8 Principle Component Analysis

A PCA was performed on the plant data to understand the relationships between the heavy metal and other properties of the plants (Fig. 5.7). The PCA scree plot suggested that 22.9% of the variation is explained by PC1 and 15.5% by PC2. Plants in PC1 are strongly associated with Al, Fe, Ti, Si, and Ni and negatively with P and Mg in plants with plaques. PC2 is associated moderately with Ba, Cd, Mn, and Se and strongly and negatively associated with Ba, K, and S. Site MW had the most variability and is associated positively with PC1 and PC2 and site SS is negatively associated with PC1 and PC2. Plants at LM had the least variability in uptake and were negatively associated with PC1. This PCA also tells how the sequestering of heavy metals differs between the upper and lower biomass, as depicted in Fig. 5.8b. Heavy metals in the upper biomass are negatively associated with PC1 and evenly with PC2. The metals in the lower

biomass are more evenly distributed, with a slight increase towards the metals on the positive side of PC1.

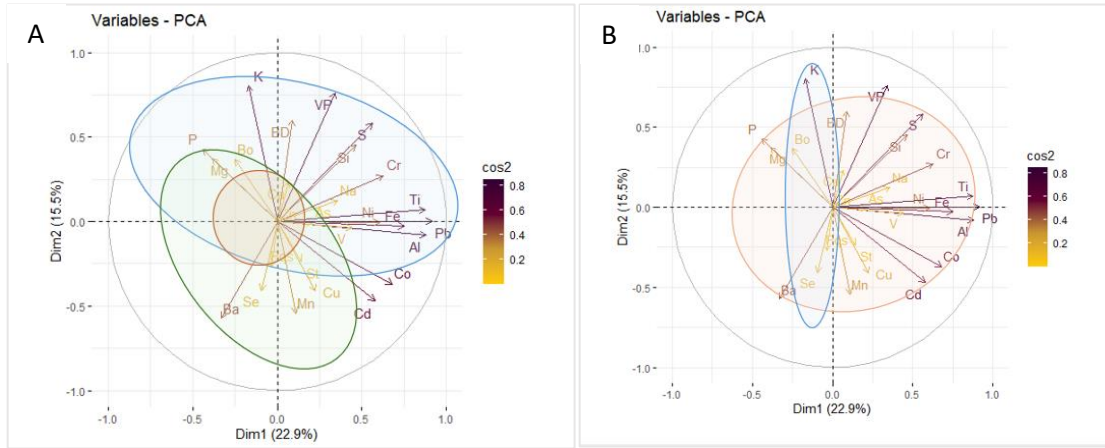


Figure 5.7 A & B. The above elliptical PCA demonstrates the associations between plant heavy metals and peat, water properties and root plaques. In Figure “a,” the red ellipse represents the plants in LM, the blue represents site MW and the green represents site SS. BD stands for Bulk density, VP for humification, and Pqs for root plaques. Plants in MW have greater variations of heavy metals, whereas those in LM have fewer variations. Plants in MW have a greater positive association with PC1, whereas LM has a greater negative association. Site SS is highly associated with PC2. The coloured numbers represent the plants in each site. In Figure “b,” the red ellipse represents the lower biomass, and the blue ellipse represents the upper biomass. The upper biomass has fewer variations of the metals.

5.3.9 Correlation Coefficient

The heavy metals within the plants were further examined by calculating correlation coefficients, which were done to examine the relationships between the sequestered heavy metals within the plants (Table 5.2). No significant correlations were found between Cr, Cu or Zn and the uptake of other heavy metals.

An additional correlation coefficient matrix was analyzed, focusing on the heavy metals present in water, peat, and plants (see Table 5.3). To differentiate among the three sites, heavy metals in plants were identified by their abbreviations, those in peat were designated by their abbreviations followed by "peat," and those in water were indicated by their abbreviations followed by “H₂O.”

The results were quite surprising; the majority of the heavy metal uptake in plants was interrelated, with only the concentrations of Ni and Zn in water showing a correlation with the uptake of heavy metals in plants. Notably, the relationship between metal sequestration in plants and their concentrations in peat and water was unique (refer to Table 5.3). The correlation coefficient revealed that the concentration of heavy metals in plants was unrelated to the concentrations of the same heavy metals in either peat or water.

Table 5.3. The relationships between heavy metals within the plant and heavy metals in the peat, water, and other parts of the plant.

Metal	Metal	R ² value	P value
As Lower Biomass	Fe Lower Biomass	0.92	<0.001
Cd Lower Biomass	Co Lower Biomass	0.79	0.047
Cd Upper Biomass	Al Lower biomass	0.82	0.044
Cd Upper Biomass	Fe Upper Biomass	0.81	0.022
Ni Total Plant	Pb Total Plant	0.68	0.008
Ni Total Plant	Ti Total Plant	0.72	<0.001
Ni Lower Biomass	Al upper Biomass	0.79	<0.001
Pb Total Plant	Ti Total Plant	0.84	<0.001
Pb Total Plant	Fe Total Plant	0.81	<0.001
Zn Upper Biomass	Na H2O	0.64	0.039

Table 5.4. Correlation coefficients between the measured biogeochemical factors within the fen. No significant relationships were found between heavy metals in the plants and root plaques or bulk density.

Metal or peat property	Metal or peat property	R ² value	P value
Dissolved Oxygen	Von Post	0.91	<0.001
Dissolved Oxygen	pH	0.82	0.016
Dissolved Oxygen	Cr Peat	0.83	0.013
Von Post	Bulk Density	0.84	0.008
Von Post	Dissolved Oxygen	0.88	<0.001
pH	Cd H2O	-0.88	<0.001
pH	Cr H2O	-0.91	<0.001
pH	Cr Peat	0.89	<0.001
pH	Cu Peat	0.81	0.022
pH	Von Post	0.77	<0.001
pH	DOC	-0.79	<0.001
As Lower Biomass	Fe Lower Biomass	0.92	<0.001
As Plant	Fe	0.95	<0.001
As Peat	Cd Peat	0.80	0.042
As Peat	K Peat	-0.88	0.002
As Peat	Pb Peat	0.87	<0.001

As Peat	St Peat	0.85	0.005
Cd Lower Biomass	Al Lower Biomass	0.82	0.019
Cd H2O	As Peat	-0.75	<0.001
Cd H2O	Cr H2O	0.99	<0.001
Cd H2O	Nitrates	0.71	0.002
Cd H2O	K Peat	0.84	0.015
Cd H2O	Ca Peat	-0.97	<0.001
Cd H2O	BD	-0.94	<0.001
Cd Lower Biomass	Co Lower Biomass	0.79	0.047
Cd Peat	K Peat	0.84	0.026
Cd Peat	K Peat	0.84	0.017
Cd Peat	Ni Peat	0.93	<.001
Cd Peat	Pb Peat	0.96	<0.001
Cd total plant	Co plant	0.79	<0.001
Cd Upper Biomass	Al Lower biomass	0.82	0.044
Cd Upper Biomass	Fe Upper Biomass	0.81	0.022
Cr H2O	Ba H2O	-0.83	0.011
Cr H2O	T Phos	0.65	0.029
Cr H2O	Nitrates H2O	0.75	<0.001
Cr Peat	Cr H2O	-0.81	0.026
Cr Peat	Ca H2O	0.81	0.025
Cr Peat	Nitrates H2O	-0.67	0.014
Cr Peat	TPhos H2O	-0.80	<0.001
Cu H2O	S H2O	0.83	0.03
Cu Peat	Ba H2O	0.87	<0.001
Cu Peat	Cd H2O	-0.76	<0.001
Cu Peat	As Peat	0.71	0.002
Cu Peat	Cd Peat	0.68	0.007
Zn Upper Biomass	Na H2O	0.64	0.039
Na Peat	Pb H2O	.85	0.014
Ni Peat	Ti Peat	0.87	0.004
Ni Peat	St Peat	0.88	0.003
Ni Peat	Pb Peat	0.83	0.043
Ni Peat	Pb H2O	0.85	0.014
Ni Total Plant	Pb Total Plant	0.68	0.008
Ni Total Plant	Ti Plant	0.72	0.001
Ni Lower	Al upper	0.79	0.001
Pb H2O	Zn H2O	0.86	0.009
Pb Peat	St Peat	0.87	0.005
Pb Total Plant	Ti Plant	0.84	<0.001
Pb Total Plant	Fe Plant	0.81	<0.001

5.4 Discussion

5.4.1 Species Richness

It is well known that species richness separates bogs and fens. Species richness is greater in fens than in bogs, with herbs being the most important species in fens and bryophytes in bogs.

Bryophytes, trees and lichen contribute to the species richness in bogs (Warner & Asada, 2006a).

As previously mentioned, fens can be further subdivided into poor and minerotrophic fens, with a further distinction between moderate, rich and extremely rich fens. Bryophyte species richness in moderate to rich fens is more diverse than in poor fens (Vitt et al., 1995). Vitt et al. (1995) also determined that the pH determines the bryophyte species richness in poor and extremely rich fens; however, in moderate fens, it is related to microhabitats. Similar conclusions were drawn by Horsakova et al. (2018), who also suggested that in poor fens, Al and Fe toxicity reduced the number of vascular species, and in extremely rich fens, the lack of phosphate and iron drove the species richness and that these conditions are in part driven by the pH. The current research found similar results, with site SS (the poorer fen) having a lower species richness than LM and MW, which were moderately rich fens.

5.4.2 Factors Affecting the uptake of Heavy metals

Root Plaques

The root plaques found on the plants at SS were generally lower than those at the other sites.

The highest root plaque development was observed in plants at LM. Plaque development was significantly associated with As, Ni, and Zn uptake in the plants. It is well known that root plaques can either aid or inhibit the uptake of metals and nutrients (Tripathi et al., 2014).

Moreover, as observed in this study, pH was positively correlated with plaque formation. Acidic pH increases the solubility of Fe and Mn and increases the formation of root plaques (J. Xu et al.,

2023). However, the effects of root plaques as a barrier or in the retention of metals remain unclear. Previous research has found that root plaque formation is negatively related to Zn (Otte, 2001; Z. Zhang et al., 2022). In contrast to the present study, Otte (2001 and Punshon et al. (2017) found that As increased in the plant biomass as root plaques increased. On the other hand, studies on *Oriza sativa* and *Phragmites australis* concluded that iron plaques inhibit the uptake of As, Cd, Cu and Cr (Batty et al 2000; Tian et al., 2023; Ye et al., 1997; Zandi et al., 2021) Ye et al. (1997) highlighted that Cu in *Typha latifolia* was higher in plants with root plaques. The relationship between iron plaques and heavy metals, as documented in the literature, remains somewhat scattered and may depend on a combination of factors (Cronk & Fennessy, 2016).

Rhizosphere Processes

The rhizosphere area dramatically influences the bioavailability of metals by altering the redox potential, pH and organic matter (Punshon et al., 2017). When a plant uptakes cations, protons are released into the peat, which in turn causes rhizosphere acidification. Furthermore, plants release up to 40% of their photosynthetic carbon into the rhizosphere, which stimulates the solubility of some heavy metals, such as arsenic (Acosta et al., 2015). While studying plants near gold mines, Acosta et al. (2015) reported twice the concentration of arsenic in the rhizosphere peats than in the surrounding peat. Furthermore, Li et al. (2020) found that rhizosphere processes increased the solubility of Pb, Cu, Fe, and Ni. The current study found an increase in As in the rhizosphere of Twig Rush compared to within the plant roots (Fig 5.3). Lead, nickel, and chromium were also found in increased concentrations in the rhizosphere compared to within the root. Furthermore, in some vascular plants, ROL occurs in the rhizosphere, which can alter the redox potential in surrounding peat (Cronk & Fennessy, 2016; Yan et al., 2022).

Redox Potential

The heavy metals in the wetlands are often in a reduced state due to anoxia (Weis & Weis, 2004). The various forms/speciation of metals determine their mobility and bioavailability. Potentially available metals include those that are water-soluble, exchangeable, complexed with large molecular weight humic materials, or precipitated as inorganic or adsorbed to hydrous oxides. Metals precipitate as insoluble sulphides, or crystalline-bound forms are unavailable for plants (Weis & Weis, 2004). It is said that most metals in the peat are insoluble due to the anaerobic condition and, they can leach out only when the conditions become aerobic (Syrovetsnik et al., 2008). Numerous studies demonstrated the capacity of peatlands as sinks for various heavy metals, including the seven metals of concern studied in this research (Borgulat et al., 2018; Syrovetsnik et al., 2008).

5.5 Bioconcentration Factor (BCF)

There are three criteria that a plant must meet in order to qualify as a hyperaccumulator. First, the plant accumulation must be 100 to 1000 fold higher in the shoots compared to non-accumulator plants (McGrath et al., 2002; Usman et al., 2012). Secondly, the BCF value must be greater than one. Lastly, the plant should not show signs of toxicity. The concentrations of heavy metals in all plants in this study were considerably lower than these values. The accumulation and concentration of heavy metals in plants differ among species at the same site and between the same species at different sites. This indicates that each plant behaves differently with respect to the processes of heavy accumulation. It has been suggested that plants may retain metals in their root by binding metals to the root's cell wall, preventing transportation to the upper biomass (Skuzza et al., 2022). The differences between the plant's accumulation and BCF values can be seen in Figure 5.2 and 5.3. Site LM demonstrated the least overall accumulation, while MW had

the highest and most varied accumulation. The number of heavy metals which each plant either moderately or highly accumulates is depicted in Figure 5.4. Moderate accumulators have a BCF of $0.1 - 1$, while higher accumulators are those with $BCF > 1$. It is clear that plants at MW accumulate greater amounts of heavy metals than other sites, while plants at SS accumulate lesser amounts. Yang et al. (2019) concluded that wetland plants are typically reported to have high metal accumulation capacity, and their ability to accumulate metals is closely related to both metal concentrations in plant tissues and plant biomass.

5.6 Translocation Factor (TF)

The transportation of heavy metals from the roots to the shoots is explained using the TF ratio. A TF ratio > 1 indicates that the plant is translocating, while a ratio < 1 suggests that the plant is retaining heavy metals in the root system. It can be seen in Figures 5.4 and 5.5 that the plants in this study generally tended to store heavy metals in the lower biomass, translocating some, usually smaller amounts, to the upper biomass. It can also be seen that each site had varying ratios of heavy metals in the upper and lower biomass. Although all plants were found to have some metals in the upper biomass, each site had two plants that translocated more heavy metals to the upper biomass than were found in the lower biomass. Thus, they had a $TF > 1$. Many works have also noted that the lower biomass of wetland plants contains higher concentrations of heavy metals than their upper biomass (Deng et al., 2020; Weis & Weis, 2004; Wu et al., 2019). It is evident that plants differ in their TF ability between sites (Fig. 5.4), but not necessarily among the species. Many plants were translocators of Zinc. Aside from zinc, two plants in LM translocated copper with a $TF > 1$ and no other metal. Similarly, for MW, two plants were found with $TF > 1$ for chromium, not other heavy metals. However, at SS, both copper and chromium were translocated. It is well known that greater concentrations of metals occur in the roots than

in the shoots of wetland plants. This is consistent with earlier studies (Deng et al., 2020; Phillips et al., 2015; Xu et al., 2023; Taylor & Crowder, 1983). In order for the metals to travel to the xylem and translocate to the upper biomass, the metals have to pass through the epidermis, cortex, endodermis and pericycle (Gupta et al., 2016). Pressure in the roots and leaf transpiration are said to result in the translocation of metals from the roots to the shoots (Mirza et al., 2014; J. Yang et al., 2017). Xu (2023) suggests that translocation to the upper biomass is a function of the concentration of the metal in the peat; the more abundant the metal in the peat, the lower the TF of the metal. This contradicted the results of Usman (2012), who concedes that plants with higher concentrations of metals in the lower biomass will also have higher concentrations in the upper biomass. The present study did not lead to similar conclusions.

5.7 Metal accumulation by different populations of *Chamaedaphne calyculata* and *Myrica gale*

Distinct populations of *Myrica gale* were collected from all three sites, and populations of *C. calyculata* were collected from LM and SS (Fig. 5.5). The same plant species were growing in sites with notable differences in pH, peat and metal composition, bulk density, DOC, redox potential etc. The heavy metal uptake of these plants was remarkably different among the populations. The roots of the plants from each population had a higher accumulation than the shoots. It is interesting to note that plants accumulated variable amounts of heavy metals, and in each site, the plants were selective on the metals they accumulated. At site MW, *M. gale* accumulated all seven metals while only six were accumulated at SS and four were accumulated at LM. In *C. calyculata*, the plants at SS accumulated five metals, whereas only three were accumulated at LM. Likewise, the translocation varied from site to site. Similar variations were

noted in metals' translocation (TF) to the upper biomass. These results suggest that factors other than plant morphology are responsible for metal uptake.

5. 8 Heavy metal uptake in fen plants

Arsenic

Arsenic is an element that is not necessary for plant development and growth, yet it can be taken up by the plant (Fitz & Wenzel, 2002). It is suggested that As competes with P to enter the plant (Carbonell et al., 1998; Rascio & Navari-Izzo, 2011). Water soluble As (V) increases as pH decreases and allows the roots to uptake As; however, As (III) follows the opposite trend (Fitz & Wenzel, 2002). Furthermore, the association of As with Fe in reduced conditions reduces the chance of As uptake (Fitz & Wenzel, 2002). The plants at MW (*M. gale*, *E. quinqueflora* and *C. mariscoides*) were the only ones to accumulate arsenic (except *C. canadensis* at LM). As noted in this study, hyperaccumulators accumulate As in the rhizomes and are transferred to the upper biomass; however, in the case of non-accumulators, most of the absorbed As remains in the roots of plants (Fitz & Wenzel, 2002; Kohda et al., 2021; Thathong et al., 2019). Presence and the relationship with other metals can influence As uptake. Silicon also demonstrated its negative impact on the uptake of As and Cd (F. Huang et al., 2024). Plants at SS had the most elevated BCF of Si, which could have inhibited the uptake of the As by plants at this site. Furthermore, iron plaque formation prevented the As uptake in *Kandelia obovate* (Liu et al., 2014; Fitz & Wenzel 2002). In the current study, root plaques were found to play a significant role in the uptake of As ($Z=-2.9$, $p<0.001$).

Cadmium

Cadmium is not essential for plant growth and development (Wright & Welbourn, 1994) however, many plants sequester it. Borgulat et al. (2018) focused on three bogs in Poland and

determined low Cd concentrations in plant leaves and attributed this to higher levels of Cd in the peat. In the current research, Cd was highest in the peat and plants at MW, which supports the above study. Slightly acidic conditions and the presence of Zn or P usually enhance Cd uptake. Some research suggests that total Cd concentration in plants is positively correlated with Cd in water; others note that Cd uptake increases with lower pH, which was not supported in this study or by Campbell and Evans (1991). Studies addressing the translocation of Cd from lower to upper biomass have conflicting results. Reddy and Patrick (1977) studied the uptake of Cd by *Oryza sativa* and found that Cd remained in the plant's roots. However in a study of *Potamogeton natans*, Cd was found to be the only heavy metal which was translocated to the upper biomass (Fritioff & Greger, 2006). Plants translocated Cd in very low quantity at site SS, only in *C. calyculata* and *M. gale*. Cadmium uptake by the plant decreases in the presence of silicon and organic matter (Simkin et al., 2021). Similarly, both Zn and Fe inhibit Cd uptake (Thomas, 2021). In contrast, the current study found that Cd accumulation was positively correlated with Fe in the upper biomass of the plant, while the concentrations of Si, Zn, and P neither inhibited nor enhanced uptake. Cd in the upper biomass was correlated to Al in the lower biomass. Total plant Cd was correlated with Al and Co accumulation (0.82 & 0.79, $p < 0.001$). This supports the study by Riaz et al. (2021) and Shamsi et al. (2007). Root plaques on the fen plants (Riaz et al., 2021) were noted to be related to the uptake of Cd.

Chromium

The uptake of chromium by plants has not been well studied since this element is not necessary for plant growth. The uptake and translocation of Cr depend on the metal's speciation (S. Ali et al., 2023). It is suggested that Cr is soluble but resists uptake (Uwiringiyimana et al., 2023). Moreover, regardless of the form of Cr (either III or VI), Cr is more likely to remain in plant

roots than to be transported to the upper portion (Pulford et al., 2001; Uwiringiyimana et al., 2023; Zayed et al., 1998; Singh et al., 2020; Sricharoenvech et al., 2024). It is argued that the vacuoles in the root cells form a barrier to translocation (Ertani et al., 2017) and act to compartmentalize and immobilize Cr (Pulford et al., 2001). Similar to other metals, Cr is said to compete with P, S and Fe for carrier binding sites during transportation; therefore, plants hyperaccumulating Fe and S also have high Cr in their tissues (Ali et al., 2023; Cervantes, 2001.; Singh et al., 2020; Ullah et al., 2023). Chromium solubility increases at high pH; therefore, deep-rooted plants may encounter more soluble Cr (Sheppard et al., 2009). *P. australis* has been found to successfully extract Cr and concentrate in high amounts in the root system (Khan et al., 2009). The present study found that *P. americanus* had the highest Cr accumulation (1.9 ug/g). However, it was not much higher than in *E. quinqueflora* (1.7 ug/g) growing at the same site. Several other metals interact with Cr. Studies by Rai (1995) and Shukla et al. (2007) suggest that Cr and Cd are positively correlated; however, this study found no correlation with Cd, although there was a strong correlation between the concentration of Cr and Fe in in the upper biomass of the plants (Singh et al., 2020). In the current research, *P. americanus* and *E. quinqueflora* had the highest BCF of Cr and high BCF for Zn (Fig. 5.3).

Copper

Copper is a biophilic element and is needed by plants. Plants' uptake of Cu depends on Cu speciation and is, in part, determined by bioavailability. Novosyolova et al. (2021) reported Cu concentrations ranging from 5.9 mg/kg to 12 mg/kg in peatland plants, which is similar to the current findings. In a study of *Artemisia*, pH was negatively correlated with Cu in the leaf and the TF (J. Xu et al., 2023). In studies of *Typha angustifolia*, Cu was positively correlated with Cr in the roots and shoots and was negatively correlated with Pb in the shoots (Bah et al., 2011),

these results were similar to those in *Sesbania drummondii* (Israr et al., 2011), but not supported by the current study. Plants are known to immobilize Cu in the upper biomass and root cortex as a means to tolerate its toxicity and then release it during low availability (Zandi, 2020). In a study of *P. australis*, the translocation of Cu was closely related to the translocation of Fe (Ubeynarayana et al., 2021; S. Xu et al., 2021). In contrast, the current research found that plants with the highest peat Cu had the lowest Cu accumulation. Xu (2020) reported that rhizosphere pH was negatively related to Cu TF, and thus, higher pH may prevent the translocation of Cu to the upper biomass. This was also not found in the present research. Others have proposed that iron plaques accumulated on the roots inhibit the translocation of Cu to the upper biomass (Shen et al., 2021; Yang et al., 2014), whereas Ye et al. (1997) found that plaques neither inhibited nor enhanced the uptake of Cu, which was supported by the current research. Iron plaques were highest in plants at LM, which had the highest concentration of Cu in peat, the lowest BCF (Fig. 5.3), and high TFs (Fig. 5.6). In this study, the plant with the lowest Cu accumulation also had the lowest Zn. Bulk density and root plaques were associated with higher accumulation but not translocation. Plants at LM and SS were observed translocating Cu to the upper biomass; this did not occur at site MW despite higher BCF in several plants compared to those at LM.

Nickel

Nickel is an essential element which is necessary for plant growth (Ofoe et al., 2023). In this study, Ni was at BDL in *P. americanus*, *E. quinqueflora* in MW and *C. calyculata* and *R. alba* in SS. Nickel is highly mobile at low pH, and at high pH low Ni uptake is reported (Rasti et al., 2020). Additionally, the presence of higher organic carbon results in a reduced nickel uptake (Rasti et al., 2020). Studies revealed that Cd, Fe, and Zn affected the uptake of Ni (Thomas, 2021). Interestingly, the current study found no Zn or Fe synergistic effects on Ni uptake.

Another noteworthy observation was the positive correlation between Ni and Ti, which is known to have a synergistic relationship. Lead and Ni were significantly correlated (0.68, $p=0.008$), and plants that sequestered nickel also sequestered lead. Lead has been found to have an antagonistic effect on the uptake and translocation of Ni in both the roots and shoots (Cai et al., 2017). The results of this study indicate that low Ni accumulation and translocation in plants are associated with low Mg and Ca ratios (Rasti et al., 2020). No plant in the study was found to translocate Ni to the upper biomass (Fig. 5.6). Roots with plaques increased uptake and translocation in *T. latifolia* (Ye et al., 1997). This was observed in the present study. Nickel in the current study was found to be positively correlated with Al, which can stimulate the uptake of other metals through transporters, particularly in acidic peats by eliciting changes in rhizosphere pH (Ofeo et al., 2022). In this study, Ni accumulation is associated with Ti, Pb and Al, Mg/Ca ratio, root plaques and higher pH.

Lead

Lead is not an essential element for the function of plants (Egendorf et al., 2020; Wu et al., 2014) but is often found at levels between 6.3-9.9mg/kg in plants. Borgulat et al. (2018) addressed levels of Pb in plants and peats in Poland bogs, finding Pb in the leaves and the roots despite its immobility at low pH (Kempter et al., 2010; Kumar et al., 1995). Other researchers found larger concentrations of Pb in the roots compared to the shoots (Deng et al., 2020). Reddy & Patrick, (1995) found that Pb uptake decreased with an increase in pH, which did not agree with the present research. Lead was found in low concentrations in the plants at MW and SS and was restricted to the roots. In a study on *Zea mays*, Cd reduced the uptake of Pb and reduced the translocation to the shoots (Miller et al., 1977). This is interesting and somewhat supporting the current research. According to Lee et al. (1998) Pb absorption in peat increases with increasing

pH from 3 and 8.5, however, Blaylock (1997) demonstrated that Pb solubility is controlled at pH between 5.5 and 7.5. High clay mineral, carbonates, Fe and Mn, phosphates, peat organic matter, and neutral pH reduce the mobility of Pb in peat, while low acidity and low peat properties contribute to lead mobilization (Egendorf et al., 2020). Lead in *T. angustifolia* was positively correlated to Zn in the roots and negatively to Ca and Cu in the roots (Bah et al., 2011). In this research, Pb in the lower biomass was related to a higher pH. It is also noted that many studies suggest that iron plaques prevent the uptake of Pb (Cai et al., 2017). However, this research also did not find supporting results.

Zinc

Zinc is an essential micronutrient in plants which is required in limited quantities (Gupta et al., 2016). Transporters uptake Zn and other divalent cations such as Cd, Ni, Pb, As through non-selective cation channels (Gupta et al., 2016). Similar to other metals in this study, Zn is absorbed into plants from the peat, and its availability can depend on other factors such as pH, redox potential, peat properties, etc. (Gupta et al., 2016). For example, Zn is known to be less soluble as pH increases, and the uptake increases with increased peat moisture and organic matter. It has been suggested that Zn translocation is related to increased root length and root hairs (Zelko et al., 2008). Zinc in peat plants varies from 8.0-33 mg/kg (Novosyolova et al., 2021) however, the current research found much higher concentrations ranging from 19 - 108mg/kg. The zinc accumulation in roots and shoots varies between plant species (J. Yang et al., 2017) and is often higher in the roots. In *T. angustifolia*, Zn has a positive relation with Pb and Ca in the roots (Bah et al., 2011), however no correlation was found in the present study. The positive correlations among Pb, Fe and Ti indicate that these heavy metals are associated with each other. Root plaques are reported to be affecting the uptake and translocation of Zn (Ye et al.,

1997) and is supported in this research ($p=0.011$). The BCF of Zinc was >1 for all plants at MW and SS but only exceeded 1 in *C. calyculata* and *C. canadensis* at LM (Fig. 5.3).

It has been suggested that sequestration may be a function of plant morphology. The current research examined the heavy metal concentration in water, peat and plants to the depths of 30cm. However, the literature suggests that while many metals remain in the upper 30cm of the peat, some exhibit vertical translocate (Smieja-Król et al., 2010; Ukonmaanaho et al., 2004), with concentration decreasing with depths (Novosyolova et al., 2021). In addition, root lengths can vary, restricting or enhancing their ability to reach metals that have vertically translocated deeper than the area studied. Schück & Greger, 2020 examined morphological plant traits such as root size and the abundance of fibrous vs wood roots and Peura et al., 2024 hypothesized that differences in plant metal concentration could be due to ranges of root depth and studies on climate change have found evidence that plant communities may change to Ericaceae species and potentially reduce sequestering abilities (Andrews et al., 2022; Robitaille et al., 2021; Pinceloup et al., 2020). These proposals are supported by the results of the graminoid plants in site MW; however, the ericaceous shrubs in site SS had higher BCFs than the graminoids. It may be more accurate to say that root morphology does not significantly affect plant uptake and plants with longer roots stabilize heavy metals deeper in the peats, making them less available to plants with shorter roots, supporting the results that the richer fens, with a higher species richness is a determining factor in heavy metal retention. However, since this study only focused on depths of 30cm, it is not possible to determine differences in metal availability versus depth, but the variations by plant and site suggest that BCF is a function of combined biogeochemical factors rather than a single or paired aspect.

5.9 Plant Conclusions

Metal uptake and translocation differed among plant populations (Deng et al., 2020). These results suggest that plant species differ in their ability to accumulate or exclude heavy metals. It has been suggested that heavy metal accumulation and translocation are species-specific (Milic et al., 2021). However, the results of this research suggest that this may also be site-specific and based more on the peat properties. Plants belonging to the same species but from different sites differ in their uptake and translocation of heavy metals

In this study, the BCF values were generally lower than 1 for all metals except Zn, Cr and Cu, indicating that the majority of the studied fen plants were unsuitable for phyto-stabilizing As, Cd, Ni, and Pb at high levels. Differences in the rhizosphere concentration of heavy metals compared to those in the roots indicate that some plants in fens may be better at rhizo-filtration, which may be why high concentrations of metals are retained in the fen. Very few plants with high heavy metal translocation factors ($TF > 1$) other than Zinc were found. Copper was translocated at LM, chromium at MW, and copper and zinc at SS. This research indicates that translocation of metals from the lower to the upper biomass is not only plant/metal specific but also site-specific, which suggests that translocation is related to combinations of the morphology of the plant and the peat properties within the fen.

6.1 Chapter 6: Thesis Conclusion

This research indicated that plants growing in acidic ecosystems, such as fens, significantly influence the sequestration of heavy metals. Generally, vascular plants employ mechanisms such as rhizofiltration and phytostabilization, which involve lower biomass sequestration of heavy metals, to reduce their mobility within the fen. This process, in turn, decreases the heavy metal load in water flowing out from the fens.

Vegetation is one of the main factors influencing heavy metal distribution in the fen. Factors such as plant distribution, species composition, uptake and retention capacities of heavy metals (Almeida et al., 2006; Reboreda & Caçador, 2007) can influence the availability of heavy metals in the water (Koretsky et al., 2008). Moreover, plant-aided retention of heavy metals in peats has been shown to influence the concentration of heavy metals in peats (Reboreda & Caçador, 2007). The effect of vegetation on heavy metal distribution is influenced by the biogeochemical processes occurring in the peats and the pollutant chemistry (Mondal et al., 2020; Ou et al., 2019; Xu et al., 2021).

Plant porewater interaction

The hydrological regime significantly influences the metal accumulation process by plants (Tang et al., 2020; Yang et al., 2020; Boostani et al., 2021; Xu, 2020). The pH, redox potential, input of heavy metals from upland sources, the affinity of metals for suspended solids (organic and inorganic matter) and the competition for binding sites in the root cells influence the availability of heavy metals in the porewater (Rothwell et al., 2006).

Utilizing porewater chemistry as a key indicator, the fens examined in this study were classified into three categories: poor, (site SS), moderately rich (site LM), and moderately rich to rich (site MW). In all sites, the heavy metal concentrations in the pore water were lesser than those in the

fen peat samples, and an overall reduction of heavy metals in the outgoing water from the fens suggests that peats could act as sinks for heavy metals. However, the porewater heavy metal concentration varied with depth, indicating that chemical, physical, and biological processes may influence their distribution in the peat. The changes in biogeochemistry, caused partly by the seasonal changes in water chemistry and vegetation, resulted in the peatlands temporarily acting as sources of heavy metals.

Heavy metal mobilization differed between fens and was believed to be largely due to changes in pH, redox potential, and synergistic or antagonistic associations with other elements. Arsenic and nickel were mostly in BDL at the outlet, suggesting that these metals were bound to peat and retained in the fens. In all fens, Cd, Cu, and Zn concentrations were elevated at the midpoints compared to the inlet during summer. This may be explained by the remobilization of heavy metals by rhizosphere oxidation (ROL) of plants and their attraction to smaller colloidal particles (DOC), which move through the low bulk density peat having large pores. The transition of fens in the fall from sink to source can be explained partly by the senescence and decomposition process of the dead plants having high BCF and TF values of heavy metals and the release of metals and nutrients into the water.

Plant peat interaction

Geo accumulation index and enrichment factors determined that the concentration of heavy metals in the fens was elevated compared to the historical background levels of North American peats (Turekian & Wedepohl, 1961). The fen inlets generally had a higher concentration of heavy metals than the midpoints, and this could be due to the settlement of heavy metals bound to the suspended solids and the absorption of heavy metals by the vegetation. Bulk density, volumetric porosity, and humification were positively associated with the heavy metals Cu, Cr, Cd, and Ni,

which have a natural affinity towards smaller colloids and are easily mobilized in the larger pores of peat with low bulk density. The correlation between bulk density and peat metal concentration suggests that reduction in pore sizes with increased bulk density results in diminished mobility of colloids, thereby enhancing the retention of metals. This agrees with an earlier study by Rezanezhad et al. (2012). Thus, fens with higher bulk density may have reduced mobility of suspended solids, resulting in an increased concentration of heavy metals in the peat. This increases the retention of heavy metals adhered to the suspended solids in closed or open pore spaces in the peat, further resulting in the retention of heavy metals in the peat (McCarter et al., 2020).

It has been largely suggested that the heavy metal uptake by plants is dependent on the concentration of heavy metals in the peat and the bioavailability in the water (Deng et al., 2020; Peura et al., 2024). However, many earlier studies have shown that there is no correlation between the heavy metal concentration in peat and water and the plant uptake (Fritioff & Greger, 2006; J. Xu et al., 2023), except with Cu and Pb (Phillips et al., 2015; Taylor & Crowder, 1983). This agrees with the present study results.

The relationship between the heavy metals and transporters and the competition for the binding sites on roots largely determined the sequestration of heavy metals in plants. The sequestration was not significantly related to heavy metal concentration in peat or water. Most metal concentrations in the plants were below the harmful level (BDL or below the level causing harm) except Cd in *P. Americanus* and Pb in *E. quinqueflora*, both from site MW and Cu in *C. calyculata* in site SS.

Several factors influence the availability of heavy metals from the peat to plants, including metal speciation, pH, and redox potential, among others. This research identified strong correlations

between peat properties and the concentration of heavy metals in the peat, particularly regarding pH and DO in relation to Cr, Cu, and Cd in both the peat and water (see Table 5.3). These findings suggest that metal speciation and their availability vary with changes in peat and water properties. However, other factors, such as DOC and bulk density, can limit their movement. It should also be noted that while metal speciation was not directly analyzed in this study, it may be linked to metal availability and uptake by plants, which could explain the lack of observed relationship between metal concentrations in peat and water and those in the plants. Furthermore, the presence of root plaques exhibited a correlation with declining pH levels, highlighting their significant relationship with the uptake of As, Ni, and Zn. While the precise role of these plaques in the sequestration processes remains unclear, their associations with Zn and Mn oxides suggest a potential role in sequestration. Studies on the role of root plaques on metal sequestration showed conflicting results, with some demonstrating inhibition while others enhancing (Tripathi et al., 2014). This study determined that the presence of root plaques significantly inhibited the sequestration of As while enhancing that of Ni and Zn.

In this study, BCF values were generally moderate to high. Several plants had extremely high BCF values, indicating that plants in fen ecosystems are good at stabilizing the seven metals of concern. Plants at site LM had significantly lower BCF values than the other sites and sequestered fewer heavy metals than the other sites. In addition, no plants at site LM sequestered Pb or N. This may result from differences in biogeochemical factors, such as an increase in root plaques. Further investigation would provide a more detailed understanding of these interactions in fens.

Conversely, site MW (rich fen) sequestered the greatest number of heavy metals and had the highest BCF values. Adsorption of heavy metals in the rhizosphere was studied in three plants,

and it was determined that many plants might utilize phytostabilization to enhance the immobilization of heavy metals rather than sequestering them into the plant cells. Furthermore, the TF values were generally below one, except for Zn in all locations. Translocation of metals was higher in SS (poor fen) and lowest at MW. This indicates that sequestration and translocation of heavy metals to the upper biomass may be a function of complex biogeochemical processes rather than a selective plant activity and that the fen plants are suitable for rhizofiltration and phytostabilization. Metal accumulation by different populations of the same two plant species (from different fens) indicated similar sequestration and translocation strategies suggesting that factors other than plant morphology/physiology are responsible for metal accumulation. However, more research is needed to clearly understand the mechanisms of plant uptake and translocation of heavy metals in fen plants and the factors affecting them. The potential of iron plaque in the rhizosphere and the uptake of heavy metals have not been understood clearly. More work on the interactions of microorganisms and their potential role in heavy metal sequestration would be beneficial to better understand the heavy metal flux in fen ecosystems.

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Appendices

Appendix A

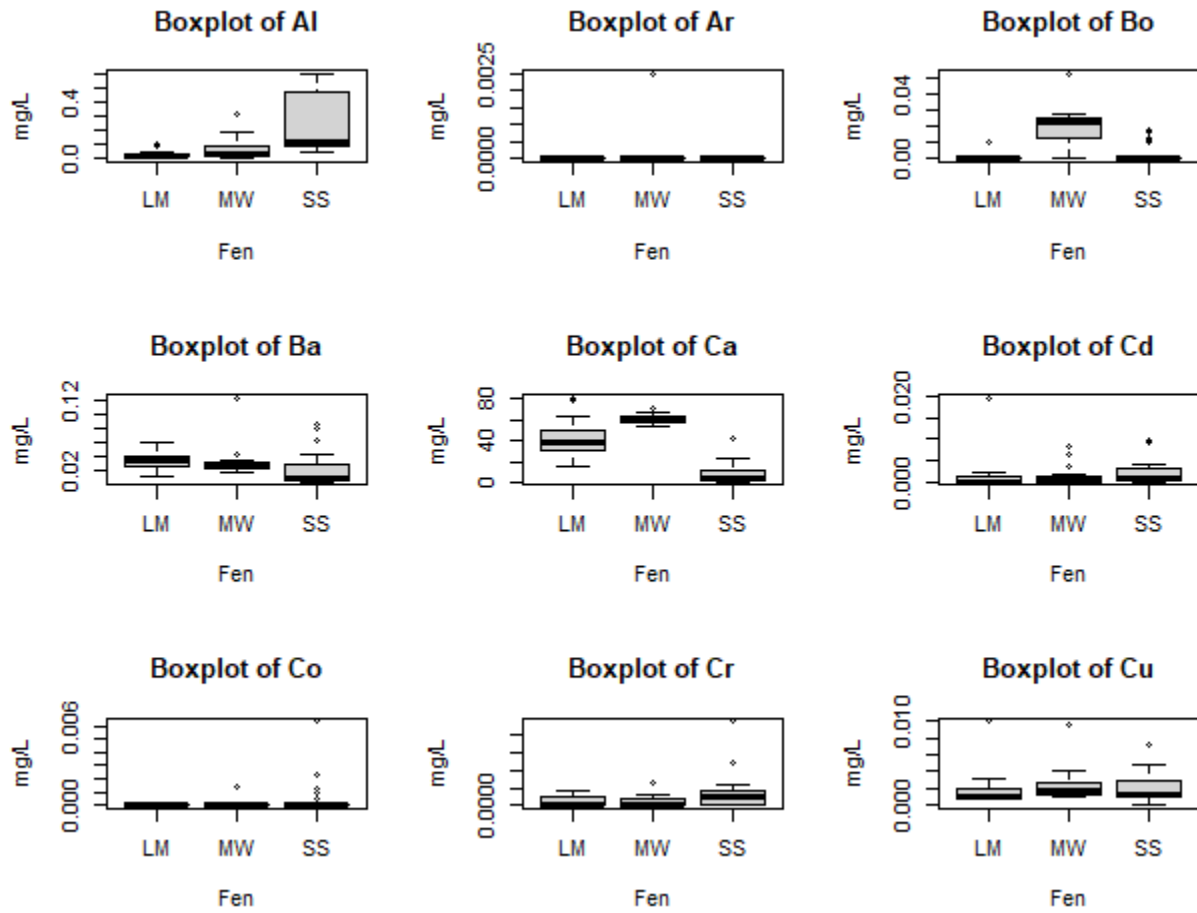


Figure A 1 Boxplots of mean water parameters and water heavy metals at each fen

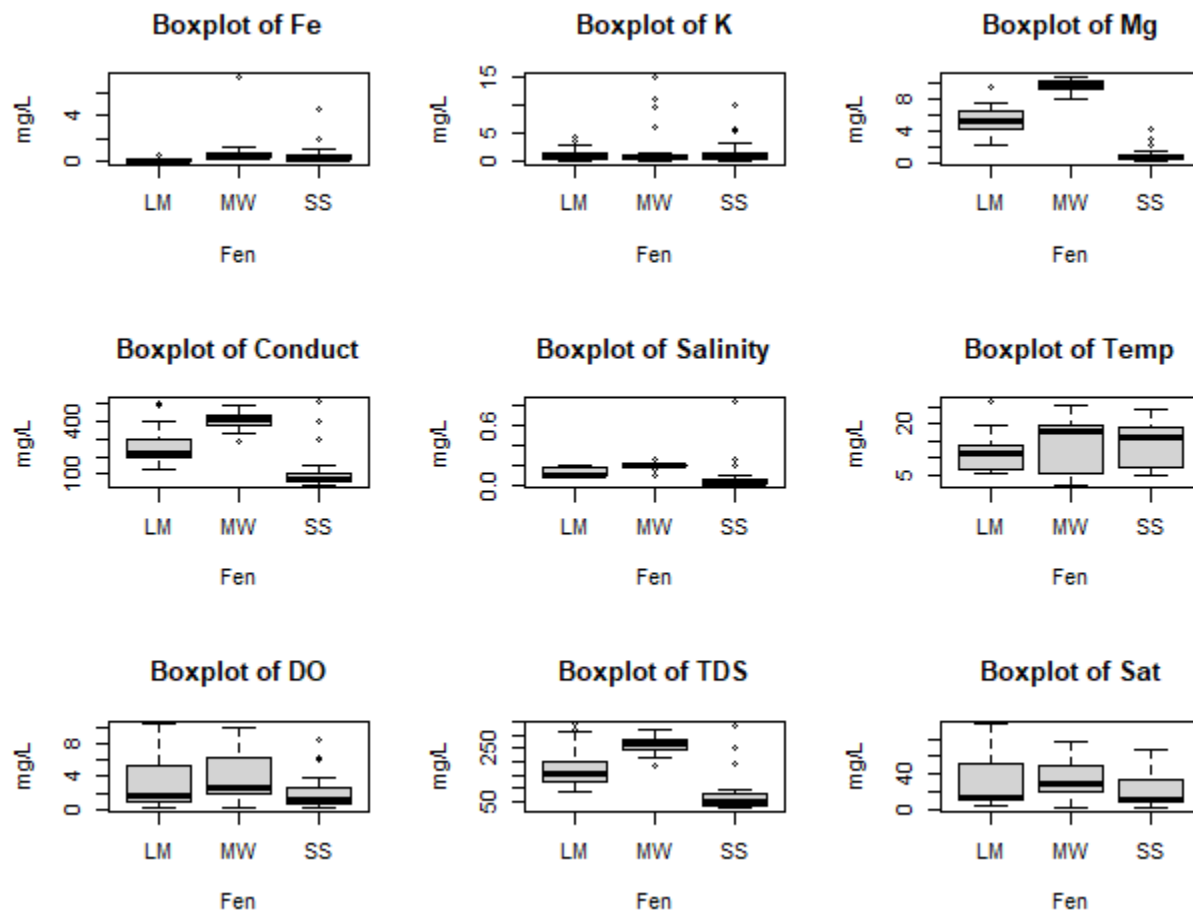


Figure A 1 Boxplots of mean water parameters and water heavy metals at each fen Cont'd

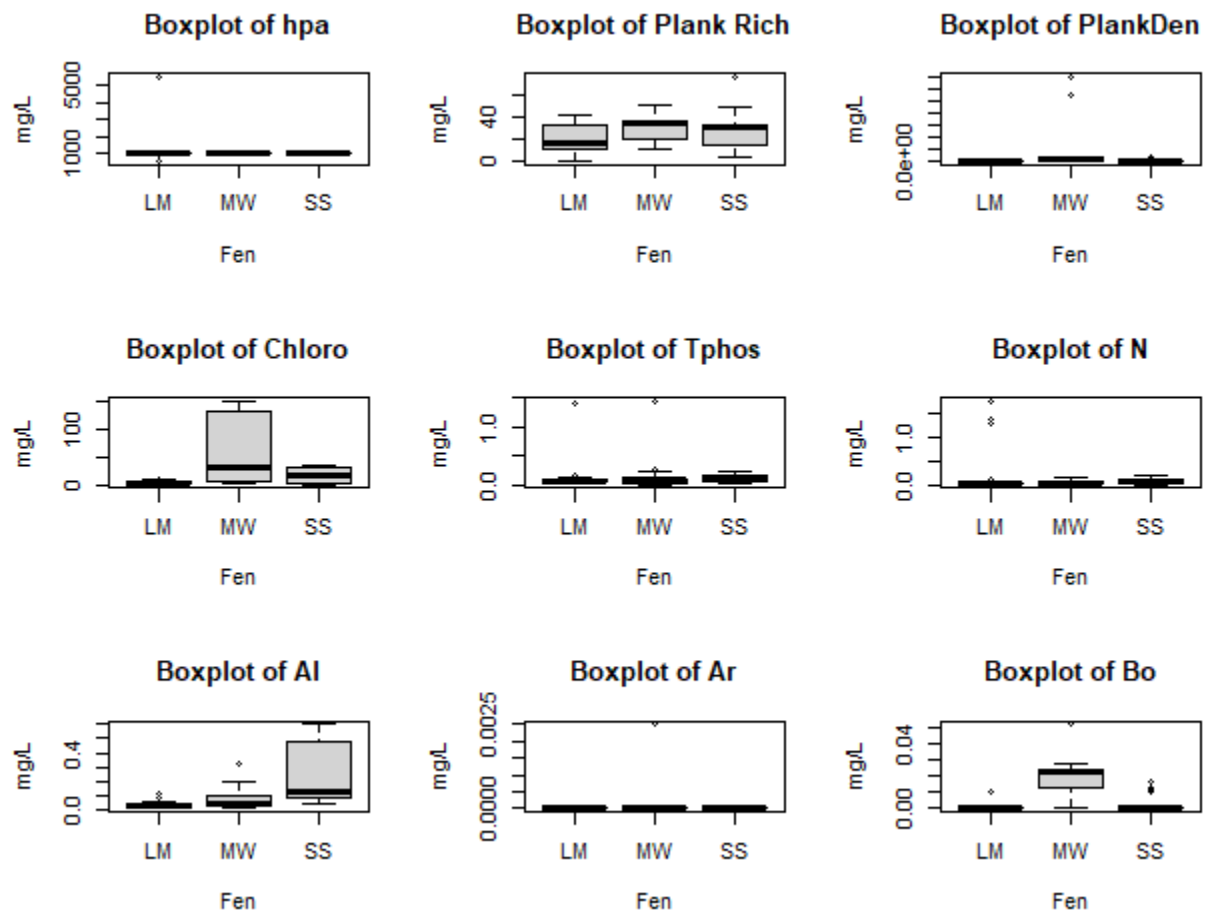


Figure A 1 Boxplots of mean water parameters and water heavy metals at each fen Cont'd

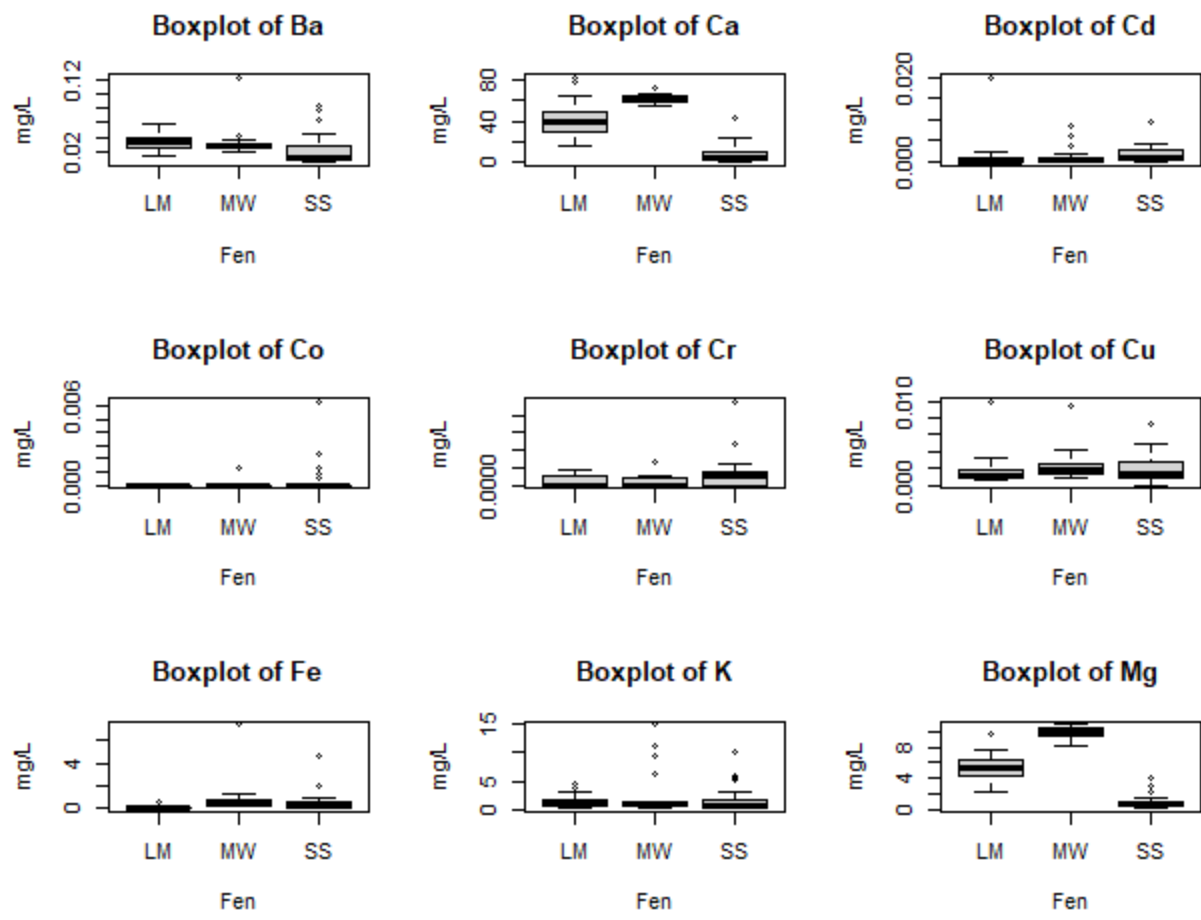


Figure A 1 Boxplots of mean water parameters and water heavy metals at each fen Cont'd

Appendix B

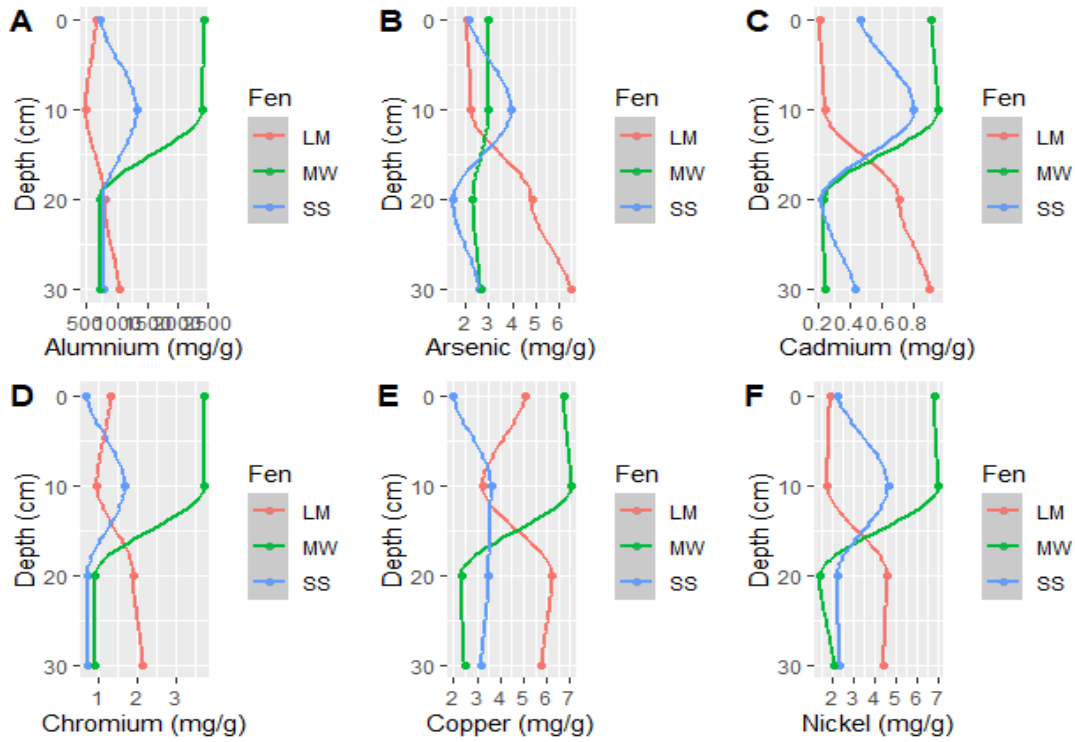


Figure B1 Heavy metals in peats at each fen

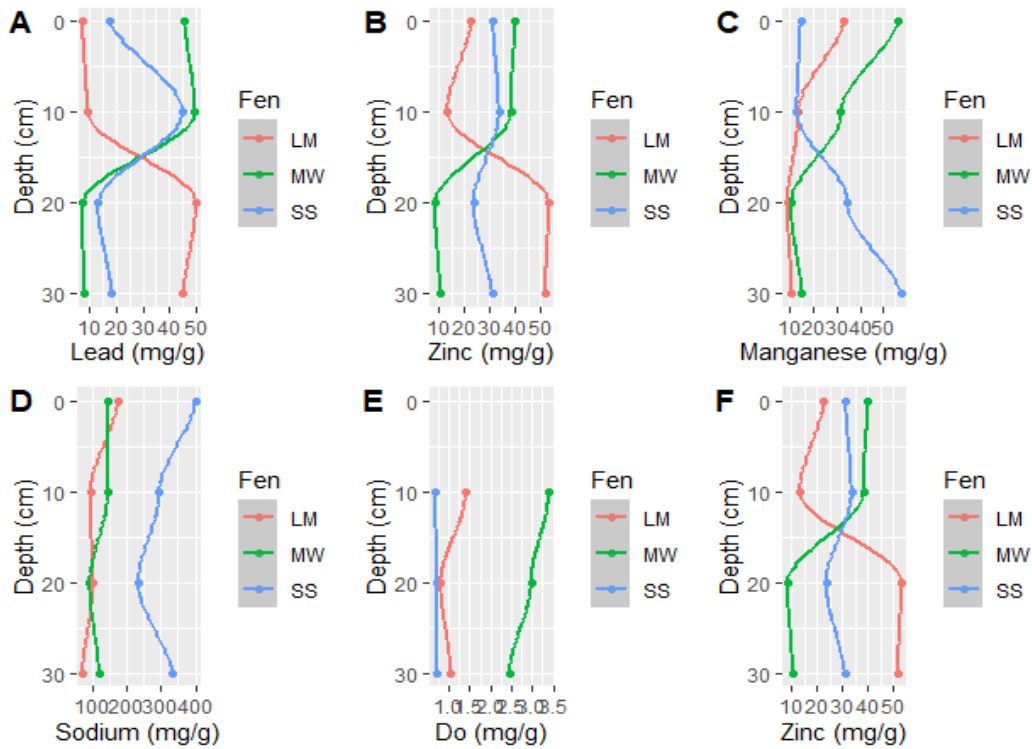


Figure B1 Heavy metals in peats at each fen, Cont'd

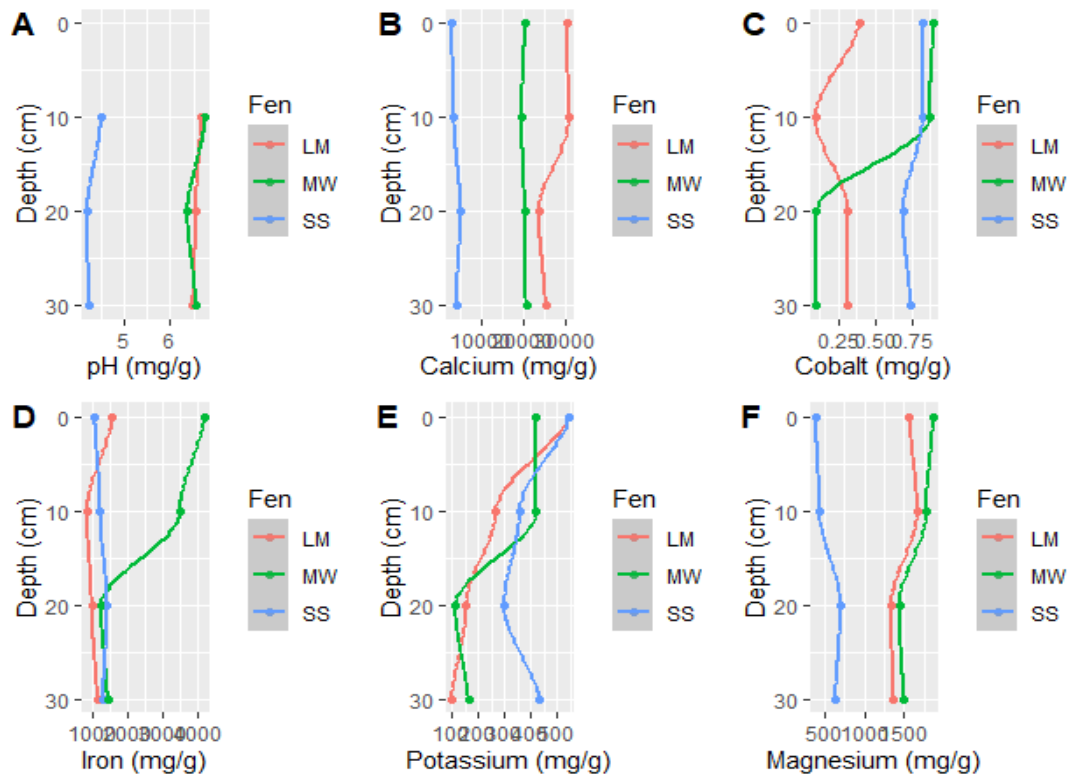


Figure B1 Heavy metals in peats at each fen, Cont'd

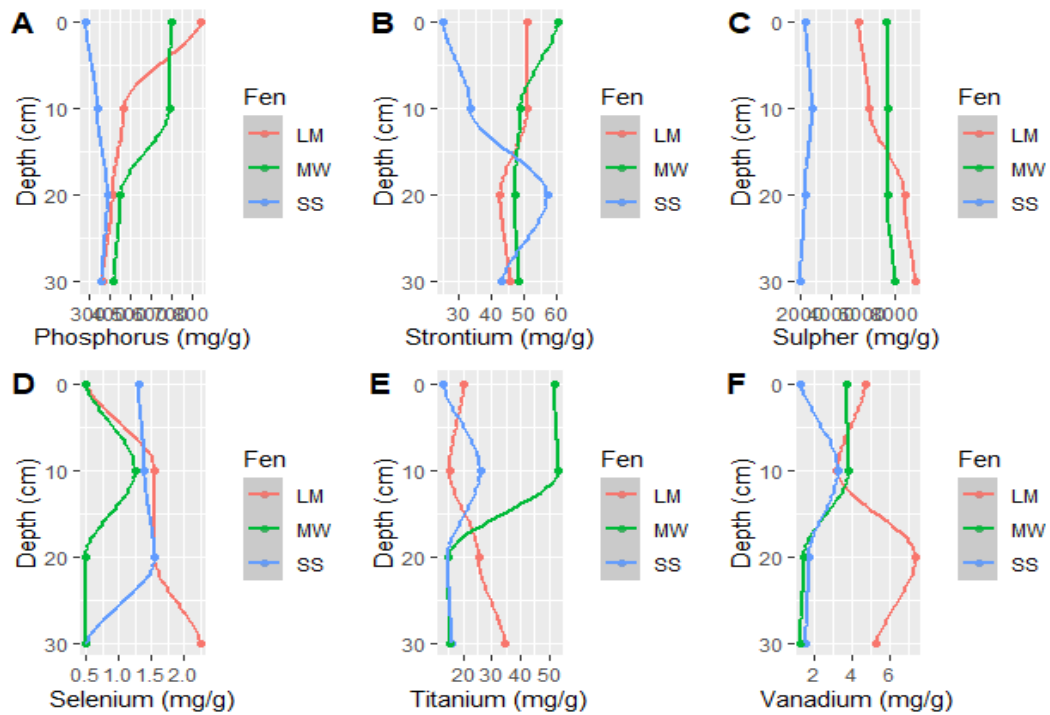


Figure B1 Heavy metals in peats at each fen, Cont'd

Appendix C

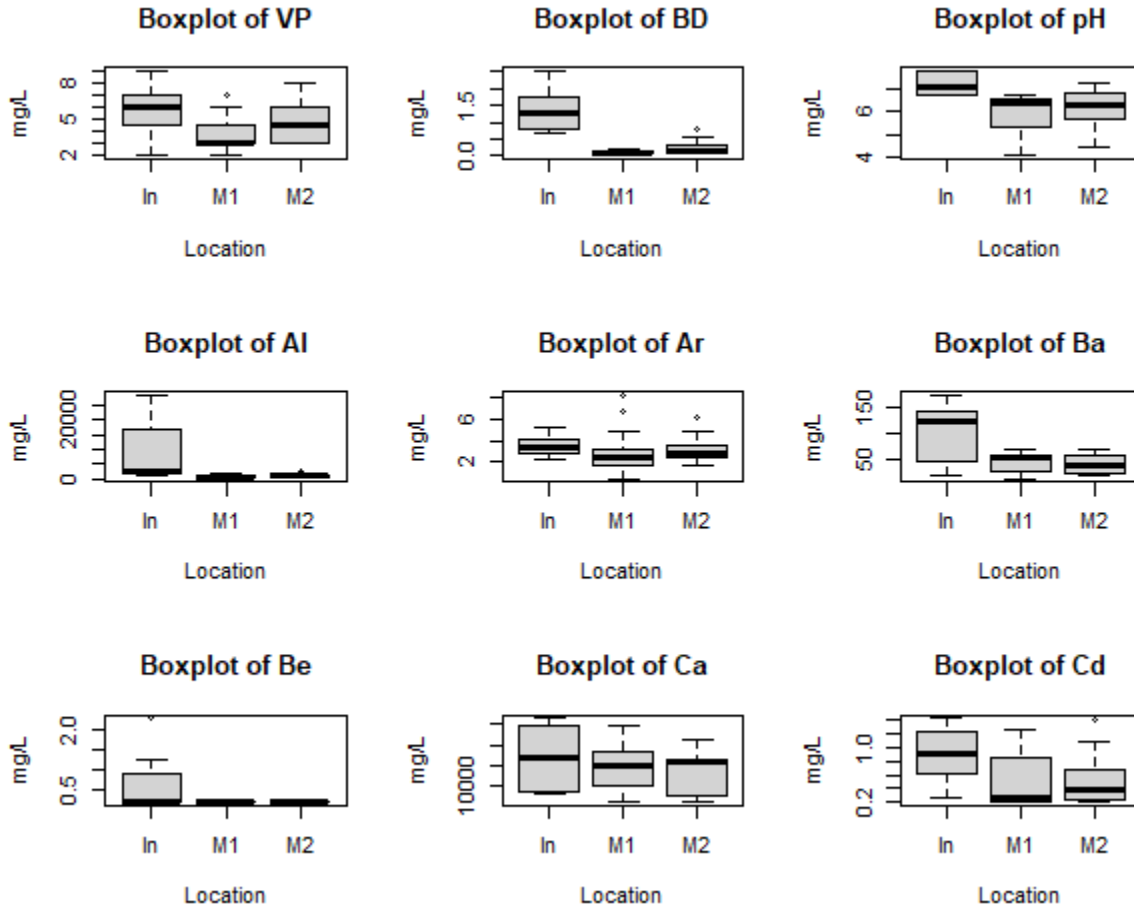


Figure C1 Boxplot of mean heavy metals in peats in the Inlet and midpoints

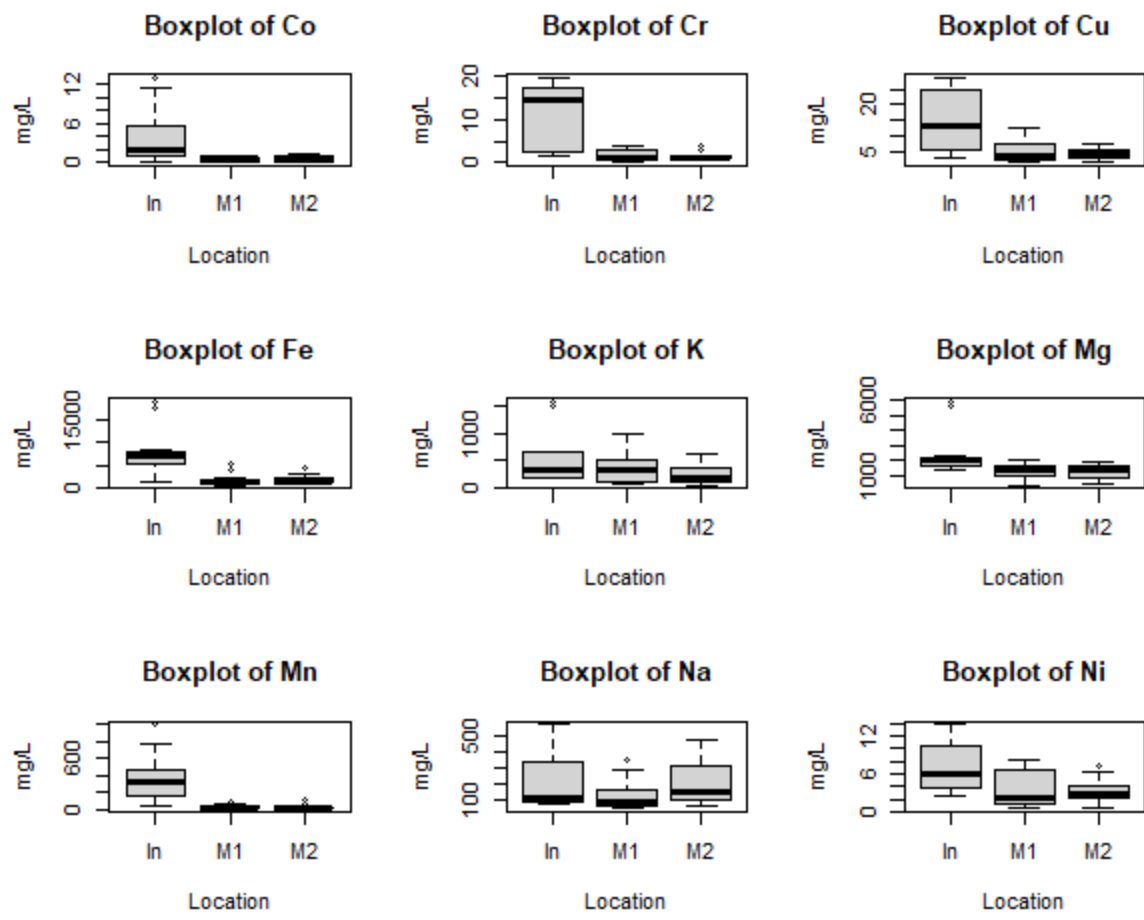


Figure C1 Boxplot of mean heavy metals in peats in the Inlet and midpoints, Cont'd

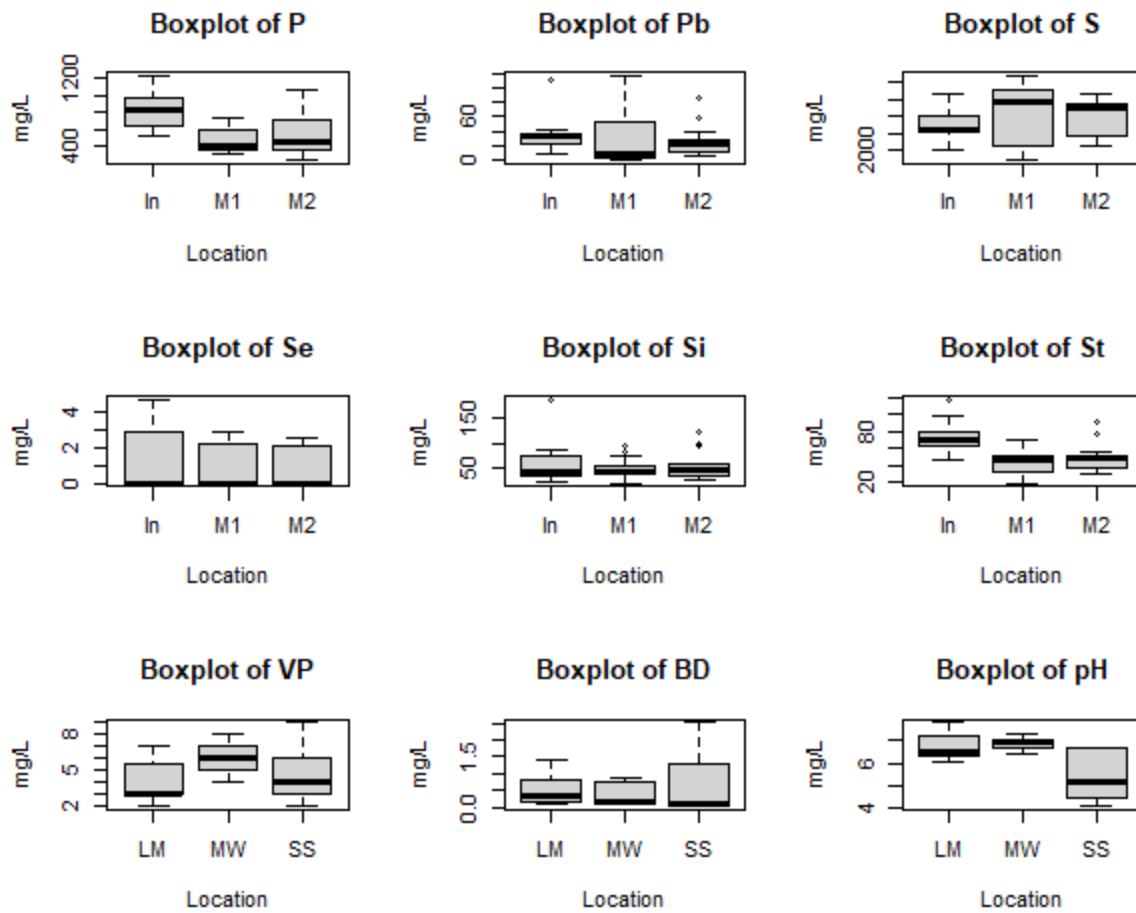


Figure C1 Boxplot of mean heavy metals in peats in the Inlet and midpoints, Cont'd

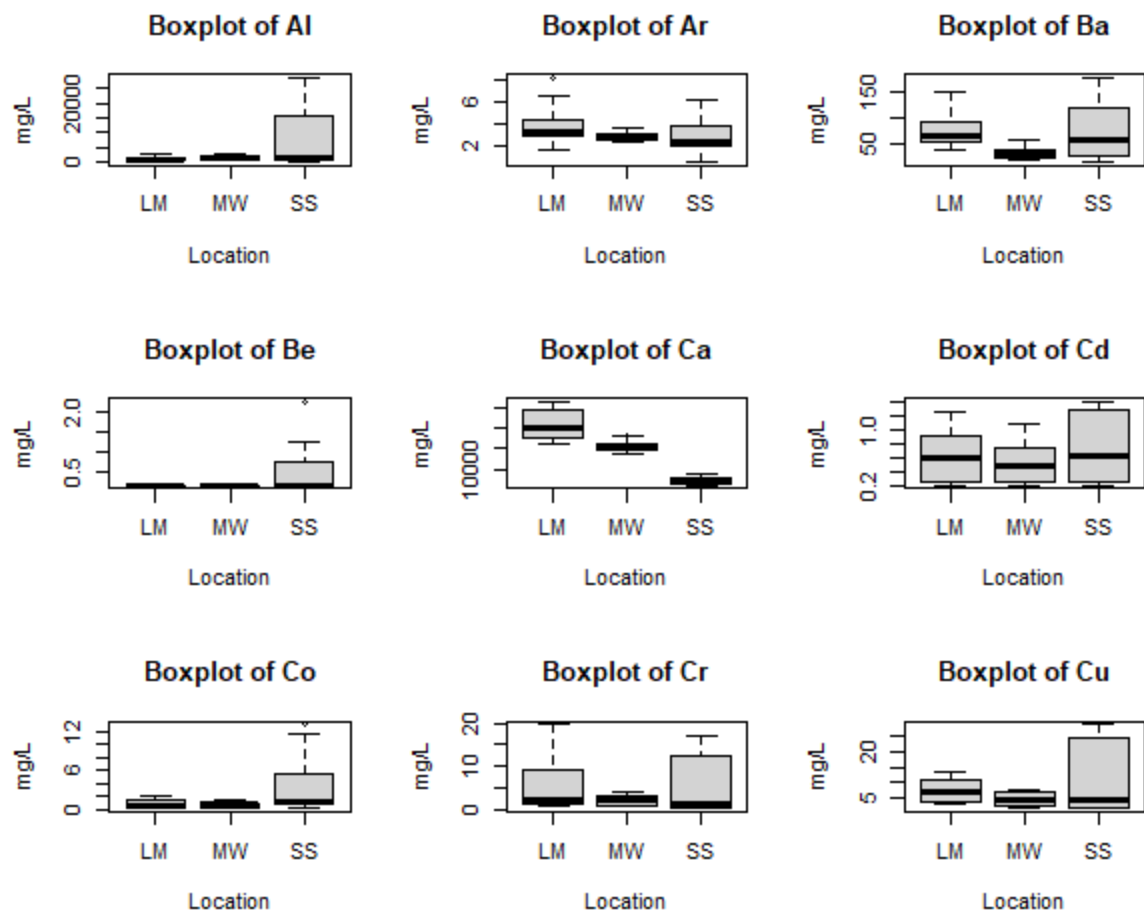


Figure C1 Boxplot of mean heavy metals in peats in the Inlet and midpoints, Cont'd

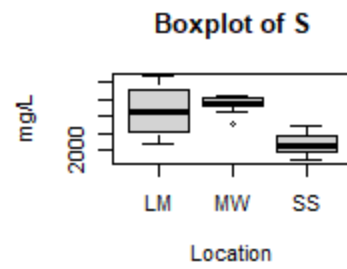
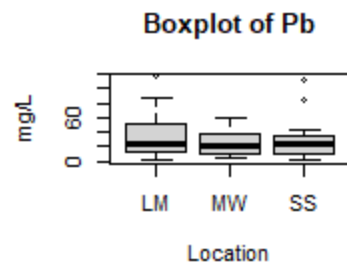
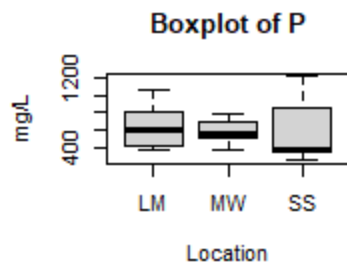
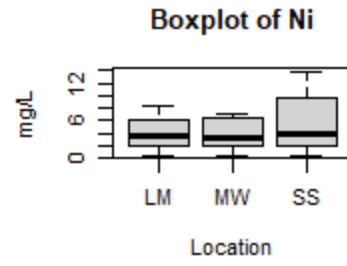
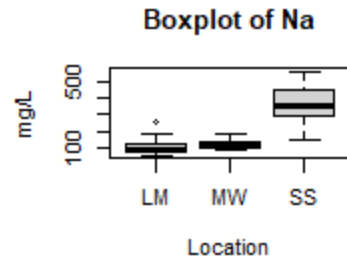
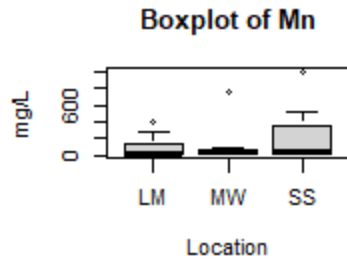
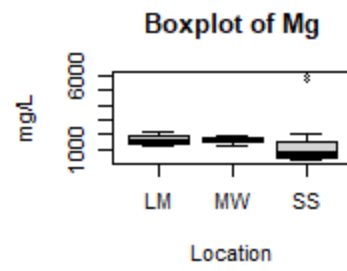
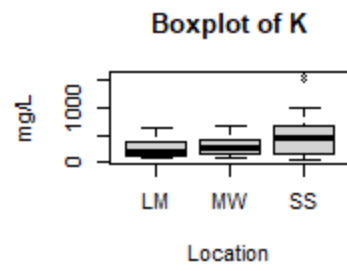
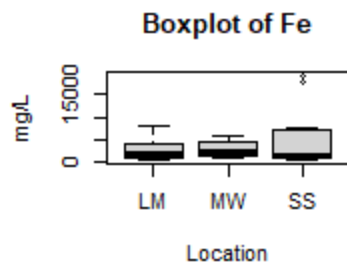


Figure C1 Boxplot of mean heavy metals in peats in the Inlet and midpoints, Cont'd

