Factors Controlling Peat Chemistry and Vegetation Composition in Sudbury Peatlands after 30 Years of Emission Reductions

A Thesis Submitted to the Committee on Graduate Studies in Partial Fulfillment of the Requirements for the Degree of Masters of Science in the Faculty of Arts and Science

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Abstract

Peatlands are prevalent in the Sudbury, Ontario region. Compared with the well documented devastation to the terrestrial and aquatic ecosystems in this region, relatively little work has been conducted on the peatlands. The objective of this research was to assess factors controlling peat and plant chemistry, and vegetation composition in 18 peatlands in Sudbury after over 30 years of emission reductions. Peatland chemistry and the degree of humification varies considerably, but sites closer to the main smelter had more humified peat and the surface horizons were enriched in copper (Cu) and nickel (Ni). Copper and Ni concentrations in peat were significantly correlated with Cu and Ni in the plant tissue of leatherleaf, although the increased foliar metal content did not obviously impact secondary chemistry stress indicators. The pH and mineral content of peat were the strongest determining factors for species richness, diversity and community composition. The bryophyte communities appear to be acid and metal tolerant, although *Sphagnum* mosses are showing limited recovery.

Keywords: heavy metals, wetland vegetation, humification, peatlands, anthropogenic emissions, secondary metabolites, bryophytes, community composition

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1 General Introduction

1.1 Wetlands and Their Key Functions

A wetland is defined as "land that is saturated with water long enough to promote wetland or aquatic processes as indicated by poorly drained soils, hydrophytic vegetation and various kinds of biological activity that are adapted to a wet environment" (NWWG 1988). Wetlands are unique ecosystems that represent a transitional area between aquatic and terrestrial systems and are the main interface for moving nutrients, pollutants, and sediments from land to water. These ecosystems are vital because of their biodiversity and irreplaceable hydrological and ecological functions; yet globally are also amongst the most vulnerable habitats (Zedler and Kercher 2005; Mitsch and Gosselink 2007). Brinson and Malvarez (2002) categorized the main stressors to wetlands that include: geomorphic and hydrologic changes (drainage or filling of wetlands, water diversions and dams, the disconnect of floodplains from high flood risk areas); climate change (global warming, increased intensity and frequency of storms and droughts); and nutrients and pollutants (eutrophication, as most wetlands occur in landscape sinks they are susceptible to collecting pollutants). Wetlands as a result are highly susceptible to changes in hydrologic, landscape, and climatic conditions, and as wetland areas are lost, the key functions they provide are also lost (Zedler and Kercher 2005). The natural physical, chemical and biological functions performed by wetlands provide great value to humans and the vegetation is an integral component of wetland ecosystems and plays an important role in its environmental function (Rydin and Jeglum 2006). It is important to note that due to the heterogeneity between wetlands, not all wetlands perform all functions and the success of the functions performed will also differ.

Biological functions

Wetlands are vital habitats due to the heterogeneity in hydrology and soil conditions, which result in a wide range of ecological niches. In Canada, wetlands provide the necessary habitat for one third of the vulnerable, threatened or endangered wildlife species and support diverse communities, wildlife, and water fowl for breeding, foraging and cover (Environment Canada

2004; Brazner 1997). Wetland flora has multiple roles in the biological functioning of wetlands including contributing to the physical habitat, and the decomposing tissue contributes to peat accumulation and fuels invertebrate food webs (Brix 1997). There are also numerous recreational and commercial values to wetlands including hunting, fishing and trapping (Mitsch and Gosselink 2007).

Water Quality and Wetlands

The water purification functions of the wetlands are dependent on the wetland substrate, microbial community present, vegetation, and water properties. When water passes through a wetland its velocity is reduced, which allows suspended sediment to settle out (estimated 80-90% of sediment) and enables biochemical reactions to occur between the plants, substrate, microbes and water column (Shutes 2001). The substrate provides a habitat for microbes and is the medium for many of the chemical transformations which occur, and the primary storage area for available nutrients and chemicals to vegetation (Mitsch and Gosselink 2000). Pollutants (e.g. heavy metals), nutrients (e.g. nitrogen (N) and phosphorus (P) from agricultural runoff), as well as other contaminants, can be taken up by plants or microbes and held in the plant tissue or peat, which can improve the water quality of the surface water and decrease the chance of issues with water quality downstream, such as toxicity and eutrophication (Mitsch and Gosselink 2007; White and Bayley 2001).

Wetlands represent a substantial portion of global terrestrial carbon reservoirs and are extensive and diverse in Canada. Approximately 30 to 50% of the soil carbon (C) pool is stored in peatlands globally, and about 85% of North America's soil C is stored within peatlands, which is important in the context of the global carbon cycle, and therefore climate change (Bridgham et al 1995; Bridgham et al 2006). Wetlands in Canada, based on the various functions they perform, generate an estimated 5 to 10 billion dollars annually in economic returns through possible flood and erosion management, the improvement of water quality, as well as for various recreational uses (Environment Canada 2004). Despite their importance, due to the complexity and variability between natural wetlands, their specific functions are still not fully understood when compared to the terrestrial and aquatic environment.

1.1.1 Characterizing Wetlands

In Canada, wetlands are classified into five classes: fens, bogs, marshes, swamps and shallow open water (NWWG 1997). Peatlands are wetlands which over time accumulate partially decomposed plant litter material and peat moss, with the rate of accumulation being marginally faster than the rate of decomposition and in Canada, are classified as having greater than 40 cm of peat accumulated (NWWG 1988). Peatlands can be grouped into two main classes; fen (minerotrophic) peatlands, which receive groundwater and precipitation, as opposed to bog (ombrotrophic) peatlands, which only gather precipitation as the dominant water source (NWWG 1988; Zoltai and Vitt 1995). The classification techniques used to distinguish between peatlands are generally based upon the following characteristics: surface morphology, water type, surface pattern, morphology of underlying mineral soil and vegetation physiognomy (Rydin and Jeglum 2006).

Bogs have a water table level at or slightly below the surface, and generally the surface is raised above or level with the surrounding terrain. As bogs receive no groundwater or surface runoff from the surrounding mineral soils, the primary water source is through precipitation. All bogs are ombrogenous and since precipitation is usually mildly acidic and contains a low concentration of dissolved minerals, surface bog waters are also quite low in dissolved minerals and are acidic (Zoltai and Vitt 1995). Peat in most bogs can show horizontal stratification with depth and many bogs are seen in the peat profile to have originally started out as fens. *Sphagnum*, which is a key element in bog vegetation, is able to acidify the surrounding environment to a degree by the exchange of mineral cations with hydrogen ions, and it is through this process, plus nutrient filtering, that *Sphagnum* under some conditions can direct wetland succession and initiate the transformation from a fen to a bog (Andrus 1986). Bogs generally have less humified peat, a low diversity of plant communities and the vegetation composition is characterised by *Sphagnum* mosses, lichens, feather mosses and ericaceous shrubs (NWWG 1997).

Fens generally have a fluctuating water table and are influenced by both groundwater and surface water movement from the surrounding catchment basins. As a result, fen water usually has a higher concentration of dissolved minerals than bogs, and fens are therefore minerotrophic. As fens vary in source water and nutrient input, which determines the level of nutrients and pH, they in turn can support a variety of vegetation and thus the plant community composition varies greatly among fens and the diversity of plant species is higher than in bogs (Weltzin et al 2000). Consequently, fens can be further classified as rich or poor. Poor fens, which are fens that are acidic and minerotrophic, are generally dominated by *Sphagnum* sp and ericaceous shrubs and able to hold an open, wooded or shrubby canopy and the vegetation composition is more similar to that of a bog (Zoltai and Vitt 1995). The pore water pH values are generally range between 4.5 and 5.5 (Vitt 1990). Moderately rich fens are those which have a slightly higher dissolved mineral content in the water and are dominated by brown mosses (i.e. *Scorpidium* or *Drepanocladus*) and sedges. Rich fens, which are alkaline, basic to neutral, are comprised of sedges, shrubs, as well as true moss species such as brown mosses and generally have higher species richness (NWWG 1997). In wetter fens grasses and some bryophytes are dominant, but in drier fens shrubs are more prominent.

Canadian peatlands cover about 14% of the land surface, which is estimated to be 1.24 million km^2 and bogs and fens comprise more than 90% of the peatlands in Canada (NWWG 1988). Wetlands locally as well as globally have been subject to human impacts, and it is roughly estimated that within the last century or two about 50% of global wetland area has been lost as a result of human activities (Zedler and Kercher 2005). Due to the low-populated regions and vastness of Canada, the total loss of wetlands in Canada has not been fully characterized, but in the populated regions there are more detailed estimates of disturbance. The greatest loss is attributed to urbanization, pollution, the conversion of wetlands to other uses (e.g. agriculture) and hydrology changes (NWWG 1997). It is estimated that Ontario contains approximately 23% of Canada's wetlands, and 6% of the world's wetlands. However the pressures which northern Ontario wetlands face are quite different from the pressures present in southern Ontario (NWWG 1988). The percent loss of wetlands in Ontario has been far greater in the south, the most populated region, with 80% to 90% wetland lost compared with areas in northern Ontario (Sudbury 45% and Thunder Bay 30% wetland loss) (NWWG 1988). Northern Ontario wetlands are heavily impacted by forestry and mining rather than by agricultural drainage and urbanization. A healthy wetland ecosystem can be attributed to supporting similar physical and chemical characteristics of natural wetlands in the region as well as sustaining a biological community (Mitsch and Gosselink 2007).

Constructed Wetlands

Constructed wetlands are built in areas where natural wetlands have been extensively demolished and can also be used in areas of anthropogenic discharge to remove various types of pollutants which are present in the wastewater that flows through the system to modify the runoff and improve water quality. These artificial wetlands have been used to treat urban and highway runoff (Shutes et al 1999), industrial waste and mine drainage (Mitsch and Wise 1998), and agricultural runoff (mainly N and P) (Kovacic et al 2000). Wetlands are constructed in order to mimic the function and structure of natural wetlands. However, as natural wetlands have extreme variability in their functional components, it is near impossible to accurately predict responses to wastewater application. Constructed wetlands on the other hand can be specifically designed to enhance the effectiveness as a treatment facility, by controlling the composition of the substrate, the types of vegetation, the location and size of the wetland, and also have control over the hydraulic pathways and retention time (Shutes 2001).

The benefits of constructed wetlands for wastewater treatment can include a relatively low cost for construction, requires less operation and maintenance, consumes less energy, and as a result, generally costs less than conventional treatment plants (Kivaisi 2001). The lifespan of the construction and frequency of dredging varies greatly depending on the use and amount of toxic materials (heavy metals, hydrocarbons) entering the system (Shutes 2001). Pollutants in surface water can be removed through assimilation into plant tissue, sedimentation, precipitation, microbial transformations and adsorption to soil particles (Shutes 2001). This is enhanced due to long retention times and the effective removal of particulate matter from the large area of sediment surface which is in contact with the flowing water. The sediment surface is also the location where microbial activity is involved in oxidation of organic matter and the transformation of nutrients occurs which can help to improve the water quality (Mitsch and Wise 1998).

1.2 Importance of Hydrophytic Vegetation

The plant communities and particular species present in a wetland has been used extensively as an indicator of wetland conditions, as it is generally assumed that the vegetation can most accurately reflect wetland health due to the relatively high species richness, rapid growth rates and direct response to environmental changes (US EPA 2002). However, it is important to first understand the contribution of wetland plants to wetland ecosystems (Mitsch and Gosselink 2007).

As plants are at the base of the food chain, the photosynthesis of wetland vegetation is a major channel of energy flow into the system and is considered the link between the inorganic environment and the biotic one. Much of the organic matter produced by macrophytes as well as algae fuels the detrital food chain, as opposed to most terrestrial ecosystems where it is directly used by herbivores (Brix 1997). Wetland vegetation strongly influences the water chemistry, hydrology and the sediment regime of wetlands (Mitch and Gosselink 2000). They are major storage sites for C and nutrients and influence methane production and nitrification-denitrification at the plant root – sediment interface (Rydin and Jeglum 2006; Ström et al 2005).

The long-term carbon accumulation in peatlands is more attributed to the low decomposition rates, rather than the high production rates of the plants, and changes in the vegetation composition can impact the rates of decomposition, plant production, and subsequently the peat accumulation rates and carbon and nutrient cycles may be altered (Scheffer et al 2001; Clymo 1983). The wetland vegetation, as well as the litter it produces, is also capable of altering the hydrology and moisture conditions of the peatlands, which can also play a part in controlling the rates of decomposition. The quality and quantity of plant litter produced is species dependent and the litter decomposition rates have also been shown to vary depending on the microbial community that is present (Strickland et al 2009). Woody biomass is high in lignin and low in N concentrations, and therefore breaks down slowly, especially in anaerobic conditions since phenol oxidase requires oxygen (Freeman et al 1997). Mosses generally have similar decomposition rates to woody biomass, and *Sphagnum* mosses are also low in N concentrations and contain insoluble phenolic acids, which makes the tissue resistant to decomposition (Aerts et al 1999; Scheffer et al 2001). The litter and its impact on microenvironmental conditions are, therefore, not only able to affect the quality of the peat, but have also been shown to alter the plant community composition (Weltzin et al 2005).

Sphagnum mosses are considered the dominant component of bog and poor fen peat, and are keystone species in terms of ecosystem function (Rydin and Jeglum 2006). *Sphagnum* mosses are able to drive peatland dynamics and shape the habitat through several key features. Under favourable conditions, these mosses are able to stimulate peatland development by reducing pH levels, low decomposition rates, and maintaining a higher water table. They are resistant to decay, tolerant to and require low concentrations of nutrients and minerals. There are numerous *Sphagnum* species, all of which have different requirements (e.g. water levels, pH, and shading) which enables *Sphagnum* to dominate along various gradients and provide successional changes as the wetlands age (Chirino et al 2006). The productivity and success of *Sphagnum* mosses is mainly attributed to the water table depth, due to its strong capillary rise functions and inability to control water loss (Proctor et al 2007). *Sphagnum* is however able to withstand desiccation of about 50-90% and can recover physiological functions upon re-wetting, although the rate of this varies depending on the species (Proctor 2000; Hájek and Beckett 2008). As *Sphagnum* resists decomposition, the underlying *Sphagnum* peat preserves relatively larger pore spaces and maintains a larger structure providing the *Sphagnum* mat with continuous capillary network from the water table, even under short periods of a lowered water table, and is able to retain relatively large amounts of water in hyaline cells (Clymo and Hayward 1982; Price 1997). Clymo and Hayward (1982) estimated that more carbon is held in the biomass of both living and dead *Sphagnum* than is fixed on an annual basis by all other terrestrial vegetation.

The wetland vegetation community composition is known to be a useful indicator of biotic integrity and ecosystem health through the species richness, diversity, non-native species richness, and community biomass and productivity (Zedler and Kercher 2004). Plant communities respond to environmental changes including anthropogenic pollution, hydrology changes and water quality (Albert and Minc 2004; Lopez and Fennessy 2002). Different plant species combinations thrive depending on the water level, anoxic conditions, substrate composition and nutrients present (Rydin and Jeglum 2006). Depending on the duration, depth, and frequency of the wetland saturation, wetland plants are typically obligate (found exclusively in wetlands) or facultative (species found in wetlands, but also could be found in upland systems). The coefficient of wetness of the plants, as well as the presence of non-native vegetation has been found to be characteristic of wetland degradation and can be used as an indicator of the wetland health (Zedler and Kercher 2004). Non vascular plants are of particular importance to poor fen communities and their sensitivity to air pollution and heavy metals is renowned (Salemaa et al 2001). As individual plant species generally have an optimal range of nutrient status and pH, measures of the plant community composition can sometimes be indicative of the local nutrient availability and chemical characteristics of the wetland. The composition of the plant community can greatly impact the diversity for other taxonomic groups as they provide a critical habitat structure and wetlands with greater structural diversity maintain greater wildlife species diversity (US EPA 2002). These taxonomic groups include fish, birds, epiphytic bacteria, periphyton and macroinvertebrates. The services provided by wetlands have only recently been recognized, but over the past two centuries peatlands have been widely decimated due to a variety of factors.

1.3 Climate Change and Wetlands

Climate change is recognized as a major threat to the survival of species and because of its location, Canada is anticipated to experience greater rates of warming than other regions in the world (Erwin 2009). Depending on the baseline frequency of disturbances, the effects on the terrestrial ecosystem will partly depend on the prior adaptation present. Climate change has the potential to alter the distribution, extent, frequency and intensity of disturbances, including fires, drought, insects and pathogens, hurricanes, windstorms, ice storms, and landslides (Burkett and Kusler 2000). For species or communities which are already at the limit of their habitat range and tolerances, the impacts would be particularly severe.

The frequency and position of wetlands in the landscape are strongly determined and dependent on the climatic conditions, and wetlands will be particularly susceptible to changes in the quantity and quality of water supply (Ferrati et al 2005). In general, lower water tables are anticipated with climate change. Due to our limited understanding of how wetland flora and fauna respond to changes in the temperature, precipitation, water level and quality and atmospheric carbon levels, it is difficult to predict wetland responses to climatic changes. Some research has shown that under extreme climatic events, such as drought, there can be sudden and dramatic changes in the abundance as well as the spatial arrangement of dominant plants (Gitlin et al 2005). However, wetlands that primarily depend on precipitation as their main water source, such as bogs, are likely to be more vulnerable to climate change (Burkett and Kusler 2000).

1.4 Consequences of Wetland Drainage and Drought

In a Canadian context, drainage is a growing abiotic influence on peatlands due to expansion of agriculture, peat extraction, mining and silviculture. The extraction of peat as an energy source, or fertilizer has received considerable attention since harvested sites rarely return to a functional peatland ecosystem, due to the impacts of drainage and extraction on the physical and hydrological conditions which are necessary for the re-establishment of *Sphagnum* (Van Seters and Price 2001; Price 1996). Peatland drainage impacts the physical structure of the peat which can lead to compaction, increases the rate of decomposition, as well as increasing the small pore size distributions and the bulk density (Sherwood et al 2013). As a result, this can impact the relationship between the quantity of water added or removed from the habitat which can lead to greater evaporation to the atmosphere and could lead to a more rapidly fluctuating water table and lower the overall water storage capacity of the peatland (Price 1996). With the loss of large diameter macropores and an increase in the smaller narrower pores, the water retention also increases which in turn decreases the free-water available to *Sphagnum* though capillarity (Chirino et al 2006). This water stress in *Sphagnum* can inhibit their re-colonization, especially if it occurs during the summer growing season (Campeau and Rochefort 1996). The successful re-colonization and dominance of *Sphagnum* is diminished even further when post-disturbed sites undergo quick re-growth of vascular and woody species which can quickly create unfavourable conditions by shading out understory species, and can reduce the biomass of *Sphagnum* mosses (Bonnett et al 2010).

There is also concern that with drainage, as well as changes in climate, the lowered water table as a result of drying could stimulate decomposition by easing the constraints posed by the anoxic conditions on microbial activity. This would further stimulate the breakdown of phenolic rich peat through phenol oxidase activity as stated by the 'enzyme latch' hypothesis (Freeman et al 1997). These lower water table positions will also increase the substrate temperature, and an increase in the nutrient availability with warmer temperatures and quicker soil mineralization rates can also have severe impacts on the vegetation (Van Seters and Price 2001). The nonvascular community is particularly at risk due to the increased availability of N favouring vascular species which would result in an increase in shading and could reduce total bryophyte cover, as well as the composition of the species present (Heijmans et al 2001). Peatlands, due to their long-term peat accumulation, have generally provided a net cooling effect by being a carbon sink, but these changes which could disrupt the decomposition or plant productivity in these systems, could also alter the function and promote the release of stored carbon back into the atmosphere (Erwin 2009).

1.5 Impact of Disturbance on Vegetation

Peatlands are vulnerable to disturbances, and from a Canadian viewpoint, an estimated 20 million ha of peatlands have been lost or severely degraded through agriculture, forestry, mining, development and extraction since 1800 (Rydin and Jeglum 2006). Disturbances, both human-induced and natural, can rapidly change the composition, structure and function of ecosystems, and thus the natural variety of plant species, and can even lead to the development of industrial barrens. The species composition of wetlands has important implications for ecosystem functioning, as well as impacting the carbon and energy exchange, and carbon dioxide and methane fluxes (Ström et al 2005).

Pollution is recognized as one of the most severe environmental stressors, although is usually quite localized. Large areas of land have been subject to elevated levels of pollutants, such as heavy metals, sulphur dioxide (SO_2), and ozone (O_3). In terrestrial and wetland environments, metal contamination is largely associated with mining, metal smelting, and refining industries (Wuana and Okieimen 2011). Metal smelters, incinerators and other industrial processes are of particular concern as they are demonstrated air emission sources for SO_2, Cd, lead (Pb), Zn, Ni and Cu (Nagajyoti et al 2010). The high temperature processing of metals, such as smelting, can emit metals in both particulate and vapour forms. The vapour forms of heavy metals, such as Cd, Cu, Pb and Zn can then combine with water in the atmosphere and form aerosols which are then able to be dispersed by dry deposition from the wind, or wet deposition through precipitating in rainfall (Nagajyoti et al 2010). Contamination is also possible through runoff from the erosion of mine wastes, and the corrosion and leaching of metals to the soil. During mining, tailings are discharged into natural depressions, including wetlands nearby, resulting in elevated concentrations (DeVolder et al 2003). The most notable areas in Canada where mining and smelting have caused environmental damage include Trail, BC, Rouyn-Noranda, QC, with the most extensive impact occurring in Sudbury, ON.

Impact of Pollution on Vegetation Physiology

The two main pathways by which heavy metals are incorporated into vascular plant tissues are through foliar absorption from stomatal and cuticle pathways by gaseous emissions and the settling of dust contaminated with heavy metals, and through root uptake with the primary route of heavy metal exposure being through root uptake. If pollutants, such as heavy metals in the substrate, are present in high enough concentrations and are bioavailable to plants, they can inhibit physiological processes including respiration, photosynthesis, cell elongation, mineral nutrition, and the plant-water relationship. Signs of this direct damage to vegetation include chlorosis and necrosis of the foliage, impeded growth rates, shortened and poorly developed roots and ultimately mortality (Marschner 1995). High concentrations of trace metals (Ni, Cu, cobalt (Co), Zn, manganese (Mn), Cd, and mercury (Hg)) are toxic to plants and lead to growth inhibition, inhibition of photosynthesis and respiration, stimulate oxidative stress, and can ultimately lead to plant death (Michalak 2006). Sulphur dioxide, on the other hand, penetrates the foliage in gaseous form through the stomata of higher plants. The effect of combinations of metals and other atmospheric pollutants (NO, NO_2, NO_x, O_3 and SO_2) can also pose cumulative toxic effects. Bryophytes, in comparison to vascular plants, do not possess any roots, have little or no developed cuticle and absorb nutrients directly from rainwater or the air; therefore they cannot prevent the passage of heavy metals or other toxic ions into their shoots or thalli (Tyler 1990). Bryophytes are therefore often used as indicators, and for monitoring air pollution. There are two categories of bryophytes in response to pollution, those which have a high capacity to absorb and accumulate, such as exposure to Pb and Zn, and those which are very sensitive, even in minute quantities, such as exposure to SO_2 (Salemaa et al 2004; Gilbert 1968).

There can also be indirect consequences to the vegetation through damage to their mycorrhizae and water relation stress, which can increase the sensitivity and vulnerability of the plant. Plants with mycorrhizal associations can be protected from metal toxicity below certain concentrations by mycorrhizae limiting the uptake through various mechanisms (i.e. chelators), and mycorrhizae have also been shown to accumulate metals themselves (Leyval et al 1997). High concentrations of heavy metals have been shown to have an adverse effect on mycorrhizae and without plants being able to form these important associations, this may have an impact on plant growth through an increased susceptibility to metal toxicity as well as impacting the other beneficial interactions between the plants and mycorrhizae (Kahle 1993). The emissions of SO_2 and metals from smelters can also lead to the severe acidification of soils and accumulation of heavy metals in the soil. As a result, this diminishes the buffering capacity of the soil and lowers the pH which increases the leaching of base cations as well as increases the concentrations of acid cations (Al, Mn, Fe) and other potentially toxic metals (Cavallaro and McBridge 1984). The susceptibility of plant species to secondary stress factors can also be impacted by air-borne pollutants. As the vitality of the plant is lowered, the resistance to pathogens can be impacted, an increase in herbivory, and the sensitivity of the species to drought and frost can also increase (DalCorso 2012).

Plant Secondary Compounds as Signs of Stress

Plants have a very complex and broad system for secondary metabolism, which involve carbon-based compounds that are not directly related to growth, reproduction, and development (Seigler and Price 1976). They are an integral component of the plant's defence system and provide numerous benefits to the plant, including anti-herbivore and antioxidant properties (Wink 1988).

Heavy metal accumulation in plants, as well as exposure to air pollutants (i.e. SO_2 and O_3) causes stress, which induces signalling cascades that activate ion channels, kinase cascades, the production of reactive oxygen species (ROS) and oxidative stress, the inhibition of enzyme activities through the displacement of essential cofactors, and blocking protein or metabolite functional groups (DalCorso 2012). Although ROS are a natural consequence of aerobic metabolism, when metal ions saturates the defence mechanisms the plant will begin to suffer oxidative stress as a result of the increased production of ROS and the inhibition of metal dependent antioxidant enzymes (Manara 2012). As a result, plant cells try to maintain a low concentration of ROS. Several antioxidants are a key part of the plants defense system to ROS, and do so by deactivating and reducing the reactivity of ROS. Phenolic compounds are one of the most important groups of secondary metabolites involved in scavenging ROS and also are able to chelate metals (Michalak 2006). Changes in the antioxidant levels and activities (such as phenolic compounds and anthocyanins) are an unspecific response to oxidative stress and can vary greatly depending on environmental factors, such as air pollution and heavy metal stress. Their occurrence in vegetation has been used as a possible early stress response in the absence of visible toxicity symptoms (Loponen et al. 2001; Pasqualini et al. 2003). As well as changes in foliar content, the roots of many plants under heavy metal stress have also been shown to exude high levels of phenolics (Rice-Evans et al 1997). Caution has to be taken, however, as these the changes in levels can be due to other stressors as well, such as drought, salinity and UV radiation.

Heavy metals and air pollutants have also been shown to directly and indirectly lead to the inhibition of photosynthesis. The reduced rate of photosynthesis is usually as a result of accumulation of metals in the leaves, disrupted chloroplast structure, blocked chlorophyll synthesis and increased chlorophyll degradation, inhibited activities of the Calvin cycle enzymes, disordered electron transport, and stomatal closure resulting in a carbon dioxide deficit (Clijsters and van Assche 1985). The chlorophyll content significantly decreases under heavy metal stress, which causes a drastic decrease in the photosynthetic rate, and thus chlorophyll content is used as an important indicator for photosynthetic activity, stress, and nutritional status (Küpper et al 2008).

Monni et al. (2001) showed that close to a Cu-Ni smelter in Harjavalta, Finland, even metal tolerant plants such as E*mpertrum nigrum* when under heavy metal stress displayed decreased chlorophyll content and organic acid in the foliage, which indicated a reduction in physiological activity. The accumulation of anthocyanin in the foliage has been noted to be in response to stress such as nutrient deficiency, ultraviolet radiation exposure, herbivory, metal toxicity in some species, and can be used to protect the photosynthetic function of the plant (Close and Beadle 2003). Increases in phenolic and lignin content have also been reported for some plants in response to exposure to elevated concentrations of Ni, Cu and Cd (Michalak 2006; Kováčik and Klejdus 2008). A study conducted on mountain birch along a strong pollution gradient from a Ni and Cu smelter determined that the quantity of the main classes of phenolic compounds (gallic acid derivatives (GAs), hydroxycinnamic acid derivatives (HCAs) and flavonoids (FLAs)) changed in response to the pollution (Loponen et al. 2001). An increase in phenolic concentrations can also impair decomposition rates in anaerobic conditions of the peat, consequently impacting peat quality (Freeman et al. 2004; Pasqualini et al. 2003).

Plant Community Composition Response to Pollution

Generally, at high enough concentrations of heavy metals (i.e. Ni and Cu) as well as exposure to elevated SO_2, species health greatly decreases, and the vegetation cover and species richness and diversity greatly decreases, even to zero, close to emission sources (Salemaa et al 2001; Buchauer 1973; Folkeson and Andersson-Bringmark 1987). The relatively vulnerable species are the most at risk of being reduced or eliminated entirely at stressed sites and may be replaced by those which are more tolerant. The species that are able to colonize metal-contaminated sites are generally metal resistant and have adapted to this stressed environment, either through avoidance or tolerance. Avoidance is achieved by preventing metal ions from entering their tissues, whereas tolerant plants are able to detoxify metal ions that have crossed the plasma membrane (Millaleo et al 2010).

In upland ecosystems, it has been well documented that when exposed to elevated levels of contaminants, the vegetation cover and composition can be drastically impacted. With a decreased vegetation cover, the rate of erosion can also increase, which can remove nutrients as well as the organic and top layers of the substrate. Salemaa et al (2001) conducted a gradient study from a Cu-Ni smelter in Finland and reported as distance from the smelter increased, the forest vegetation cover and species richness also increased. Within the immediate area of the smelter (<1km) the understorey vegetation was dead, and the overstory which still contained pines that were stunted in growth, damaged and suffering from needle discolouration. Adjacent to a Zn smelter in Pennsylvania, USA, an area of about 500 ha was devoid of any vegetation and where vegetation was present it was sparsely covered with tolerant species (Buchauer 1973). The combined effects of SO_2 and heavy metals have been studied and have shown sensitive species only occurring at an appreciable distance from the source, and the diversity and richness was vastly impacted close to the source (Le Blanc et al 1974). Folkeson and Andersson-Bringmark (1987) also conducted a study of the impacts of metal emissions with essentially no SO_2 or other acidifying compounds on vegetation in the vicinity of Gusum, Sweden and the vegetation cover significantly decreased closer to the foundry as well as a reduction in biomass, length, and weight of the various species.

In the Sudbury, Ontario, Canada region there is a prominent Ni and Cu smelter which has received a great deal of attention (Gunn et al 1995; SARA 2009; Hutchinson and Whitby 1974; Gundermann and Hutchinson 1995). Previous work has shown that tree density, species richness and the Shannon diversity index increased with distance from the smelter, and within very close proximity to the emission source (<3km) the forest was found to be devoid of any vegetation (Freedman and Hutchinson 1980). Any species which did appear closer to the smelter were tolerant to the pollutant stresses and were in isolated patches. Gignac and

Beckett (1986) found that in peatlands throughout the Sudbury area, similar impacts were found, with severe devastation to the vegetation community within 10 km of the smelter and the species that were colonizing in impacted sites were suspected to be metal-tolerant species, such as *Betula papyrifera* and *Pohlia nutans*. In comparison to upland ecosystems there has been considerably less work conducted in disturbed peatlands and the impact to vegetation.

1.6 Industrial Impact on the Sudbury Landscape

The first settlement in the Sudbury district by Europeans was at Wanapitei Post in 1822. The logging industry developed soon after and remained dominant until the 1920s, which greatly contributed to mass deforestation; however the impact was minimal compared to the later requirements of trees for the roast yards (Winterhalder 1996). A major consequence of the increased area being cut down was an increase in the soil erosion, which was particularly problematic on the already shallow soils on the slopes. Extraction of Cu and Ni from the Sudbury basin began in the late 1880s, and the Sudbury region is noted as one of the world's major ore deposits of Ni and Cu. Open roast yards were originally used to remove the sulfur from the Cu-Ni ore. From 1885 to 1929 eleven roast yards operated in Sudbury and over this period, about 10 million tonnes of SO_2 was released (SARA 2009). Vast amounts of lumber were required for this process, which not only led to a depletion of the supply by 1929, but also increased the frequency of fires and erosion (Gunn 1995).

The damage of the roast beds and ground level emissions of SO_2 was quite localized and caused mass destruction to the surrounding vegetation and acidification of the soils (Winterhalder 1996). The widespread impact to the landscape in Sudbury can be attributed to the smelter fumes, which contained SO_2 and metal particulates, particularly Ni and Cu. The effects of the smelters were extremely widespread with large areas of land rendered completely barren or semi-barren. The combination of extensive logging, smelting, fires and erosion resulted in a severely anthropogenic disturbed landscape. Following the mining and smelting operations, which commenced in 1882, 17000 ha of land were completely barren and 72000 ha of land were left semi-barren with stunted vegetation (Amiro and Courtin 1981). One of the most significant impacts of the barren landscape was soil erosion, which stripped the landscape of a significant portion of its topsoil, and left the remaining soil deficient in P, N and calcium (Ca). The erosion rate also increased the amount of sediment that was washed into the lakes, which caused severe damage to the shoreline and resulted in siltation (Pearce 1976). A lack of vegetation cover left the barren areas susceptible to high wind speeds which could have increased wind-blown deposition of metals from uplands and the surrounding area (Tanentzap et al 2007).

Sudbury's Ni and Cu smelting complex represented one of the largest point sources of SO_2 in the world in the early 1960's, contributing an estimated 4% of the global emissions (SARA 2009). Nieboer et al. (1972) showed that lichens, which are known to be good indicators of atmospheric pollution levels, decreased drastically close to the smelters. A similar decrease in diversity closer to the smelters was recorded for vascular plants (Amiro and Courtin 1981; Gorham and Gordon 1960; Freedman and Hutchinson 1980). Lake acidification combined with extremely elevated concentrations of toxic trace metals (Cu and Ni) in the Sudbury area was also very widespread and over 7000 lakes within a 1700000 ha area were acidified to a point where significant biological harm was expected (Keller et al 2007; Nriagu et al 1982).

The annual emission of SO_2 reached a peak of 2560 kt in 1960 (Potvin and Negusanti 1995). The provincial government of Ontario imposed limits on the smelter emissions in 1969 and 1970 to improve local air quality. In 1971 the smelter operation at Coniston was closed and in 1972 a 381m "Superstack" at Copper Cliff smelter began operating in order to disperse the by-products away from the city of Sudbury and Falconbridge closed its pyrrhotite plant. This resulted in the release of SO_2 being reduced from 2.5 million tonnes per year at the beginning of the decade to less than 1 million tonnes per year at the end and the particulate emissions also was halved to about 15000 tonnes (Potvin and Negusanti 1995). The containment of the mine waste and tailings drainage was also vastly improved in the 1970s which reduced the acidity and metal concentrations in the water prior to being released into the lakes and streams (Winterhalder 1996). In the 1990s the Ontario government implemented the Countdown Acid Rain program which further reduced emissions. This control strategy had target emissions of 365 kt of SO_2

per year to be met by 1994, and the Sudbury smelters did better than meeting the target (Gunn 1995). By 2010 the annual SO_2 emissions had been reduced to below 200 kt (OMOE 2012).

In addition to these reductions in the smelter air pollution, in 1978 a large-scale land reclamation program began resulting in over 3400 ha being limed and seeded and over 9 million trees have been planted (Gunn et al 1995). There have been widespread improvements in the surface water chemistry which has enabled a variety of organisms to recolonize the aquatic systems and the landscape has largely been re-vegetated (Gunn et al. 1995; Keller et al 2007). However, despite these improvements, many of the impacted lakes in the Sudbury region are still acidic with elevated metal levels and are showing a delayed and limited biogeochemical recovery (SARA 2009; Szkokan-Emilson et al 2011). The Sudbury Soil Risk Assessment (SARA) identified that this delayed recovery could be attributed to nutrient limitation, and not solely the metal toxicity. SARA (2009) also identified the integral part that wetlands play in the environment and the current knowledge gap that exists for the role they play in the recovery of the lakes and regulating and maintaining healthy aquatic systems.

Despite wetlands being abundant throughout this region, with over 33000 ha of wetlands in the city of Greater Sudbury, and many of which are connected to the 47000 ha of streams, lakes and rivers in the vicinity, relatively little work has focused on these systems (Monet 2013). A few studies conducted in the 1980s indicated that peatlands located in close proximity to the smelters were heavily contaminated with Cu and Ni, and the vegetation community (both vascular and non-vascular) were severely impaired (Gignac and Beckett 1986; Taylor and Crowder 1983). Although the acid and metal emissions have declined substantially since this time, the peatland systems have been largely un-investigated with a particular gap in the knowledge of the vegetation in these systems. There is a need for substantial studies to be conducted on these wetland systems investigating the potential recovery of the vegetation community post-emission reductions, and whether any differences in the vegetation are due to inherent variances in the wetlands or due to the historical and present day contamination.

The objective of my research is to characterize the peat and plant chemistry along with the vascular and non-vascular community composition in 18 peatlands with spatial variability in their Ni and Cu surface peat contamination. It was predicted that Ni and Cu concentrations would be higher close to the main smelter at Copper Cliff. The plant tissue Ni and Cu concentrations was predicted to increase with increasing peat concentrations and the plant secondary chemistry would indicate signs of stress under elevated metal exposure. It was also predicted that there would be a decrease in species richness and diversity at the most contaminated sites and that there would be a greater impact on the non-vascular community than the vascular community composition due to greater sensitivity to pollution stressors.

2 Methods

2.1 Study Area

2.1.1 Sudbury Geology

The Sudbury area (46°30' N, 81°00' W) is located on the Southern Province of the Canadian Shield in central Ontario, Canada and has a mean elevation of 300m above sea level and was totally glaciated in the most recent of the Pleistocene glacial advances. The Sudbury basin is unique to Precambrian shield geology as it lies near the junction of three major geologic subdivisions, with the Superior Province to the northwest and the Grenville Province to the southeast (Rousell and Card 2009).

2.1.2 Sudbury Climate

The Sudbury area experiences a continental climate. The average daily temperature in January is -13.6°C, increasing to 19°C in July. The total annual precipitation averages 650 mm of rainfall and 240 mm of snowfall (water equivalent), and is distributed relatively uniformly throughout the year (Environment Canada 2011).

2.1.3 Study Sites

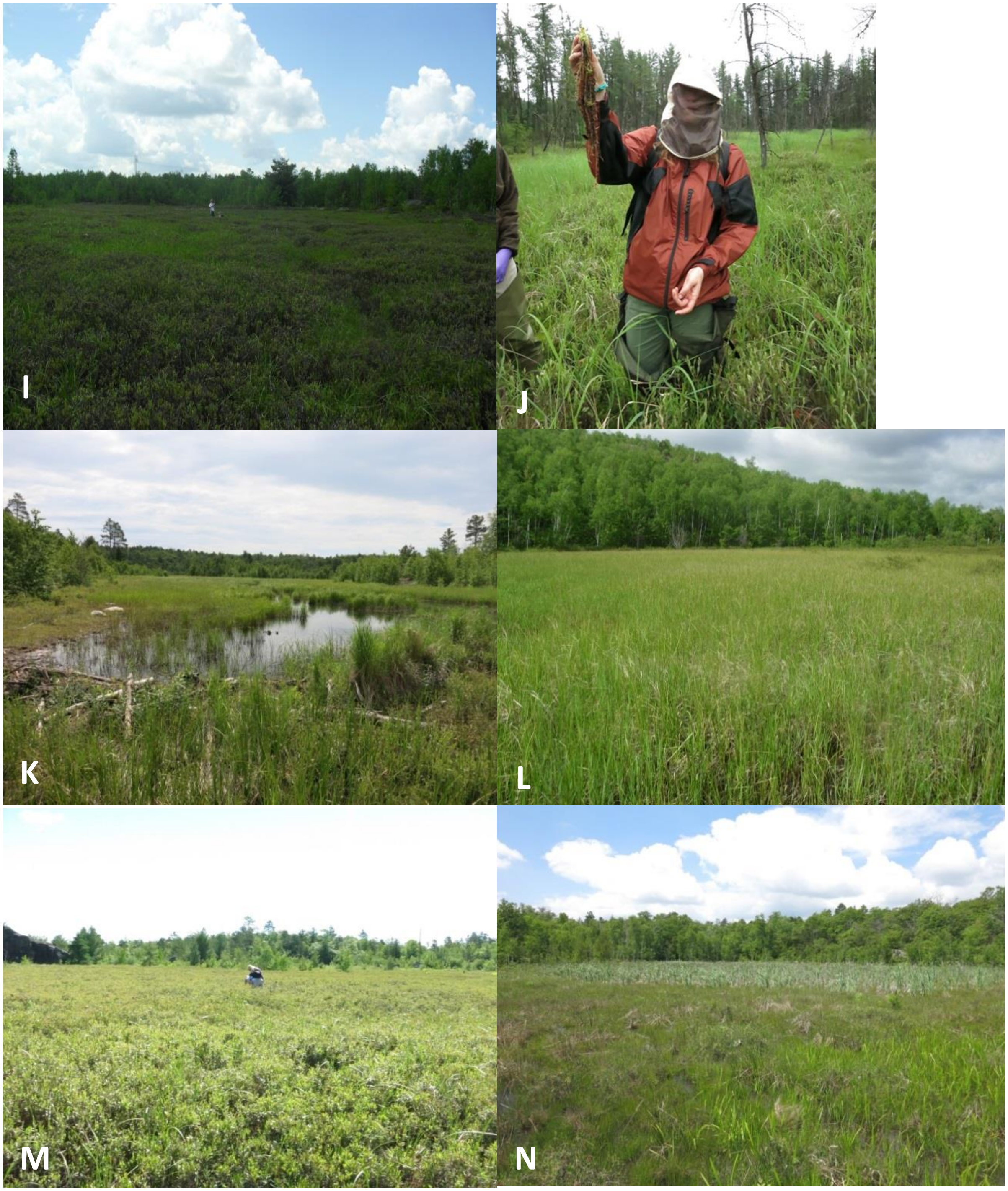
It is estimated that a quarter of the Sudbury area is comprised of wetlands, with fens dominating the region (SARA 2009). Eighteen peatlands were chosen for this study based on similar size (0.20 ha to 5.86 ha), vegetation, pH range of 3.4 – 5.0, organic matter accumulation to at least a depth of 45 cm, and attempted to constrain the Ca^{2+} content in the water of less than 12 mg L^{-1}, however two of the peatlands exceeded this. Although these limitations were put in place to attempt to keep the general characteristics the same, and suggestive of a poor fen or a bog, they vary in other aspects and due to spatial distribution are expected to vary in impact and contamination (Table 2.1) (Figure 2.1).

The peatlands were located in areas ranging from 'high disturbance' based on damage to upland vegetation, to the three peatlands within the Rockcut, Ashigami and Matagamasi lake catchments to be 'low disturbance' based on the corresponding surface Ni and Cu concentrations as a result of proximity to Copper Cliff smelter, and to a lesser extent, Falconbridge smelter and Conisiton smelter (Figure 2.2). The water table at all the peatlands that were assessed falls between 5 and 23 cm below the surface (Table 2.1).

Table 2.1 - Wetland study sites and summary characteristics (surface peat pH was assessed August 2012 and water table fluctuation below the surface from July 2010 to July 2011 using the electric tape method).

Wetland Code	Area (ha)	Drainage Water Body	Latitude	Longitude	Distance from Copper Cliff (km)	Peat pH	Fall pore water Ca ppm	Water Table Fluctuation (cm)
SLV	1.07	Silver Lake	46.4318	-81.0171	6.00	3.44±0.02	9.31±4.55	8.9
LU	3.08	Lake Laurentian	46.4551	-80.9678	7.53	3.90±0.15	10.3±0.5	5.4
MUD	0.20	Mud Lake	46.4544	-81.1652	8.30	3.90±0.15	19.6±8.5	27.5
BR	0.92	Broder Lake	46.3954	-80.9671	11.46	4.07±0.09	4.40±0.41	5.9
CRO1	0.86	Crowley Lake	46.3891	-80.9741	11.70	3.85±0.17	6.77±0.83	9.3
LON	0.22	Long Lake	46.3694	-81.0667	11.78	3.99±0.10	6.42±1.38	8.0
C2	2.09	Clearwater Lake	46.3696	-81.0613	12.13	3.31±0.03	11.2±3.3	N/A
C3	0.42	Clearwater Lake	46.3661	-81.0497	12.18	3.94±0.21	7.70±2.51	N/A
WHT2	1.09	Whitson Lake	46.5745	-80.9938	12.18	3.80±0.07	26.4±1.2	N/A
CRO2	1.03	Crowley Lake	46.3847	-80.9662	12.45	4.14±0.09	4.62±1.71	12.8
DH17	0.29	Daisy Lake	46.4541	-80.9000	12.62	4.31±0.08	12.8±6.5	7.8
C1	5.86	Clearwater Lake	46.3656	-81.0462	12.65	4.38±0.28	7.86±4.38	8.1
D5	2.05	Daisy Lake	46.4541	-80.8893	13.44	4.48±0.07	3.03±0.45	9.7
WHT1	1.56	Whitson Lake	46.5899	-80.9916	13.88	4.43±0.08	25.4±3.7	4.7
D4	1.05	Daisy Lake	46.4549	-80.8824	13.93	4.24±0.05	1.98±0.85	14.3
RCK	0.46	Rockcut Lake	46.7275	-80.9266	29.86	3.59±0.05	4.38±0.58	9.7
ASH	0.41	Ashigami Lake	46.6458	-80.6144	39.15	3.80±0.12	6.87±1.76	23.1
MAT	0.47	Matagamasi Lake	46.7134	-80.6192	42.99	3.47±0.09	7.50±0.87	11.8


A
B
C
D
E
F
G
H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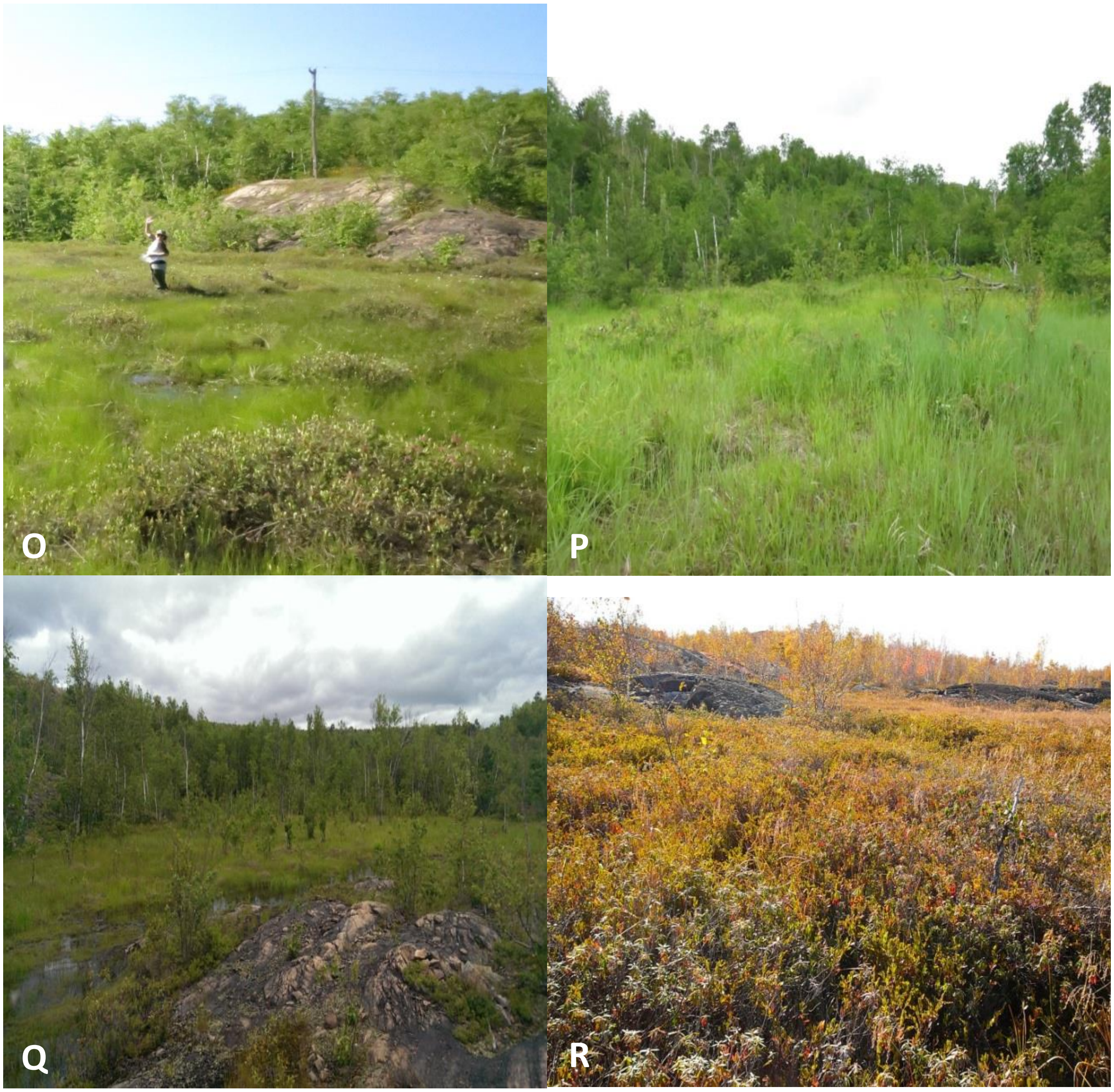

Figure 2.1 – Photos of the study sites (A: C2, B: LON, C: MUD, D: RCK, E: C3, F: DH17, G: CRO1, H: BR, I: WHT2; J: MAT; K: C1; L: WHT1; M: ASH; N: CRO2; O: SLV; P: D5; Q: D4; R: LU)

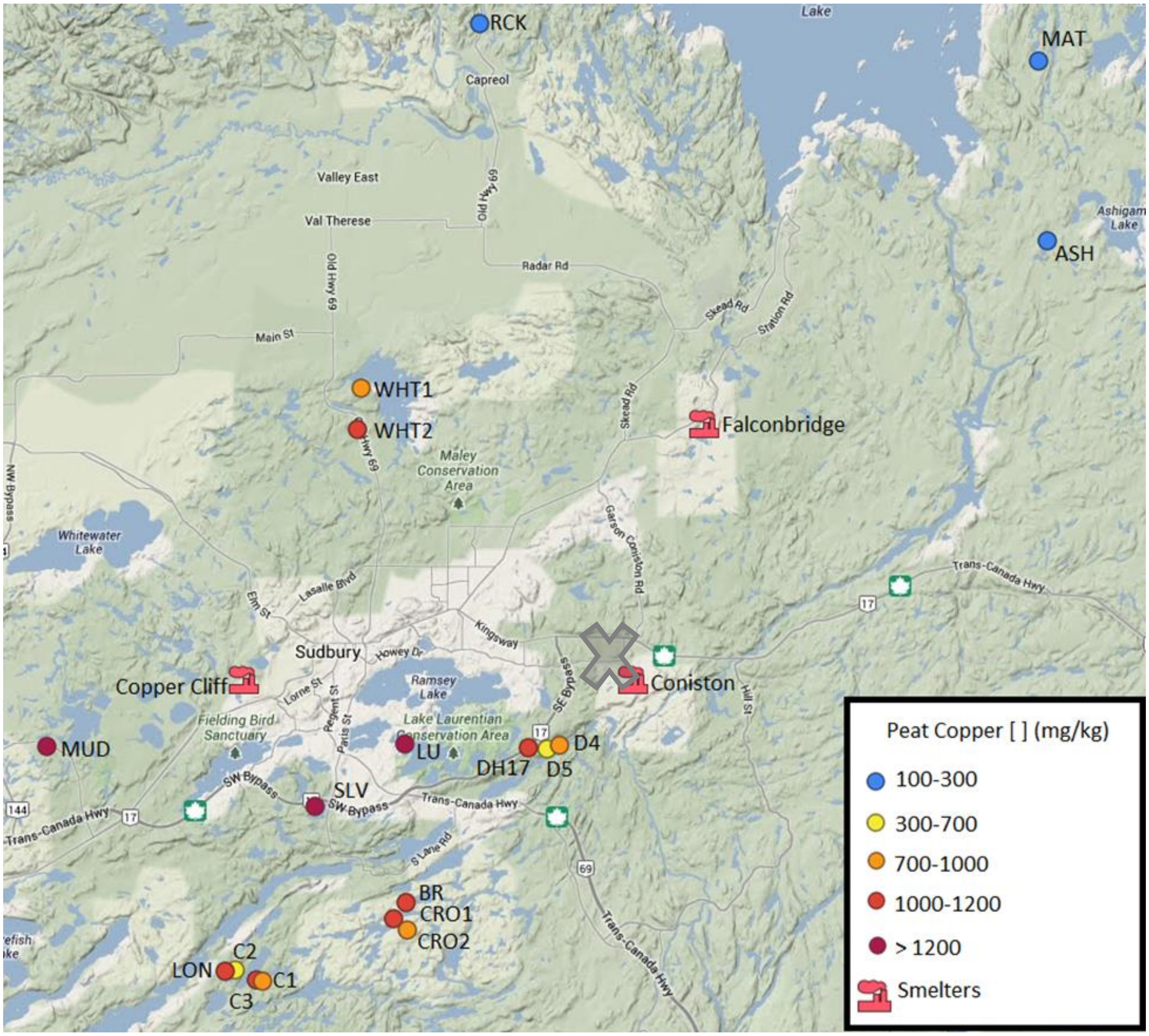

Figure 2.2 - Location of the eighteen sampling sites in the Greater Sudbury Area, Ontario with their corresponding concentration of Cu in the surface (0 -15 cm) peat (sampled October 2011), and the locations of the three smelters: Copper Cliff, Falconbridge and Coniston (decommissioned).

2.2 Field Sampling

All field sampling was conducted during August 2012 and June 2013. Peat, pore water, plant tissue sampling and vegetation assessment was conducted along a transect through the center of the wetland, avoiding the edge. This was to eliminate variances in the chemistry and composition of the substrate near the edge which would influence the vegetation community.

Samples of two co-dominant species (*Chamaedaphne calyculata* and *Kalmia angustifolia*) that were present at the majority of sites were collected with five replicates for each species per wetland. Tissue samples included new foliage which was not visibly damaged, samples of stems, as well as roots into separate clearly labeled paper bags. The roots were washed gently with deionized water to remove any soil or dust deposits prior to analyses. *C. calyculata* was present at 17 and *K. angustifolia* present at 16 of the 18 study sites. The roots, stem, and new foliage were collected for metal and nutrient analysis, and a subset of new foliage was collected and stored immediately at -18°C to determine chlorophyll, anthocyanin and total phenolic content. Leatherleaf (*C. calyculata*) is an evergreen, perennial ericaceous shrub which forms large, dense stands in bogs and poor fens. It has an extensive root system and the vegetative growth is able to promote the successful establishment of other woody plants (Swan and Gill 1970). Sheep laurel (*K. angustifolia*) is also an evergreen, perennial ericaceous shrub and forms well-developed and closely interlaced networks of rhizomes.

At each site, during August 2012, five peat samples were collected using a trowel from three depths (0-15cm, 25-35cm, 45-60cm) by digging a pit. Fresh peat samples were classified using the von Post humification scale (H1 to H10) based on the degree of decomposition of the peat (Appendix 7.1 - Table 7.1).

Prior to the community assessment, a species-area curve was used to determine how many quadrats would be necessary to characterize the species present. Sixteen $1m^2$ quadrats were used for the vascular vegetation and twenty $25cm^2$ quadrats for the nonvascular vegetation community composition assessment (Figure 2.1). Within each quadrat all vegetation was identified to species, and the vascular plant species nomenclature and authority names follow Fernald (1950), and Gleason and Cronquist (1991) and the bryophytes and lichens follow Schuster (1953). For the vascular vegetation assessment each species' percent cover was visually estimated and recorded, and for nonvascular the total bryophyte and total lichen percent cover was recorded, as well as the presence of each species. If the presence was less than 5% in the quadrat, the cover was visually estimated to the nearest 0.25%, and if between 5-20% the cover was visually estimated to the nearest 0.5%. Species were identified using field guides and a sample of each species was collected for confirmation of species identification in the lab. The vascular taxa collected were preserved in a plant press and then transferred to a herbarium, however the bryophytes were simply air dried and kept in a paper packets as pressing the plants would ‘lose’ the diagnostic traits. The coefficients of wetness, which are the estimates of the probability for which a species occurs in wetlands (Appendix 7.5 - Table 7.9), were recorded for the vascular taxa from each site, averaged and regarded as a wetness index for each peatland.

Figure 2.3 - Images showing the quadrats used for vascular (left) and non-vascular (right) vegetation community composition analysis.

Pore water of the study sites was sampled in October 2011 with three replicates per wetland. Autumn and summer water chemistry has been shown to explain more of the variation in species data than other times of the year (Hájek and Hekera 2004), but during the summer pore water collection there was a drought limiting the sample collection. Pore water was collected from three sampling wells in the center of each wetland using a 1.9 cm PVC pipe with slit openings covered in nylon mesh and the samples were extracted from the wells using polyethylene syringes and tubing after first purging the wells. The pore water was analyzed for metal and nutrient content using ICP-OES and the free metal ion concentrations were calculated using the Windermere Humic Aqueous Model, version 7 (WHAM) (Tipping 1994).

2.3 Laboratory Analyses

i. Metal and Nutrient Analysis

Peat and vegetation samples were oven dried at 60°C for 72 hours and then pulverized and thoroughly mixed prior to analysis. The ground dried sample (0.2 g) was added to 2.5 mL of concentrated nitric acid (trace grade assay 67-70% HNO_3) and left to cold-digest at room temperature for 24 hours, followed by a digest under reflux at 100°C for 8 hours. Samples were then filtered using coarse VWR filter papers and diluted ten times with B-pure water prior to analysis by inductively coupled plasma optical emission spectrometry (ICP-OES) for sodium (Na), potassium (K), Ca, magnesium (Mg), P, aluminum (Al), iron (Fe), Mn, Ni, Cu, Zn and Co. The precision of the results was confirmed by the analysis of certified NIST-1515-SRM apple leaves. For all elements, the recovery was between 85 – 120% except for Na (>1000%) due to suspected contamination, and subsequently was not included in the analyses, and there was a low recovery of Fe (66%). To determine if there was any impact of atmospheric deposition on the surface of the foliage, a subset of *C. calyculata* was washed and a subset left unwashed and analyzed using ICP-OES to determine any differences in the foliar metal and nutrient concentrations. The difference in the Ni and Cu concentration between the washed and unwashed *C. calyculata* foliage was typically less than 15%. The results from the unwashed foliage were used as there was no clear indication of surface deposition on the foliage.

Carbon, N, and sulphur (S) content of the peat and vegetation was analysed by weighing the ground dried sample (0.40 – 0.80 mg) and adding a 1:2 tissue:tungsten oxide (WO_3) ratio. The tissue and tungsten oxide mixture was packed in foil and quantified using an elementar vario MACRO analyzer. The precision of the results was confirmed using blanks and sulfadizine for recalibration, as well as QA standards (NIST-1515-SRM).

ii. Anthocyanins

Total anthocyanin concentrations of new foliage were determined for both *C. calyculata* and *K. angustifolia* using the spectrometric method derived from Kwee and Niemeyer (2011). Foliage was dried at 60°C for 72 hours and was ground using a Retsch MM300 mixer-mill. The ground sample (0.02 – 0.2 g) was extracted into 1.0 mL of acidified methanol (15% hydrochloric acid, v/v) on a shaker for 30 minutes and then centrifuged at 13000 rpm for 30 min. The supernatant was removed and the absorbance was measured at 535 nm versus a blank of acidified methanol (15% hydrochloric acid, v/v) on a spectrophotometer. The extract was compared to a calibration curve prepared with ≥95% Kuromanin chloride HPLC grade ($C_{21}H_{21}ClO_{11}$) (Sigma-Aldrich; Oakville, Ontario) at 26 concentrations ranging from 0.5 to 24 mg L^{-1} (Figure 2.2). Total anthocyanin content per sample was calculated using a modified equation described by Abdel-Aal and Hucl (1999) and converted to mg g^{-1} dry weight (Equation 2.1).

$$[2.1]\ C = (A/\varepsilon) \times (V/1000) \times MW \times (1/SW) \times 10^3$$

Where C is the concentration of total anthocyanin (mg g^{-1}), A is the absorbance reading, Ɛ is the molar absorptivity of Kuromanin chloride in acidified methanol (mean value of 27979.52 cm^{-1} M^{-1}, calculated using Beer's Law), V is the total volume of the extract (10mL), MW is the molecular weight of Kuromanin chloride (484.84 g mol^{-1}), SW is the sample weight, and 10^3 is the conversion factor.

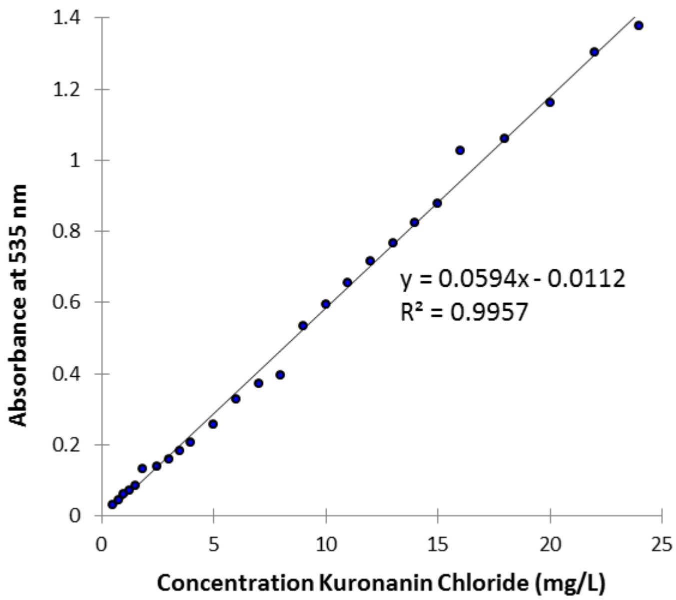

Figure 2.4 - The standard curve of Kuromanin chloride in acidified methanol (15% v/v).

iii. Total Phenolic Content

The total phenolic content was determined using the Folin-Ciocalteu reagent method, modified from Ainsworth and Gillespie (2007). Between 0.15-0.2 g of the fresh foliage was homogenized with 2 mL of 80% $CH_3OH:H_2O$ (80% methanol, 20 mL MilliQ; 80:20 v/v) in a ball mill grinder (Retsch MM300) at 4°C for 5 minutes at 30 Hz. The samples were centrifuged at 10000 rpm for 10 minutes. In a 2mL Eppendorf tube 20 µL of supernatant was added, mixed with 1580 µL of MilliQ water and 100 µL of F-C reagent (SigmaAldrich, Oakville, Ontario), mixed thoroughly using a vortex mixer and allowed to incubate at room temperature for 5 minutes. Subsequently, 300 µL of 20% Na_2CO_3 (20% sodium carb powder, 80 mL MilliQ) was added and then vortexed briefly. Samples were left to sit at room temperature for 2 hours and then the supernatant absorbance was measured at 760nm versus a blank of 80% methanol on a Perkin-Elmer Lambda-25 UV-Vis Spectrometer and samples were diluted if necessary. Quantification was completed using a standard curve of certified reference grade gallic acid (Sigma-Aldrich, Oakville, Ontario) using 6 concentrations between 10 mg L^{-1} and 100 mg L^{-1} (Figure 2.3).

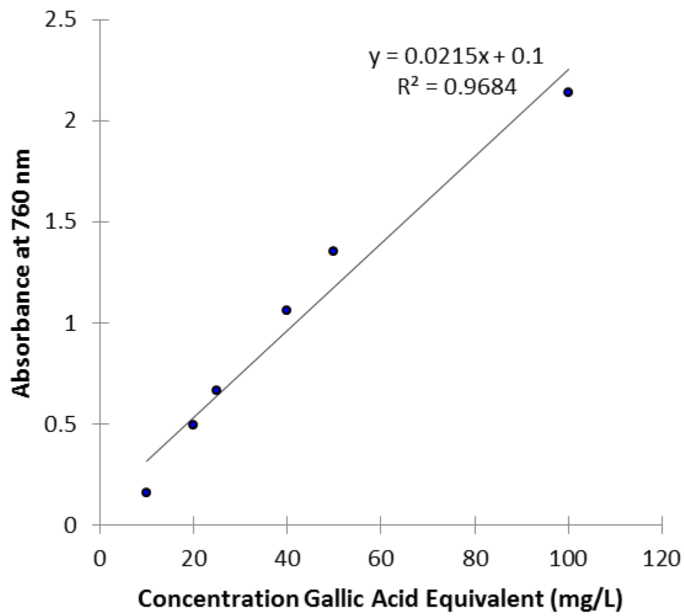

Figure 2.5- The standard curve of Gallic Acid in 80% methanol.

iv. Chlorophyll

Chlorophyll extraction was determined using a spectrometric method derived from Bruinsma (1963), Linder (1974) and Lewandowska and Jarvis (1977). As the leaves were small, four whole leaves were cut up, avoiding major veins or necrotic areas. Half of the leaves were dried at 105°C for 24 hours to determine the dry weight and the other half was placed into 15mL centrifuge tubes with 10 mLs of 100% acetone, macerated and stored overnight at 4°C to leach the chlorophyll from the leaves. The absorbance of the leachate was measured at 662 nm and 644 nm on a spectrometer and the content of chlorophyll a, chlorophyll b and chlorophyll *a*+*b* were calculated (Equation 2.2, Equation 2.3, Equation 2.4).

[2.2] Chl a = $9.78*A_{662} – 0.99*A_{644}$

[2.3] Chl b = $21.40*A_{644} – 4.65*A_{662}$

[2.4] Chl a+b = $5.13*A_{662} + 20.41*A_{644}$

Where chl is the chlorophyll content in mg L^{-1} and A is the absorbance.

v. Other analyses

The pH of the surface peat samples, once dried and sieved at 2 mm, was analyzed by adding 1g of soil with 50 mL of 0.01 M $CaCl_2$, stirred for 20 minutes and then left to equilibrate for 40 minutes. The pH of the solution was then measured using a calibrated LAQUA pH/ion/conductivity meter.

2.4 Statistics

Relationships between the surface von Post, Ni and Cu concentrations at the three depths and distance from Copper Cliff were tested using regression (correlation) and differences between the depths and sites were tested using ANOVA with XLStat. A principal component analysis (PCA) using XLSTAT Version 2014.1.01 was done in order to characterize peatland chemistry. Relationships between the chemical variables in the surface peat were assessed using the PCA and the results reported in each case as a biplot, showing ordination axes 1 and 2, as well as axes 2 and 3, as all three axes yielded important information. Relationships between the species richness and pH, and the plant Cu and Ni concentration and the peat and pore water (total and free ion) were tested using regression (correlation) analysis using XLStat. Relationships between the plant secondary chemistry (anthocyanin, total phenol, and chlorophyll content) and plant tissue, peat and pore water chemistry were also evaluated using regression (correlation) analysis (XLStat). Relationships between the percent cover of vascular, bryophyte, frequency of *Sphagnum* and Ni and Cu peat concentrations were tested using regression (correlation) analysis using XLStat.

Canonical correspondence analysis (CCA) was used to test whether the community structure was more strongly related to the pollutant gradient than expected by chance, rather than the community structure in general. In order for the CCA to work effectively, the number of environmental variables had to be reduced to less than the number of sites. The results from the PCA, helped to remove redundancy from the variables and highly correlated variables were excluded. The variables chosen represent the natural variability and anthropogenic disturbance in the wetlands as showcased by the three main explanatory axes in the PCA, as well as possible limiting factors for the plant community.

The CCA was applied to vascular species present at > 15% of the wetlands and non-vascular species present at >10% of the wetlands in order to reduce the noise and eliminate rare species, using XLSTAT Version 2014.1.01. Vascular plants and bryophytes differ in important traits related to growth and reproduction, and therefore can respond differently to changes in the environmental conditions (Hájek et al 2011). To account for these different requirements and limitations, a separate set of explanatory variables was chosen for the vascular and non-vascular analyses to represent the possible limiting factors for each. For the vascular vegetation 7 physico-chemical factors were entered (peat pH, free ion Cu concentration in the porewater, porewater Cl, surface peat Cu, surface peat %C, surface peat CN Ratio, surface peat K) as explanatory variables and the normalized percent cover of 30 species were used. For the non-vascular vegetation 5 physico-chemical factors were entered (peat pH, surface peat Cu, surface peat CN ratio, the vascular vegetation cover, surface von Post) and the percent frequency of 12 species were used. The significance of the relations was tested using the Monte Carlo permutation test, selecting variables that had an $F > 1.4$ and $p<0.05$ (Appendix 7.4 - Table 7.7, Table 7.8) (van Dobben and de Vires 2010). The results are reported in each case as a biplot, showing ordination axes 1 and 2, as the first orientation is by far the most important and the others (axes 1 and 3, and 2 and 3) do not yield as important information.

3 Results

3.1 Peat chemical and physical properties

The peatlands sampled are all acidic (surface peat pH 3.44 – 4.48) and exhibit great spatial variability in peat chemistry (Table 3.1). Both Ni and Cu were strongly correlated with each other (r_p=0.84, p=< 0.0001) as well as with distance from the main smelter in Sudbury, Copper Cliff (Figure 3.1). Increasing distance from the smelter, the peat Ni concentrations significantly decreased from 920 to 120 mg kg^{-1}, and Cu concentrations fell from 1685 to 169 mg kg^{-1}. No other peat chemistry variables (including pH), or other metals emitted from the smelter such as Co, Fe and Mn, were significantly related to the distance from the smelter, although there was considerable variation in peat chemistry among the peatlands. The concentrations of Fe and Al, for example, both range from about 4 g kg^{-1} to 20 g kg^{-1} and the C content also varied greatly from 12% to 51% (Appendix 7.2 – Table 7.2). These differences reflect the inherent peatland differences as sites varied from those with a relatively high mineral content to those primarily organic. The sites D4 and D5 had the highest Al (21 mg kg^{-1} and 19 mg kg^{-1} respectively) and Fe (15 mg kg^{-1} and 17 mg kg^{-1} respectively) concentrations with lower %C content and the sites with the lowest %C content, under 20% included, C1, D4 and D5 compared to RCK which was primarily organic (>40% C) (Appendix 7.2 Table 7.2).

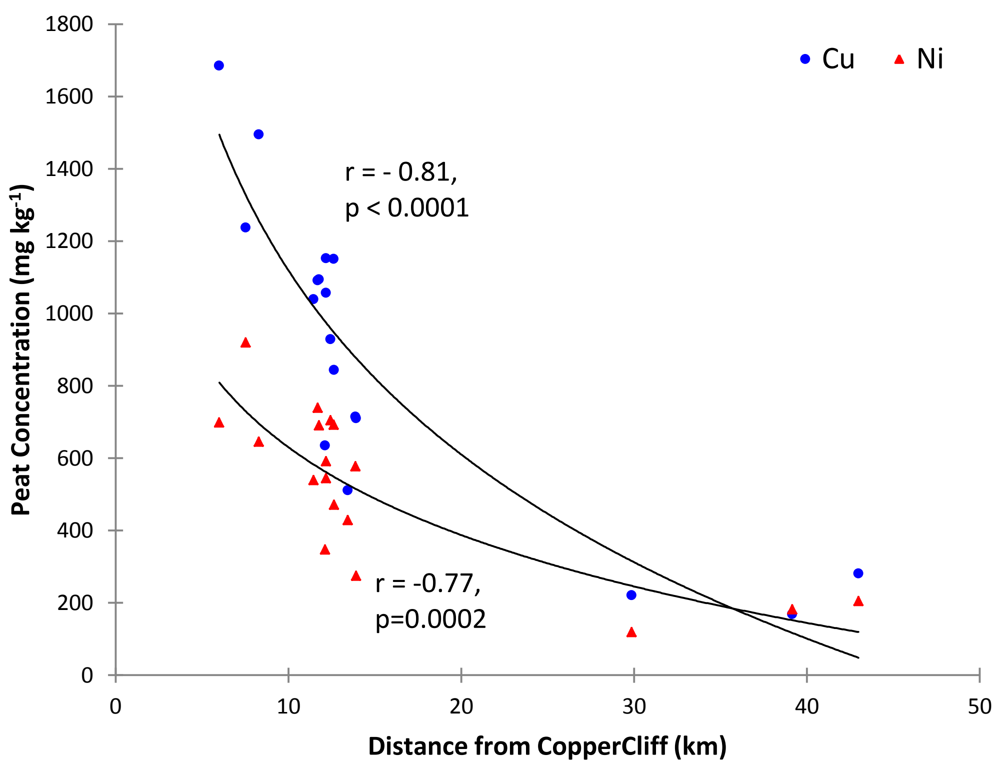

Figure 3.1 - Relationship between the Ni and Cu surface peat concentrations and distance from the Copper Cliff smelter.

Table 3.1- Surface peat chemistry and humification status (von Post) and the correlation coefficients (*d*) for total metals, nutrients, peat pH and von Post of the peatland averages with distance to the Copper Cliff smelter.

	Surface Peat (0-15 cm)				
Variables	Average	±SD	Max	Min	*d*
Na g kg^{-1}	0.61	0.19	1.24	0.34	-0.29
K g kg^{-1}	0.75	0.19	1.12	0.55	0.15
Ca g kg^{-1}	3.38	1.81	7.10	0.72	-0.06
Mg g kg^{-1}	0.77	0.53	2.31	0.33	0.06
P mg kg^{-1}	780	187	1116	466	0.14
Al g kg^{-1}	7.65	5.22	21.0	1.72	-0.19
Fe g kg^{-1}	7.04	3.91	17.3	3.09	-0.03
Mn mg kg^{-1}	56.9	35.0	147.2	18.2	0.40
Ni mg kg^{-1}	521	221	920	120	-0.76 **
Cu mg kg^{-1}	890	420	1685	169	-0.81 ***
Co mg kg^{-1}	12.0	3.35	20.5	5.59	0.13
Zn mg kg^{-1}	48.5	15.9	81.2	17.0	-0.28
%N	1.88	0.46	2.50	0.71	-0.16
%C	40.5	12.0	51.1	12.1	0.03
%S	0.71	0.26	1.25	0.22	0.02
CN Ratio	21.8	5.40	31.9	12.9	0.22
pH	3.95	0.35	4.48	3.31	-0.31
von Post	H4	1.3	H8	H2	-0.73*

* $p < 0.05$; ** $p<0.001$; ***$p<0.0001$

The first two axes in the PCA explained approximately 55% of the variability in the peat chemistry and the third axes explained an additional 14% of the variability (Figure 3.2). The first axis (38.6%) represents primarily a mineral to organic gradient in the peat, with negative loadings for Al, Fe, Mg and positive loadings for C, N and S. The second axis (16.8%) represents primarily a pH fertility gradient, with a negative loading for peat pH and a positive loading for CN Ratio. The third axis (13.9%) primarily represents the smelter metal deposition gradient and is positively loaded with Ni, Cu (Table 3.2).

The two sites clearly separated from the other sites are D4 and D5 with a significant negative loading on the first axis. They are characterized by having a more profound mineral influence (higher Al, Mg and Fe content) and lower C content. The sites with the highest Ni and Cu concentrations are LU, SLV, MUD and D5 and those with the lowest are MAT, ASH and RCK.

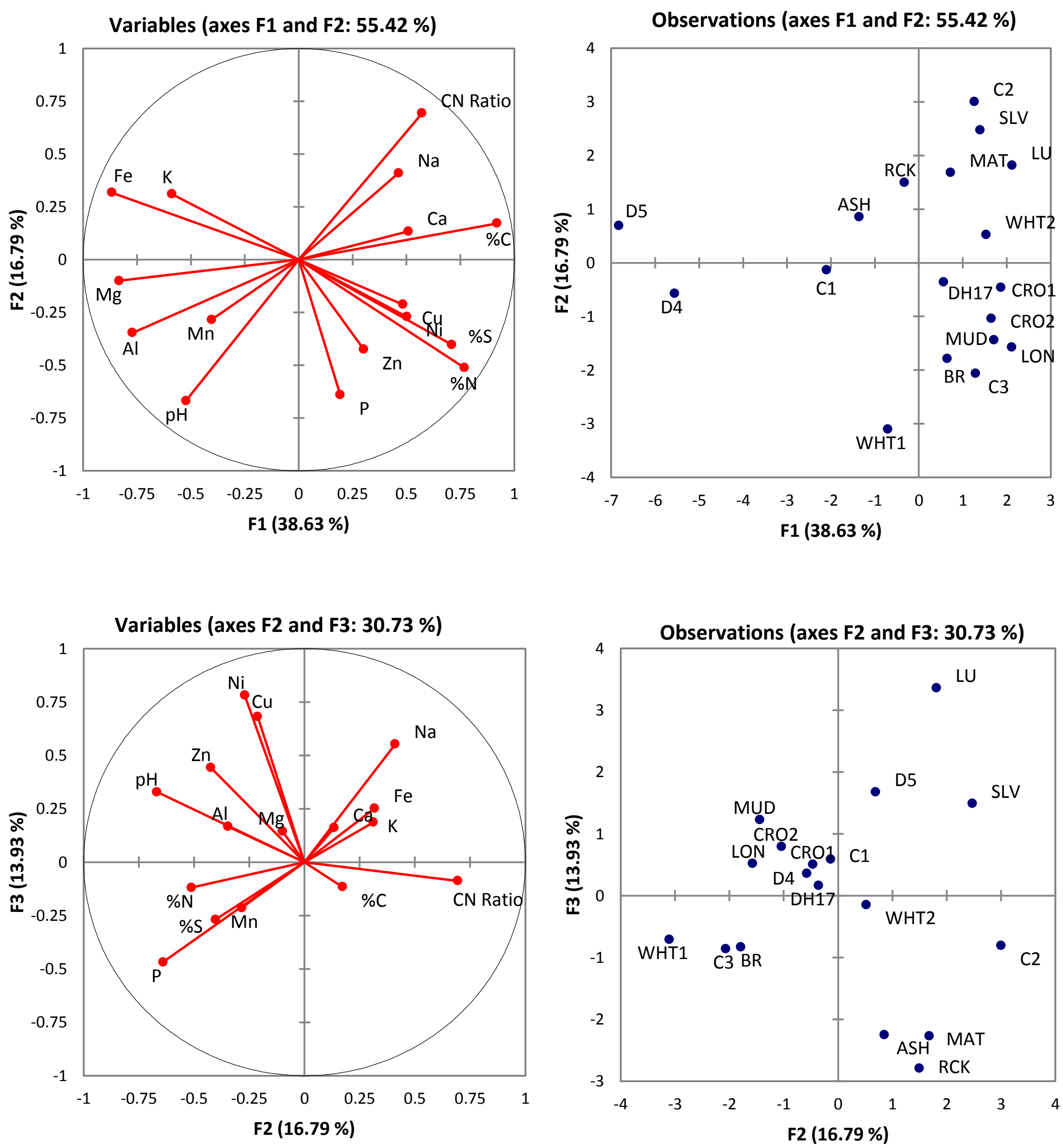

Figure 3.2 - Principal component analysis for surface peat chemistry showing the variable and wetland site loadings.

Table 3.2 – PCA factor loadings for the peat chemistry variables.

Variable	F1	F2	F3		Variable	F1	F2	F3
pH	-0.523	-0.669	0.328		Mn	-0.404	-0.284	-0.214
Na	0.463	0.410	0.552		Ni	0.502	-0.20	0.781
K	-0.588	0.311	0.186		Cu	0.483	-0.212	0.682
Ca	0.509	0.135	0.161		Zn	0.302	-0.425	0.443
Mg	-0.834	-0.100	0.145		%N	0.769	-0.512	-0.120
P	-0.193	-0.641	-0.468		%C	0.920	0.172	-0.115
Al	-0.771	-0.346	0.167		%S	0.710	-0.403	-0.269
Fe	-0.867	0.318	0.252		CN Ratio	0.572	0.694	-0.087

3.1.1 Vertical Composition of the Peat

The Cu and Ni concentrations at the 'middle' (25 - 35 cm) and 'deep' (45 - 60cm) depths are much lower than the concentrations found at the surface and were not related to the distance from Copper Cliff (Figure 3.3, Figure 3.4). The Ni and Cu content from the surface and middle peat collected at MAT did not significantly differ and Ni was elevated in the middle layer compared to the surface at ASH.

The humification status of the surface peat (0 -15 cm) assessed using the von Post scale was between H7 (very decomposed) to H2 (only partially decomposed). As expected, the humification index of the peat increased with depth with the exception of the furthest site, MAT, where there was no difference between the surface and middle peat (H3). There was also a significant correlation between the von Post ranking of the surface (r_p=0.69, p=0.002), middle (r_p=0.50, p=0.035) and deep (r_p=0.56, p=0.024) peat and the surface peat Cu contamination (Figure 3.5).

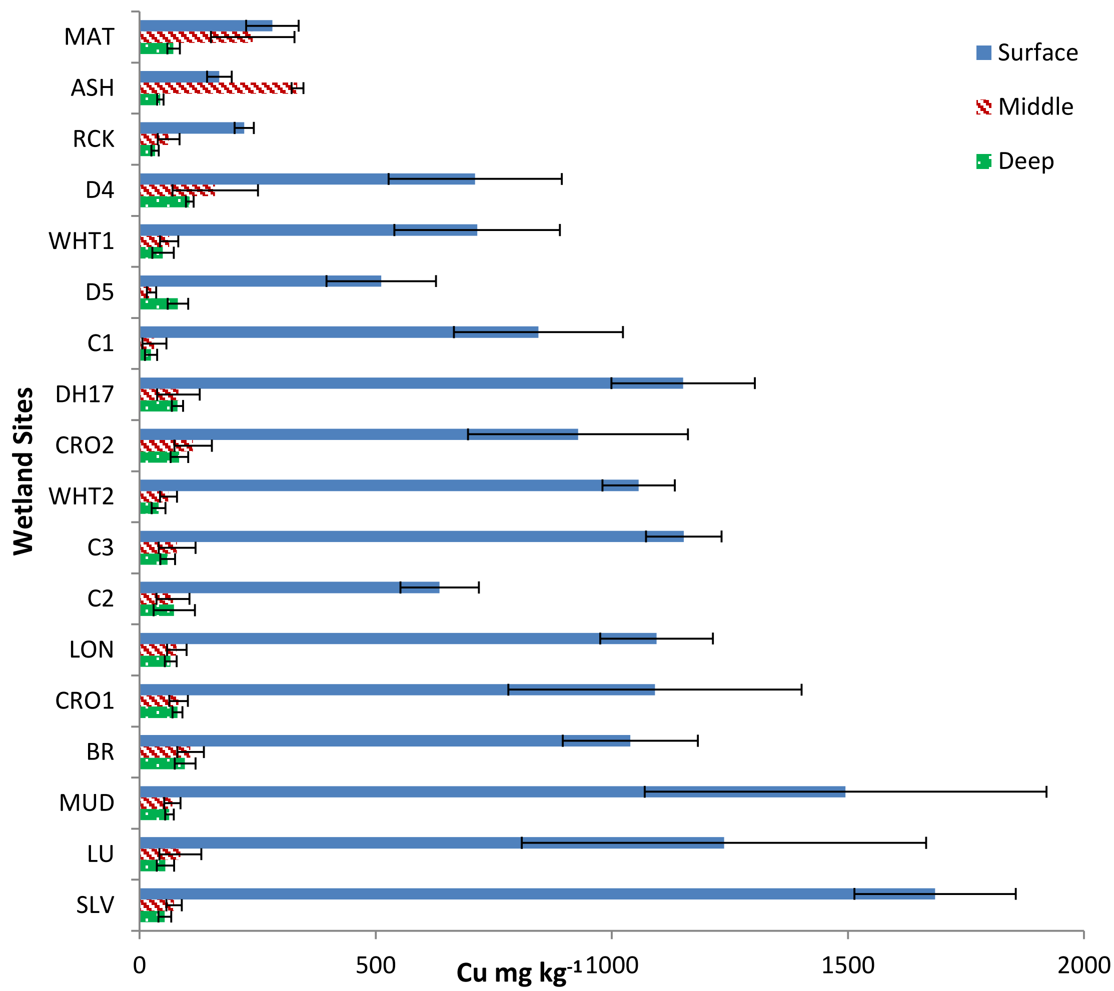

Figure 3.3 – The peat Cu concentration at all of the eighteen study sites at three different bulk depths: surface (0 – 15 cm), middle (25 – 35 cm), deep (45 – 60 cm) ordered in decreasing distance from Copper Cliff.

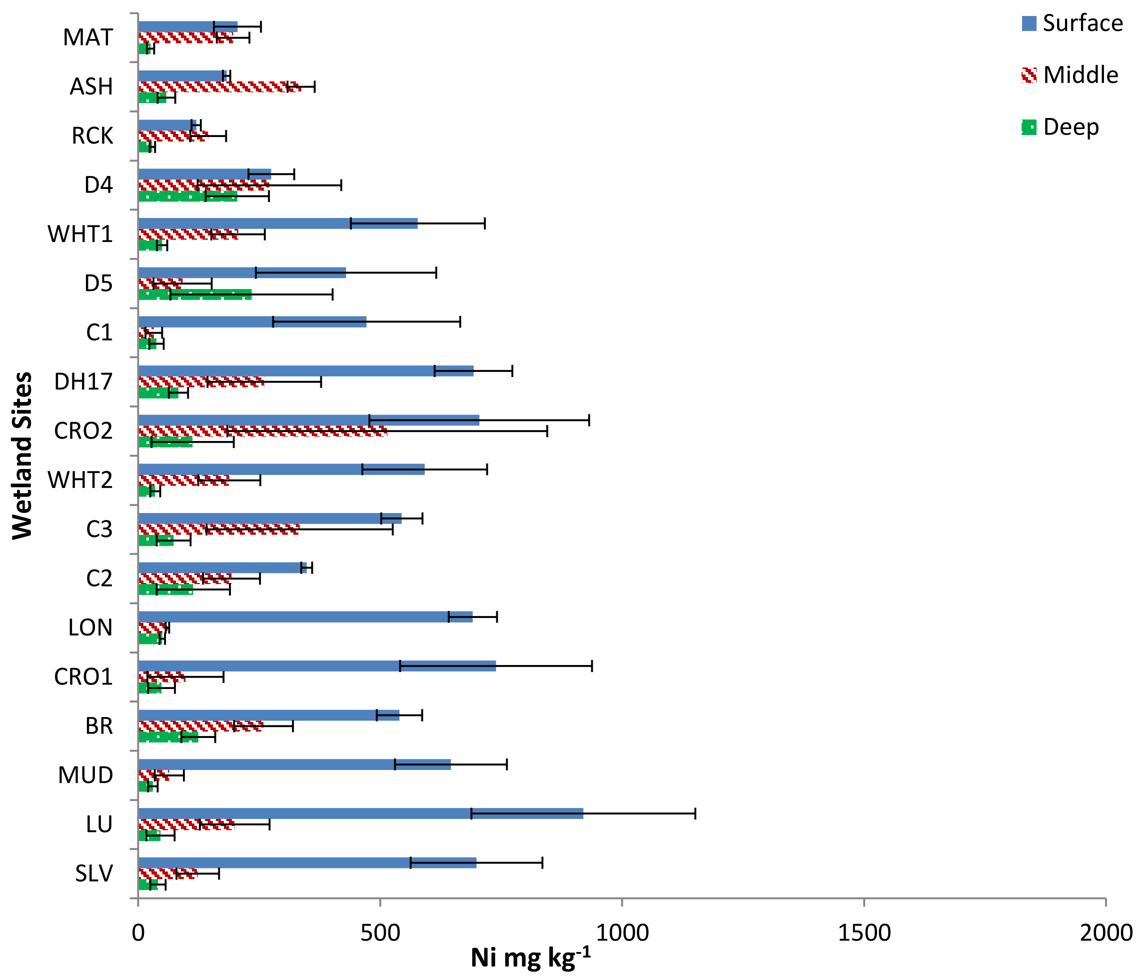

Figure 3.4 - The peat Ni concentration at all of the eighteen study sites at three different bulk depths: surface (0 – 15 cm), middle (25 – 35 cm), deep (45 – 60 cm) ordered in decreasing distance from Copper Cliff.

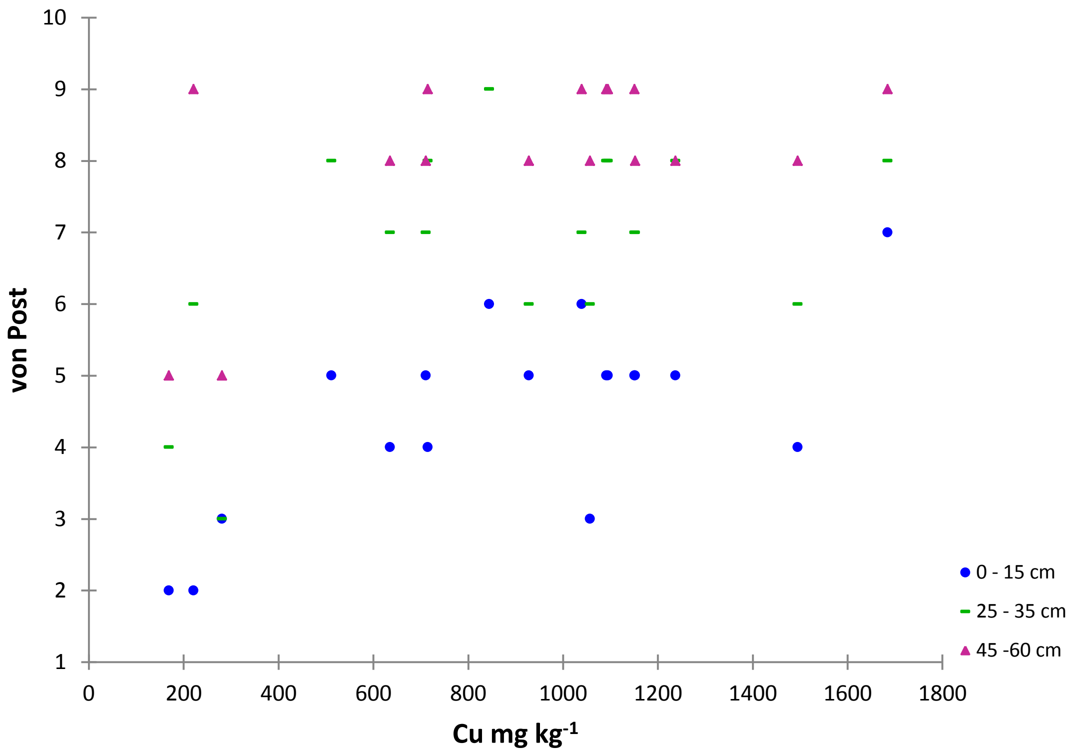

Figure 3.5 - The relationship of peat von Post humification index of the peat at three depths and the Cu contamination in the surface peat at each of the 18 study sites.

3.2 Chemical characteristics of the vegetation

The average Ni concentration in *C. calyculata* foliage was 23.6 mg kg^{-1} with a range of 3.6 - 47.7 mg kg^{-1}; foliar Cu averaged 9.6 mg kg^{-1} and was between 4.3 – 27.6 mg kg^{-1}. The average Ni concentration in the *K. angustifolia* foliage was 16.5 mg kg^{-1} with a range of 7.0 – 27.3 mg kg^{-1}; the foliar Cu averaged 6.1 mg kg^{-1} and ranged between 4.2 – 7.4 mg kg^{-1} (Table 3.3, Table 3.4). There was a significant positive correlation between the surface peat concentration and plant tissue chemistry for Ni and Cu in *C. calyculata* (Figure 3.6). In *K. angustifolia* the relationship was less strong and only evident for Ni (foliage r_p=0.43; stem r_p=0.68, p=0.004; root r_p= - 0.12). There was no correlation with the plant tissue concentrations and the total or free Ni and Cu pore water concentrations in soil solution, except for the roots of *K. angustifolia* and free Cu (r_p=0.50, p=0.05) (Table 3.3, Table 3.4).

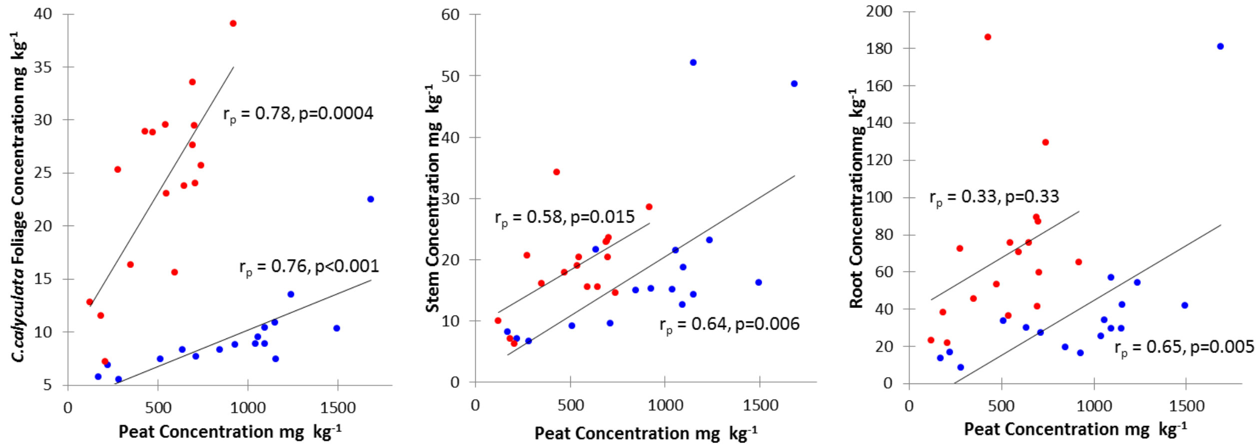

Figure 3.6 – The relationship between the surface (0-15cm) peat Cu and Ni concentrations and the *C. calyculata* foliar, stem and root concentrations.

Table 3.3 – The Cu concentrations of the fall pore water (total and free ion), surface peat (0-15cm), and *Chamaedaphne calyculata* and *Kalmia angustifolia* tissue content in all 18 wetlands sampled, in order of increasing distance from Copper Cliff.

	Pore Water		Peat	*C. calyculata mg kg⁻¹*			*K. angustifolia* mg kg⁻¹		
Sites	**Total ppb**	**Free Ion ppb**	**mg kg⁻¹**	**Foliage mg kg⁻¹**	**Stem mg kg⁻¹**	**Root mg kg⁻¹**	**Foliage mg kg⁻¹**	**Stem mg kg⁻¹**	**Root mg kg⁻¹**
SLV	231	116	1685±171	22.5±5.6	48.7±9.6	181±54.5	6.79±2.10	32.6±12.2	10.7±2.6
LU	77.9	216	1238±428	13.5±2.3	23.1±7.5	54.5±13.3	7.12±1.21	29.0±21.6	41.2±13.6
MUD	64.2	182	1495±425	10.4±0.38	16.2±4.9	41.8±8.54	5.89±1.97	10.1±6.8	26.6±9.1
BR	335	74.0	1039±143	8.90±1.69	15.1±7.6	24.5±12.7	7.32±1.41	14.7±5.3	20.1±13.3
CRO1	83.5	20.2	1091±310	8.93±1.32	12.6±3.2	56.9±25.7	4.51±1.47	9.51±4.23	22.9±4.0
LON	174	19.3	1095±120	10.4±1.3	18.7±8.7	29.6±9.2	6.47±1.62	29.5±6.9	9.48±5.15
C2	131	105	635±72	8.34±0.76	21.6±6.0	30.2±8.8	5.15±1.51	15.0±4.3	46.0±33.1
C3	89.7	86.5	1152±80	7.48±0.67	14.3±3.9	42.7±25.7	4.35±2.15	8.30±4.09	19.8±17.3
CRO2	240	6.66	928±233	8.81±1.56	15.2±2.5	16.6±5.4	4.65±1.54	22.5±4.0	19.7±8.9
DH17	61.8	98.4	1151±152	10.9±3.4	24.0±3.1	30.0±7.8	7.40±2.27	15.0±10.6	14.2±8.3
C1	316	43.8	844±149	8.35±2.49	15.0±5.2	19.8±8.6	N/A	N/A	N/A
WHT2	123	48.4	1057±77	9.51±2.31	21.5±4.2	34.0±13.4	5.97±1.07	12.2±7.3	16.3±8.4
D5	153	38.3	512±116	7.47±1.48	9.11±2.16	33.5±18.5	4.24±2.05	4.87±1.07	32.5±11.2
WHT1	85.4	14.1	715±175	N/A	N/A	N/A	N/A	N/A	N/A
D4	148	61.1	711±183	7.67±0.18	9.49±0.06	27.4±11.2	5.45±1.48	31.9±18.3	35.7±11.4
RCK	50.1	167	221±20	6.89±2.55	7.07±3.48	17.0±4.7	6.50±2.48	9.41±5.61	91.6±40.0
ASH	186	58.9	169±26	5.75±1.26	8.20±2.50	13.6±4.5	6.03±1.35	5.68±2.01	8.20±2.61
MAT	72.7	49.1	281±56	5.53±1.72	6.60±0.81	8.68±2.65	5.26±1.05	11.3±4.2	24.4±14.6

Table 3.4 - The Ni concentrations of the fall pore water (total and free ion), surface peat (0-15cm), and *Chamaedaphne calyculata* and *Kalmia angustifolia* tissue content in all 18 wetlands sampled, in order of increasing distance from Copper Cliff.

	Pore Water		Peat	*C. calyculata*			*K. angustifolia*		
Sites	Total ppb	Free Ion ppb	mg kg^{-1}	Foliage mg kg^{-1}	Stem mg kg^{-1}	Root mg kg^{-1}	Foliage mg kg^{-1}	Stem mg kg^{-1}	Root mg kg^{-1}
SLV	194	419	699±136	29.5±5.8	20.3±3.0	87.3±15.8	21.4±6.2	20.1±3.7	22.9±8.7
LU	318	535	920±231	39.1±4.2	28.6±7.3	65.0±15.4	25.1±8.0	26.2±4.9	45.7±13.9
MUD	418	632	646±116	23.8±3.0	15.6±4.1	75.8±7.1	18.6±3.9	17.1±5.7	53.6±7.4
BR	677	202	540±47	29.6±10.6	18.9±6.6	36.6±6.7	18.1±7.6	26.3±8.5	16.5±22.6
CRO1	125	85.5	740±198	25.7±1.2	14.5±2.8	129±52	17.2±5.5	21.5±6.4	70.6±17.7
LON	572	94.7	691±50	33.6±2.2	22.9±4.9	89.4±27.3	15.1±6.4	35.1±5.5	26.4±12.1
C2	236	171	348±11	16.4±3.2	15.1±3.9	45.8±20.4	27.3±6.8	21.7±6.3	45.6±19.6
C3	107	240	545±43	23.1±2.2	20.3±1.8	75.5±38.2	15.9±2.2	22.1±2.1	38.3±21.9
CRO2	222	54.1	405±227	24.0±1.8	23.5±2.8	59.6±18.8	11.4±1.5	27.7±4.2	68.1±22.2
DH17	69.2	426	693±80	27.7±6.8	23.1±4.5	41.4±17.4	17.0±4.2	19.8±3.8	26.1±9.2
C1	929	250	471±193	28.8±5.9	17.8±6.2	53.5±18.6	N/A	N/A	N/A
WHT2	136	311	592±129	15.6±3.4	15.5±4.0	70.5±35.7	10.8±2.2	12.0±2.6	24.6±6.6
D5	506	119	429±186	28.9±6.2	24.3±16.7	186±91	14.4±2.2	13.0±1.3	21.8±13.1
WHT1	131	267	578±138	N/A	N/A	N/A	N/A	N/A	N/A
D4	298	174	275±47	25.3±6.0	20.6±2.6	72.7±23.3	22.1±4.6	18.6±6.6	25.0±21.8
RCK	199	154	120±10	12.8±5.1	9.94±3.52	23.1±6.6	8.08±1.4	10.0±2.4	49.4±15.8
ASH	534	110	182±7	11.5±2.1	7.11±1.54	38.5±12.5	6.98±1.54	7.28±2.50	33.6±15.8
MAT	197	103	205±49	7.2±2.3	6.26±0.82	21.8±7.4	9.1±2.2	10.7±3.0	85.2±42.1

The foliar N, P, K concentrations for both species significantly differed among the sites. The *C. calyculata* foliage had an average N content of 12.1 mg g^{-1} (10.6 – 13.8 mg g^{-1}), P content of 0.64 mg g^{-1} (0.46 – 0.88 mg g^{-1}) and K content 3.40 mg g^{-1} (2.25 – 4.18 mg g^{-1}). All of the sites except one had an N:P ratio over 14.5 and all of the N:K ratios were above 2.1. The *K. angustifolia* foliage had an average N content of 12.9 mg g^{-1} (9.3 – 11.7 mg g^{-1}), P content of 0.99 mg g^{-1} (0.43 – 0.54 mg g^{-1}) and K content 4.53 mg g^{-1} (2.78 – 3.67 mg g^{-1}). All of the sites except one had an N:P ratio above 14.5 and all of the N:K ratios were above 2.1.

Although there was a significant difference in the anthocyanin, total phenolic and chlorophyll among the sites ($p<0.0001$) there was no relationship between the Cu and Ni concentrations in the foliage or surface peat and the anthocyanin, chlorophyll or total phenolic content in either species as indicators of smelter related stress (Table 3.3). The anthocyanin content of *C. calyculata* was negatively correlated with the foliar P (r_p=-0.51, p=0.043) and K (r_p=-0.60, p=0.014) and was positively correlated with N (r_p=0.68, p=0.003) and S (r_p=0.56, p=0.023). There was also a negative relationship between anthocyanin content in *K. angustifolia* and foliar P (r_p=-0.35), K (r_p=-0.34), and N (r_p=-0.18), although not significant and a positive correlation with Fe (r_p=0.55, p=0.032). There was no relationship in either species with the nutrient content (N, P or K) and the chlorophyll or total phenolic content.

Table 3.5 - Summary of foliar nutrient status, chlorophyll, anthocyanin and total phenolic content in *Chamaedaphne calyculata* and *Kalmia angustifolia*.

	C.calyculata Foliage				*K.angustifolia Foliage*			
Variables	Average	Stdev	Max	Min	Average	Stdev	Max	Min
Total Phenol (mg g^{-1} DW)	155.3	45.1	275.6	75.6	488.1	82.0	633.6	207.7
Anthocyanin (mg g^{-1} DW)	0.28	0.04	0.33	0.02	1.11	0.32	3.28	0.41
Chlorophyll a+b (mg g^{-1} DW)	2.18	0.52	3.63	1.37	0.97	0.23	1.52	0.55
Chlorophyll a (mg g^{-1} DW)	1.52	0.35	2.52	0.94	0.66	0.14	0.90	0.38
Chlorophyll b (mg g^{-1} DW)	0.66	0.17	1.12	0.40	0.31	0.11	0.64	0.03
N:P Ratio	19.9	4.0	33.6	12.2	22.3	4.5	35.1	12.0
N:K Ratio	3.72	0.78	6.11	2.38	3.28	0.66	4.91	2.03

3.3 Vegetation Community Composition

3.3.1 Vegetation Species Diversity and Richness

The peatlands can be separated into three groups based on their dominant vegetation class by those which are shrub dominant (C2, LON, MUD, RCK, C3, DH17, CRO1, BR, WHT2, MAT, LU), sedge dominant (C1, WHT1, ASH, CRO2, SLV), and sedge/grass dominant (D5, D4). A total of 77 vascular species across 23 families and 22 nonvascular species across 13 families were identified at all of the sites (Appendix 7.5 – Table 7.10, Table 7.11). The most frequent vascular taxa were *Calamagrostis canadensis*, *Chamaedaphne calyculata*, *Kalmia angustifolia*, *Glyceria canadensis*, *Juncus canadensis* and *Kalmia polifolia*. The vascular species richness ranged from 7 to 24 and the Shannon-Weiner diversity index was between 0.850 and 2.775 (Table 3.6). The most frequent nonvascular taxa among all of the sites were *Cladopodiella fluitans*, *Warnstorfia fluitans, Polytrichum commune, Sphagnum fallax, Pohlia nutans* and *Mylia anomala*. The non-vascular species richness ranged from 2 to 12 (Table 3.6).

Species richness and diversity varied significantly among sites ($p < 0.0001$), but richness and diversity were not correlated with distance to the smelter or the Ni and Cu surface peat concentrations. The diversity index was most strongly correlated with the peat pH, which was not related to distance from the smelter (Figure 3.2). The pH of the peat and the autumn pore water pH were correlated ($r_p=0.81$, $p=<0.0001$). The vascular species richness was negatively correlated with the CN ratio in the peat ($r_p=-0.48$, $p=0.04$), the available iron (FeIII) in the pore water calculated from WHAM ($r_p=-0.60$, $p=0.008$) and both the bryophyte and vascular species richness is positively correlated with peat pH (Figure 3.7).

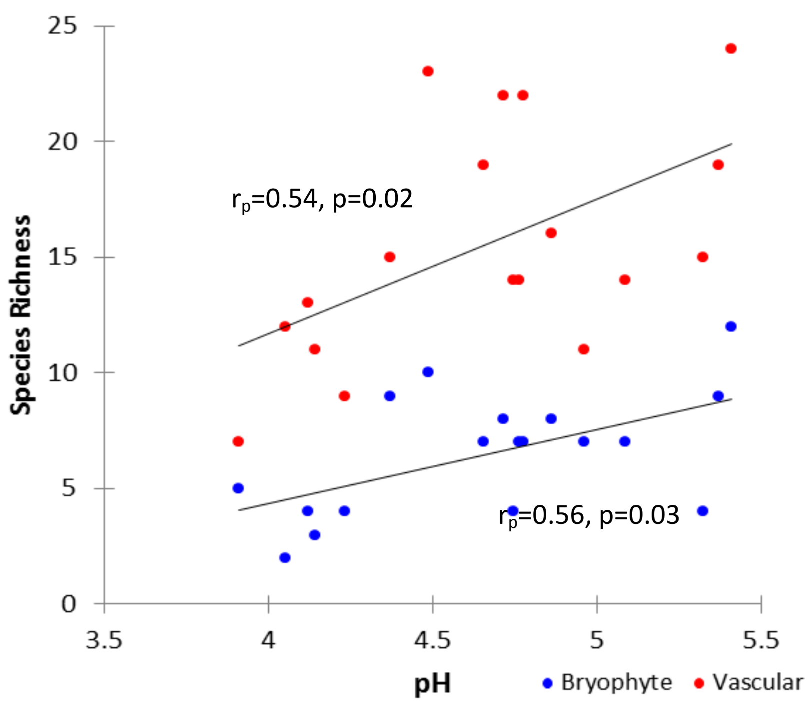

Figure 3.7- Relationship between the vascular and nonvascular vegetation species richness at each of the wetlands with the pore water fall pH (Oct 2011).

Table 3.6 – The vegetation species richness, Shannon-Weiner diversity index, mean wetness index, and dominant species found at the 18 peatlands surveyed in Sudbury, Ontario in order of increasing distance from the Copper Cliff smelter.

Site	Vascular Richness	Non-Vascular Richness	Shannon's Index	Wetness Index	Vascular Dominant sp.	Non-Vascular Dominant sp
SLV	11	3	1.687	-4.5	*Rhynchospora alba*	*Cladopodiella fluitans*
LU	9	4	1.406	-4.5	*Chamaedaphne calyculata*	*Cladopodiella fluitans*
MUD	15	9	1.566	-3	*Chamaedaphne calyculata*	*Pohlia nutans*
BR	11	7	1.646	-4.5	*Juncus canadensis*	*Cladopodiella fluitans*
CRO1	16	8	1.840	-3	*Kalmia angustifolia*	*Cladopodiella fluitans*
LON	14	7	1.531	-4	Chamaedaphne *calyculata*	*Mylia anomala/ Cladopodiella fluitans*
C2	7	5	0.850	-3	*Chamaedaphne calyculata*	*Pohlia nutans*
C3	22	8	2.273	-4	*Chamaedaphne calyculata*	*Cladopodiella fluitans*
WHT2	14	7	1.328	-4	*Scirpus atrovirens*	*Pohlia nutans*
CRO2	24	12	2.775	-4	*Rhynchospora alba*	*Cladopodiella fluitans*
DH17	14	2	1.618	-4.5	*Chamaedaphne calyculata*	*Cladopodiella fluitans*
C1	19	7	1.873	-4.5	*Scirpus atrovirens*	*Warnstorfia fluitans*
D5	19	9	2.111	-2	*Schizachne pupurascens*	*Polytrichum commune*
WHT1	15	4	1.670	-5	*Dulichium arundinaceum*	*Sphagnum squarrosum*
D4	22	7	1.701	-2	*Muhlenbergia uniflora*	*Polytrichum junniperinum*
RCK	13	4	1.484	-3	*Myrica gale*	*Pohlia nutans*
ASH	23	10	1.757	-4.5	*Carex magellanica*	*Sphagnum fallax*
MAT	12	2	1.736	-4.5	*Chamaedaphne calyculata*	*Sphagnum fallax*

The wetness index for each site was below zero, and the majority were between -3 and -5, with the exception of D4 and D5 which had a wetness index of -2 (Table 3.4). The vascular vegetation cover, which was calculated as the total sum of the cover of all species regardless of overlap, was strongly negatively correlated with Ni and Cu concentration in the surface peat (Figure 3.8). To a lesser extent, but still significant, the vascular vegetation cover increased with the peat nutrients Mg (r_p=-0.54, p=0.022) and K (r_p=-0.52, p=0.027). The average percent cover of bryophytes at the study sites ranged from 10% to 100% and from 0% to 0.25% for lichens, but was not found to be correlated with any peat or pore water variables measured. The majority of the wetlands surveyed had a bryophyte cover over 50% with the exception of four sites (C1, C2, WHT1 and WHT2). *Sphagnum* species did not appear until beyond 8 km and reached a maximum richness of 5 *Sphagnum* sp. at the furthest site surveyed. The percent frequency of combined *Sphagnum* sp. in the recorded quadrats increased with increasing distance from the smelter (Figure 3.9) and also was negatively correlated with the surface von Post (r=-0.62, p=0.007). The three furthest sites (MAT, ASH, RCK) had a *Sphagnum* frequency between 85% and 100%, four 'medium-disturbance' sites (C3, WHT1, CRO2, D5) had a frequency between 45% and 70% and the rest of the sites had a frequency less than 20%.

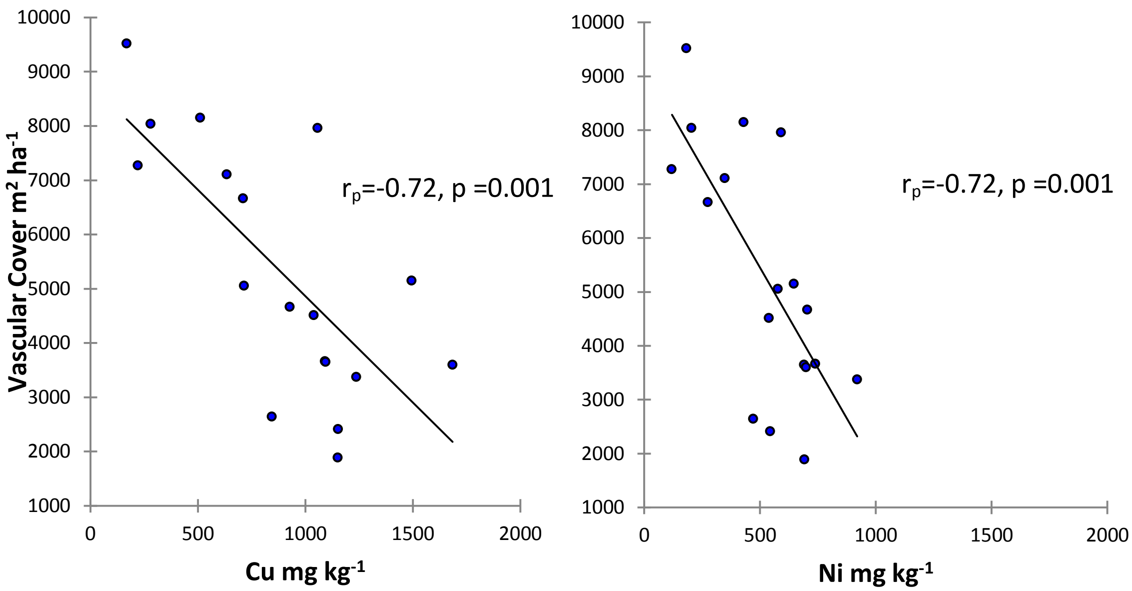

Figure 3.8 - The total vascular vegetation cover compared with the surface peat Cu (left) and Ni (right) concentrations.

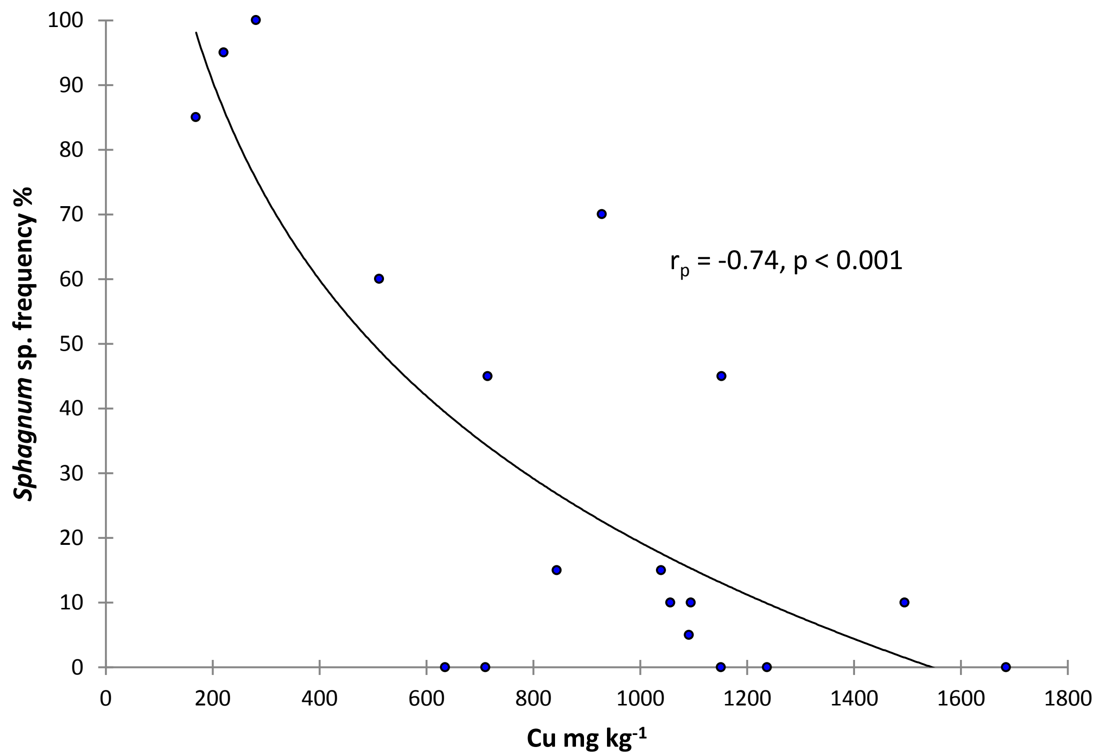

Figure 3.9 – The relationship between the % frequency of *Sphagnum* sp. in the 20 x 25cm^2 quadrats for each wetland and surface peat Cu concentration.

3.3.2 Vegetation Community Compositions Assessed through CCA

The first two CCA axes explained 58.9% (axis 1 = 37.6%; axis 2 =21.3%) of the vascular species-environmental variance (Figure 3.10). The first axes (Eigenvalue 0.317) is best correlated with the pH and CN ratio of the peat interpreted as a gradient of the elevated mineral to higher organic content in the substrate. Axis 2 (Eigenvalue 0.179) was best correlated with the Cu pollution gradient and chloride concentrations (influence of road salt) in the peat porewater and is interpreted as a gradient of anthropogenic disturbance. There is some interaction between the axes as Cu and Cl loads on both axis 1 and 2. The sites that are more minerotrophic and have a lower Cu contamination (D4 and D5) are dominated by a variety of grasses including *Muhlengergia uniflora, Poa sylvestris, Calamagrostis canadensis* and *Schizachne purpurascens*. The sites which have a higher mineral content and Cu content (DH17, C1, BR) have a higher occurrence of sedges including *Carex utriculata, Rhychospora alba*, and *Dulichium arundinaceum*. The sites with a lower Cu contamination, lower pH and more of an organic substrate (ASH, MAT, C2 and RCK) and have a higher occurrence of sedges and shrubs such as *Chamaedaphne calyculata*, *Carex magellanica*, *Carex leptalea*, *Typha latifolia* and *Carex livida*. The sites with the highest Cu content (SLV, LU and MUD) had the highest occurrence of *Scirpus atrovirens, Rhododendron groenlandicum* and *Kalmia polifolia.*

The first two CCA axes explained 68.2% of the non-vascular species-environmental variance (axis 1 37.4%; axis 2 30.8%). The first axis (Eigenvalue 0.282) is most correlated with the peat Cu and is interpreted as the smelter deposition gradient, and the second axis (Eigenvalue 0.232) is most strongly correlated with the CN Ratio of the peat and the vascular vegetation cover. The species occurring at the wetlands with the lowest peat Cu concentration, MAT, ASH and RCK, were *Sphagnum fallax* and *Sphagnum fimbriatum,* and including species present at <10% of the sites, *Sphagnum cuspidatum* and *Sphagnum fuscum* were also occurring only at one of the lowest Cu and Ni contamination sites. At the sites with the highest peat Cu and Ni concentrations (SLV, LU, MUD and BR) *Cladonia chlorophaea*, *Cladopodiella fluitans* and *Mylia anomala* were the most frequent. The two sites D4 and D5 separated out again having the highest frequency of *Polytricum commune* and *Sphagnum squarrosum* as well as the occurrence of *Mnium stellare* at D5.

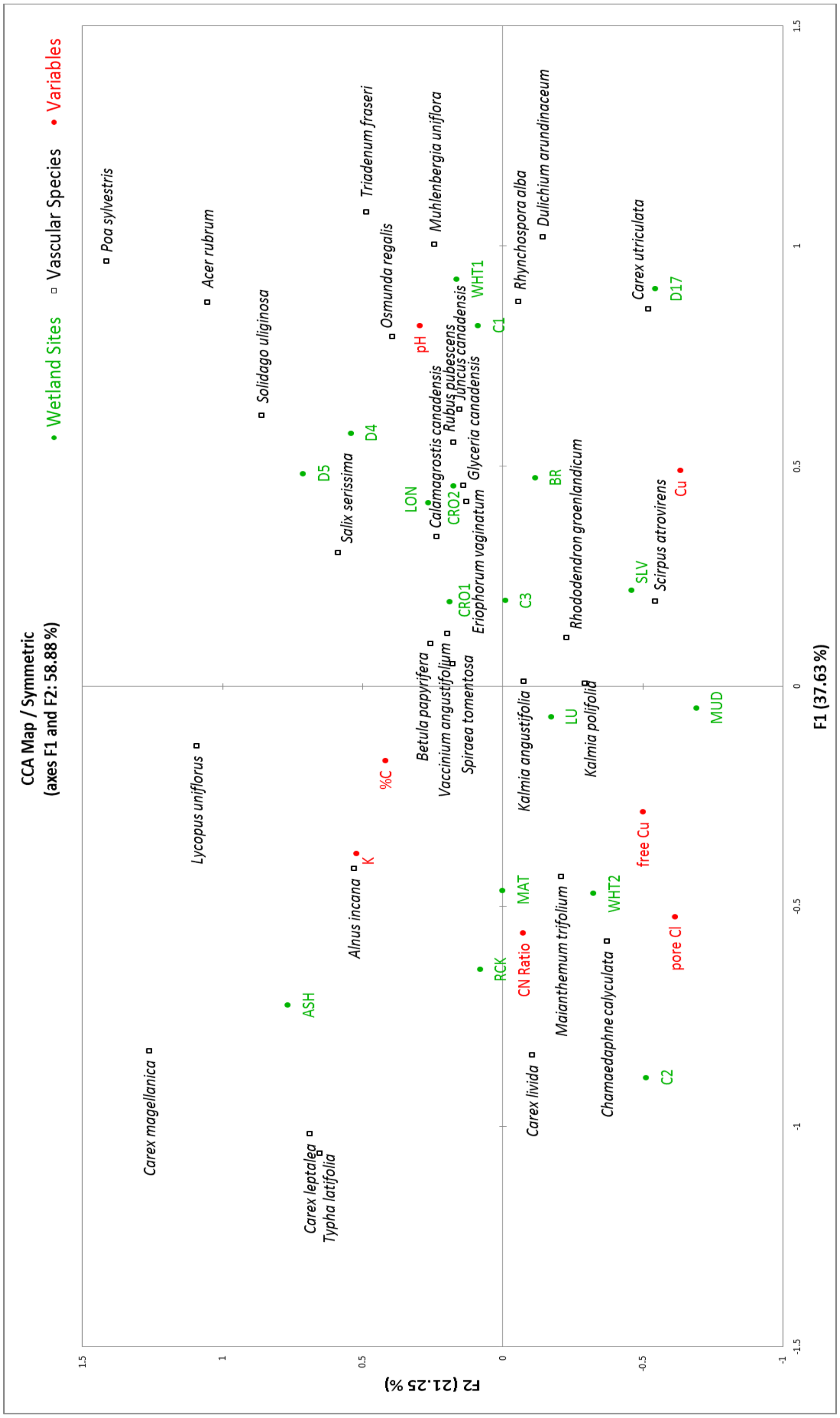

Figure 3.10 - Biplot of CCA analysis of the Sudbury data (Appendix 7.4 - Table 7.7) and the vascular species present at greater than 15% of the wetlands surveyed.

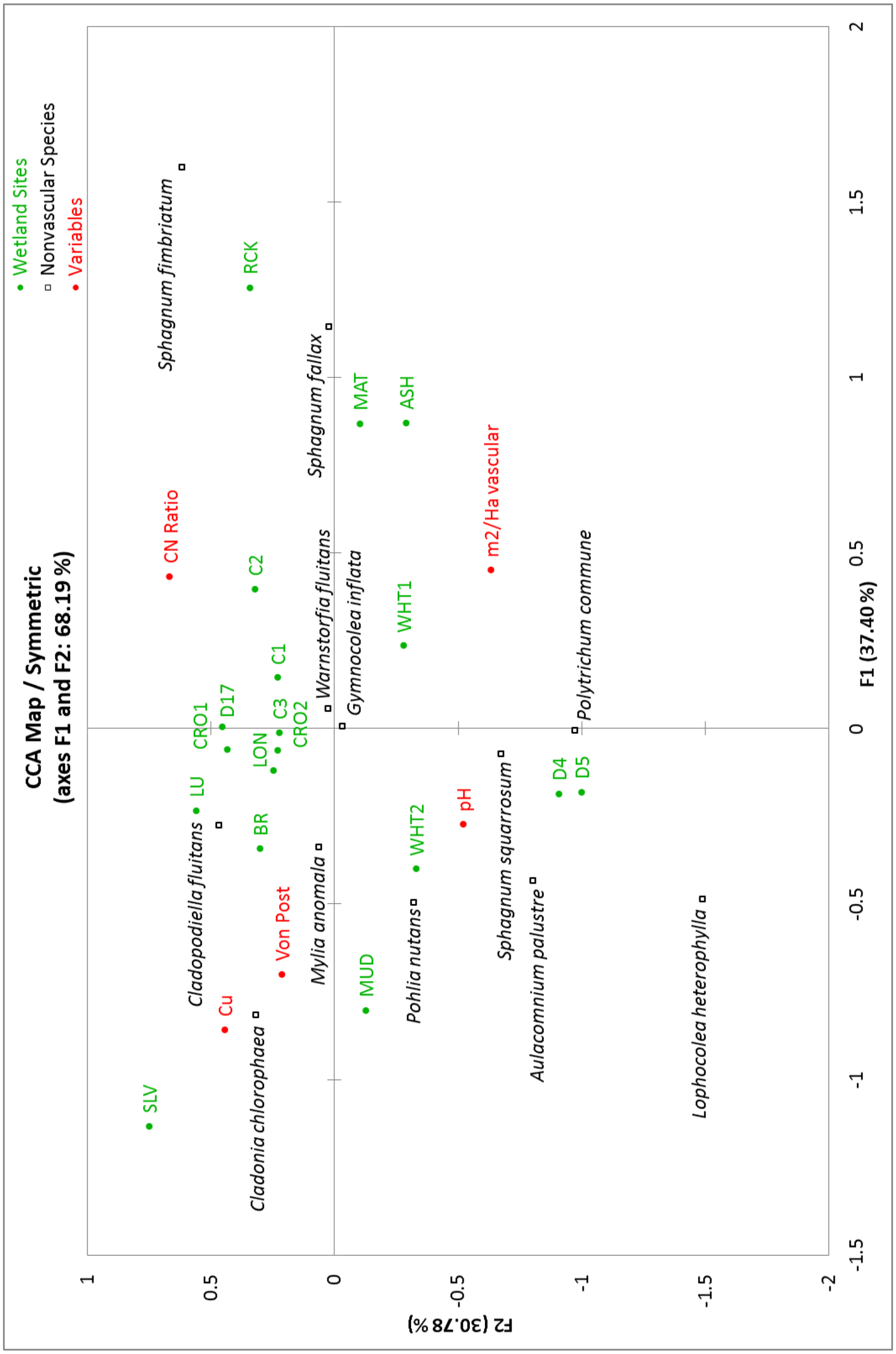

Figure 3.11 – Biplot of CCA analysis of the Sudbury data (Appendix 7.4 - Table 7.8) and the nonvascular species present at greater than 10% of the wetlands surveyed.

4 Discussion

There is great spatial variability in the concentrations of Cu and Ni in surface peat, and are greatly elevated close (< 10 km) to the main Copper Cliff smelter similar to levels found in peatlands in the 1980s (Gignac and Beckett 1986). Species richness and diversity of vascular and non-vascular plants, however is most strongly correlated with the pH of the peatlands, which varies naturally and is not related to distance from Copper Cliff. Metal concentrations in peat are more strongly related to plant tissue concentrations of Ni and Cu than the pore water concentrations, particularly for *C. calyculata*. There is no evidence, however, of plant stress (as indicated by high total phenols, anthocyanin and altered chlorophyll) caused by elevated metal (Ni and Cu) levels. Plant community composition, however, appears to be influenced by the Ni and Cu pollution gradient, with the majority of bryophytes being acid and metal tolerant, and the vascular vegetation cover and frequency of *Sphagnum* strongly decreases closer to Copper Cliff.

Chemistry of Peatlands along a Historical Deposition Gradient

The Cu and Ni concentrations in surface peat decrease with distance from the Copper Cliff smelter. No such relationship is found for peat sampled at depths greater than 15 cm indicating that the elevated Cu and Ni is due to aerial deposition. Although the emission reductions in Sudbury have significantly improved the air quality and metal deposition, the peat Ni and Cu concentrations close to the smelter are comparable to values reported in the 1980s. Gignac and Becket (1986) for example, reported metal concentrations within 10 km of the smelter to range from 500-1300 mg kg^{-1} of Cu and 600-800 mg kg^{-1} of Ni in the surface peat. Taylor and Crowder (1983) reported maximum metal concentrations within the immediate vicinity of the smelter of 6912 Cu mg kg^{-1} and 9372 mg kg^{-1} Ni, and within 10 km Cu ranged around 500 – 2000 mg kg^{-1} Cu and 1000 – 2000 mg kg^{-1} Ni in the wetland soils. This study found sites within a 10 km radius of the main smelter, Copper Cliff, to be contaminated with 1238 – 1685 mg kg^{-1} of Cu and 646 – 920 mg kg^{-1} of Ni showing that even though major emission reductions were implemented in 1970 and have been gradually declining since then, the surface peat is still contaminated with elevated levels of Ni and Cu. Peatlands in central Ontario about 300 km away from Copper Cliff contained average Ni and Cu peat concentrations of 10 mg kg^{-1}, which is respectively about 90 and 170 times lower than what was found in this study (Landre et al 2010).

The Sudbury Ni and Cu deposition gradient has been also well documented for the aquatic (Semkin and Kramer 1976; Keller et al 2007) and terrestrial (Freedman and Hutchinson 1980, Amiro and Courtin 1981) systems. This Ni and Cu deposition signature was only present in the surface peat of the peatlands sampled. A similar vertical distribution of metals with depth was found in fens near a Ni smelter in Flin Flon, Manitoba, which showed enrichment in metals and a decrease with distance only in the surface 15 cm of peat (Zoltai 1987). Nieminen et al (2002) similarly analysed peat cores in the vicinity of a Ni and Cu smelter in S.W. Finland and found Ni and Cu were half the concentration at 9 cm than at the very surface. They also found consistently lower Ni values compared with Cu. Based on the emission reports from Copper Cliff, Falconbridge, and Coniston there is not a significant difference between the Ni and Cu that was emitted with the majority being emitted from Copper Cliff, although a dust analysis in 1971 showed twice the amount of Cu relative to Ni occurring at Copper Cliff (SARA 2009). Copper is known to form much more stable complexes with natural organic ligands than Ni, which is much more mobile in the peat, and can explain the comparatively higher concentrations of Cu relative to Ni in the surface peat (Nieminen et al 2002).

The contamination evident in the surface peat is a result of the past, as well as current emissions from the smelting activities in the Sudbury area (SARA 2009; Szkokan-Emilson et al. 2014). As the main metallic contaminants emitted from the smelting process are Ni and Cu, this is probable reason as to why Ni and Cu are present in such high concentrations in close proximity to the source. Freedman and Hutchinson (1980) found about 40% of the emitted Ni and Cu was deposited within 60 km. Previous studies identified a significant decrease in other pollutants with increasing distance to the smelter, including S, however in this study there was no correlation between the sulphur concentration in the peat and distance. This may be attributed to the 90% emission reduction in SO_2 emissions and due to the nature of a gaseous emission, more than 97% of the sulfur emitted is deposited beyond 60 km (Freedman and Hutchinson 1980). The current level of SO_2 emissions is between 130 – 150 kt current progresses to reduce it to 20 kt. It is also suggested that the majority of the current S deposition in the Sudbury area is not attributed to the Sudbury smelters, but instead is from long-range transport (Szkokan-Emilson et al 2014).

The pH and the substrate composition (organic matter and mineral content) can greatly impact the availability of nutrients, chemical behaviour and availability of metals, such as Cu and Ni, in the peat (Freedman and Hutchinson 1980). The pH, as well as all other measured metals and nutrients, did not exhibit any relationship with the distance from the smelters and the variability is likely due to other driving factors, such as the groundwater inputs, local geology, mineral content in the peat, and vegetation composition (Gignac and Beckett 1986; Hájková et al 2006). The pH range for the peatlands selected for this study were also within the same range of those peatlands surveyed by Gignac and Beckett (1986). The study sites also exhibited a gradient from relatively high mineral content, which contain larger amounts of Al, Mn, and Fe, to more organic substrate. The mineral content could be entering these systems through the settling of wind-blown dust, leaching and erosion from the surrounding mineral soils (Szkokan-Emilson et al 2014). The pore water and peat of bogs and poor fens is generally low in concentrations of nutrients (i.e. N and P) and important mineral elements (i.e. Ca, Mg, K) (Gignac 1989). These limitations can impact species distribution with pH, conductivity and especially Ca concentrations being shown to be the most important (Gignac 1989).

Chemistry of the Vegetation

Both species analyzed (*C. calyculata* and *K. angustifolia*) are suggested to be resistant of metal contamination, harsh soil conditions and are considered to be early successional in peatland formation (Gignac and Beckett 1986; Glaser et al 1990), which would explain their abundance throughout the study sites, even at the higher contamination sites. Leather leaf requires acidic conditions to become dominant, and is able to thrive in both dry and wet, as well as minerotrophic and ombrotrophic conditions. Sheep-laurel is able to thrive on a variety of substrates ranging from dry jack pine forests to wet *Sphagnum* bogs. In the 1980s C.*calyculata* was one of the only species found growing in the immediate vicinity of the Sudbury smelters and was present in all peatlands surveyed beyond 2km, and K.*angustifolia* appeared at all of the peatlands onwards from 12 km (Gignac and Beckett 1986; Amiro and Courtin 1981). In this study both leatherleaf and sheep laurel were present at the most contaminated peatlands sampled (<10 km from Copper Cliff) and nearly all of the wetlands onwards. It has been shown though that when a significant overstory establishes, both the leatherleaf and sheep-laurel cover tends to thin (Glaser et al 1990; Mallik 2012).

The metal concentration in *C. calyculata* foliage at uncontaminated sites has been reported to range from 0.78-3.39 mg kg^{-1} for Ni and 2.31 – 6.59 mg kg^{-1} for Cu (Mackun et al 1993; Gotelli et al 2008). In the present study, foliar *C. calyculata* Ni concentrations exceeded this range and the positive correlation between the tissue Ni and Cu concentrations and the "total" peat concentrations suggests that elevated peat metal levels are leading to increased metal uptake. There were poor relationships between the total and free ion pore water Cu and Ni concentrations and the plant tissue Cu and Ni content, although generally the bioavailable fraction of metals in a soil is thought to be the free metal ion in the soil solution (Marschner 1995). The relationships were less strong for the dissolved metal and free ion than the peat, which could be due to the great temporal and spatial variability in the pore water compared with the peat concentrations. The surface peat, which is where the rooting zone for the species occurs, is a better predictor of uptake due to it better representing the total concentration of metal and is where the rooting zone for the species occurs. Otte et al (1993) also found that the bioavailable concentrations of heavy metals in plants are not better predictors for uptake than the total metal concentration in the soil. The poor relationship may also be due to external factors regulating metal availability, such as the pH, redox potential and desiccation, and factors that impact uptake, such as the availability at the root surface, root exudates, and the presence of mycorrhizal associations (Alloway 2012). A study by van der Welle et al (2007) showed that although total metal content is generally a better predictor for uptake than the bioavailable metal, the biogeochemical differences as a result of soil characteristics (pH, redox potential, acidification potential) and the plant-soil interactions provide a much more reliable prediction of the uptake and metal availability for wetland plants. In the Sudbury area during the fall there was an acid pulse, and was not specifically measured when the vegetation was collected, which may have further muted any relationship between the bioavailable Ni and Cu at the time it was measured and the tissue content. This acid pulse has been noted following prolonged dry conditions and water table decline when the conditions in the peat become favourable for the oxidation of metals, and can undergo SO_4 related acidification resulting in the mobilization and release of base cations and metals into the pore water and outflow (Szkokan-Emilson 2014).

The concentration of Ni and Cu in *K. angustifolia* foliage from uncontaminated substrate was approximately 25 mg kg^{-1} for Ni and 20 mg kg^{-1} for Cu (Bagatto and Shorthouse 1999). The foliar concentrations from this study were within the range of uncontaminated sites and there was little relationship between the peat and plant tissue of Cu and Ni in *K. angustifolia*. Plants colonizing metal-contaminated soils are generally resistant and have adapted to this stressed environment, one strategy is for plants to limit the translocation of heavy metals and maintain a low level of contaminants in their aerial tissues over a wide range of substrate concentrations (Baker 1981).

The Ni and Cu concentrations in *C. calyculata*, and *K. angustifolia* to a lesser extent, were highest in the roots, which was anticipated as metals that are taken up from soil are largely found bound to the cell walls and near the uptake site, which is why typically 75-90% of the metal taken up is found to be in the root (Greger 2004). The Ni concentration was higher than Cu in both species and the distribution between the foliage and stem was comparable; however the Cu content in the stem for both species was generally higher than the foliage. Nickel is essential in small quantities for some plant species and has been shown to compete with Fe^{2+} and Zn^{2+} for physiological and biochemical processes, and in turn roots can uptake Ni by Fe and Zn transporters (Pandey and Sharma 2002). As Cu is an essential nutrient in plants, these species may be able to prevent the uptake by down-regulating the expression of Cu-transporters (Harmens et al 1993). Due to the increased regulation on Cu, this may explain the lower concentration of Cu in both species compared with Ni.

There was no strong indication that the Cu and Ni levels in the peat or plant tissue were impacting the foliar concentrations of chlorophyll, total phenolic content or anthocyanin content. A rise in anthocyanin content is expected under heavy metal stress in order to preserve the plant from toxicity; however this was not true for either species analyzed for Ni and Cu (Heller and Forkmann 1988). The assessments of the secondary chemistry, especially the total phenolic content, were rather crude though and more detailed analyses targeting the specific compounds may be insightful as although a correlation was not evident with the bulk analysis, this does not rule out metals having an impact on the secondary chemistry of the plants. Loponen et al (2001) found that along a metal pollution gradient with increasing distance there was no significant change in the total phenolic content in *Betula pubescens* foliage. However, there were significant differences in the main classes of phenolic compounds; flavonoids increased and gallic acid derivatives decreased with increasing distance to the smelter. There were significant differences in the foliar chlorophyll, anthocyanin and total phenol content among the sites sampled that could be attributed to natural variability, or other stressors such as nutrient deficiency, pathogen attacks, wounding and UV light (Michalak 2006). There was stronger indication that nutrients are impacting the secondary chemistry rather than the metal contamination, as under nutrient deficient conditions, particularly K- and P-deficiency, the anthocyanin content of both species increased. Anthocyanin accumulation is a distinctive trait of P-deficiency in numerous plants, although N- and K-deficiency has also been shown to induce elevated anthocyanin concentrations (Steyn et al 2002).

The ratio of N:P and N:K in plant tissue is considered to be a useful indicator if the vegetative growth is N-, K- or P-limited. The critical ratios established in aboveground vascular plants are N:P = 14.5, N:K = 2.1 to determine which nutrients may be posing as the limiting factor (Olde Venterink et al 2003). From the two species analysed it appears that two wetlands are N-limited (C1 and C2), the rest are P- or P+N co-limited sites, and all of the sites may be K- or K+N co-limited. As the majority of the wetlands are P or K limited, rather than just N limited, this may be the reason for the increase in foliar anthocyanin content under decreasing P and K concentrations, rather than N content. Van Duren et al (1997) found that disturbed fens which had been drained or subjected to prolonged lowered water tables were K-limited, whereas the undrained poor fens were N-limited. Subsequent rewetting did not change the type of nutrient limitation, which may explain the majority of K limitation over N limitation in the peatlands in this study if their hydrology had been significantly altered. The toxicity and tolerance of plants to heavy metal stress is highly species specific and is not solely dependent on the metal bioavailability and substrate factors impacting it (pH, substrate composition, moisture content, soil aeration, temperature), but also by differences in uptake and excretion rates, the storage capacity, and other physiological, molecular or biochemical changes (Marschner 1995). When plants are deficient in essential nutrients, the potential for toxicity can be enhanced. Wallace (1984) reported that Cu toxicity to plants is elevated when they are P-limited, but despite evidence of P deficiency in the present study there was no clear indication of toxicity in the two species assessed.

Vegetation Community Composition and Diversity

Species richness and diversity of vascular and non-vascular plants was not correlated with distance from the Copper Cliff smelter, or the Cu / Ni contamination in the peat, which contrasts with past studies industrial disturbed upland (Salemaa et al 2001; Amiro and Courtin 1981; Freedman and Hutchinson 1980) and wetland (Gignac and Beckett 1986; Crowe et al 2002) ecosystems with a similar pH range. However, due to the nature of peatlands, such as poor fens and bogs, the diversity and richness is not anticipated to be as high as in other systems, such as rich fens. In the Sudbury area during the peak of emissions, the most important cause of ecological damage was attributed to SO_2, but the toxic impacts of acidification, Ni, Cu, Al and indirect impacts (e.g. erosion, increase in fires) were also thought to be important (Hutchinson and Whitby 1974; Winterhalder 1996). Gignac and Beckett (1986) found that with an increase in the Cu and Ni concentrations in the peat surface there was a severe decrease in the number of vegetative species, and industrial barrens were created in the immediate vicinity of the smelter (<2 km). To date, there are still numerous areas sparsely vegetated and heavily contaminated with Ni and Cu, but through a combination of natural recovery and reclamation efforts since the emission reductions in Sudbury, extensive regrowth and vegetation in the terrestrial environment have been observed (Gunn et al 1995; Meadows and Watmough 2012). Post-disturbance succession of the wetlands is expected, however the severity of the disturbance would impact the successful colonization of fen plants depending on the impact of erosion to the peat surface, changes in the pH and metal and nutrient content, hydrology, the competition and facilitation of the species present, and if the residual peat is devoid of plants and a viable seed bank (Salonen 1987).

This study found that neither the variation in the species richness, Shannon-Wiener diversity index nor the evenness were correlated with the pollution gradient, contrasting previous studies which reported the pollution gradient to be the main driving factor for richness and diversity on smelter damaged lands with a similar pH range (Gignac and Beckett 1986; Amiro and Courtin 1981). The vegetation richness and diversity was instead more strongly correlated with pH of the peatland. Numerous studies have shown relationships between pH and vegetation (Gough et al 2000; Hájková et al 2006) and an increase in vascular vegetation species richness with increasing pH has also been reported for wetlands located in the Netherlands (Vermeer and Berendse 1983). Hájková et al (2006) found that fen vegetation distribution was strongly correlated with pH, and with various studies which examined primary influences driving plant distribution found that the most influential chemical variable on vegetation composition was the pH and composition of the substrate (Hájková and Hájek 2003; Goslee et al 1997; Hájková et al 2006). The pH is an environmental variable which is also related to the nutrient and toxic element availability and the species richness generally declines at both highly acidic, which can increase Al toxicity and Ca deficiency preventing germination and survival, and alkaline soils due to fewer species being adapted to these conditions (Marschner 1995). The maximum range of pH values measured in this study may be an optimal range and favorable for more species, resulting in higher overall species richness, however the more general reasons behind community differences and varying pH still remain to be investigated thoroughly. A weaker correlation was found in the ‘fen-like’ peatlands surveyed between the bryophyte species richness and pH. Previous work has also shown this less pronounced relationship in poor fens for bryophyte richness and pH, but when this was considered against all peatlands (bog-fen) no patterns in richness was apparent with pH or other variables measured in uncontaminated peatlands showing the importance of separating different wetland classes (Vitt et al 1995).

The composition of the vegetation may be affected by the metal contamination without changes in diversity or richness as certain species are more tolerant to metals than others. In the present study, the metal contamination gradient is not greatly impacting the ability of plants to grow to the extent that was observed in the 1980s (Gignac and Beckett 1986). However the CCA analysis showed that the most important variables explaining the variation in species composition of the peatland vascular vegetation was the pH and mineral to organic content of the peat, and to a lesser extent, the Cu-Ni pollution gradient, which is consistent with the relationship between the pH and species richness. The first two PCA axes attributed to the pH and mineral to organic gradient in the peat explained 55% of the variability in the peat chemistry and species diversity which corresponded with the first axis in the vascular CCA and the second axis in the nonvascular CCA. The third PCA axis attributed to the pollution metal gradient explained 13% of the peat chemistry variability and corresponded to the second axis in the vascular CCA and the first axis in the nonvascular CCA. Fens are inherently variable in their species richness, and the gradients in pH, mineral and nutrient concentrations, hydrology and light are well-known driving factors contributing to vegetation patterns in fens, the two most important gradients influencing vegetation variation being pH-base richness and moisture-aeration (Kotowski et al 2001; Vitt and Slack 1975; Rydin and Jeglum 2006). Brumelis and Carleton (1989) assessed the vegetation composition in disturbed wetlands from logging and mechanical disturbance and also found the dominant influence on the vascular vegetation composition to be the site nutrient regime, with the disturbance and successional influence to be secondary.

The most frequent taxa recorded at the sites surveyed are expected in poor fens and also were found in the majority of the wetlands (>10 km of the smelter) studied by Gignac and Beckett (1986), suggesting they are tolerant of acidic and metal contaminated conditions. The species identified in the CCA as having a higher presence at the organic, less contaminated sites are not seemingly evident of being highly sensitive to metals. *T. latifolia* for example, has been shown to have internal Cu and Ni tolerance mechanisms (Taylor and Crowder 1983) and *C.calyculata* is known to be highly tolerant of acidic and disturbed sites, including heavy metal contamination (Gignac and Beckett 1986). Several other studies conducted in boreal peatlands have also found a primary gradient from the more ombrotrophic species (towards the center of the biplot) while the more minerotrophic species are toward the right edge of the biplot (Anderson and Davis 1997; Jeglum and He 1995; Lachance and Lavoie 2004). Although some species have been shown to be metal tolerant, this study cannot conclude the resistance of the species to metals and this could be further investigated to fully assess the tolerance and sensitivity of the peatland plant communities present.

The varying dominance of *Sphagnum* sp. as well as the variable mineral content and elevated water Ca and Mg content shows the variability in peatlands and indicates that not all of the study sides are true poor fens and are either undergoing transition or were formed more recently as a result of erosion, road construction or the degradation to the Sudbury landscape (Zoltai and Vitt 1995). Compared with average chemistry outlined by Zoltai and Johnson (1987) the fall porewater chemical composition of WHT1 and WHT2 have a much higher pH (>5) and Ca concentration (about 25 mg L^{-1}) which is more indicative of a moderate-rich fen rather than a poor fen, although this changes temporally and was much lower in the spring. The vegetation community at both D4 and D5 are significantly different from the other surveyed sites including the presence of species expected in terrestrial upland habitats, a higher wetness index, and differences in the peat chemistry (higher mineral content). Although the wetness index at these two sites are below zero, which indicates a predominance of wetland species, it is higher than any of the other sites due to the presence of facultative species including *Deschampsia flexuosa*, *Apocynum androsaemifolium* and *Schizachne purpurascens* (Wilhelm 1989). The elevated peat mineral content (Al, Fe, Mn) and lower C and N content compared to the other sites may be attributed to the surrounding area which suffered a heavy loss of terrestrial upland vegetation and upland soils due to the smelting practices and subsequent erosion of the mineral soil into the peatlands (Szkokan-Emilson et al. 2011). Furthermore, the high occurrence of *P. commune* at D4 and D5, as identified in the CCA, as well as the presence of *A. palustre* are indicative of fens bordering mineral soil (Rydin and Jeglum 2006).

The total vascular vegetation cover increased with decreasing Cu and Ni concentrations in the peat and with distance from Copper Cliff. Salemaa et al (2001) also found that with increasing distance from the Cu-Ni smelter at Harjavalta, Finland, the total coverage of the upland vegetation also increased. Vegetative cover has also been found to be strongly linked with the hydrology and wetness of the site with less total vegetation cover on drier sites (Jeglum and He 1995). Changes in the total vegetative cover can greatly impact bryophyte species, but no clear relationship between the bryophyte percent cover and vascular vegetation cover was identified in this study, and the cover of specific bryophyte species was not assessed. It is generally thought that the influence of vascular plants on the growth and development of *Sphagnum* to be of less importance than *Sphagnum* to vascular vegetation (Malmer et al 1994). Shade tolerance in nonvascular species has been well identified, although the tolerance ranges vary between species and studies have shown opposing results with the impact of shading to decrease (Clymo and Hayward 1982) and increase (Murray et al 1989) the growth of *Sphagnum*.

Bryophyte Community Composition

When focusing on the restoration and recovery of peatlands, priority is often given to vascular vegetation, although bryophytes are of equal importance (Kotowski et al 2001; Mitsch and Gosselink 2007). A great amount of research has examined the functional role of bryophytes in bogs, but comparatively, little is known about their function in fens which limits knowledge of keystone vegetation groups and indicators of restoration (Clymo and Hayward 1982). *Sphagnum* mosses are considered to be an integral component of bog and poor-fen communities, although are less dominant in richer fens, and the rehabilitation of the peatlands hinges on the growth of *Sphagnum* (Moore and Bellamy 1974). The conditions generally required for *Sphagnum* to recolonize a bare peat surface successfully includes an increase in high pore-water pressures, a high and stable water table, and a high soil moisture content (Price 1997; Grosvernier et al 1997). The full recovery of a *Sphagnum* peatland is promoted through the successional series W. *fluitans*, *S. cuspidatum* as carpet mosses, *S. fallax* as a lawn species, low hummocks to be colonized by *S. magellanicum*, and *S. rubellum*, and *S. fuscum* on higher hummocks (Rydin and Jeglum 2006). Both *W. fluitans* and *S. fallax* were present at >50%

of the wetlands, although were not dominating, but there was a lack of *S. rubellum*, *S. cuspidatum*, and *S. magellanicum* was not found at all. This may indicate that although colonization of the peatlands is occurring, it is at a lower rate than is expected and more time is needed for these species to become established and thrive. However, this rate of recolonization may be further inhibited if there are no colonies in the vicinity and the peatland conditions are not conducive for reestablishment.

Along the Ni and Cu spatial variability, *Sphagnum* began to appear at a distance of 8 km or greater from the Copper Cliff smelter and reached a maximum species richness of 5 at the furthest site. Although the *Sphagnum* species richness was not correlated with distance from Copper Cliff, the frequency of *Sphagnum* recorded in the quadrats increased with distance from Copper Cliff. Gignac and Beckett (1986) similarly found that in the Sudbury peatlands *Sphagnum* began to appear at 10 km and beyond 30 km stabilized to a *Sphagnum* richness of about ten. However they also surveyed the edge of the wetland which can vary in substrate composition and therefore host different species, resulting in a higher overall species richness. The diversity of *Sphagnum* throughout the majority of the sites surveyed, including richness and the frequency, was not as high as expected in a poor fen, although the species present are expected in a poor fen community (Rydin and Jeglum 2006). As *Sphagnum* mosses were not present at the peatlands studied by Gignac and Beckett (1986) or in the peatlands present now in this high impact zone within 10 km of Copper Cliff, it can be assumed that *Sphagnum* mosses have been absent for quite some time within this zone. Although their disappearance may be speculated to be originally due of the SO_2 emissions and other disturbances at the peak of emissions due to the sensitive nature of *Sphagnum*, it can be argued that since the emission reductions, it seems the recovery of *Sphagnum* in these peatlands is being limited factors other than the air quality. Factors which may be currently restricting full recovery and the ‘re-entry’ of *Sphagnum* at these sites may include the hydrology, no species in the vicinity to colonize the peatlands, and the peat humification and quality. Within a range of environmental conditions studied by Mulligan and Gignac (2001), the depth to water table was considered to be the most important factor regulating *Sphagnum* species distribution, and *S. fallax*, and to a lesser extent

S. magellanicum, and *S. angustifolium* exhibited a wide tolerance and distribution to habitat environmental factors.

The peat humification status was also correlated with distance to Copper Cliff with more humified surface peat closer to the smelter and less humified peat at the furthest sites. The primary mechanisms for peat accumulation are slow decomposition rates which are regulated through saturated, anaerobic soils and cool climate conditions (Yavitt *et al.* 1997). The humified peat may be a result of the history of absent and reduced *Sphagnum* cover at these sites, attributed to the previous emissions and disturbance (Gignac and Beckett 1986). *Sphagnum* mosses comprise up to 90% of the peat due to the recalcitrant and antibacterial nature of *Sphagnum* which inhibits decomposition when compared to vascular plant tissues, as well as their ability to maintain a high water table (Andrus 1986; Turetsky 2003; Hájek et al 2011). The accumulation of peat alters the hydrology of the system and the pore water biogeochemistry, which in turn makes the conditions for favourable and advantageous for *Sphagnum*, and consequently *Sphagnum* is often deemed an ecosystem engineer (van Breemen 1995). Their prolonged absence at these peatlands could have resulted in a larger fluctuating water table, which could increase aerobic conditions, preferential for increased decomposition rates (Freeman et al 1997) and enable the dominant litter to be of other species which may have compounds able to be decomposed quicker (Scheffer et al 2001). The higher humification status of the peat closer to Copper Cliff may also be attributed to other site disturbances such as erosion which would have negatively affected the vegetation cover and altered the surface peat to expose the more humified peat below. There were also mass amounts of logging and deforestation occurring in the area and these wetlands may have been logged and been subject to mechanical disturbance. The impact of extracting logs by skidding has been shown to severely reduce vegetation cover, result in *Sphagnum* mortality and due to disturbance of the surface peat, can create niche habitats for fast growing weed species, expose deeper more humified peat and convert the nutrient status of the wetland (Brumelis and Carleton 1989).

The absence of *Sphagnum* sp. at the most disturbed sites (none found at SLV or LU) may have produced a positive feedback loop attributed with a lower vascular vegetative cover, more humified peat, and possibly a lowered water table. This is of concern as losses in the key individual functional types, such as *Sphagnum*, can lead to further shifts in the vegetative composition and can weaken key ecosystem functions, such as carbon accumulation and water quality (metal release) (Dieleman et al 2014). It has been shown that peatland remnants with strongly humified peat are not favorable for the redevelopment of *Sphagnum* carpets due to the wide water table fluctuations and high water tensions, which may further impact recolonization of *Sphagnum* at the sites currently devoid of *Sphagnum* (Smolders et al 2003; Price 1997).

A low incidence of *Sphagnum* reflects the loss of natural functions (shrinking and swelling, regulating runoff and evaporation) that previously limited the water table fluctuations to a narrower range near the surface (Van Seters and Price 2001). Conversely, the sites with the highest frequency of *Sphagnum* (MAT, ASH, RCK) had the least humified peat, which may be attributed to the resistance of *Sphagnum* to decomposition, and were also the furthest from the smelter which could have resulted in the surface peat being less disturbed than the peatlands in close proximity to the smelter (Clymo and Hayward 1982). Unsupported ^{210}Pb concentrations conducted at selection of the sites show that the peak layers have similar ranges of values indicating a similar deposition time frame. Assuming similar background deposition, about 3-5 cm of peat has accumulated at the sites devoid of *Sphagnum* (LU, MUD); compared to the least contaminated sites which are dominated by *Sphagnum* (RCK, ASH) where the peak occurs much deeper in the profile and over 10 cm of peat has accumulated. Due to the uniform humification with depth at SLV and LU, it is estimated that the peat has a more uniform pore structure with higher bulk densities and high water retention capacity (Price 1996).

The water table fluctuation and depth are of particular importance as they have a major control on the decomposition dynamics and the water chemistry, although these were not specifically measured for this study (Chirino et al 2006; Sherwood 2013; Weltzin et al 2000). The impact of drought in these systems has been shown to decrease the pH and mobilize sulphate and metal ions in the water outflow from the peatlands (Szkokan-Emilson et al 2013). The Sudbury area experienced a summer drought in 2011 and 2012 and with climate change disruptions to these systems, will likely increase and become more prevalent which may also pose additional stressors, not related to the variability in metal contamination, on the vegetation composition. Lowered water tables with the consequent increase in aerobic conditions at the surface peat have been shown to accelerate rates of organic matter decomposition and substantial C losses from bogs and fens, but the response of C sink/source behaviour of the peatlands has been shown to vary greatly between wetlands (Scheffer et al 2001; Moore and Bellamy 1974; Fenner and Freeman 2011).

The distribution of peatland bryophyte species typically are controlled by four main gradients: open to shaded, ombrotrophic to minerotrophic, from the margin to the center, and wet to dry (Gignac and Vit 1990). For the variables measured, the largest impact on the bryophyte species distribution was related to the spatial variability in the Ni and Cu contamination, and the ombrotrophic to minerotrophic gradient. Mosses and lichens are unable to prevent the passage of heavy metals into their tissues because they have no protective cuticle and obtain nutrients directly from the rainwater and air (Clymo and Hayward 1982; Salemaa et al 2004). In contrast, the vascular vegetation has, to some extent, greater control over which elements are taken up by their roots, which may contribute to the larger impact that the metal contamination is appearing to have on the bryophytes as opposed to the vascular vegetation.

Large areas in Sudbury were severely devastated with industrial barrens and impacted vegetation. The most frequent nonvascular taxa found throughout the study sites, *C. fluitans*, *W. fluitans* and *P. nutans,* are not surprisingly been shown to be metal tolerant, often the first to colonize harsh conditions, and *S. fallax* and *M. anomala* are also notorious colonizers (Gignac and Beckett 1986). *P. nutans* especially has been shown to accumulate higher concentrations of Ni and Cu compared to other species and able to survive in close proximity to smelters (Salemaa et al 2004). For this study, only the center of the peatlands were surveyed which eliminates the edge effect, as other work has noted a pronounced variation in the abundance of species as a function of distance from the edge (Gignac and Becket 1986; Campbell et al 2003). Several studies have investigated the metal tolerance on upland species, but this has not been readily done for wetland species, and most research conducted on wetland plants has been primarily on hyper-accumulating species.

It is important to note that all of the wetlands studied have been impacted with metal deposition to some degree. To completely remove the Ni and Cu smelter metal signature from the peat, sites further away as a reference or to compare uncontaminated vegetation composition would be necessary. Furthermore, greater restrictions and spatial variability when choosing the sample sites may have proved to be beneficial to try and constrain the characteristics of a fen or a bog with the main difference between sites being the Ni and Cu contamination. Without experimental exposures, however, it is challenging to identify the contribution of the metal contamination to the plant species instead of other environmental factors, such as drought, nutrient limitation, impact of erosion, or other anthropogenic disturbances (road construction).

5 General Conclusion

It is evident that the peatlands in Sudbury, Ontario are still heavily contaminated with Ni and Cu and decline logarithmically in the surface peat with distance from the main smelter, Copper Cliff. The Cu and Ni concentrations in plant tissues of *C. calyculata* are correlated with peat Cu and Ni concentrations, respectively, but there is very little relationship between plant chemistry and the total or free-ion concentration in the pore water, indication peat concentrations to be a better predictor of uptake. In the two abundant species, *Chamaedaphne calyculata* and *Kalmia angustifolia,* there is no obvious impact of the Ni and Cu contamination on secondary compounds (total phenolic content, chlorophyll or anthocyanin concentration) that would indicate plants are stressed due to metal contamination. Instead there is a stronger indication that nutrient (P or K) limitation may be having a greater influence on secondary plant chemistry (anthocyanin content). The metal concentrations in the peat are comparable to the levels found in Sudbury peatlands with a similar pH range by Gignac and Beckett (1986), suggesting that the higher richness and diversity could be attributed to the lower SO_2 rather than the Ni and Cu concentrations or the pH. The pH of the wetlands is the most important factor controlling the plant and bryophyte communities (richness and composition), however there is evidence that the vascular plant communities, and more so the bryophyte communities, remain affected by the historical deposition gradient. The historical disturbance and elevated metal concentrations have resulted in the bryophyte community dominated with species that are suggested to be acid and metal tolerant, as well as being colonizers to disturbed peatlands. Due to the severe historical disturbance to the peat surface through erosion, contamination, and the lack of vegetation cover, a delayed recovery was expected. The recovery of *Sphagnum* appears to be the most limited, with no species found within 8 km of the smelters and the frequency of *Sphagnum* significantly decreases with in close proximity to the smelter which reflects the loss of natural functions of the peatlands, and sites closer to the smelter also have surface peat which is more humified than sites located further from the smelter, which can also indicate a wide water table fluctuation. A wetland conceptual model for the current as well as historical stressors on the Sudbury peatlands, as well as the attributes that can be monitored as a sign of recovery has been summarised (Figure 5.1).

It can be argued that the peatlands have undergone recovery since emission reductions when compared with peatlands with similar metal contamination and pH range studied by Gignac and Beckett (1986). However, despite the >90% emission reductions, there is variability in the "recovery" of peatlands within the same range of Ni and Cu content as indicated by the vascular cover and presence of *Sphagnum* mosses, which should be further explored as the ecosystem function at these disturbed sites may be impacted. As *Sphagnum* is a key component of poor fen and bog communities and helps stabilize the hydrology of these systems, further assessment to determine why *Sphagnum* is not colonizing the peatlands within close proximity to the smelter is needed. Focus on where *Sphagnum* is occurring on a greater scale within the high impact zone (<10 km of Copper Cliff) to determine what are the limiting factors for *Sphagnum* in this vicinity and which *Sphagnum* species could be focused on to promote recovery and colonization of these more contaminated and disturbed peatlands would be beneficial. To restore the peatlands which are still showing limited signs of recovery consideration into raising the water table, mulching, and reintroducing *Sphagnum* would be beneficial (Figure 5.2). More in depth secondary chemistry analyses, such as the different classes of phenolic compounds, flavonoids and terpenoids, to assess for metal stress in the plant species present could also prove to be beneficial if a marker for metal stress is found.

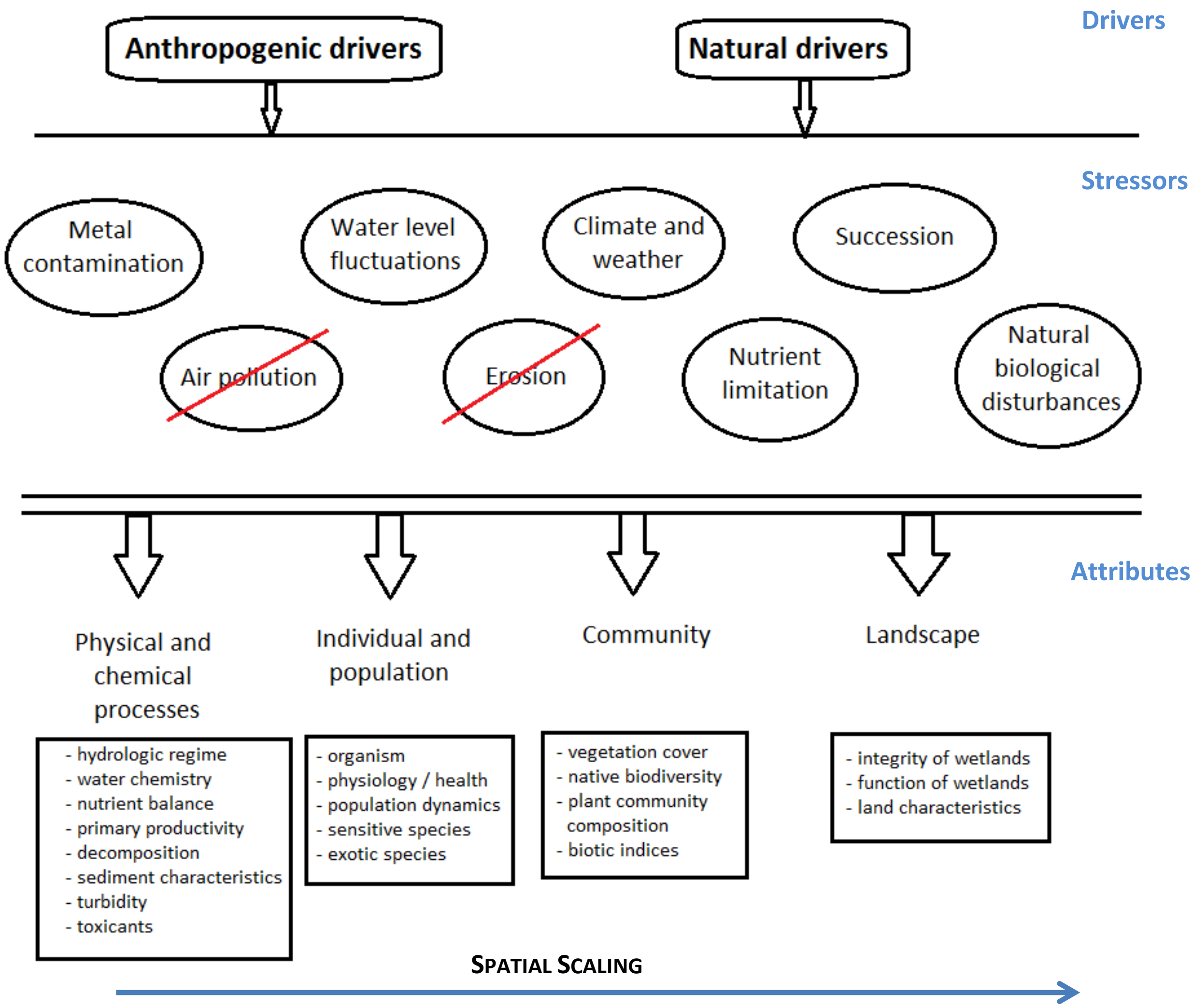

Figure 5.1 – The conceptual model of wetland ecosystem drivers and stressors with the elimination of the historical impact of SO_2 air pollution and erosion.

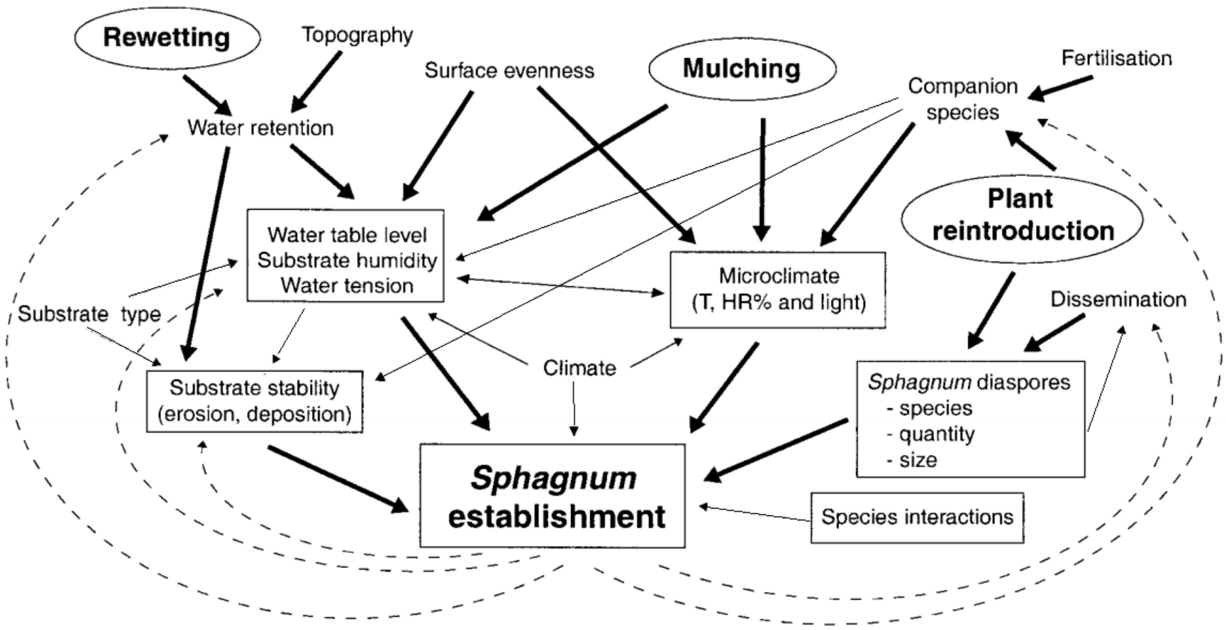

Figure 5.2 – Adapted from Gorham and Rochefort (2003), the interaction and suggested routes for remediation techniques in the re-establishment of *Sphagnum* mosses on impacted peatlands.

Overall, the vast improvements to the richness, diversity and community composition on a whole is indicative of the natural re-vegetation and recovery, albeit limited, of the smelter disturbed peatlands surrounding Sudbury, Ontario. Although more time is needed to improve the vegetation composition and peatland conditions, it would be suggested to further assess the status of bryophytes, in particular *Sphagnum* mosses in the Sudbury peatlands, as the ecosystem function may be impacted due to their absence, and reintroduction of these species may prove to be beneficial.

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7 Appendix

7.1 von Post classification of peat

The von Post was assessed in the field by squeezing a sample of peat and observing the colour of the solution expressed between the fingers, the proportion of the original sample that remains in the hand, and the nature of the fibers.

Table 7.1 - The von Post scale of Humification (source Ekono 1981).

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

7.2 Peat Metal and Nutrient Analysis

Table 7.2 - Surface peat (0-15cm) peat metal and nutrient chemistry analyses for all of the peatlands in order of increasing distance from Copper Cliff**.**

	Na g kg^{-1}	K g kg^{-1}	Ca g kg^{-1}	Mg g kg^{-1}	P g kg^{-1}	Al g kg^{-1}	Fe g kg^{-1}	Mn mg kg^{-1}	Ni mg kg^{-1}	Cu mg kg^{-1}	Co mg kg^{-1}	Zn mg kg^{-1}	N%	C%	S%	CN Ratio
SLV	0.65±0.22	0.57±0.20	2.04±0.15	0.33±0.08	0.52±0.07	6.80±0.76	8.91±3.30	18.2±5.0	699±130	1685±171	12.4±2.7	43.8±7.7	1.63±0.22	51.1±1.5	0.37±0.05	31.9±408
LU	1.24±0.34	1.02±0.17	5.84±2.33	0.40±0.07	0.61±0.08	3.36±0.78	7.87±0.73	47.1±13.8	920±231	1238±428	17.3±4.4	64.7±20.2	1.86±0.23	49.2±0.5	0.67±0.09	26.8±3.3
MUD	0.80±0.49	0.80±0.20	4.05±2.85	0.71±0.25	0.97±0.11	6.42±2.86	4.73±1.02	54.3±18.1	646±116	1495±425	10.2±1.5	69.9±30.6	2.50±0.32	45.0±2.7	0.76±0.09	18.2±2.1
BR	0.57±0.06	0.59±0.06	1.74±0.29	0.38±0.04	1.12±0.10	10.5±2.6	3.09±0.11	42.5±7.7	540±47	1039±143	10.4±0.9	43.0±12.6	2.11±0.20	40.0±2.3	0.76±0.09	18.8±0.9
CRO1	0.59±0.07	0.63±0.18	4.31±1.53	0.54±0.07	0.62±0.10	3.96±0.79	4.25±1.79	63.2±24.3	739±198	1091±310	15.3±4.6	52.7±15.3	2.39±0.28	48.3±1.0	0.86±0.09	20.5±2.4
LON	0.58±0.04	0.76±0.14	3.41±0.80	0.64±0.07	0.79±0.15	4.53±1.50	3.99±1.46	54.5±12.1	691±50	1095±120	13.2±3.1	81.2±4.8	2.30±0.68	46.5±1.4	1.25±0.19	22.2±8.7
C2	0.71±0.08	0.83±0.24	5.43±1.04	0.38±0.01	0.63±0.06	1.72±0.05	8.18±2.18	29.1±0.6	348±11	635±83	8.36±0.20	38.7±8.1	1.73±0.23	48.4±1.2	0.70±0.16	28.5±4.0
C3	0.47±0.11	0.60±0.09	1.85±0.17	0.44±0.10	1.09±0.23	9.82±1.75	3.68±0.16	35.4±3.9	545±43	1152±80	9.00±1.13	55.3±7.6	2.25±0.36	43.7±1.0	0.99±0.25	19.8±3.9
WHT2	0.60±0.34	0.66±0.05	7.10±3.10	1.15±0.49	0.85±0.14	3.83±0.16	5.75±1.48	40.7±17.2	592±129	1057±77	13.0±2.2	38.4±3.5	1.85±0.10	48.1±2.3	0.91±0.29	26.1±2.4
CRO2	0.69±0.11	0.59±0.15	4.66±2.13	0.65±0.19	0.71±0.13	6.85±3.04	3.23±1.49	45.6±7.9	705±227	928±233	12.1±3.6	62.8±30.3	2.29±0.26	46.1±1.4	0.83±0.21	20.4±2.5
DH17	0.58±0.15	0.55±0.07	1.74±0.38	0.43±0.06	0.76±0.11	11.1±3.4	6.07±1.88	25.2±4.1	693±80	1151±152	12.3±1.7	21.3±1.5	2.01±0.24	47.3±2.0	0.75±0.15	23.9±3.6
C1	0.51±0.11	0.67±0.10	2.52±0.60	0.59±0.13	0.60±0.27	5.35±1.74	7.66±2.66	39.2±5.9	472±193	844±179	9.35±3.32	42.9±15.7	1.31±1.04	17.6±13.2	0.39±0.34	14.1±1.9
D5	0.47±0.03	1.12±0.20	1.73±0.40	2.31±0.53	0.47±0.12	18.6±2.7	17.27±4.14	92.4±12.8	429±186	512±116	12.0±1.6	45.2±2.1	0.71±0.26	12.1±5.8	0.22±0.10	16.6±3.4
WHT1	0.34±0.18	0.59±0.22	4.84±1.26	1.02±0.49	0.98±0.12	10.6±6.4	6.81±2.71	136±107	578±138	715±175	11.3±1.3	60.2±7.1	2.28±0.55	36.6±8.0	0.84±0.23	16.2±1.4
D4	0.49±0.19	1.04±0.40	0.72±0.16	1.72±0.98	0.89±0.24	21.0±4.5	15.29±0.81	62.5±22.6	275±47	711±183	11.8±1.5	41.3±14.0	1.34±0.21	17.3±3.4	0.24±0.07	12.9±1.3
RCK	0.63±0.04	0.82±0.07	0.98±0.08	0.36±0.11	0.80±0.12	5.68±0.43	6.68±1.42	36.3±2.7	120±10	221±20	5.59±0.49	17.0±1.8	1.95±0.36	41.9±6.0	0.81±0.10	21.7±3.1
ASH	0.46±0.10	1.08±0.08	3.95±0.78	1.07±0.37	0.77±0.08	3.06±0.89	9.31±2.23	147±68	183±8	169±26	20.5±0.4	44.6±5.0	1.88±0.40	43.7±1.4	0.79±0.28	24.1±5.0
MAT	0.57±0.03	0.58±0.18	3.97±1.09	0.63±0.06	0.87±0.07	4.66±0.35	3.88±1.22	54.6±15.4	205±49	281±56	11.5±1.2	49.1±24.3	1.53±0.19	45.7±1.1	0.58±0.13	30.2±2.9

Table 7.3 - Middle peat (25-35cm) peat metal and nutrient chemistry analyses for all of the peatlands in order of increasing distance from Copper Cliff**.**

	Na g kg^{-1}	K g kg^{-1}	Ca g kg^{-1}	Mg g kg^{-1}	P g kg^{-1}	Al g kg^{-1}	Fe g kg^{-1}	Mn mg kg^{-1}	Ni mg kg^{-1}	Cu mg kg^{-1}	Co mg kg^{-1}	Zn mg kg^{-1}	%N	%C	%S	CN Ratio
SLV	0.45±0.04	0.11±0.02	4.11±0.96	0.47±0.08	0.38±0.09	5.74±0.76	3.25±1.96	17.9±3.2	123±44	73.1±16.1	7.67±1.32	20.8±4.2	1.39±0.16	53.6±1.1	0.32±0.04	38.9±5.0
LU	0.43±0.11	0.09±0.03	10.65±1.79	0.72±0.14	0.52±0.07	5.33±0.4.	2.55±0.27	54.1±11.2	199±72	86.4±44.3	19.4±8.1	15.2±9.6	1.80±0.12	51.5±0.8	0.43±0.05	28.7±2.2
MUD	0.42±0.37	0.10±0.05	9.41±1.28	0.72±0.15	0.69±0.13	6.95±1.18	3.08±0.93	51.6±12.5	106±99	69.4±17.5	5.65±2.47	20.2±10.3	1.88±0.34	51.7±2.1	0.46±0.04	28.3±5.0
BR	0.37±0.16	0.15±0.04	5.88±1.55	0.67±0.13	1.54±0.45	15.6±2.8	1.90±0.41	109±28	342±194	108±28	11.0±5.2	41.8±30.8	2.00±0.15	40.2±4.3	0.60±0.08	20.1±1.5
CRO1	0.13±0.03	0.09±0.02	13.43±2.05	1.67±0.35	0.56±0.08	5.36±0.54	2.03±0.52	84.6±27.3	150±135	82.7±19.7	7.47±4.32	26.5±22.4	1.75±0.14	50.8±1.0	0.46±0.08	29.3±2.7
LON	0.50±0.03	0.23±0.08	11.30±2.59	1.14±0.14	0.85±0.20	8.86±3.73	3.41±0.69	117±40	60.3±3.6	79.6±20.8	4.36±2.98	32.7±24.0	1.86±0.21	45.5±3.9	0.53±0.08	24.7±2.4
C2	0.62±0.02	0.19±0.06	3.41±0.50	0.30±0.08	0.47±0.12	2.6±0.5	1.68±0.49	24.7±6.2	192±59	70.6±35.0	4.98±1.24	26.3±4.3	1.58±0.22	51.6±1.8	0.44±0.14	33.3±5.7
C3	0.50±0.05	0.27±0.12	5.27±0.89	0.68±0.08	1.37±0.27	15.7±2.9	2.84±0.32	99.5±30.9	333±193	79.4±37.1	72.3±21.2	10.3±4.9	1.89±0.32	41.3±8.3	0.57±0.10	21.8±1.1
WHT2	0.62±0.03	0.15±0.07	6.12±2.64	0.71±0.24	0.89±0.24	8.57±1.87	3.22±0.66	44.9±16.1	188±64	60.9±17.9	33.6±13.4	8.97±1.90	1.77±0.13	49.2±2.6	0.40±0.13	27.9±3.0
CRO2	0.28±0.19	0.18±0.10	12.21±2.34	1.35±0.27	0.68±0.19	6.90±1.69	2.71±0.33	98.4±50.4	422±353	94.1±55.0	9.94±5.58	66.7±58.5	1.83±0.29	48.7±1.5	0.55±0.15	27.3±6.0
DH17	0.55±0.15	0.11±0.02	16.17±1.53	1.14±0.16	0.94±0.17	13.4±2.4	3.58±0.45	94.2±16.7	260±117	82.2±44.8	24.0±9.1	18.1±5.8	1.96±0.12	46.7±2.1	0.47±0.05	23.8±1.5
C1	0.63±0.05	0.62±0.30	3.18±1.21	1.87±0.51	0.15±0.15	16.8±11.3	8.50±3.76	64.5±11.7	49.0±40.6	31.3±25.6	22.0±6.1	5.08±2.02	0.22±0.25	3.63±4.73	0.06±0.05	16.1±3.6
D5	0.56±0.03	0.97±0.11	1.35±0.30	3.99±0.29	0.25±0.14	14.5±2.3	14.44±0.63	164±52	91.6±60.0	25.1±9.6	13.8±3.5	46.9±9.0	0.20±0.15	3.30±2.45	0.17±0.15	16.2±1.5
WHT1	0.49±0.17	0.45±0.12	9.84±4.10	1.49±0.34	0.74±0.20	15.0±1.2	4.97±1.04	120±27	206±55	62.6±19.2	24.5±25.3	38.4±39.1	1.39±0.47	29.7±10.5	0.37±0.11	21.4±1.0
D4	0.61±0.04	3.27±0.58	2.59±1.64	7.57±1.25	0.61±0.14	45.9±7.6	34.48±6.36	577±286	271±148	160±91	31.6±6.7	156±27	0.42±0.10	5.58±1.44	0.09±0.02	13.2±1.9
RCK	0.49±0.05	0.23±0.05	2.07±1.07	0.27±0.06	0.95±0.12	6.57±0.77	1.91±0.28	60.7±28.0	144±37	61.5±22.8	5.44±1.41	43.5±10.9	2.52±0.65	42.2±5.0	0.60±0.12	17.4±3.2
ASH	0.37±0.05	0.17±0.04	6.99±0.95	0.66±0.10	0.75±0.12	5.16±0.77	5.64±1.20	165±67	289±111	289±90	15.8±3.7	187±19	2.320.19	47.1±2.2	0.87±0.18	20.4±2.2
MAT	0.49±0.06	0.25±0.18	3.48±1.16	0.51±0.09	0.83±0.10	5.22±0.67	2.72±0.53	45.1±12.4	196±33	239±89	10.7±1.6	66.1±24.8	2.13±0.30	48.5±0.6	0.87±0.14	23.2±3.4

Table 7.4 – Deep peat (45-60cm) peat metal and nutrient chemistry analyses for all of the peatlands in order of increasing distance from Copper Cliff**.**

	Na g kg^{-1}	K g kg^{-1}	Ca g kg^{-1}	Mg g kg^{-1}	P g kg^{-1}	Al g kg^{-1}	Fe g kg^{-1}	Mn mg kg^{-1}	Ni mg kg^{-1}	Cu mg kg^{-1}	Co mg kg^{-1}	Zn mg kg^{-1}	%N	%C	%S	CN Ratio
SLV	0.43±0.08	0.13±0.03	4.02±0.60	0.49±0.04	0.27±0.04	7.66±1.15	1.95±1.10	11.9±2.9	40.6±15.8	53.5±13.6	3.6±0.8	7.28±0.73	1.21±0.12	52.9±1.2	0.32±0.04	44.1±5.5
LU	0.41±0.06	0.12±0.04	13.7±3.2	1.02±0.10	0.35±0.05	4.8±0.7	2.55±0.71	25.7±15.7	61.2±42.3	54.7±18.5	12.8±12.2	7.68±1.70	1.59±0.06	51.7±1.0	0.35±0.06	32.5±1.8
MUD	0.31±0.28	0.11±0.02	10.7±1.6	0.95±0.14	0.72±0.22	9.92±1.06	3.33±0.80	72.8±19.6	30.3±9.9	63.0±9.2	2.7±0.6	7.47±5.05	1.51±0.07	48.6±4.8	0.36±0.01	32.0±2.2
BR	0.16±0.13	0.15±0.04	8.28±2.12	1.05±0.19	1.24±0.29	16.3±2.8	2.09±0.07	86.3±30.8	124±35	96.3±22.3	5.5±1.6	16.8±4.9	1.81±0.17	42.8±3.4	0.56±0.06	23.7±0.8
CRO1	0.14±0.03	0.09±0.02	13.4±2.0	2.00±0.31	0.49±0.03	6.08±0.86	2.05±0.36	67.4±9.2	48.1±27.7	80.3±10.6	3.75±0.88	8.4±4.9	1.59±0.11	51.8±0.8	0.39±0.04	32.6±2.4
LON	0.36±0.16	0.22±0.06	10.5±1.9	1.24±0.25	0.72±0.15	10.2±3.7	3.39±0.30	62.0±19.7	49.5±5.8	65.8±12.7	2.49±0.88	11.0±6.0	1.57±0.10	41.9±1.5	0.49±0.08	26.7±1.6
C2	0.64±0.08	0.15±0.05	3.93±0.79	0.44±0.13	0.31±0.07	3.10±0.98	1.52±0.32	27.1±8.4	114±76	73.1±43.8	4.23±1.44	23.6±10.5	1.27±0.11	53.4±0.7	0.35±0.08	42.2±4.2
C3	0.53±0.06	0.37±0.28	5.07±1.47	1.02±0.39	1.21±0.13	18.5±2.9	3.42±1.31	82.9±29.5	73.0±34.8	59.1±15.6	22.6±7.4	4.0±1.6	1.33±0.63	33.5±15.6	0.35±0.16	25.3±1.0
WHT2	0.53±0.05	0.16±0.05	5.56±2.14	0.96±0.42	0.85±0.36	12.4±3.5	3.74±1.60	41.5±15.7	34.9±10.3	40.2±14.8	12.0±2.1	3.19±0.68	1.30±0.44	37.8±14.7	0.24±0.07	29.0±5.2
CRO2	0.19±0.19	0.19±0.04	9.84±2.18	1.34±0.29	0.69±0.08	10.2±1.7	2.24±0.39	42.2±17.0	112±85	84.2±19.0	4.45±1.67	21.5±16.7	1.73±0.16	47.7±1.0	0.56±0.16	27.8±2.1
DH17	0.52±0.14	0.10±0.03	18.5±3.3	1.54±0.24	0.87±0.37	16.9±6.6	3.61±0.91	65.9±20.2	82.8±20	80.3±11.7	122±2.7	788±1.47	0.14±0.07	2.40±1.14	0.12±0.06	17.9±2.0
C1	0.62±0.03	1.15±1.02	3.18±0.61	4.58±1.89	0.13±0.08	15.1±6.5	12.9±2.2	162±84	37.5±14.8	23.9±13.0	30.7±4.7	7.7±1.8	0.04±0.02	0.62±0.57	0.02±0.01	14.5±5.0
D5	0.68±0.07	1.47±0.11	2.78±0.56	4.03±0.37	0.19±0.08	15.1±1.3	13.7±0.8	139±30	234±168	81.4±21.7	17.0±5.7	55.1±5.7	0.30±0.05	3.92±0.38	0.10±0.02	13.3±1.7
WHT1	0.54±0.03	0.33±0.04	9.93±4.95	2.48±0.49	0.57±0.09	10.5±3.0	7.32±1.20	113±12	61.5±29.0	49.5±22.9	35.1±4.3	4.90±0.11	0.74±0.48	15.7±10.6	0.19±0.08	21.1±1.3
D4	0.58±0.06	3.21±0.33	2.31±1.18	7.21±0.66	0.50±0.07	45.1±5.5	32.5±4.7	556±159	205±66	106±8	31.3±6.8	147±18	1.58±0.15	45.1±3.7	0.42±0.05	28.7±3.3
RCK	0.49±0.07	0.19±0.06	1.57±0.93	0.46±0.43	0.83±0.33	7.50±1.45	1.71±1.08	48.3±17.5	28.9±5.5	32.7±7.8	2.2±1.1	18.6±5.9	1.69±0.96	28.5±14.0	0.30±0.15	17.9±2.6
ASH	0.40±0.10	0.18±0.03	9.65±2.41	0.71±0.07	0.65±0.10	5.34±0.66	4.1±1.14	130±69	58.0±18.1	43.7±7.0	10.2±5.4	23.5±3.4	2.05±0.13	49.3±1.4	0.65±0.15	24.2±1.8
MAT	0.38±0.09	0.14±0.02	3.91±1.14	0.44±0.12	0.78±0.07	6.57±0.89	1.57±0.36	16.3±4.6	25.7±7.3	72.0±13.1	5.4±1.1	14.6±4.5	2.16±0.17	50.2±1.9	0.42±0.06	23.4±2.7

7.3 Vegetation Tissue Analysis

Table 7.5 – Summary table for the metal and nutrient analysis of *Chamaedaphne calyculata* foliage, stem and root tissue from all of the study sites

	Foliage				Stem				Root			
Variables	Avg	Stdev	Max	Min	Avg	Stdev	Max	Min	Avg	Stdev	Max	Min
Na, g kg^{-1}	0.16	0.04	0.24	0.12	0.31	0.10	0.44	0.11	0.43	0.09	0.68	0.34
K, g kg^{-1}	3.4	0.49	4.18	2.25	1.84	0.38	2.59	1.32	1.40	0.34	2.22	0.80
Ca, g kg^{-1}	8.33	1.03	10.02	6.22	2.29	0.28	2.73	1.86	2.19	0.50	3.19	1.45
Mg, g kg^{-1}	1.34	0.16	1.62	1.08	0.47	0.07	0.59	0.33	0.45	0.08	0.60	0.34
P, mg kg^{-1}	635	110	879	462	290	77	412	197	275	92.3	524	156
S, mg kg^{-1}	1447	138	1633	1178	419	75	527	226	870	367	1722	456
Al, mg kg^{-1}	213	58	292	35	123	29	185	56.7	450	207	860	180
Fe, mg kg^{-1}	159	54	265	82	218	142	617	70.6	3380	2007	8341	410
Mn, mg kg^{-1}	863	505	2041	146	690	332	1423	135	659	283	1165	166
Ni, mg kg^{-1}	23.7	8.4	39.1	7.2	18.6	7.15	34.3	6.2	69.0	40.5	186	21.9
Cu, mg kg^{-1}	9.49	3.87	22.5	5.5	18.5	13.0	52.1	6.6	49.0	39.0	181	8.68
Zn, mg kg^{-1}	19.4	2.79	25.5	15.7	27.4	10.6	47.1	12.2	97.8	78.4	287	16.2
N%	1.21	0.10	1.38	1.07	0.44	0.06	0.56	0.34	0.44	0.08	0.64	0.31
C%	52.5	0.3	53.0	51.8	50.0	0.6	51.0	48.9	48.1	1.3	50.4	46.0
S%	0.16	0.01	0.19	0.14	0.09	0.03	0.19	0.05	0.13	0.04	0.20	0.07
CNRatio	43.8	3.7	49.8	38.0	118	18	154	91	117.8	23.3	158.6	78.8

Table 7.6 – Summary table for the metal and nutrient analysis of *Kalmia angustifolia* foliage, stem and root tissue from all of the study sites

	Foliage				Stem				Root			
	Average	Stdev	Max	Min	Average	Stdev	Max	Min	Average	Stdev	Max	Min
Na, g kg^{-1}	0.29	0.03	0.36	0.26	0.36	0.05	0.49	0.30	0.28	0.17	0.47	0.05
K, g kg^{-1}	3.67	0.48	4.53	2.78	1.11	0.17	1.34	0.76	1.17	0.18	1.57	0.85
Ca, g kg^{-1}	5.73	1.32	8.88	3.66	1.45	0.12	1.64	1.27	1.17	0.33	1.69	0.62
Mg, g kg^{-1}	0.71	0.19	1.10	0.47	0.35	0.04	0.41	0.26	0.31	0.07	0.43	0.21
P, mg kg^{-1}	547	131	990	433	218	30	282	184	250	63	402	167
S, mg kg^{-1}	751	101	942	617	296	32	365	243	500	182	880	261
Al, mg kg^{-1}	46.4	12.9	69.1	22.1	52.5	19.2	102.9	22.1	332	208	885	49
Fe, mg kg^{-1}	57.6	24.5	134	36.2	169	81	312	26	2851	2490	9365	138
Mn, mg kg^{-1}	464	239	937	127	317	108	486	138	236	89	346	84
Ni, mg kg^{-1}	16.2	5.95	27.3	6.98	19.3	7.5	35.1	7.28	44.0	18.1	85.2	23.0
Cu, mg kg^{-1}	5.82	1.06	7.40	4.24	16.3	9.6	32.6	4.87	27.5	20.4	91.6	8.20
Zn, mg kg^{-1}	14.9	3.20	19.5	6.18	24.2	10.2	49.1	10.57	40.8	19.4	74.7	9.52
N%	1.17	0.10	1.29	0.93	0.34	0.03	0.39	0.28	0.37	0.07	0.45	0.23
C%	52.8	0.4	53.5	52.3	51.9	0.6	52.8	50.0	49.0	0.5	50.0	48.2
S%	0.13	0.01	0.15	0.12	0.08	0.02	0.14	0.06	0.13	0.14	0.63	0.06
CNRatio	45.8	4.3	56.5	41.3	157	13	188	139	143	30	212	112

7.4 CCA Explanatory Variables

Table 7.7– Correlation coefficients for the selection of environmental variables and site scores of axis I and II of the vascular vegetation CCA

Variable	Pseudo-F	P	F1	F2
pH	2.803	0.002	0.531	-0.110
free Cu	1.983	0.006	0.067	-0.535
pore Cl	1.797	0.012	-0.124	-0.595
Cu	1.823	0.006	0.367	-0.340
%C	1.534	0.034	0.534	-0.217
CN Ratio	1.512	0.017	-0.473	0.070
K	1.504	0.021	-0.432	0.534

Table 7.8- Correlation coefficients for the selection of environmental variables and site scores of axis I and II of the non-vascular vegetation CCA.

Variable	Pseudo-F	P	F1	F2
pH	1.177	0.072	-0.219	-0.280
Cu	1.721	0.001	-1.136	0.079
CN Ratio	1.557	0.004	0.098	0.556
m^2/ha vascular cover	1.712	0.002	-0.782	-0.693
von Post	1.589	0.006	-0.390	0.033

7.5 Vegetation Species Identified

Table 7.9 – Wetland category definitions and corresponding coefficients of wetness for vascular vegetation taxa.

Wetland Category	Coefficients of Wetness	Definition
Upland (UPL)	5	Occurs almost never in wetlands under natural conditions (estimated <1% probability)
Facultative Upland (FACU)	2, 3, 4	Occasionally occurs in wetlands, but usually occur in non-wetlands (estimated 1%-33% probability)
Facultative (FAC)	-1, 0, 1	Equally likely to occur in wetlands or non-wetlands (estimated 34% - 66% probability)
Facultative Wetland (FACW)	-2, -3, -4	Usually occurs in wetlands, but occasionally found in non-wetlands (estimated 67% - 99% probability)
Obligate Wetland (OBL)	-5	Occurs almost always in wetlands under natural conditions (estimated >99% probability)

Table 7.10 – All nonvascular species identified in the 18 peatlands surveyed in Sudbury Ontario with increasing distance from Copper Cliff and their corresponding percent frequency in the twenty 25cm^2 quadrats per wetland or if they were observed (OBS).

	SLV	LU	MUD	BR	CRO1	LON	C2	C3	WHT2	CRO2	D17	C1	D5	WHT1	D4	RCK	ASH	MAT
Aulacomnium palustre (Hedw.) Schwägr.			10										5				5	
Cladonia chlorophaea (Florke ex Sommerf.) Sprengel			5		5													
Cladonia cristatella Tuck.																	5	
Cladonia rei Schaerer		OBS																
Cladonia sp.										5								
Cladopodiella fluitans (Nees) Jörg.	100	100	50	80	100	75	70	100	10	60	100	5	10		65	5	70	
Dicranum scoparium Hedw.					5													
Gymnocolea inflata (Huds.) Dumort.						5	15	0	10	5					5			
Lophocolea heterophylla (Schrad.) Dumort.									5						10			
Mnium stellare Reichard ex Hedw.													5					
Mylia anomala (Hook.) Gray		OBS	25	10	25	75		60	15	25	OBS		35					
Pohlia nutans (Hedw.) Lindb.	OBS	OBS	90	0			75	5	60	5		5	35		5			
Polytrichum commune Hedw.	OBS		10	15	15	20		5		15		5	65	5	100	15	30	
Polytrichum juniperinum Hedw.															OBS			
Warnstorfia fluitans (Hedw.) Loeske			40	10	20	55	60	55	5	5		40	40	20			35	
Sphagnum centrale C.E.O. Jensen										OBS								
Sphagnum cuspidatum Ehrh. ex Hoffm.								OBS										30
Sphagnum fallax H. Klinggr.				15		5	OBS	40		45		15	5			60	85	100
Sphagnum fimbriatum Wilson			5	OBS	5							5		OBS		40	OBS	
Sphagnum fuscum (Schimp.) H. Klinggr.										OBS							5	
Sphagnum rubellum Wilson					OBS					5							OBS	
Sphagnum squarrosum Crome			5	5		5		10	10	35		OBS	50	45	OBS		5	

Table 7.11 - All vascular species identified in the 18 peatlands surveyed in Sudbury Ontario with increasing distance from Copper Cliff and their corresponding percent frequency in the eighteen 1m^2 quadrats per wetland.

	Wetness	SLV	LU	MUD	BR	CRO1	LON	C2	C3	WHT2	CRO2	D17	C1	D5	WHT1	D4	RCK	ASH	MAT
Acer rubrum L.	FAC			12.5			12.5		6.25	6.25				12.5		43.75			
Alnus incana (L.) Moench	OBL						6.25			6.25	31.25						6.25	62.5	
Andromeda glaucophylla Link	OBL																		6.25
Apocynum androsaemifolium L.	UPL															6.25			
Aronia melanocarpa (Michx.) Elliott	FACW										6.25								
Aster sp.																6.25			
Betula papyrifera Marshall	FACU			6.25		12.5										43.75	6.25		
Calamagrostis canadensis (Michx.) P. Beauv.	OBL		18.75	6.25	6.25	31.25	56.25		43.75	25	25	12.5	93.75	81.25	56.25	18.75	81.25	12.5	93.75
Carex brunnescens (Pers.) Poir.	FACW											25							
Carex crinita Lam.	FACW													50		25			
Carex lacustris Willd.	OBL							6.25					6.25						
Carex leptalea Wahlenb.	OBL																6.25	18.75	50
Carex livida (Wahlenb.) Willd.	OBL		50						25	75			6.25				93.75	6.25	
Carex magellanica Lam.	OBL						100		50		18.75							6.25	43.75
Carex trisperma Dewey	OBL							75											
Carex utriculata Boott	OBL			75						6.25			37.5		87.5				
Carex sp.														43.75		50			
Carex sp									25										
Carex sp					6.25														
Carex sp				43.75															
Carex sp		25																	
Chamaedaphne calyculata (L.) Moench	OBL	100	100	100	100	93.75	100	100	100	100	68.75	93.75	6.25	12.5			100	100	100
Deschampsia flexuosa (L.) Trin.	UPL													12.5		50			
Drosera rotundifolia L.	OBL										62.5							68.75	
Dryopteris cristata (L.) A. Gray	OBL										31.25								
Dulichium arundinaceum (L.) Britton	OBL	18.75			81.25	12.5					12.5	6.25	31.25		37.5				
Equisetum pratense Ehrh.	FACW													75		31.25			
Eriophorum vaginatum L.	OBL	93.75	18.75		43.75	81.25	6.25		56.25		87.5	50				62.5	12.5	6.25	
Galium palustre L.	OBL														6.25				
Glyceria canadensis (Michx.) Trin.	OBL	50	87.5		12.5		6.25		56.25	37.5	68.75	62.5	50	31.25	6.25	50		12.5	18.75
Iris versicolor L.	OBL								12.5										6.25
Juncus canadensis J.Gay ex Laharpe	OBL	43.75			100	37.5	56.25		87.5	25	37.5	100	75	6.25	18.75	6.25		6.25	
Juncus effusus L.	OBL															6.25			
Juncus pelocarpus E.Mey.	OBL														43.75			31.25	
Juncus sp.									6.25										
Kalmia angustifolia L.	FAC	37.5	81.25	56.25	12.5	100	93.75	100	37.5	75	93.75	12.5		6.25		6.25	56.25	25	31.25
Kalmia polifolia Wangenh.	OBL	12.5	75	6.25	12.5	93.75	75	81.25	25	18.75	100	6.25					6.25		100
Lycopus uniflorus Michx.	OBL										37.5		6.25		18.75			25	
Lysimachia terrestris (L.) Britton, Sterns & Poggenb.	OBL														43.75				
Lysimachia thyrsiflora L.	OBL														6.25				
Maianthemum trifolium (L.) Sloboda	OBL			31.25		25				6.25									31.25
Muhlenbergia uniflora (Muhl.) Fernald	OBL	50									18.75	75	12.5	18.75		81.25			
Myrica gale L.	OBL																93.75		
Osmunda regalis L.	OBL								6.25		25		6.25						
Picea mariana (Mill.) Britton, Sterns & Poggenb.	FACW															6.25		31.25	
Pinus resinosa Aiton	FACU					6.25													
Poa sylvestris A.Gray	FAC												12.5	25		6.25			
Pogonia ophioglossoides (L.) Ker Gawl.	OBL																	25	
Rhododendron groenlandicum (Oeder) Kron & Judd	OBL	25	43.75	75	12.5	56.25	37.5	43.75	25	31.25	81.25	6.25				6.25		25	
Rhynchospora alba (L.) Vahl	OBL				12.5	12.5			75		75	18.75	18.75						
Rhynchospora fusca (L.) W.T.Aiton	OBL	43.75																	
Rubus pubescens Raf.	FACW						6.25		6.25				6.25						
Salix eriocephala Michx.	FACW																	6.25	
Salix serissima (Bailey ex Arthur) Fernald	OBL			43.75										37.5	12.5			25	
Schizachne purpurascens (Torr.) Swallen	FACU													100					
Scirpus atrovirens Willd.	OBL	18.75	6.25	18.75		12.5				81.25		6.25	56.25				6.25		
Solidago rugosa Mill.	FAC													87.5		12.5			
Solidago uliginosa Nutt.	OBL										31.25			18.75		6.25		6.25	
Sparganium emersum Rehmann	OBL														37.5				
Sparganium eurycarpum Engelm.	OBL										6.25								
Spiraea alba Du Roi	FACW																		6.25
Spiraea tomentosa L.	FACW			6.25					37.5				6.25					18.75	
Symphyotrichum lateriflorum (L.) Á. Löve & D. Löve	FACW													25					
Thuja occidentalis L.	FACW										6.25								
Triadenum fraseri (Spach) Gleason	OBL						18.75		37.5			18.75	43.75		93.75			43.75	
Typha latifolia L.	OBL									12.5					6.25			25	
Vaccinium angustifolium Aiton	FACU			6.25		12.5		25	6.25		6.25			43.75		31.25	6.25		
Vaccinium macrocarpon Aiton	OBL								6.25										
Vaccinium myrtilloides Michx.	FACW			6.25													6.25		
Vaccinium oxycoccos L.	OBL																	12.5	12.5
Viola conspersa Rchb.	FACW													18.75		6.25			
Unknown Grass sp.																			
Unknown Grass sp.													12.5		6.25				
Unknown Orchid sp.							12.5		12.5		12.5								
Unknown Sedge sp.						6.25													
Unknown Sedge sp.						6.25													
Unknown Violet sp.											50		18.75						