INVESTIGATION INTO THE POTENTIAL FOR ESTABLISHING A SELF-SUSTAINABLE WETLAND ECOSYSTEM OVER PYRITIC MINE TAILINGS

By

Paula Treacy

Submitted to the Higher Education and Training Awards Council in fulfilment of the requirements for the Degree of Doctor of Philosophy

April 2003

Research conducted at the
School of Science, Institute of Technology, Sligo,
under the supervision of
Mr. J. P. Timpson, Head of School of Science
Institute of Technology, Sligo

"We shall not cease from exploration
And the end of all our exploring
Will be to arrive where we started
And know the place for the first time"

From the "Four Quartets'' by T.S. Eliot

ACKNOWLEDGEMENTS

The successful completion of this research would have been impossible were it not for the commitment and assistance of a large number of individuals to whom I am greatly indebted. From the beginning, my supervisor, Mr. Pat Timpson encouraged my return from the United States to Sligo to commence this work. It was his knowledge and previous experience in the rehabilitation of mine tailings that facilitated the commencement of this work. I am indebted to him for introducing me to the world of environmental science and for his valuable critique of the work.

During the course of this experiment I was assisted by a host of angels in various guises. To those who laboured with me in the wetlands, Margaret Cullagh, Anne Leahy, Vince Murray, and Helen Murray, many thanks. Most particularly, I extend my thanks to Joseph Meehan whose incredible generosity with his time enabled me to complete the field ecology work. I doubt it would have been possible without him. Another individual who was tremendously generous was Dr. Ron Stanley from the Commonwealth of Pennsylvania Department of Environmental Protection who supplied me with numerous research papers and books of major relevance. I am also very grateful to a number of individuals on the staff of the Institute of Technology, Sligo for their constant guidance and assistance including Margaret O' Dwyer, Deirdre Cox, Breege Fahy, Rosemary O'Reilly, Eamonn Grennan and Don Cotton. I am also particularly grateful to Michael Breen and Ewen Speed whose knowledge regarding SPSS was invaluable.

Special thanks are due to many close friends who were particularly supportive during the highs and lows of performing research work including John and Mette, Rosie and Simon, Nora and Hansi, Noreen and Rosemarie, and of course Cecily, whose late husband Andy started original work several years ago investigating the potential for establishing reeds on mine tailings. Also, I am especially thankful to Eamonn for providing food, shelter and spiritual sustenance during my sojourns near Silvermines. Likewise, I am hugely indebted to Tom and Ursula Cullagh for providing me with a home away from home during my time at Lisheen Mine.

Throughout the entire gruelling process my entire family have been overwhelmingly supportive. Therefore I extend warm thanks to Fran, Cathy and Rhoda, with a particular note of gratitude to Una, Mimi, Martin and Gerard for their help in producing the text, and to Rita and Tony for the necessary computing technology. Heartfelt thanks to Angie and Gerry for providing a wonderful home base in Sligo. My deepest thanks are reserved for my parents whose constant care and nurturing, particularly during the write-up, ensured this work would be completed.

Finally, it is important to acknowledge the financial support of Enterprise Ireland, Lisheen Mine and the Institute of Technology, Sligo, who made this work possible. I extend many thanks to Margaret Stokes at Lisheen Mine for her continual support throughout the project.

DECLARATION

This thesis has not previously been submitted to this, or any other college. With acknowledged exception, it is entirely my own work.

Paula Treacy

ABSTRACT

Research was conducted to investigate the potential for ecologically engineering a sustainable wetland ecosystem over pyritic mine tailings to prevent the generation of acid mine drainage. Ecological engineering is technology with the primary goal being the creation of self-sustainable ecological systems. Work involved the design and construction of a pilot-scale wetland system comprising three wetland cells, each covering 100 m^2. Approximately forty tonnes of pyritic mine tailings were deposited on the base of the first cell above a synthetic liner, covered with peat, flooded and planted with emergent wetland macrophytes *Typha latifolia, Phragmites australis,* and *Juncus effusus*. The second cell was constructed as a conventional free water surface wetland, planted identically, and used as a reference wetland/experimental control.

Wetland monitoring to determine long-term sustainability focused on indicators of ecosystem health including ecological, hydrological, physico-chemical, geochemical, and biotic metrics. An integrated assessment was conducted that involved field ecology in addition to ecological risk assessment. The objective of the field ecology study was to use vegetative parameters as ecological indicators for documenting wetlands success or degradation. The goal of the risk assessment was to determine if heavy-metal contamination of the wetland sediments occurred through metal mobilisation from the underlying tailings, and to evaluate if subsequent water column chemistry and biotic metal concentrations were significantly correlated with adverse wetland ecosystem impacts. Data were used to assess heavy metal bioavailability within the system as a function of metal speciation in the wetland sediments.

Results indicate hydrology is the most important variable in the design and establishment of the tailings wetland and suggest a wetland cover is an ecologically viable alternative for pyritic tailings which are feasible to flood. Ecological data indicate that in terms of species richness and diversity, the tailings-wetland was exhibiting the ecological characteristics of natural wetlands within two years.

Data indicate that pH and conductivity in the tailings-wetland were not adversely impacted by the acid-generating potential or sulphate concentration of the tailings substrate and its porewater. Similarly, no enhanced seasonal impacts from sulphate or metals in the water column, nor adverse impacts on the final water quality of the outflows, were detected.

Mean total metal concentrations in the sediments of the tailings-wetland indicate no significant adverse mobilisation of metals into the peat substrate from the tailings. Correlation analyses indicate a general increase in sediment metal concentration in this wetland with increasing water depth and pH, and a corresponding decrease in the metal concentrations of the water column. Sediment extractions also showed enrichment of Cd, Fe, Pb and Zn in the oxidisable fraction (including sulphides and organic matter) of the tailings-wetland sediments. These data suggest that adsorption and coprecipitation of metals is occurring from the water column of the tailings wetland with organic material at increasing depths under reducing conditions. The long-term control of metal bioavailability in the tailings wetland will likely be related to the presence and continual build-up of organic carbon binding sites in the developing wetland above the tailings.

Metal speciation including free-metal ion concentration and the impact of physico-chemical parameters particularly pH and organic matter, were investigated to assess ecotoxicological risk. Results indicate that potentially bioavailable metals (the sum of the exchangeable and reducible fractions) within the tailings wetland are similar to values cited for natural wetlands. Estimated free-metal ion concentrations calculated from geochemical regression models indicate lower free-metal ion concentrations of Cd in the tailings wetland than natural wetlands and slightly higher free-metal ion concentrations of Pb and Zn.

Increased concentrations of metals in roots, rhizomes and stems of emergent macrophytes did not occur in the tailings wetland. Even though a substantial number of *Typha latifolia* plants were found rooting directly into tailings, elevated metals were not found in these plant tissues. *Phragmites* also did not exhibit elevated metal concentrations in any plant tissues. *Typha* and *Phragmites* populations appear to be exhibiting metal-tolerant behaviour.

The chemistry of the water column and sediments in Silvermines wetland were also investigated and were much more indicative of a wetland system impacted by heavy metal contamination than the tailings-wetland. Mean Cd, Fe, Mn, Pb and Zn concentrations in the water column and sediments of Silvermines wetlands were substantially higher than in the pilot wetlands and closely approximate concentrations in these matrices contaminated with metals from mining. In addition, mean sulphate concentration in Silvermines wetland was substantially higher and is closer to sulphate concentrations in waters associated with mining. Potentially bioavailable metals were substantially elevated in Silvermines wetland in comparison to the pilot wetlands and higher than those calculated for natural river sediments. However, Fe oxy-hydroxide concentrations in Silvermines sediments are also much higher than in the pilot wetlands and this significantly impacts the concentration of free-metal ions in the sediment porewater. The free-metal ion concentrations for Pb and Zn indicate that Silvermines wetland is retaining metals and acting as a treatment wetland for drainage emanating from Sivermines tailings dam.

TABLE OF CONTENTS

APPENDICES

LIST OF TABLES

LIST OF FIGURES

CHAPTER ONE

INTRODUCTION

1.1 MINING IN IRELAND AND LONG-TERM SUSTAINABILITY

The arrival of copper-bronze metallurgy was an important development, both in economic and social terms, in the Neolithic to Bronze Age transition in Ireland. The rapid spread of this new technology owed much to the availability of raw material, with the result that Ireland emerged as one of the most prolific metal producers in Bronze Age Europe (O'Brien, 1995). Over four millennia later, at the commencement of the 21st century, Ireland is again considered an important metal mining country. This time in regard to zinc, of which it is one of the most important producers in Europe.

The Lower Carboniferous limestones and dolomites of the Irish midlands are host to a variety of base metal ore deposits, particularly zinc, which have provided reserves for a range of mines since the 18th century as outlined below:

Mine	Period	Reserves (Mt = million tonnes)
*Abbeytown	1785 - 1961	1.1 Mt at 3.8% Zn, 1.5% Pb, 40g/t Ag
*Tynagh	1965 - 1980	9.9 Mt at 5.7% Zn, 7% Pb, 1% Cu, 23g/t Ag
*Gortdrum	1967 - 1975	3.8 Mt at 1.2% Cu, 25g/t Ag
*Silvermines	1968 - 1982	17.7 Mt at 6.4% Zn, 2.5% Pb, 23 g/t Ag
*Tara	1977 - in production	70 Mt at 10.1% Zn, 2.6% Pb, 11g/t Ag
*Galmoy	1996 - in production	6.5 Mt at 13% Zn, 1.5% Pb
**Lisheen	1999 - in production	19 Mt at 11.6% Zn, 1.9% Pb, 26g/t Ag

*Source: Arthurs, 1994.
**Source: Minorco Lisheen, Environmental Baseline Report, 1995a.

In particular, the Silvermines area in County Tipperary has a long history of mining spanning over a thousand years. In the twentieth century, intensive mining commenced here with the development of Europes then largest zinc and lead mine in 1968. This position was usurped by Tara Mines in County Meath, considered a world class deposit when production started in 1977. The most recent base metal mines to open in Ireland are Galmoy in County Kilkenny which commenced production in 1996 and Lisheen in County Tipperary which commenced production in 1999.

The Lisheen orebody is the largest of its kind to have been discovered in Northern Europe in the last ten years. With its development, Ireland has resumed its role as a leader in zinc production in Europe. Exercising a leadership role in mining today necessitates scrupulous adherence to environmental considerations and sustainable development. This awareness arises from the disastrous consequences to the environment and human health that have occurred through inadequate environmental management at mine sites. Corporations that adopt and practice sustainable development recognise that they are responsible not just to shareholders but to a broad range of stakeholders whose long-term interests are affected by corporate decisions and actions. Collectively the mining industry is pathfinding a global strategy for mining and sustainable development. To facilitate this, a group of global mining companies recently launched a Global Mining Initiative to work through the World Business Council on Sustainable Development in Geneva, in dialogue with leading Non Governmental Organisations, to develop a comprehensive global strategy for the mining industry (Cooney, 2000).

A fundamental goal of a sustainability strategy for this industry involves achieving long-term closure objectives including eventual 'walk-away' solutions for remediating mine waste. This is based on the understanding that society may have limited motivation, or ability, to ensure today's mining waste does not present a threat to the environment for centuries to come. Equally the mining industry has a moral obligation to avoid passing the burdens of today's mining industry to future generations who will inevitably bear those of their own (Vick, 2002). Society expects the minerals industry to run its operations with minimal environmental impact and to fully rehabilitate mining sites and mine waste following closure.

1.2 SULPHIDE TAILINGS AND ACID MINE DRAINAGE

Using ore and metal analyses, Coughlan and Case (1957) argued that production of the earliest copper and bronze in Ireland was based on the use of sulphide ore. Similarly, the base metal mined in Silvermines in the latter half of the 20th century and in Lisheen today are extracted from sulphide ore. Processing of these ores to extract minerals produces concentrates by froth flotation from milled ore called tailings. This fine-grained waste material is piped as a slurry to a tailings dam where the solids settle out. Large tailings dams are significant features of the landscape near all recent Irish mines.

The valuable minerals in sulphide orebodies occur in sulphide form. Iron sulphides usually occur in association with such ores, principally as pyrite but also as pyrrhotite and marcasite (Vick, 2002). Ordinarily having no commercial value, these iron sulphides are rejected and transported with other processing wastes to the tailings impoundment.

Acid mine drainage (AMD) is produced when pyrite is oxidized on exposure to oxygen and water to form ferric hydroxides and sulfuric acid under the following reactions:

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO^{2+} + 2H^+ \quad (1)$$

$$Fe^{2+} + 1/4\ O_2 + H^+ \rightarrow Fe^{3+} + \ ½\ H_2O \quad (2)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_2 + 3H^+ \quad (3)$$

$$FeS_2 + 14Fe^{3+} + H_2O \rightarrow 15Fe^{2+} + 2SO^{2+} + 16H^+ \quad (4)$$

(Singer and Stum, 1970)

The generation of acidic conditions in tailings and the accompanying mobilisation of metal cations in solution proceeds by these complex series of chemical reactions on the surfaces of sulphide mineral grains, aided at key stages by the bacteria *Thiobaccillus ferroxidans* and *Thiobacillus oxidans* as catalysts (Vick, 2002). The movement of acidic, metal-bearing water or AMD out of a tailings deposit can cause considerable harm to the environment. For example, the Avoca River in County Wicklow has been heavily polluted by acidic water draining out of disused mines and spoil heaps. The discharge is leach liquor runoff from a strongly pyritic rock sequence that is uncontrollable; the dissolution of soluble metal compounds from the ore or waste rock results in AMD (O'Sullivan, 1995). Figures 1.1 and 1.2 outline the impact of acidity and heavy metals arising from the discharge of AMD to a riverine system.

Uncontrollable discharges of AMD produce long-term environmental problems. For example, Vick (2002) notes that mines worked by the Romans in Spain and the Vikings in Scandinavia continue to generate acidic drainage today, and the effects of AMD were known to medieval miners like Georgius Agricola who described the arguments of early detractors of mining in 1556 as follows:

"...Further, when the ores are washed, the water which has been used, poisons the brooks and streams, and either destroys the fish or drives them away....Thus it is said, it is clear to all that there is greater detriment from mining than the value of the metals which mining produces."

Though it took over 400 years for contemporary critics of mining to seize upon the observations of their predecessors, by the 1980s AMD was becoming recognised as mining's environmental Achilles heel (Vick, 2002). Consequently, the United States Environmental Protection Agency has singled out AMD from abandoned coal mines as being the greatest water quality problem in the Appalachian region of the United States (U.S. Office of Surface Mining, 1995).

1.3 USE OF WETLANDS TO PREVENT AMD POLLUTION

For several years, scientists have recognised that constructed wetlands offer an inexpensive, natural, low maintenance, and potentially long-term solution to treating AMD without chemical additives (Brodie, 1991; Perry and Kleinmann, 1991; Brodie *et al.*, 1993; Eger *et al.*, 1993; Hedin *et al.*, 1994; Sikora *et al.*, 1995; and Reed *et al.*, 1995). Mitsch (1992) attributes the use of wetlands for mine drainage control to the observation of volunteer *Typha* wetlands near acid seeps in a harsh environment where no other vegetation could grow. By 1996, several hundred wetlands had been constructed in the United States to normalise stream pH levels and remove heavy metal contaminants using the United States Bureau of Mines procedures (U.S.Bureau of Mines, 1994, 1996; Kleinmann, 1996). A large body of this work concentrated on the treatment of AMD from coal mine waste (Hedin *et al.*, 1994) and formed the basis

Figure 1.1 Impact of acidity arising from the discharge of AMD to a lotic (river) system (Gray,1999).

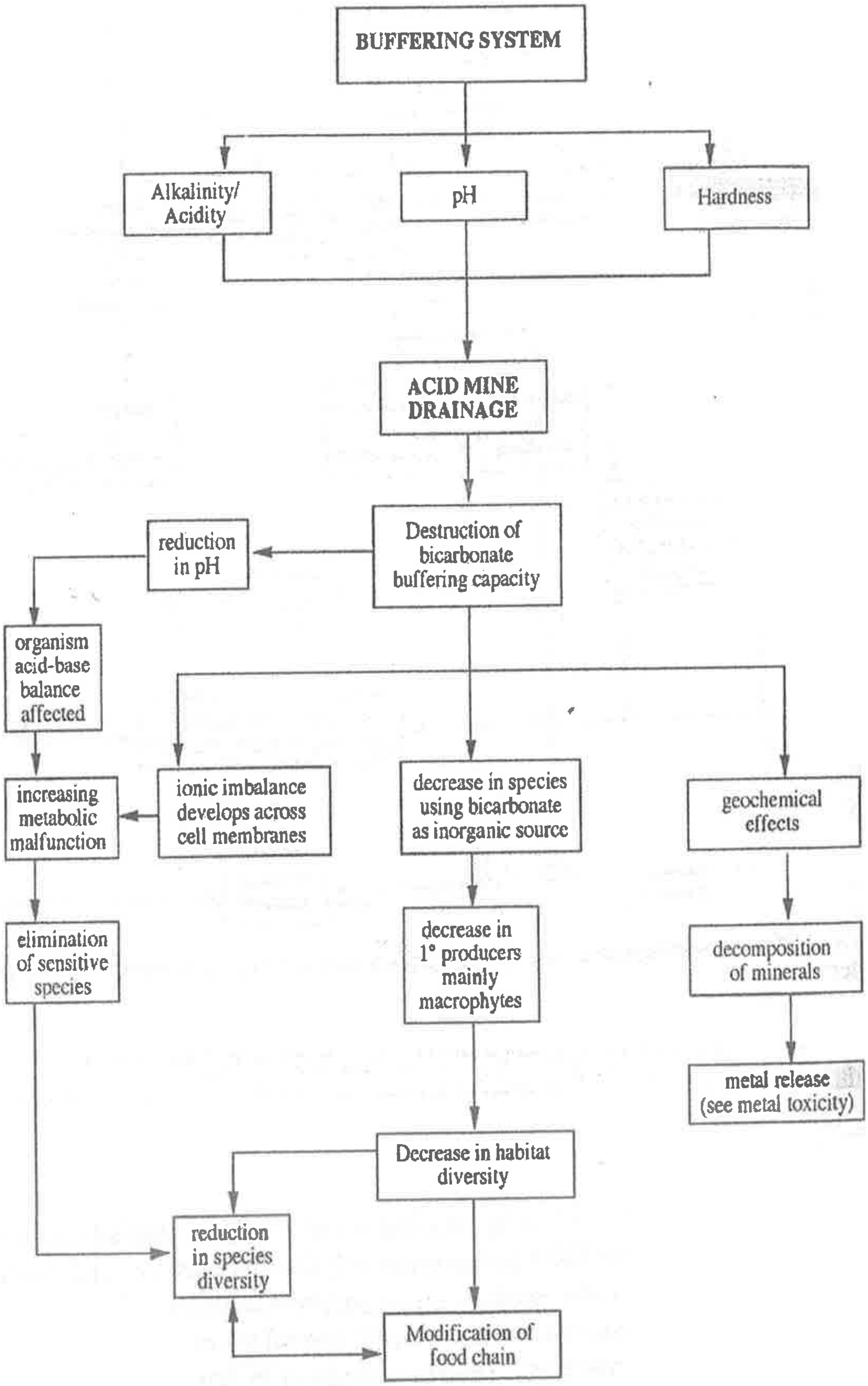
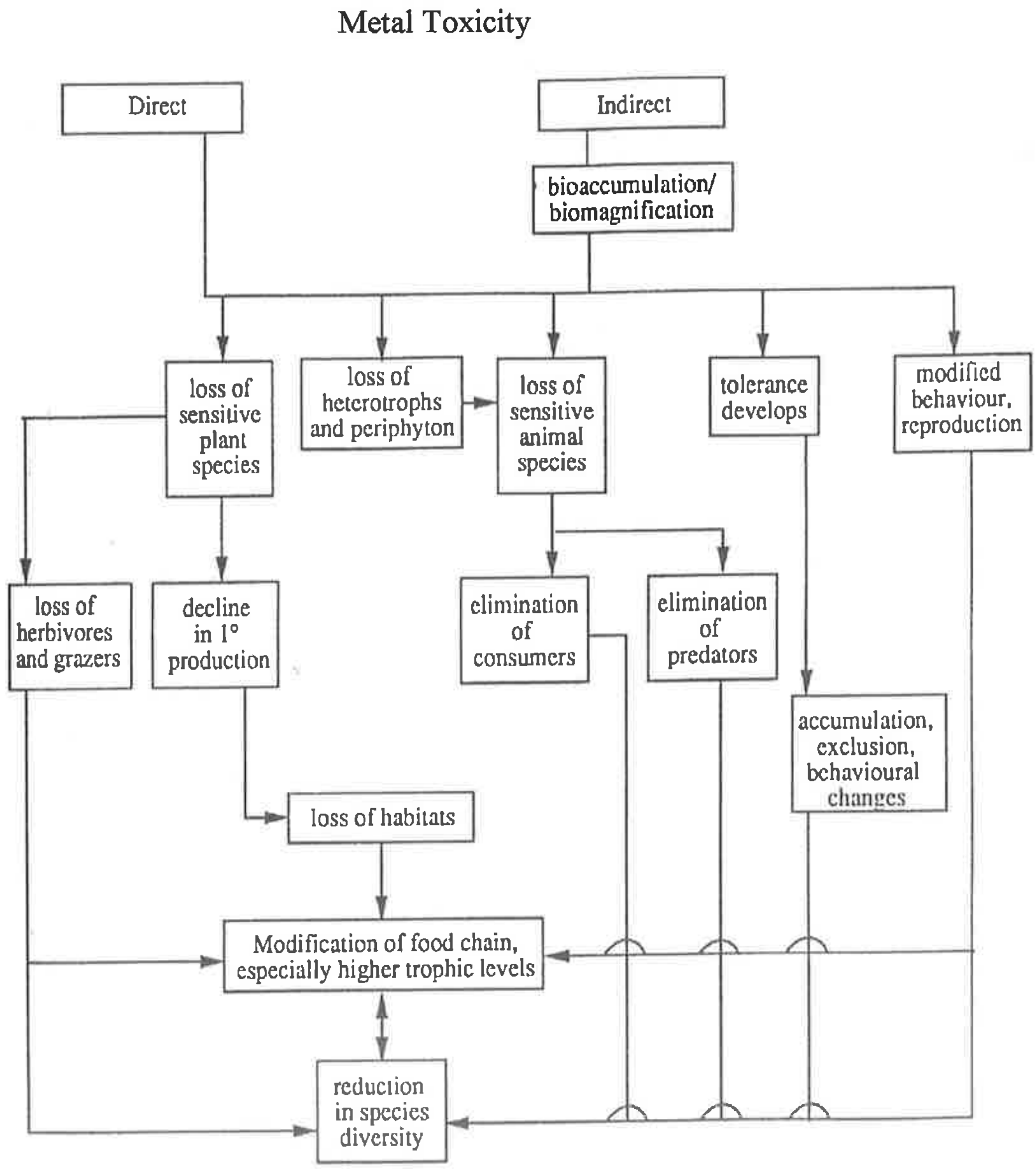


Fig. 1.2 Impact of heavy metals arising from the discharge of AMD to a lotic system (Gray, 1999).



of successful research and field work on wetland systems for treating AMD from metalliferous tailings.

The most common AMD control strategy is treatment of contaminated water at the discharge point. From Equations (1) through (4) it is clear, however, that pyrites can remain in their reduced state in undisturbed strata, as long as they are anaerobic. A better alternative for pollution control at mine sites, therefore, is inhibition of sulphide oxidation at the source (Perry and Kleinmann, 1991; Nawrot and Sandusky, 1993; U.S. EPA, 1995a). Flooding and saturation are the best techniques for inhibition/prevention of pyrite oxidation (Kleinmann, 1996; DaSilva, 1996; Nawrot, 1995).

In recognition of this, scientists have been examining the use of flooding and saturation techniques to prevent pyrite oxidation and consequently establish long-term sustainable management strategies for AMD-generating tailings. This includes work performed in Canada by the Mine Environmental Neutral Drainage Program where water covers are considered one of the most important technological developments for decommissioning acid-generating tailings (Feasby, 1996). Half of the 500 million tonnes of waste rock generated each year by Canadian surface mining includes acid-producing sulphide ores (NR Can, 1995) and permanent submergence has been endorsed by certain provinces of Canada where physiographic, climatic and geologic factors are often favourable to long-term dam stability (Vick, 2002). In addition, a substantial amount of work has been performed by U.S. EPA in evaluating water covers at acid-generating metalliferous tailings impoundments in the United States (U.S. EPA, 1995a).

Permanent submergence is only feasible at tailings dams designed specifically for this purpose. However, concerns have been raised regarding the geochemical security of permanent submergence for tailings dams because the majority of tailings dam failures have been attributed in one way or another to inadequate impoundment water control (ICOLD, 2001). A systematic survey of tailings dam failures and accidents (USCOLD, 1994) shows that of the 106 failures identified from a variety of causes, only nine involved inactive tailings dams despite their vastly greater numbers (Vick, 2002). Flood overtopping was found to be the dominant cause of these failures, with those from other common instability mechanisms almost entirely absent. A considerable body of tailings dam field performance experience therefore shows that tailings dam failure does not occur under post-closure conditions if overtopping is prevented and surface water is removed from the impoundment (Vick, 2002).

In light of the benefits of flooding tailings to prevent sulphide oxidation combined with the necessity to reduce the risk of overtopping, it makes sense to minimise the water depth over the impoundment surface. Consequently, a promising technology yet to see widespread application is that for 'saturated covers'. This involves hydraulically depositing a chemically inert layer of fine tailings or other such material that retains a high moisture content, to produce a surface layer over tailings that can reduce infiltration and oxygen diffusion without the need for surface water or a compacted soil cover (Vick, 2002; Nicholson et al., 1989).

In the same manner, the remediation approach proposed for the tailings dam at the zinc/lead mine in Lisheen, County Tipperary, also recognises that keeping tailings wet via a wetland cover will prevent AMD generation.

1.4 USING A WETLAND COVER TO REMEDIATE MINE TAILINGS

Upon closure, Lisheen Mine will have generated 6.63 million tonnes of pyritic tailings that will be deposited in a Tailings Management Facility (TMF) with a final surface area of approximately 64 ha and embankment walls measuring 15.5 m high (see Figure 1.3). The mine's rehabilitation plan (Minorco Lisheen, 1995b) calls for the deposition of layers of organic-enriched crushed limestone, using the existing tailings distribution system, over the tailings upon closure. The tailings will then be handplanted with reed rhizomes and other wetland vegetation. The core intent underlying this plan is that the limestone layer, water cover and organic matter produced by the vegetation will inhibit excessive pyrite oxidation in the tailings and prevent the generation of AMD. The plan's ultimate aim is for the TMF to remain as a landscaped artificial dam containing an ecologically sustainable reed marsh similar to the margins of many Irish calcareous marl lakes. The build up of organic matter over time will reduce further the depth of water cover in the impoundment, eventually leading to a bog or wet woodland (Minorco Lisheen, 1995b).

Fig. 1.3 Lisheen's Tailings Management Facility at Lisheen Mine, Co. Tipperary (Source, Lisheen Mine).

Natural peat development at mine sites is not an unknown phenomenon in Ireland. Upland blanket-bog development and waterlogged sediments uniquely preserved the Bronze Age mines at Mount Gabriel in the Mizen Peninsula in West Cork which operated between 1700 and 1500 BCE (O'Brien, 1995).

In addition, recent scientific research has shown that wetlands naturally occurring over metalliferous tailings have successfully reduced acidity and metal levels in tailings drainage (MEND, 1993a; 1993b). Also, wetlands have been established on low-pH infertile mine spoil which result from surface-mining operations in the United States. These wetlands have taken on the botanical and biogeochemical characteristics of natural wetlands within 3-4 years (Sistani, Mays, and Taylor, 1999).

The primary objective of rehabilitating the tailings dam at Lisheen Mine is to foster a wetland system over pyritic tailings that is robust enough to be self-sustaining. This entails fostering the regeneration of a living system with the capacity for self-preservation and self-perpetuation.

1.5 AIMS AND OBJECTIVES OF THESIS

The overall aim of this thesis is to investigate the potential for creating such a self-sustainable wetland ecosystem over pyritic mine tailings using the principles of ecological engineering. Therefore it was essential to conduct research trials which involved the following practical objectives:

1. **Design and Construct a Wetland Pilot Plant Research Facility**

   A pilot-scale research facility was designed and constructed in Sligo at the Institute of Technology in 1998 to facilitate the collection of preliminary data to determine the potential for a wetland cover to be ecologically engineered on tailings (see Figures 1.4 and 1.5). The pilot system comprises three wetland cells with pyritic mine tailings deposited on the base of the first cell above a synthetic liner to model Lisheen's TMF (referred to as the TMF wetland throughout this thesis). A wetland cover was grown over these tailings. The

Figure 1.4 One of three wetland cells in the pilot research facility at Institute of Technology, Sligo.

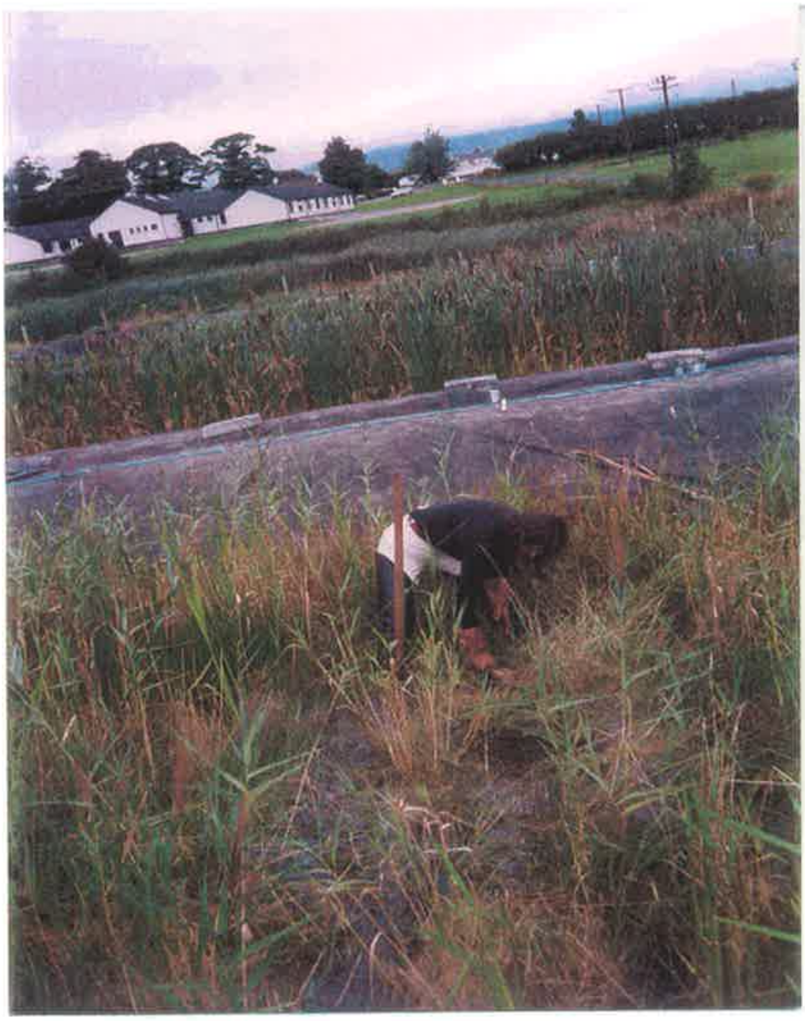


Figure 1.5
Field ecology work underway in the TMF Wetland cell. The parallel cell is the Reference/Control Wetland.

second cell was constructed as a conventional treatment wetland (without tailings) given Lisheen's closure plan also proposes the construction of a secondary wetlands to treat any overflow from the TMF. The third was designed as an experimental control. Given the water quality discharging from the TMF wetland throughout the course of this experiment was within regulatory guidelines, it was not necessary for the second cell to act as a treatment wetland and consequently it was used as the reference wetland/experimental control.

2. Develop a Research Methodology Rigorous Enough to Accurately Characterise the Environmental Health of the Research Wetlands

The complexity surrounding metal mobilisation in wetlands required the use of a range of environmental indicators to conduct an integrative assessment that evaluated the ecological, hydrological, physico-chemical, sediment geochemical and biotic interactions within the wetland system which were then compared these with the reference wetland. This research methodology involved conducting a field ecology study, in addition to an ecological risk assessment, to determine ecosystem health and sustainability. The objective of the field ecology study was to use vegetative parameters as ecological indicators for documenting wetlands success or degradation. The goal of the risk assessment was to determine if heavy-metal contamination of the wetland sediments occurred through metal mobilisation from the underlying tailings and to evaluate if subsequent water column chemistry, sediment metal concentrations and biotic accumulations of metals were significantly correlated with adverse wetland ecosystem impacts.

3. Use Data from Pilot Facility to Investigate Research Hypothesis

Data generated from the pilot plant was ultimately used to evaluate the potential for a healthy wetland ecosystem to be effectively established on pyritic tailings.

4. **Provide Recommendations for Lisheen's Scaled-Up Research Trials at Field Level**

Data from this study was then used to provide baseline data and recommendations for Lisheen's proposed field-scale trials.

1.6 SILVERMINES WETLANDS

The above work was complemented by concurrent work carried out near Silvermines Village, County Tipperary that consisted of evaluating the treatment efficiency of wetlands receiving run-off from pyritic zinc-lead tailings deposited in the Gortmore tailings dam. This dam received tailings from the major zinc-lead mine at Silvermines operated by Mogul Ltd. during 1968 to 1982. Figure 1.6 outlines the location of this tailings dam. Figures 1.7 and 1.8 illustrate the surface of the Gortmore tailings dam and wetlands surrounding the easterly wall of this dam.

The purpose of the work carried out at Silvermines was two-fold. Firstly, it was important to characterise the wetlands at the Gortmore site to understand the role they are playing in terms of pollution prevention and environmental protection, given they are treating drainage emanating from the tailings dam. Secondly, since Lisheen mine had not started producing tailings at the commencement of this research work, the tailings required for the pilot plant were taken from the Gortmore TMF. These tailings were deemed the most suitable given they were produced from sulphide ore and are highly pyritic zinc-lead tailings which are potentially acid-producing.

Characterisation of the wetlands at Silvermines involved quantifying their spatial aspects, identifying mobilised metal contaminants in the water column and sediments of the wetlands, and assessing the important processes governing contaminant fate and transport within them. Total metals analysis and extractions of sediments were conducted to determine potentially bioavailable species of metals in these wetlands. This facilitated an examination of whether the water column chemistry has a more important adverse influence on this wetland system than sediment chemistry.

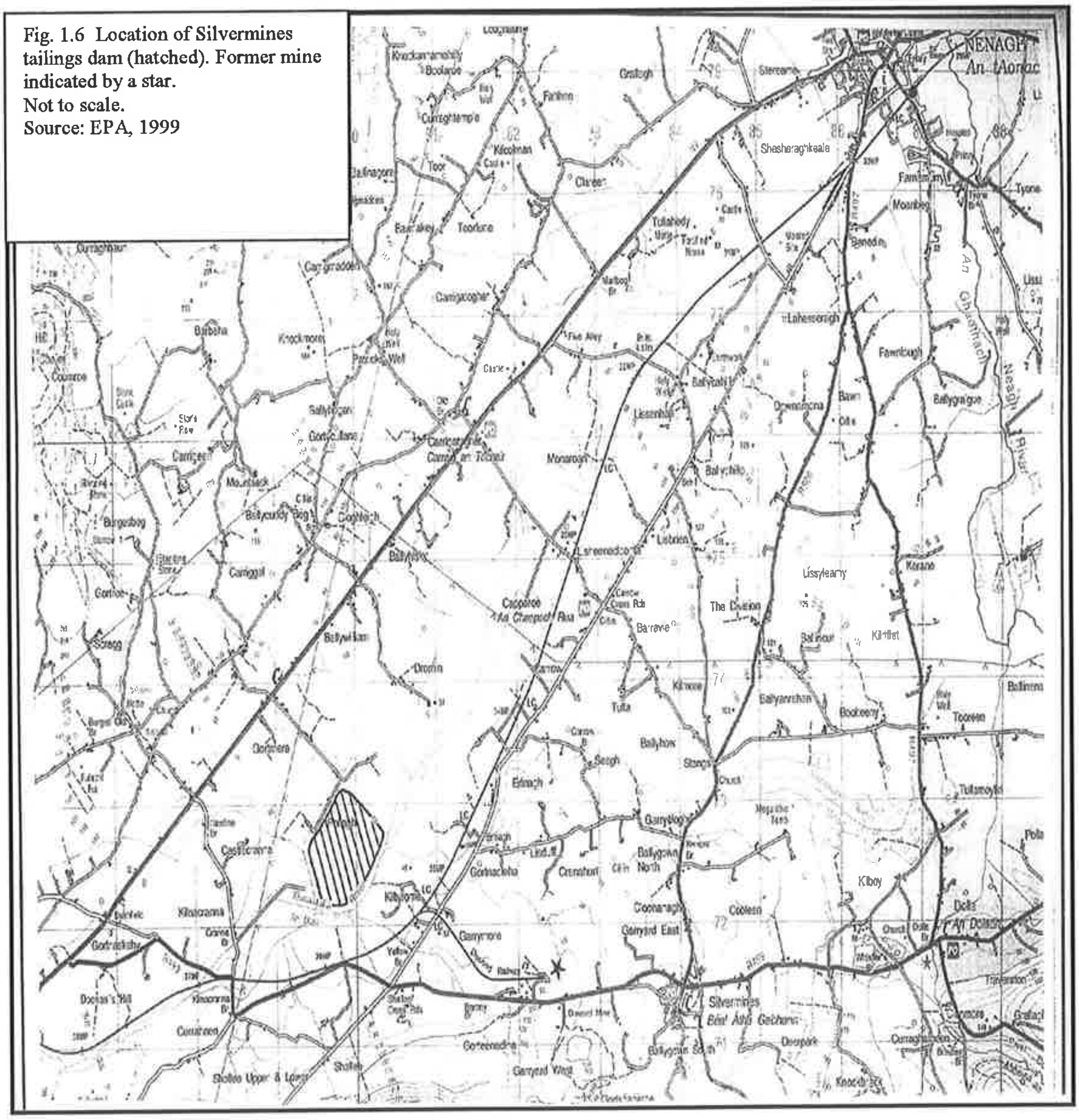


Fig. 1.6 Location of Silvermines tailings dam (hatched). Former mine indicated by a star.
Not to scale.
Source: EPA, 1999

Figure 1.7 Tailings dam at Silvermines with obvious acid burn in foreground.

Figure 1.8 Wetlands surrounding easterly wall of tailings dam at Silvermines.

The wetland system at Silvermines could then be compared with the pilot plant to compare treatment wetlands and wetland covers for rehabilitating pyritic mine tailings.

1.7 ORGANISATION OF THESIS

The organisation of this thesis follows the systematic approach to evaluating various multi-media environmental matrices carried out in the integrated assessment of the pilot wetlands. Chapters Two, Eight and Nine have sections designated to the ecological, hydrological, physicochemical, sediment geochemical and biotic aspects of the study. Chapters Four, Five, Six and Seven outline the results of each specific indicator group. The content of each Chapter is as follows:

- Chapter Two begins with a discussion of the use of ecological engineering in the design of self-sustainable land reclamation projects. This is followed by an outline of the use of environmental indicators to conduct integrative assessments that evaluate the complex interactions within a wetland system, in order to assess its overall environmental health and sustainability. The selection of specific ecological, hydrological, physico-chemical, sediment geochemical and biotic indicators for evaluation in the pilot plant are then based on a review of the current scientific literature.

- Chapter Three outlines the methodologies used in the design and construction of the wetlands, the various sampling and statistical protocols employed, and the specific laboratory procedures for analysing a variety of environmental matrices with appropriate quality control requirements.

- Chapters Four, Five, Six and Seven outline the results of the ecological, hydrological and physico-chemical, sediment, and biotic indicator analyses respectively.

- Chapter Eight presents the results of comprehensive correlation and regression analyses conducted to investigate the wide range of relationships between the various indicators and their impact on environmental health.

- Chapters Nine and Ten present a discussion of the overall results of the research work and the subsequent conclusions that can be drawn from the project. The final Chapter also makes several recommendations for Lisheen's field-scale trials.

CHAPTER TWO

LITERATURE REVIEW

2.1 ECOLOGICALLY ENGINEERING SELF-SUSTAINABLE ECOSYSTEMS

According to Mitsch (1992) ecological engineering is technology with the primary tool being self-designing ecosystems; the components are all of the biological species of the world. Both basic and applied ecology provide important fundamentals to ecological engineering but do not define it completely. Ecological engineering is the "prescriptive" discipline of ecology (Mitsch, 1992).

Ecological engineering as defined by Odum *et al.* (2000) is the development of partnership designs with nature. It is necessary because a sustainable civilisation requires an harmonious fit between economic use of the earth's materials and the environmental system (Odum *et al.*, 2000). Ecological engineering is a way to fit heavy metal industries into a prosperous society by tying into nature's cycle of elements (Odum *et al.*, 2000).

The principles of ecological engineering in relation to wetlands and mining waste were examined by Odum *et al.* (2000) in a joint study undertaken over an eight-year period. The study examined wetlands treating lead discharges from a Superfund[1] site in Florida and lead and zinc discharges from mining and processing in Poland running into wetlands for over 400 years. The results indicate that wetlands are one of the main places where toxic metals are filtered, immobilised, and returned to the geologic part of the earth cycle, mostly isolated from the living biosphere. From evidence of many kinds the authors realised that wetlands and their humic peat, as they have evolved over geological time are a mechanism for making the biosphere safe (Odum *et al.*, 2000).

[1] A Superfund site is one that has been placed on the U.S. National Priority List under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). Under CERCLA, U.S. EPA has established a comprehensive programme for identifying, investigating and remediating hazardous waste sites.

The primary goal of this thesis is to investigate the potential for creating a self-sustainable wetland ecosystem over pyritic mine tailings using the principles of ecological engineering. General design principles for ecologically engineering wetlands are outlined in Table 2.1 (Mitsch, 1992). The main design principle is to ensure the system ultimately requires minimal maintenance and is self sustainable.

According to Haigh (2000) self-sustainable land reclamation strives to lend a helping hand to the re-establishment of natural processes. This is not the same as recreating the original landscape, rather the ambition is to promote the self-creation of a natural control system and to plan for the emergence of a new healthy natural system.

The primary requirements for a healthy ecosystem are system sustainability and integrity where these refer to the capability of an ecosystem to remain intact, to self regulate in the face of stress and to evolve towards increasing complexity and integration (Burton, 1992). At present, only one environmental system is capable of self-creation, self-regeneration, and self-improvement. It is the same system that is responsible for many of the long-term successes of early reclamation projects; it is nature (Haigh, 2000).

The essence of nature is that it does not require to be looked after. It is self-creating, self-preserving and self referenced or autopoietic (Jantsch, 1980). The only way to guarantee the reproductive capacity of reclaimed land is to develop its living system. Self-sustaining behaviour is the particular property of living systems, the signature of nature and the goal of successful land reclamation (Haigh, 2000).

The practical goal of this research was to develop a methodology robust enough to adequately characterise the environmental health of the pilot tailings wetland and to determine if it is a self-sustaining ecosystem. Therefore a wide range of environmental indicators were selected to assess the environmental health of this system.

Table 2.1 General Principles of Ecological Engineering of Wetlands (Mitsch, 1992)

1.	Design the system for minimum maintenance. Instead, the system of plants, animals, microbes, substrate and water flows should be developed for self-maintenance and self-design.
2.	Design a system that utilises natural energies, such as potential energy of streams as natural subsidies to the system.
3.	Design the system with the landscape, not against it. Floods and droughts are to be expected. Outbreak of plant diseases or invasion of alien species are often symptomatic of other stresses and may indicate faulty design rather than ecosystem failure.
4.	Design the system to be multi-objective, but identify at least one major objective and several secondary objectives.
5.	Give the system time. Wetlands are not functional overnight and several years may elapse before nutrient retention or wildlife enhancement are well developed. Strategies that try to short circuit ecological succession or over-manage it often fail.
6.	Design the system for function, not form. If initial plantings and animal introductions fail, but the overall function of the wetland, based on its initial objectives, is intact, then the wetland has not failed.
7.	Do not over-engineer wetland design. Ecological engineering recognises that natural systems should be mimicked, not simplified, to accommodate biological systems.

2.2 USING ENVIRONMENTAL INDICATORS TO ASSESS ENVIRONMENTAL HEALTH

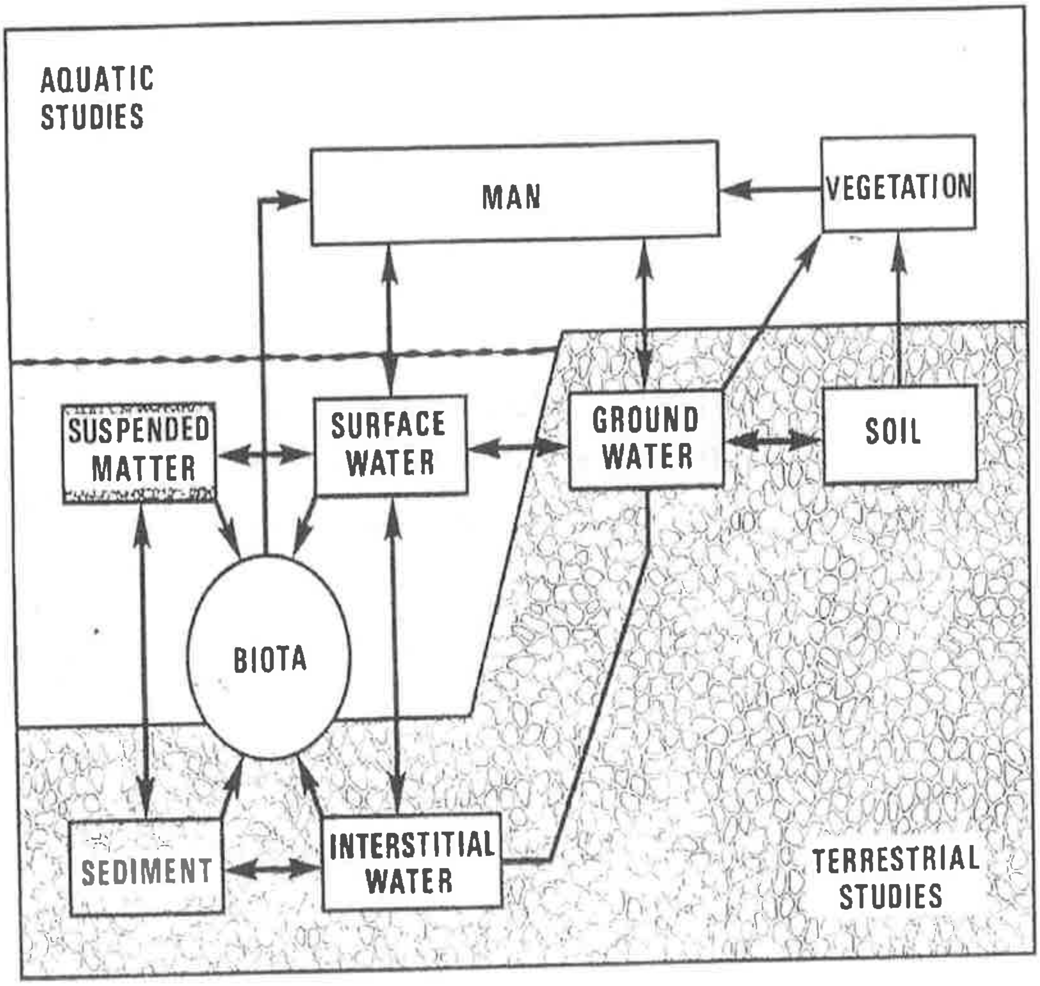
Once excess trace metals enter a system, they remain bound to soil components, become incorporated into plant tissues, or can be ingested by animals over an extensive time period (Marcus 1991). Estimates of residence time in soils for trace metals in temperate climates range from 1000 to 3000 years for copper, lead, and zinc (Kabata-Pendias and Pendias 1992). Animals can potentially take in heavy metals by consuming plants with trace metals on the plant surface, within the plant tissues, or by ingesting soil (Adriano 1986; Haygarth and Jones 1992) and changes in community structure may be caused by bioaccummulation of metals within wetland food webs (Nelson *et. al*, 2000).

Studies of AMD impacted watersheds in the U.S. indicate that both water column and sediment toxicity from heavy metals are significantly correlated with benthic macroinvertebrate community impacts including reduced diversity and abundance in impacted areas and species shifts from intolerant to tolerant taxa (Rutherford and Mellow 1994; Cherry *et al.* 1995; Soucek *et al.*, 2000a and 2000b).

In the pilot system it was necessary to determine if the tailings placed in the TMF wetland cell will generate AMD and have a toxic impact on the ecological health of the saturated wetland cover above them. Potential stressors in this wetland system include increases in the concentration, availability or toxicity of metals (specifically Cd, Fe, Mn, Pb and Zn); increased acidification; and potentially high levels of sulphate. To evaluate the health of the pilot wetland ecosystem it is important to quantify the major contaminants, determine if metal mobilisation is occurring throughout the system and assess any potential effects on the sediments, the water chemistry and the biota. (Figure 2.1 is a schematic presentation of the complexity of the metal interactions that can occur in aquatic systems.)

According to Adamus (1992) few experiments in which wetland communities are intentionally exposed to a stressor and subsequently monitored have been conducted in natural outdoor settings; most have involved limited-time, single species assays

Figure 2.1 Schematic presentation of metal reservoirs and the complexity of metal interactions in aquatic systems (Salomons and Förstner, 1984).



under laboratory conditions. The interpretation of this data can be confounded by differences between laboratory test conditions and field conditions that are typical of wetlands (e.g. altered toxicant mobility and toxicity due to increased organic carbon; interactions between hydroperiod effects and chemical toxicity) (Adamus, 1992). In human health risk assessment the individual is the primary focus, whereas ecological risk assessment must deal with populations, communities and ecosystems and their attendant interactions and complexities (Gentile, 2000).

Consequently, Warren-Hicks *et al.* (1989) suggest that links between adverse ecological effects and environmental pollutants are best established 'by demonstrating a pattern of effects between ecological, toxicological and chemical data'. Thus, wetland monitoring to determine long-term sustainability focuses on ***indicators*** of ecological health; these may be physical, chemical, or biological samples or measurements of processes (Adamus, 1992). Table 2.2 outlines selected indicators of wetland health in constructed and natural wetlands (Mitsch, 1992) and indicators proposed by the U.S. Environmental Protection Agency as part of its planning for their nationwide Environmental Monitoring and Assessment Program (Adamus, 1992).

Ideally, monitoring of a wetland should encompass as many indicators, and as many micro-habitats within the wetland as possible, given available resources (Adamus, 1992). Only whole system investigations conducted for extended time periods can simulate the most complex responses of ecosystems to pollutants and provide enhanced knowledge of how ecology, hydrology and geochemical processes affect metal toxicity in natural systems. This requires an integrative assessment using a variety of environmental indicators to determine ecosystem health.

2.2.1 Integrative Assessments to Determine Ecosystem Health

Integrative assessments have been defined as investigations involving attempts to integrate measures of environmental quality to make an overall assessment of the status of the ecosystem (Chapman *et al.*, 1992). Therefore, integrative assessments use environmental indicators to make functional and structural assessments of ecosystems. A functional approach towards ecosystem assessment focuses on the

Table 2.2 Selected indicators of wetland health in constructed and natural Wetlands (Mitsch, 1992) and indicators proposed by U.S. EPA as part of the Environmental Management Assessment Program (Adamus, 1992).

Selected Indicators of Wetland Health in Constructed and Natural Wetlands

Hydrological Indicators
- Depth and hydroperiod
- Hydrologic inflows
- Retention time

Chemical Indicators
- Chemical removal efficiencies
- Chemical loading rates
- Sedimentation rates

Substrate/Soil Indicators
- Metals
- Organic content
- Soil texture
- Nutrients

Biotic Indicators
- Vegetation composition
- Peak biomass
- Diurnal dissolved oxygen
- Aquatic metabolism

Indicators Proposed by U.S. EPA for use by EMAP Wetlands

Physical
-Wetland extent and diversity
- Landscape and wetland pattern
- Hydroperiod
- Sediment and organic matter accretion
- Chemical contaminants in sediment, tissue of plants and animals

Biological
- Vegetation: species composition, spectral greenness, and % cover
- Birds: community composition, bioaccumulation
- Amphibians: community composition, bioaccumulation

successful functioning of various systems that describe the dynamics or changes in the system over time (Cairns et al., 1992). Natural and constructed wetlands can have a variety of functions as outlined in Table 2.3. A structural approach involves assessing the numbers and kinds of species and other component parts of the system at any point in time. Structural data can be used to assess how well the system is meeting its functional requirements. By measuring the community-level responses as well as the individual and population-level responses to a stressor, causal mechanisms become more evident (Adamus, 1992).

An integrative approach for assessing the wetlands serves to:

- Identify pollution-degraded areas from control conditions
- Determine the extent of pollution induced degradation of sediments
- Provide empirical evidence of sediment quality
- Determine contaminant concentrations associated with water chemistry effects
- Describe ecological relationships between sediment properties and biota
- Allow ecological interpretation of physical, chemical and biological properties
- Generate data to identify bioindicators and calibrate models
- Use a preponderance of evidence rather than relying on single measurements to predict if degradation will occur

(Chapman *et al.*, 1992)

In the pilot plant a combination of both structural and functional information was used to characterise ecosystem health. This approach was used to establish relationships between component parts of the wetland ecosystem over the tailings to determine system dynamics over time.

The key functions of the pilot TMF wetland were determined to be toxicant retention and pollution prevention, sediment retention, creation of faunal habitat, creation of aquatic habitat and ultimately self sustainability. Characterising aquatic herbage, the water column, sediments, and the potential for interaction between these metrics using selected indicators, facilitated an understanding of the entire integrated aquatic environment in the pilot wetlands. This characterisation was achieved using a combination of an extensive field ecology study and an ecological risk assessment.

Table 2.3 Wetland function and functional definitions (Kent *et al.*, 1992).

Wetland Function	***Definition***
Aquatic habitat	To provide living, feeding, and breeding habitat for aquatic organisms.
Faunal habitat	To provide living, feeding, breeding and migratory habitat for semiaquatic and terrestrial amphibians, birds and mammals.
Toxicant retention	To adsorp toxic materials via wetland plants and soil.
Sediment retention	To adsorp and stabilise alluvial and suspended sediments via wetland plants and soil.
Flood attenuation	To provide temporary storage, reduction in velocity, or reduction in crest of flood waters.
Groundwater recharge	To recharge groundwater through the movement of surface water down through the soil to an underlying aquifer.
Nutrient metabolism	To remove or transform of nutrients, especially nitrogen and phosphorus via wetland plants, bacteria and soils.

The field ecology study involved using ecological indicators to assess ecosystem structure. A variety of indicators including hydrological, physico-chemical, sediment and biotic metrics were used in the ecological risk assessment. This involved the physico-chemical analysis of the water column, sediment chemical analysis, and plant tissue chemical analysis.

Specific ecological, hydrological, physico-chemical, sediment and biotic indicators suitable for this study were selected based on a review of the current literature. The scientific basis underpinning this selection of relevant appropriate environmental indicators is discussed in Sections 2.2 through 2.6.

2.3 ECOLOGICAL INDICATORS

2.3.1 Habitat Assessment and its Effect on Ecological Health

The objective of the field ecology study was to use vegetative parameters as ecological indicators for documenting wetlands success or degradation. Ecological indicators are used in the identification and enumeration of species to determine community composition, vegetation cover, plant distribution, similarity, species richness, diversity, density, dominance and indicator species (Brower *et al.*, 1990; Kent *et al.*, 1992). Growth studies for productivity and biomass are also indicators of ecological health (Brower *et al.*, 1990).

Table 2.4 outlines examples of analytical metrics, indices, and procedures used for wetland community studies (Adamus, 1992). To optimise detection of an ecologically degraded condition, it is usually best to use several of these in combination (Schindler 1987). Where only few metrics can be used, Adamus (1992) recommends the following ranking of metrics in descending order of relative sensitivity from the existing literature:

1. Clustering and Ordination Procedures
2. Similarity Indices
3. Number of Species (per unit area)
4. Diversity Indices, Biomass, Abundance

Table 2.4 Examples of analytical metrics, indices, and procedures used for wetland community studies (Adamus, 1992).

Similarity (comparative) indices. Metrics that reflect number of species or functional groups in common between multiple wetlands or time periods. May be weighted by relative abundance, biomass, taxonomic dissimilarity, or caloric content of the component species. Includes Jaccard Coefficient, Bray-Curtis coefficient, rank coefficients, overlap indices, "community degradation index" and others.

Cluster analysis and ordination. Procedures that detect statistical patterns and associations in community data. Can be used to hypothesize relationships to a stressor. Includes principal components analysis, reciprocal averaging, detrended correspondence analysis, TWINSPAN, canonical correlation and others.

Tolerance indices. Metrics that reflect proportionate composition of tolerant vs, intolerant taxa. "Tolerance" usually means tolerance to organic pollution; tolerance to many toxicants and physical habitat alterations may not be well reflected by available indices.

Functional group (guild) analysis. Procedures in which individual species are assigned to functional groups (species assemblages) based on similar facets of their life history, sensitivity, or other factors.

Indices of biotic integrity. Indices that are a composite of weighted metrics describing richness, pollution tolerance, trophic levels, abundance, hybridization, and deformities. Widely used in stream fish studies.

Clustering and ordination procedures were not carried out in the pilot system due to time constraints. However, extensive use of biostatistical procedures were used to examine ecotypic variation and bivariate correlations between ecological and environmental science parameters. This facilitated detection of statistical patterns of associations in community data. The remaining metrics have been used in combination to assess the ecological health of the pilot wetland.

2.3.1.1 Vegetative/Species Composition

Species composition is an important indicator of overall ecological health and was used in the pilot system to compare the vegetative cover that developed over the tailings to that of the Control. Common emergent plants used in treatment wetlands in the United States include *Scirpus validus* L. (soft-stem bulrush), *Typha latifolia* L. and *Typha angustifolia* L. (cattails), *Carex* spp. L. (sedges) and floating-leaved aquatic plants such as *Nymphaea odorata* L. (white water lily) and *Nuphar luteum* (L.) Smith (spatterdock) (Mitsch, 1992). Throughout the United States *Typha* spp. is championed by some and disdained by others as it is a rapid coloniser of limited wildlife value (Odum, 1987). *Phragmites australis* Cav. (Reed grass) is used extensively in constructed wetlands in Europe.

The importance of species composition as an indicator of ecological change over time is outlined by Mitsch (1992) in regard to experimental wetlands constructed in 1989. A total of fourteen new species were observed in these wetlands in 1990 that were not observed in 1989. However, ten species present in 1989 did not reappear in 1990, with several of these upland species. Factors that may be responsible for the establishment of new species include recruitment from seed bank (both the remnant seed bank and a newly forming one), introduction of seeds by waterfowl or wildlife, or wind deposited seeds (Mitsch, 1992).

A study conducted by Sistani *et al.*, (1999) used vegetative indicators to examine the biogeochemical changes taking place in wetlands constructed on coal mine spoil to determine the rate at which these constructed wetlands would develop the ecological characteristics of natural wetlands. A multicell wetland system was constructed with individual cell substrates consisting of coal-mine spoil or topsoil and planted with

Typha latifolia (cattail), *Panicum hemitomon* L. (maidencane), *Pontederia lanceolota* L. (pickerelweed), and *Scirpus validus* (soft stem bulrush). Survival of *Typha latifolia* and bulrush was lowest on the acidic coal mine spoil while *Panicum hemitomon* and *Pontederia lanceolota* survival did not appear to be pH dependent. *Pontederia lanceolota* spread most rapidly compared to other planted species because it spread by rhizomes and also produced seeds which were moved through the cells by water currents. Beginning in the second year of planting and more so in the third, there was a significant invasion of native wetland vegetation in areas where planted species failed to become established and open water existed. Four years after planting, all cells had a complete cover of emergent vegetation (Sistani *et al.*, 1999).

A study conducted by McCabe and Otte (2000) examining the potential for revegetation of mine tailings under wetland rather than dryland conditions examined *Glyceria fluitans* (L.) R. Br. (floating sweetgrass) following its discovery growing in a lead/zinc mine-tailings pond. In two outdoor experiments *Glyceria fluitans* grew successfully on alkaline tailings containing elevated metal concentrations (Zn and Pb) but did not survive on saline tailings originating from Silvermines (as used in the pilot plant) that contained much higher salt content ($MgSO_4$) and lead and iron concentrations. *Glyceria fluitans* grown on tailings from Silvermines died after a period of three to four months following initial transplantation and again after a repeat transplantation (McCabe and Otte, 2000). It is important to note that *Glyceria fluitans* was planted directly into tailings whereas in the pilot plant, a peat substrate was placed over the tailings as the immediate planting medium for wetland plants.

The pilot wetlands were assessed to determine the composition of emergent vegetation, the length of time for this vegetation to become established, and to evaluate the impact of pH on species composition. However, vegetation success, which has been the primary indicator of the success of constructed or restored wetlands, should be measured more by the success of the original objective of the wetland than by the success of individual species (Mitsch, 1992). Therefore, species composition in the pilot plant was used as an important ecological indicator to assess the overall objective of the system which is to create a sustainable living wetland ecosystem.

2.3.1.2 Diversity, Density and Biomass

The United Nations Environment Programme and World Wide Fund for Nature describe ecosystems as healthy when they have a high level of biodiversity, productivity and habitability (Burton, 1992). According to Brower *et al.*, (1990) high species diversity indicates a highly complex community, for a greater variety of species allows for a larger array of species interactions. Diversity can be used as an index of maturity on the premise that communities become more complex and more stable as they mature. However, this is a subject of considerable discussion for ecologists. Some ecologists support the concept of species diversity as a measure of community stability (the ability of community structure to be unaffected by disturbance of its components) while others have concluded there is no simple relationship between diversity and stability (Brower *et al.*, 1990).

In the pilot plant it was important to evaluate diversity as a potential bioindicator of ecosystem health. Bagatto and Shorthouse (1999) found the best reclamation strategy at a series of mine tailings sites occurs where a diverse vegetation of herbs, shrubs, and deciduous trees resulting primarily from natural colonisation leads to a more substantial litter and ground cover. Consequently, they recommend that assessments of both ecosystem function and sustainability should include measures of biodiversity in addition to direct measurements of substrate characteristics and biotic accumulation of metals. For example, their study showed that plants from tailings restored to a more diverse state have higher concentrations of metals (Cu and Ni) than those from younger, less vegetated habitats. These observations may seem to contradict the assumption that plants from a healthier ecosystem should have lower concentrations of metals; however, they can be explained when the reduced ability of later successional plants to exclude metals from their tissues is considered (Bagatto and Shorthouse, 1999).

Alternatively, in Yellowstone National Park, where tailings and associated trace metals from past mining have been deposited along 28 km of riverbank, data analysis shows that metals and acidity associated with tailings adversely affect plant biomass, density, and diversity (Stoughton and Marcus, 2000). The primary finding of this research was that metals in floodplain soils associated with dispersion of tailings exert a threshold relation over vegetation. Vegetation diversity, density and biomass all varied widely up to a certain trace metal level, at which point mean diversity, density, and biomass dropped significantly. Likewise at soil pH levels below 6.5, mean vegetation density and biomass decreased in a threshold relationship similar to that of the metals. The relationship between pH and vegetation diversity, however, was not as strong as the links between pH and density or biomass (Stoughton and Marcus, 2000).

The empirical relationships between vegetation parameters, trace metals, and pH levels documented by Stoughton and Marcus offer insights into how the impact of mine tailings and ecological mechanisms can influence community structure in the riparian zone. It was based on research in other areas where high trace metal levels and low pH levels also led to decreased vegetation diversity, density, and biomass (Macnicol and Beckett 1985, Kabata-Pendias and Pendias 1992, Levy *et al.*, 1992). Stoughton and Marcus concluded that metals and acidity associated with tailings affect plant biomass, density, and diversity; however, changes in density of individual species may provide a better estimate of plant health, while diversity measures illustrate broad vegetation patterns.

Additionally, the net primary productivity and biomass of the macrophytic community in constructed wetlands can be used to give an overall indication of the ecological health of wetlands and their relative stage of succession (Mitsch, 1992). Estimates of the productivity of macrophytes in four constructed wetlands, as determined by peak biomass, showed productivity was moderate during the first growing season and increased substantially in all wetlands during the second (Mitsch, 1992). The wetland that had the lowest peak biomass production in both years was receiving low flow and appeared to be the least "healthy" wetland.

In the pilot system the wetlands were allowed to mature for two growing seasons before exhaustive ecological sampling was carried out to quantify and compare diversity and density indices and biomass production in the tailings wetland and reference wetland.

2.3.1.3 Wetland Vegetation and Fauna

In addition to inhibiting metal mobilisation, a key goal of creating a wetland cover over pyritic tailings is to provide habitat for fauna. A beneficial attribute of reclaiming mining sites is their extensive use by fauna of various types due to their location in rural areas away from dense human habitation (Sistani *et al*., 1999).

Wetland vegetation is an important factor in assessing the potential habitat value a wetland ecosystem has for fauna. Wetlands designed for habitat value should take into account the potential for low dissolved oxygen (D.O.) concentrations and trace element bioaccummulation associated with vegetation community types. For example, Nelson *et. al* (2000) produced data from wastewater mesocosms suggesting that the quality of wetland habitat (as measured by invertebrate taxa richness and abundance) for invertebrates increases from open water with low D.O. under a continuous cover of *Lemna* spp. (duckweed), to tall emergents with low D.O. but large amounts of detrital food, to short emergents that provide some detrital food but also allow for light penetration to water, and finally to open water with oxygen-producing submerged macrophytes. Invertebrate taxa richness was positively related to D.O. concentrations that were, in turn, related to vegetation communities (Nelson *et. al*, 2000). Providing environmental attributes appropriate for invertebrate production can enhance wildlife, specifically waterfowl production.

The potential habitat value of the tailings wetland is considered closely in evaluating data gathered from the pilot plant during the ecological fieldwork.

2.4 HYDROLOGICAL INDICATORS

Hydrology is the most important variable in wetland design (Mitsch, 1992) and an underlying assumption in the assessment of wetland ecological health is the existence of a hydrologically sound water balance (Kent *et. al*., 1992). If the proper hydrologic conditions are developed initially, the chemical and biological conditions will respond accordingly (Mitsch and Gosselink, 1986). Improper hydrologic conditions will not correct themselves as will the more adaptable biological components of the system (Mitsch, 1992).

A hydrological assessment of the pilot wetlands required considering factors such as morphology (surface area and maximum depth), hydroperiod (pattern of water depth over time), seasonal patterns, frequency of flooding and the optimum depth for enhanced faunal habitat.

2.4.1 Flooding - Influence of Wetland Morphology and Hydroperiod

Ensuring tailings are saturated is fundamental to ensuring the inhibition of pyrite oxidation. Flooded, predominantly mineral wetland soils and sediments are near neutral in pH and favour metal immobilization, though some predominantly organic wetland soils may be moderately to strongly acidic (Gambrell, 1994). Under non-flooded, oxidized conditions, changes can occur in soil pH, redox potential, metal mobility, and nutrient availability (Gambrell 1994), which can affect plant growth (McCabe and Otte, 2000). For example, recent experiments investigating wetland plant growth on tailings conclude a low water table could adversely affect the use of wetland plants to facilitate tailings rehabilitation and recommend adequate care is taken in the design of the water supply for a wetland cover to ensure the tailings remain flooded at all times (McCabe and Otte, 2000).

Snodgrass *et al.* (2000) sampled fish and selected water chemistry variables (dissolved organic carbon, sulfate, and pH) in nine southeastern depression wetlands in the U.S. to determine relationships among wetland morphology, hydrology, water chemistry, and bioaccumulation of mercury (Hg) in three fish species. Variation in fish Hg concentrations among wetlands was related to variation in morphometric and hydrological characteristics, specifically depth and hydroperiod. The authors hypothesized that the effects of repeated flooding on Hg cycling in sediments is an important process controlling the bioavailability of Hg in wetlands. Additionally, the positive correlation observed between degree of water level fluctuation and fish Hg concentrations suggests that management of water level fluctuations can be used to control the bioavailability of Hg in aquatic systems (Snodgrass *et al.*, 2000).

The results suggest that leaching of Hg from sediments during the drying and reflooding cycle and binding of Hg species by dissolved organic carbon in the water column are primary factors controlling the bioavailability of Hg in southeastern depression wetlands in the United States (Snodgrass *et al.*, 2000).

Caldwell and Canavan (1998) also reported that concentrations of total Hg and MeHg in water and sediment were highest at a site in a New Mexico reservoir that experienced periodic drying and flooding compared with five sites in deeper water. These results, as well as those of Snodgrass *et al.* (2000) suggest that intermittent or periodic flooding associated with changes in water levels in reservoirs and wetlands can also enhance MeHg production and (or) bioavailability.

Studies by Sistani *et al.* (1999) show that wetlands can be established on low-pH infertile sites which result from surface-mining operations with little input beyond grading the soil to create depressional wetlands with sufficient runoff area to supply water. The authors conclude that wetland creation is an economical and ecologically viable alternative for sites which are feasible to flood.

It was important in the pilot plant to examine the hydrological balance within the wetland cells and whether water depth is related to metal mobility. The wetland hydrology was examined on a seasonal basis to investigate the impact of rainfall and evapotranspiration on water depth and the potential for dessication of sediments and oxidation of the tailings.

2.4.2 Water Depth and Faunal Habitat

Water depth also can significantly impact fauna habitat. Results of a study by Nelson et. al (2000) support conclusions by others (Schwartz and Gruendling, 1985, Batzer and Resh 1992) about the importance to wetland macroinvertebrates of shallow (approx. 0.5m depth) open water. Nelson *et al.* (2000) determined that while emergents provide important cover for waterfowl, the importance of open water for wildlife should not be underestimated. They found chironomids, crucial for waterfowl food, were largely absent from heavily vegetated wastewater wetland mesocosms. Often treatment wetlands are designed with limited open water areas and dense coverage of emergent vegetation to maximise nutrient removal capacity, however; this may limit the usefulness of some constructed wetlands as invertebrate habitat and therefore limit their value to waterfowl. The authors suggest that some combination of oxygen-producing open water and detritus-producing emergent plant zones maximises invertebrate biodiversity.

Sartoris and Thullen (1998) also suggest that interspersion of emergent vegetation and open water habitats in the design of wastewater treatment wetlands would create alternating aerobic and anoxic environments, along with providing a mosaic of habitat types for fauna use.

Therefore, in the pilot plant study an evaluation of the impact of water depth on habitat was appropriate.

2.5 PHYSICO-CHEMICAL INDICATORS – WATER CHEMISTRY

2.5.1 Selected Physico-chemical Indicators: pH, Conductivity, Sulphate, Metals, Dissolved Oxygen

In the pilot plant a complete evaluation of water column chemistry parameters was essential to determine the impact of the tailings on the water column and overall ecosystem health and sustainability. This included an evaluation of pH, conductivity, sulphate, metal concentrations, temperature and D.O.

In a study of an AMD impacted watershed in southwestern USA, Soucek *et al.* (2000b) found several water column chemistry parameters (pH, conductivity and metal concentrations) were good indicators of both sediment and water column toxicity. Stations that had significantly altered water chemistry (low pH, high conductivity, and high water column Fe and Al) and significantly higher sediment Fe concentrations had significantly decreased benthic macroinvertebrate richness and abundance relative to unimpacted stations. The high percentages of water (with acidic pH and elevated metals) in sediment samples probably account for the correlation of water chemistry parameters with sediment toxicity. These results suggest that water column chemistry has a more important adverse influence on this system than sediment chemistry (Soucek *et al.*, 2000b). An earlier study by McCann (1993) also suggested that waterbome metals have a greater influence on aquatic biota than sediment-bound metals in an area influenced by mining activities.

Emerson *et al.*, (1999) outline another study conducted in the United States where the pH values of a river range from 3.5 to 6.5 as a result of acidity generated by nearby mining spoils from pyrite mines. In the pilot plant it was important to monitor pH to determine if the tailings are adversely impacting the acidity of the water column and to determine if any correlation exists between metal mobility and pH.

Conductivity is an indirect measure of salinity, which reflects the osmotic concentration of the solutes. Since polluted waters have a higher conductivity than natural waters, this measure is often used as an index of pollution (Brower *et al.*, 1990). O'Sullivan *et al.* (1999) conducted a range of experiments on wetland systems treating runoff from Pb/Zn mine tailings. They found average conductivity measurements were positively correlated with the sulphate concentrations of the water in inflow and outflow ponds. The data indicate that sulphate is one of the more important ions determining conductivity in this particular type of water, as would have been expected from the high concentrations of sulphate present. Thus conductivity may be used to monitor the retention of sulphates in these systems (O'Sullivan *et al.*,1999).

The formation of highly insoluble sulphide from soluble sulphate in waterlogged wetland soils is particularly important. This process leads to the precipitation of sulphur and the co-precipitation of metals, including Fe, Zn, Pb and Cd in the form of sulphides (O'Sullivan *et al.*, 1999; Sikora *et al.*, 1995; and Gambrell, 1994). Once metal sulphides have precipitated, they are stable and insoluble providing the soil remains anaerobic (Mclntire and Edenbom 1990; Dvorak *et al.* 1992). Therefore, levels of sulphate and metals tend to be reduced in water after passage through wetlands.

Given, sulphate is a potential contaminant in the pilot plant, monitoring conductivity in addition to sulphate concentration indicated the impact of the tailings on sulphate concentrations in the wetland system.

The metals of potential concern in the pilot study include Cd, Fe, Mn, Pb, and Zn and they exist in natural waters as dissolved cations. In lakes under lentic conditions, one normally expects to find a relationship between the metal concentration in the water column and the metal concentration in the sediments because of the establishment of an equilibrium between metals in the dissolved and absorbed phases (St-Cyr and Campbell, 2000). Seasonal sampling and analysis of the water column was undertaken to determine if metal contamination from the tailings impacted the overlying water column of the wetland.

Lau and Chu (2000a), suggest that an increase in temperature (namely in summer) may elevate contaminant release from sediments to overlying water. Therefore, it was essential to conduct more extensive metal analysis of the water column in summer to determine if there is enhanced temporal metal availability for biota in the water column at this time. This work was essential in the assessment of temporal variability in contamination upon the ecosystem as a whole.

Wetlands are considered to be the most productive ecosystems in the world and measurements of their productivity are indicative of the health of the system (Mitsch and Gosselink, 1986). Measurement of diel changes in D.O. gives a good estimate of water column productivity in a wetland. Strong diel swings in D.O. in the water column are common and to be expected in natural wetlands. If D.O. does not change in the summer it could indicate that either the wetland is starved for nutrients or it has been impacted by toxic materials (Mitsch, 1992). Nelson *et. al* (2000) measured low concentrations of D.O. in bulrush wetland mesocosms constructed for wastewater treatment while higher concentrations of D.O. were measured in open water mesocosms containing submerged *Potamogeton pectinatus* L. (pondweed). The relationship between D.O. and mesocosm plantings was also suggested by Canonical Correspondence Analysis conducted by the authors where plant height was almost directly opposed to D.O. The negative relationship of plant height to D.O. may be related to shading of oxygen-producing submerged plants and production of oxygen-consuming biomass.Variations in D.O. in these wastewater wetlands were positively correlated with macroinvertebrate richness but not with abundance (Nelson et. al, 2000).

Submerged plants benefit invertebrates by releasing oxygen into the water column, whereas emergent plants lose oxygen to the atmosphere (Sculthorpe 1967) and shade benthic and plankton communities (Nelson *et. al*, 2000). Plants also contribute large amounts of oxygen-demanding detritus in the water column upon death or senescence, and the humic substances produced may inhibit algae growth (Vymazal, 1995, Nelson *et. al.*, 2000).

In the pilot plant it was necessary to investigate periodic variations in D.O. to ensure the tailings wetland will support aquatic life.

2.6 SEDIMENT INDICATORS

Wetland substrate plays an important role in plant development and chemical processes with substrate characteristics such as organic content, texture, nutrients, and metals playing important roles in wetland design and construction (Mitsch, 1992).

In treatment wetlands contaminant immobilisation into underlying sediment occurs across the sediment-water interface, allowing the sediment to provide an historical archive of pollution levels (Cundy *et al,* 1997, Lau and Chu, 2000b). Metals are not necessarily fixed permanently by the sediment, however, but may be recycled via biological and chemical agents, both within the sedimentary compartment and also back to the water column (Forstner, 1985). Because of the capability of contaminant release sediment will act as a potential source when the overlying water is less polluted (Lau and Chu, 2000a). Sediment contamination not only threatens biological life through bioconcentration (bioaccumulation from water) and biomagnification (bioaccumulation from food), but also affects the contaminant dynamics of ecosystems (Lau and Chu, 2000b).

The primary task in this thesis was to evaluate if tailings under a wetland cover may be regarded as a potential future source of pollution by contaminating wetland sediments. The pilot plant facilitated an investigation of the potential remobilisation of metals under changing environmental conditions at the tailings-sediment interface and the interface between sediments and the water column. This required an understanding of metal speciation and bioavailability in aquatic systems.

2.6.1 Metal Speciation and Bioavailability in Aquatic Systems

Elevated total concentrations of metals in sediments do not necessarily result in problem releases to water or excessive plant uptake (Gambrell, 1994). It is now well established that the total metal concentration in a sediment sample is rarely adequate to interpret the reactivity of the metal in biological or environmental processes. In addition to the particular metals present and their concentrations, the chemical forms or species of metals present and the processes affecting transformations between these forms are important to assessing ecotoxicological risk (Gambrell, 1994). Metal speciation in aquatic media is the real key to a better understanding of metal availability to biota (Gambrell, 1994; Mota and Correia Dos Santos, 1995; Campbell, 1995; and St. Cyr and Campbell, 2000).

Chemical speciation is defined as the distribution of an individual chemical element between different chemical species or groups of species (Turner, 1995). Only part of the metals present in sediments or sludges are involved in short-term geochemical processes and/or are bioavailable (Förstner, 1985). There are five major mechanisms of metal accumulation in sedimentary particles (Gibbs, 1973; Förstner, 1985):
-adsorptive bonding on fine-grained substances;
-precipitation of discrete metal compounds;
-co-precipitation of metals by hydrous Fe and Mn oxides;
-associations with organic molecules; and
-metals incorporated in crystalline minerals.

Sequential extraction procedures are used to estimate the chemical speciation of metals in line with their accumulation in these sedimentary particles. Sequential extractions have been used to distinguish among ion-exchangeable metals, a carbonate fraction, a reducible fraction (typically hydrous oxides of iron and manganese), an oxidizable fraction (sulfides plus organic matter), and a residual fraction (Förstner, 1985; Burton, 1992; Apte and Batley, 1995). The selectivity of these separations is clearly operationally defined, and further limited by the reprecipitation and readsorption that can occur as metals released from heterogeneous phases interact with other solubilized components or with activated sediment surfaces (Apte and Batley, 1995).

The assessment of environmental effects of trace metals in particulate matter must predominantly consider the most mobile fraction of these elements, which is that introduced by human activity and bound to the sediment in sorbed, precipitated or co-precipitated (carbonates and hydrous Fe-Mn oxides) and organically complexed forms (Forstner, 1985). Water-soluble metals are considered the most mobile and plant available; exchangeable metals are considered weakly bound and may be displaced relatively easily to the water-soluble form (Gambrell, 1994). Together metals in the soluble and exchangeable form are considered readily mobilised and available (Gambrell, 1994). Figure 2.2 illustrates the potential bioavailability of different metal species and Figure 2.3 illustrates the sediment/water interface and those species of contaminants most mobile and consequently most likely to be released into the water column. Figure 2.4 summarises the major processes and mechanisms in the interaction between dissolved and solid metal species in surface waters and sediments.

In the Mai Po marshes in Hong Kong, Lau and Chu (2000b) determined less than 10% of contaminants (nutrients and heavy metals) in sediments (surface and bottom) were water soluble. This suggests that the release of contaminants across the sediment-water interface to overlying water may be relatively low. Also, the authors determined that the total and soluble concentrations of metals (Cd and Zn) in sediments were highly temporally dependent, with higher concentrations occurring at warmer temperatures. Water solubility of contaminants helps determine their bioavailability and toxicity in the aquatic ecosystem (Lau and Chu, 2000b).

In the final analysis, it is the concentration and speciation of the metal in the immediate micro-environment of the organism that is important in determining the bioavailability and toxicity of a metal (Mason and Jenkins, 1995). Therefore, in the pilot system a combination of total metal analysis and sediment extractions were carried out on sediment samples to evaluate metal speciation and bioavailability in the pilot wetland. It was essential that speciation studies were conducted in summer given the potential for enhanced concentrations of soluble metals in summer.

Figure 2.2 Availability of metal forms for biological uptake (Baudo, 1982 as cited in Salomons and Förstner, 1984).

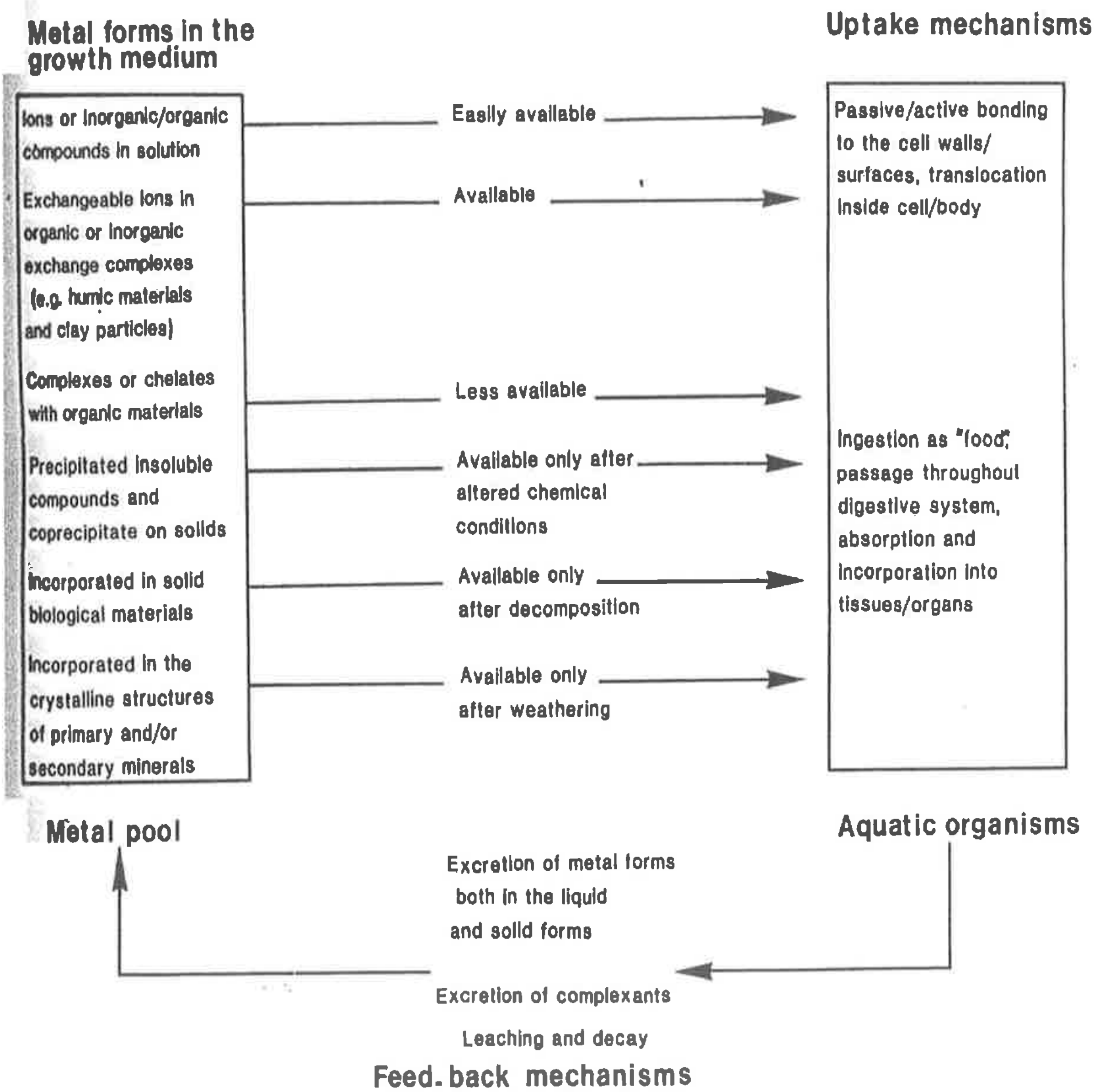


Figure 2.3 Cross-section of the sediment/water column interface and the prevalent forms of contaminants. Forms presented in italics are considered the most mobile and therefore are the most likely to be released into the water column (Burgess and Scott, 1992).

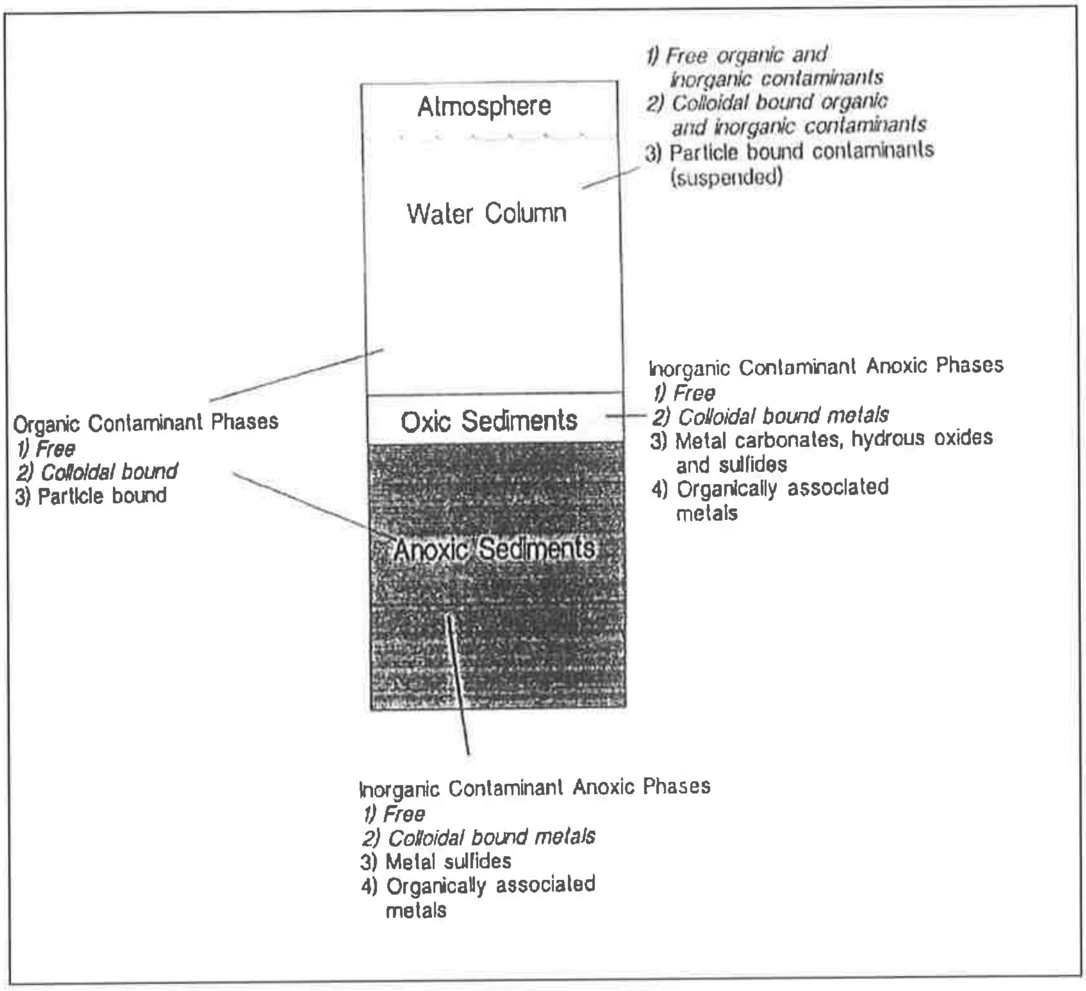
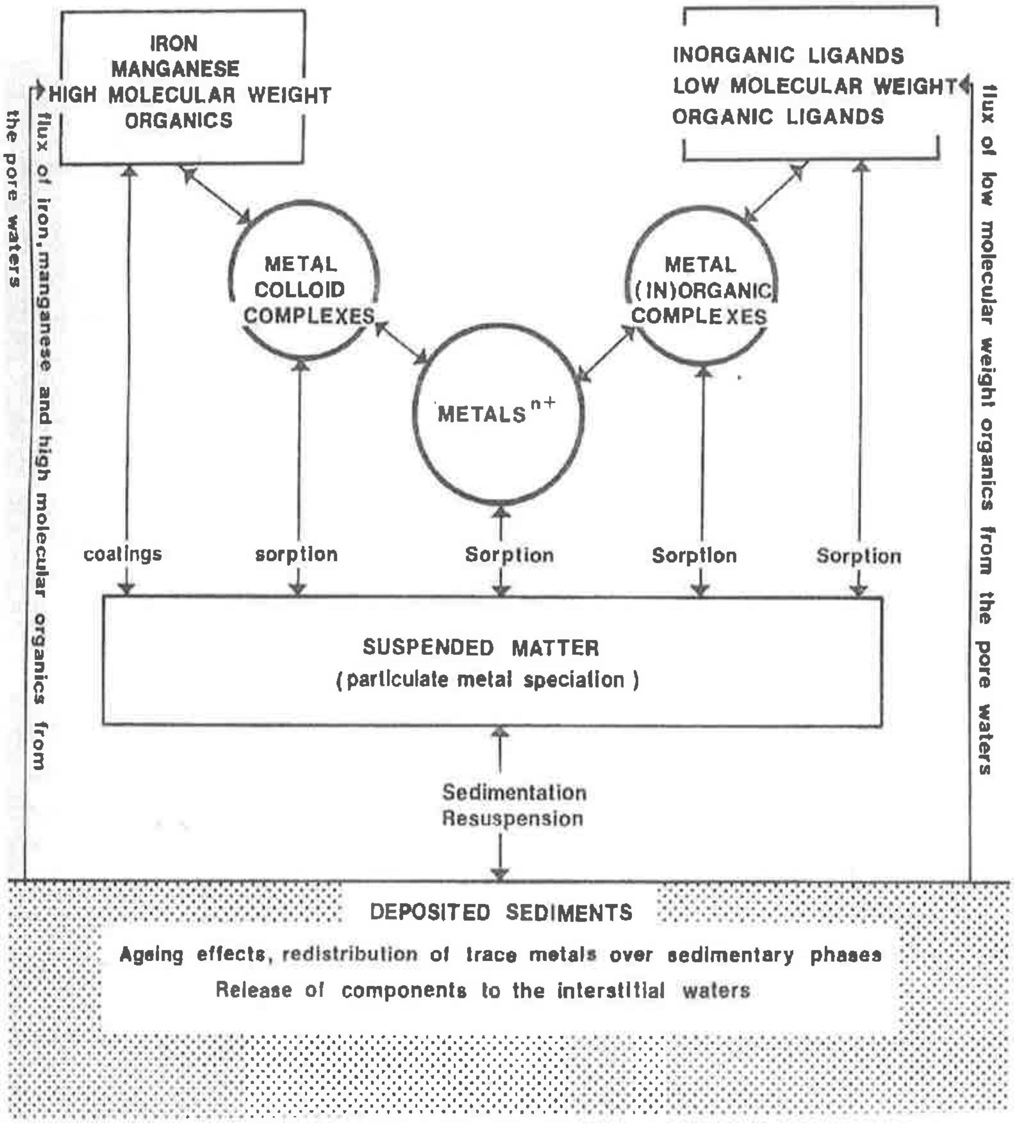


Figure 2.4 Summary of major processes and mechanisms in the interactions between dissolved and solid metals species in surface waters (Salomons and Förstner, 1984).



2.6.2 Impact of the Physico-chemical Environment on the Potential Remobilization and Bioavailability of Metals in Sediments

The impact of changing environmental conditions on metal speciation, accumulation, transport and bioavailability in wetland sediments is essential in the assessment of the potential remobilisation of metals. These changing environmental conditions include:

- varying pH and redox potential over time,
- organic carbon bonding sites,
- the presence of other metals that may either act synergistically or competitively,
- other potential ligands, and
- effects of plants and benthic organisms

(St Cyr and Campbell, 2000; Wood and Shelley, 1999; Sparling and Lowe, 1998; Campbell, 1995; Förstner, 1985; Campbell and Stokes, 1985; Spry and Wiener, 1991).

2.6.2.1 pH and Speciation

Low pH conditions in surface water or sediments can significantly increase metal bioavailability (Wood and Shelley, 1999). Wetland sediment pH is typically 6.0 to 7.0 for mineral soils and can be less than 6.0 for organic soils (Faulkner and Richardson, 1989). Typically adsorption of metals in soil and sediment increases from near nil to near 100% as pH increases through a critical range 1-2 units wide (Benjamin *et al.*, 1982; Förstner, 1985). This means that a small shift in pH in surface water, as may occur in lakes, causes a sharp increase or decrease in dissolved metal levels.

Changes in the pH of the environment can influence the uptake of metals in at least two ways: firstly by affecting metal speciation directly and secondly by affecting the biological surface (Campbell and Stokes, 1985). As reported by Simkiss and Taylor (1995) Campbell and Stokes compiled data on Cd, Mn, Pb, and Zn to investigate how acidification of the freshwater ecosystem might influence metal speciation. Over the pH range of 7 to 4 they found that Pb showed speciation changes, while Cd, Mn, and Zn showed little effect. When the biota were exposed to these metals there were two sets of responses. For Pb a decrease in pH caused an increase in metal availability while for Cd and Zn a decrease in pH caused a decreased biological uptake

Alternatively, Adriano (1986) reports that in soils with a pH between 4.2 and 6.6, Zn is mobile and Pb is slowly mobile. Förstner (1985) also expects that changes from reducing to oxidizing conditions (with corresponding reduction in pH) will strongly increase the mobility of metals such as Cd, and probably to some extent also of Zn and Pb. However, mobility is characteristically lowered for Mn and Fe under oxidizing conditions (Förstner, 1985).

Species differentiations can be used for the estimation on the remobilization of metals under changing environmental conditions (Förstner, 1985). For example, in the estuarine environment changes in pH and redox potential affects the *exchangeable fraction* in particular; however, these changes could also influence other easily extractable phases, e.g. carbonate and manganese oxides (Förstner, 1985). Lowering of pH will affect, according to its strength, the *exchangeable*, then the *easily reducible* and in some cases parts of the *moderately reducible* fraction, the latter consisting of Fe-oxyhydrates in less crystallized forms (Förstner, 1985). In strongly *reducing* environments, e.g. in. highly polluted sediments, the *moderately reducible fraction* is affected by redox changes, especially when Fe is present in the form of coatings (Jenne, 1977; Förstner, 1985). The effects on organically bound metals are more complex, however, it has been argued that this fraction is highly susceptible to environmental changes (Förstner, 1985).

2.6.2.2 Sediment Organic Content and Speciation

The general organic content of soils is significant in the retention of chemicals in a wetland (Mitsch, 1992). Mineral soils generally have lower cation exchange capacity than do organic soils, with the former dominated by various metal cations and the latter by the hydrogen ion (Mitsch, 1992). Organic soils can therefore remove some contaminants (metals) through ion exchange. It appears there is a trade-off in using organic sediments for metal retention. On one hand the organics provide a large capacity for binding metals, but on the other hand, they drive down pH which reduces the amount of metal that can partition to the organic carbon (Wood and Shelley, 1999).

Wetland soils generally vary between 15 and 75% organic matter (Faulkner and Richardson, 1989) with higher concentrations in peat building systems such as bogs and fens and lower concentrations in open wetlands such as riparian wetlands (Mitsch, 1992).

Natural organic matter behaves as a simple hydrophilic ligand in solution which enhances complexation and reduces metal toxicity (Campbell, 1995). Humic substances, the dominant component of natural organic matter, are traditionally divided into three operational fractions: fulvic acids, humic acids and humin (Turner, 1995). In aquatic systems dissolved organic carbon (DOC) includes both humic and fulvic acids. Humic substances in water are derived from two sources: leaching of soil organic matter (which in turn derives from degradation of higher plant debris) and excretion of organic material from aquatic organisms (Turner, 1995).

Humic matter is high, particularly in peatlands. Seventy percent of the DOC in wetland surface waters is humic matter, and it constitutes close to 90% of the organic matter in some wetland sediments (Weber 1973, Thompson-Roberts and Pick, 2000). In aquatic systems with a high content of organic substances, humic matter, plays a dominant role in the final distribution of metal (Mota and Correia Dos Santos, 1995).

A system dynamics model developed by Wood and Shelley (1999) to investigate the bioavailability of metals in sediments demonstrated that the amount of organic carbon in sediment plays the biggest role in controlling metal bioavailability. The organic carbon in the deep anaerobic sediment appears to have the largest influence on metal bioavailability even at moderately low pHs. The authors conclude that long term control of metal bioavailability is more related to the build up of organic carbon binding sites in a developing wetland. Thus, if control of metals toxicity is an important design criteria for wetlands, then seeding of the area with organic rich soils may prove beneficial even if otherwise unnecessary for quick successional development (Wood and Shelley, 1999).

Metals are normally associated with fine-textured, organic-rich sediments (Martin, 2000). A polish study of metal mobility in wastewater treatment wetlands attributed decreased concentrations of Pb and Zn to the increased content of suspended organic matter, whereas decreased Cd content was ascribed to a decrease of the fine grained mineral fraction of sediments (Obarska-Pempkowiak and Klimkowska, 1999). Manganese concentration was controlled by redox conditions in the various sections of the system, and was substantial in ditches rich in organic matter.

Finally, the significant positive relationship between sediment organic content and sediment Hg for wetlands obtained in a study by Thompson-Roberts and Pick (2000) also provides evidence for the importance of wetland sediments as metal-binding sites. The authors propose that despite containing more Hg, organic-rich wetland sediments may not pose a greater Hg risk to organisms given organic-rich sediments also provide the anoxic conditions necessary for sulfide production and hence additional sequestering of Hg.

2.6.2.3 Impact of Competing Metals

Different metals are transported and behave differently in sediment due largely to differences in solid-water partitioning, both in the surface water and in sediment pore water (Wood and Shelley, 1999). Occasionally, anomalously low metal concentrations are observed in algae from heavily polluted areas, particularly where other metals are present in high concentrations and hence compete for uptake sites (Langston and Spence, 1995). Elevated levels of Zn and Mn, for example, significantly reduce the accumulation of Cd in *Fucus vesiculosus* (Bryan *et al.*, 1985). These observations demonstrate the need to be aware of conditions in the pilot plant, such as the presence of other potentially interfering metals or ligands, when evaluating field data.

Since a variety of metals exist in wetland sediments, interest in a particular metal must account for individual metal competition for binding sites dependent on metal sulfide solubility products (Wood and Shelley, 1999). The first metals released from the sulfide bond are, in the following order: Fe>Zn>Cd>Pb. Since Cd is both more soluble than Pb in sulfides and with organic complexes, it along with Zn will probably produce the highest pore water concentrations in sediments with competing metals. A wetland receiving inflow with a mix of heavy metals, will likely exhibit toxicity in sediment from zinc or cadmium first, before lead becomes a problem (Wood and Shelley, 1999).

In the pilot plant the relationships between pH, organic matter and competing metals on metal speciation and bioavailability are thoroughly investigated.

2.6.3 Free-Metal Ion Concentration and Bioavailability

Recent scientific research has determined that biological availability of dissolved trace metals can be correlated more directly with chemical speciation, often through the activity of the free-metal ion (Campbell, 1995)[2]. The free-metal ion concentration is the concentration of metal in the solid sediment phases in equilibrium with the porewater and can be represented as $[M^{z+}]$ (Apte and Batley, 1995). There are frequent references in the literature to the free-metal ion as the 'toxic' or 'bioavailable' species (Petersen, 1982; Gavis *et al.*, 1981; Turner, 1984; and Petersen and Healy, 1985, as cited in Campbell, 1995).

A convincing body of evidence has been developed to support the tenet that the biological response elicited by a dissolved metal is usually a function of the free-metal ion concentration. Campbell (1995) sites several examples where the activity of the free-metal ion is a better indicator of metal bioavailability to aquatic plants and organisms than total metal concentration. For example, Anderson *et al.* (1978) examined the effects of Zn on the growth of a coastal diatom *Thalassiosira weissflogii* and discovered Zn ion activity rather than total Zn concentration determines the growth rate of *T. weissflogii* under Zn limiting conditions. In addition, the activity of the free-metal ion rather than the concentration of total metal was found to determine Zn bioavailability to test algae *Scenedesmus subspicatus* and *Chlamydomonas variabilis* (Bates *et al.*, 1982).

Investigations of biological availability of trace metals, therefore, require means of determining the concentrations of the free-metal ions. The free-ion concentration is determined not only by the total dissolved metal concentration, but also by the concentration and nature of the ligands (organic carbon) present in solution and the potential competition for the metal binding site, by the hydrogen ion, H^4, and by the hardness cations, Ca^{2+} and Mg^{2+} (Campbell, 1995).

Free metal ion concentrations can rarely be measured directly because concentrations are normally very low, sample volumes are small, and separation artifacts abound (Adams, 1994; St. Cyr and Campbell, 2000). Consequently, the use of partial sediment extractions and geochemical models to estimate porewater metal concentrations (i.e. dissolved free metal ions [M^{Z+}]) has been suggested as a means of circumventing methodological problems (Campbell and Lewis, 1988; St Cyr and Campbell, 1996; 2000). Tessier (1992) and Tessier *et al.,* (1993) have developed equations for determining the free-metal ion concentrations of Cd, Pb and Zn to estimate dissolved [Cd^{2+}], [Pb^{2+}], and [Zn^{2+}] at the root-sediment interface. These equations are outlined in Chapter 6. While the equation used to estimate [Cd^{2+}] has been refined and tested over a wide geographical area (Tessier *et al.,* 1993), the geochemical models used to calculate [Pb^{2+}] and [Zn^{2+}] are less well tested (Tessier, 1992).

St-Cyr and Campbell (2000) used sequential extractions and these published equations to assess the bioavailability of sediment-bound metals (Cd, Pb, and Zn) in the St. Lawrence River using a rooted aquatic plant as the biomonitor species. In general, metal concentrations in plant tissues correlated more closely with estimates of bioavailable sediment-bound metals (i.e. [Cd^{2+}], [Pb^{2+}], [Zn^{2+}]) than with total metal concentrations in sediments (St-Cyr and Campbell, 2000).

These equations (Tessier, 1992; Tessier *et al.,* 1993) were applied to specific metal and physico-chemical data from the pilot plant and from Silvermines wetlands to obtain estimates of the bioavailable concentrations of free-metal ions in these systems. This facilitated a comparison between these wetland systems and with natural wetland sediments in Canada.

2 A full review of the Free Ion Activity Model can be found in Campbell, 1995.

2.7 BIOTIC INDICATORS

2.7.1 Bioavailability of Metals to Plants/Bioindicator Concept

In the case of vascular plants, Adamus (1992) recommends relative sensitivities to pollutants might be elucidated by measuring exposure of a host of species to a particular substance, and then monitoring the varying degrees to which the substance accumulates in tissue or alters germination and other physiological processes. The quantification of metal content in plants facilitates an investigation of eco-physiological indicators of sub-lethal stress in assessing wetland plant health (McNaughton *et al.*, 1992).

Bagatto and Shorthouse (1999) determined that grasses (*Agrostis gigantea* Roth. and *Poa compressa* L.) growing on tailings contained higher concentrations of Cu and Ni in their shoot and root tissues compared with those from control sites. Furthermore, accumulation of these two metals is higher in root than in shoot tissues. The authors also determined that concentration of metals within tailings plants is a good indicator of elevated levels in tailings substrates, but is not adequately sensitive in gauging more subtle improvements in ecosystem function.

Plant and soil scientists generally agree that soil pH and redox potential exert the greatest influence on trace metal bioavailability in plants (Adriano 1986, Barbour *et al.*, 1987, Kabata-Pendias and Pendias 1992, Alloway 1995). Acidification of wetlands due to acid deposition, acid mine drainage, or natural causes, especially when the pH is below *5.5* (Irving, 1991), can elevate the concentration of selected metals in solution and increase their bioavailability and concentrations in aquatic plants (Lehtonen, 1989; Sprenger and McIntosh, 1989; Albers and Camardese, 1993, as cited in Sparling and Lowe, 1998). Jackson *et al.* (1993) demonstrated that low sediment pH coupled with elevated sediment metal concentrations and mildly oxic redox potential could increase macrophyte concentrations of several metals.

Rooted, emergent plants can be exposed to metals through the air, water, and soil; but submerged species are not aerially exposed and non-rooted species may have limited contact with the soil (Crowder, 1991). Sparling and Lowe (1998) examined the influence of soil type under two regimens of water acidification on metal uptake by four species of aquatic macrophytes: two emergents, *Polygonum sagittatum* L. (smartweed) and *Sparganium americanum* L. (burreed); and the submerged *Potamogeton diversifolius* L. (pondweed) and *Utricularia vulgaris* L. (bladderwort). Soils were important to plant metal concentrations in all species, but especially in the emergents. Regression equations computed by the authors showed that metal concentrations in emergent wetland plants were more frequently influenced by soil type than by water treatment.

Thompson-Roberts *et al.*, (1999) measured total Hg in sediments, water, and four species of aquatic macrophytes, *Nuphar variegatum* Smith. (yellow pond lily), *Myriophyllum spicatum* L. (eurasian water milfoil), *Elodea canadensis* Michaux. (common waterweed), and *Potamogeton crispus* L. (curly leaf pondweed) in twenty-three wetlands along the St Lawrence River. The authors measured low concentrations of Hg in *Nuphar variegatum* compared to other aquatic plants and explained this result from the observations that rhizomes of some aquatic plants can change their rhizospheric oxidation (Jaynes and Carpenter 1986) and pH (Crowder 1991) which may alter the uptake of Hg. In addition, Fe and Mn oxides can scavenge Hg, making it less available to plants (Crowder 1991). At several sites, the remaining three species accumulated Hg over and above sediment concentrations. The highest concentrations of plant Hg and the highest bioconcentration factors came from sites with low organic matter and correspondingly low total sediment Hg. Given, *Nuphar variegatum* was determined an 'excluder' of Hg and the remaining three, 'accumulators' of Hg, none were deemed appropriate bioindicators of sediment Hg contamination.

Analysis of aquatic organisms has been used increasingly as a direct measure of the abundance and availability of metals in the environment, and has led to the adoption oft the bio-indicator concept (Langston and Spence, 1995). Biological availability of most metals can vary by several orders magnitude between clean sites and those that are most contaminated. Generally, for nonessential metals at least, the quantity and form of the element in water, sediment, or food determine the degree of bioaccumulation (Langston and Spence, 1995). The ability to reflect such gradients in contamination is clearly of overriding importance in the selection of indicator organisms (Langston and Spence, 1995).

The rationale for using biological indicators to assess contamination and impact, stresses there should be a reasonable correlation between metal contamination in some compartment of the environment (sediment/water/food) and concentrations in the tissue(s) of the selected plant or organism (Langston and Spence, 1995). Roots are better bioindicator organs than shoots for detecting metal contamination in sediments, particularly in running water (St-Cyr and Campbell, 2000).

Bagatto and Shorthouse (1999) outlined the need to identify appropriate bioindicator species and communities for studies of the accumulation of heavy metals in arthropods and plants from mining activities. These bioindicators will contribute to the assessment of soil quality and identification of the best route to the development of sustainable ecosystems over mine tailings.

In the pilot system three species of wetland rooted emergents *Typha latifolia, Phragmites australis,* and *Juncus effusus* were monitored for tissue accumulation of metals to examine the potential phytotoxic impacts of contamination on wetland species. Emergents were selected for analysis because metal accumulation is more influenced by soil type for these plants and the wetland sediments were expected to have higher concentrations of potentially bioavailable metals then the water column. This research investigated if these species are potential bioindicators for use in future work in assessing wetlands for rehabilitating tailings.

2.7.1.1 Metal-Tolerant Eco-Types

Genetic mutation, natural selection, or adaptation can result in evolution of tolerant ecotypes, i.e. local forms of a species that have become tolerant of contaminants (Adamus, 1992). This can alter competitive relationships and ultimately, community structure (Adamus, 1992). It has been documented to occur in communities of macrophytes (Christy and Sharitz, 1980; Adamus, 1992).

Some plant populations colonizing mine spoils have developed behavioral tolerances over time, as demonstrated by lower shoot tissue metal concentrations in tolerant populations (Kruckeberg and Wu 1992). Plant adaptation to increased metal levels can occur rapidly, sometimes within a few years of the disturbance (Tyler *et al.*, 1989; Stoughton and Marcus, 2000).

Bagatto and Shorthouse (1999) determined concentrations of Cu and Ni were significantly different between species of tailings grasses. They suggest the only plants able to survive in the early stages of tailings colonization are metal tolerant and are replaced by less tolerant (high accumulating) species as soil quality improves. Plants that dominate habitats with severe conditions are sometimes restricted to these habitats because they are poor competitors on less extreme sites (Barbour *et al.*, 1987; Stoughton and Marcus, 2000).

Some plants display striking techniques for sequestering metals. For example, previous experiments (McCabe and Otte, 1997; 2000) have indicated that *Glyceria fluitans* can grow in elevated zinc concentrations. Another striking example of this sequestering strategy is found in prokaryotes such as the thermophylic green alga, *Cyanidium caldarium* (Mason and Jenkins, 1995). This species is extremely tolerant of low pH environments and adapted strains have been shown to grow readily in acid mine drainage waters rich in metals Cu, Ni, and Cr (Wood and Wang, 1983). Grown under these conditions, *Cyanidium caldarium* can accumulate metals to the point at which they represent as much as 20% of the dry weight of the cell (Wood and Wang, 1983).

This work will assess wetland species for potential metal tolerance and assess the potential for using metal-tolerant ecotypes in the field-scale trials.

2.7.2 Bioavailability – Free-Metal Ion Concentration and Plants

Campbell *et al.* (1988) considered the bioavailability of metal species from sediments in terms of two types of organisms: Type A organisms living in intimate contact with the sediment, but not capable of ingesting it, and Type B organisms able to ingest sediment and take up metals from the particulate phase. The former may include benthic algae and rooted aquatic plants, the latter benthic invertebrates. Type A organisms are said to respond to free metal ions and other bioavailable metal forms in the interstitial water (Apte and Batley, 1995).

Jackson *et al.* (1991), working with data from a broad literature review, reported a significant positive relationship between metal concentrations in the above-ground tissues of aquatic plants (of all growth forms: emergent, submerged, with floating leaves, and free-floating plants) and the total metal concentrations in the underlying sediments but reported that both organic and Fe content as well as sediment pH and redox potentials contribute to ameliorate this relationship (Jackson *et al.*, 1991, 1993; St-Cyr and Campbell, 2000)

Given reported improvement of predictions when these variables are taken into consideration and the accumulated evidence that aquatic organisms tend to respond to variation in the free-metal ion concentrations (Campbell 1995), St-Cyr and Campbell (2000) chose to focus on these combined facts when considering metal geochemistry in predicting metal uptake by aquatic plants. These authors used sequential extractions and published geochemical models (Tessier *et al.*, 1992; 1993) to assess the bioavailability of sediment-bound metals (Cd, Pb, and Zn) using a rooted aquatic plant, *Vallisneria americana* Michx, as the biomonitor species.

However, while the authors determined *Valisneria* root Zn concentrations were significantly related to total metal concentrations in the underlying sediments, no relationships were obtained for the other metals studied including Cd and Pb. This inability to predict plant metal levels (particularly in the leaves) on the basis of total metal concentrations in the sediments contrasts with the results previously obtained by Jackson *et al.* (1991).

In the case of Zn, normalizing the readily extractable metal concentrations in the sediments with respect to the iron oxyhydroxide concentrations improves the relationship between this metal in *Vallisneria* roots and in sediments (St Cyr and Campbell, 2000). This role of sediment iron oxyhydroxides in controlling metal availability to various aquatic species has been reported by Campbell and Tessier

(1996). Some geochemical basis for this improved relationship exists, as under certain circumstances it can be considered as a surrogate measure for free Zn^{2+} in the interstitial water surrounding the root (St-Cyr and Campbell, 2000).

Ultimately, St-Cyr and Campbell determined that free metal ion concentrations $[M^{z+}]$ in the sediment interstitial water appeared to be a more mechanistically meaningful measure of metal availability to rooted aquatic plants. In general, metal concentrations in plant tissues correlated more closely with estimates of bioavailable sediment-bound metals ($[Cd^{2+}]$, $[Pb^{2+}]$, $[Zn^{2+}]$) than with total metal concentrations in sediments (St-Cyr and Campbell, 2000).

Given, in the pilot plant plant, metal concentrations and free-metal ion concentrations in wetland sediments were determined in subsequent years, it was not possible to investigate direct correlations between these data. However, the role of the free-metal ion concentrations in the sediment interstitial water of the pilot wetlands are considered in relation to the potential bioavailability of metals to plants in these ecosystems based on the work performed by Tessier *et al.*, (1993) and St Cyr and Campbell (2000).

2.7.3 Impact of Plants on Metal Mobility

Wetland plants provide an important conduit for gas exchange between the atmosphere and saturated, anaerobic soils. Perhaps the most important influence plants have on gaseous fluxes into anaerobic soils is oxygen transport from stems to the roots and the subsequent release of 0_2 into the rhizosphere (Emerson *et al.*, 1999; Armstrong *et al.*, 1994; and Brix 1993). Recently, microbial ecologists have become more cognizant of the potential for the rhizosphere of vascular wetland plants to provide an aerobic habitat in an otherwise anaerobic environment (Emerson *et al.*, 1999).

Plants can directly affect redox potential (Eh) and pH, two metal mobility regulating soil factors in waterlogged soils, through radial oxygen loss into adjacent sediments (Wright and Otte, 1999). Micro aerobic zones can be created around the surface of roots in the deep sediment, but the effect of such zones is difficult to predict. The most significant effect would likely be the oxidation conditions for formation of sulfates, potentially releasing sulfide bound metals (Gambrell, 1994; Wood and Shelley, 1999). This has been observed in salt marsh sediments where decreased pyrite accumulation occurred under roots compared with unvegetated soil, (Hsieh and Yang 1997; Wright and Otte, 1999). The process behind the formation of iron plaques on root surfaces also may be root-induced oxidation of the precipitated and immobile sulfides, thereby releasing precipitated metals followed by Fe precipitation around the root as oxyhydroxide (Otte 1991). Emerson *et al*., (1999) discovered substantial numbers of bacteria associated with the root Fe-plaque of different wetland plants. The finding of both acidophilic and neutrophilic Fe oxidizers in acidic root systems indicates that the rhizosphere may be a dynamic environment with respect to pH.

In recognition that vegetation can modify the local geochemistry of natural soils, Wright and Otte, (1999) conducted a study into the effects of wetland plants on the metal mobility in stagnant, waterlogged Zn-Pb mine tailings. They discovered *Typha latifolia* caused decreased pH and increased soluble Zn near (as far as 1cm) and below the roots, while *Glyceria fluitans* showed little effect on the sediment chemistry. The overall influence of plants on Eh, pH and metal mobility remained localised. *Typha latifolia* oxidised the rhizosphere and the surrounding sediment, raising Eh of the tailings possibly as far as 3cm. However, this oxidation did not decrease the porewater metal concentrations as expected. Overall, Fe and Zn mobility in stagnant Pb—Zn tailings was affected little by the presence of *Typha latifolia* and *Glyceria fluitans* beyond a narrow halo surrounding the roots. The authors advocate direct study of vegetated tailings soil is necessary for valid conclusions about metal mobility conditions (Wright and Otte, 1999).

In the pilot plant penetration by roots into tailings may enhance water and oxygen penetration resulting in acidity and increased metal mobility to higher levels. The action of plants on metal mobility in the pilot plant may be important particularly at the peat/tailings interface.

The above ecological, hydrological, physico-chemical, sediment and biotic indicators were investigated in the pilot plant. The results of these investigations are outlined in Chapters Four, Five, Six, and Seven respectively.

CHAPTER THREE

MATERIALS AND METHODS

3.1 DESIGN AND CONSTRUCTION OF PILOT WETLAND PLANT

3.1.1 Closure Plan for Lisheen's Tailings Management Facility

Upon closure Lisheen Mine will have generated 6.63 million tonnes of pyritic tailings that will be deposited in their Tailings Management Facility (TMF) which will have a final surface area of approximately 64 ha with embankment walls measuring 15.5 m high (see Figure 1.3).

Lisheen's closure plan (Minorco Lisheen, 1995b) for the TMF calls for the deposition of 0.2 m layers of organic-enriched crushed limestone over the tailings using the existing tailings distribution system. The water over the tailings will be drawn down and the cover handplanted with reed rhizomes and other wetland vegetation. Slow release fertilizer may also be used. After planting and initial growth, groundwater is to be pumped back into the impoundment for some months after which water levels are allowed to rise naturally by rainwater input. The height of the water level will be adjusted to allow optimum growth of the wetland plants. Water levels will be managed to allow a mean maximum depth of 0.5-0.7 m above the flat tailings surface. The plan calls for spring/summer drawdowns to be carried out for two subsequent years to encourage reed spread and further plant establishment from seed. From the fourth year onwards a natural water fluctuation will be allowed to establish, and the response of the vegetation monitored (Minorco Lisheen, 1995b).

It is anticipated that the limestone layer, water cover and organic matter production by the vegetation will inhibit excessive pyrite oxidation in the tailings and prevent the generation of acid mine drainage (AMD) (Minorco Lisheen, 1995b). The closure plan also calls for the construction of secondary wetlands to treat any overflow from the TMF, if necessary.

The ultimate aim of the closure plan is that the TMF will remain as a landscaped artificial dam containing an ecologically sustainable reedmarsh similar to the margins of many Irish calcareous marl based lakes. The build up of organic matter over time will reduce further the depth of water cover in the impoundment, eventually leading to a bog-like system or wet woodland.

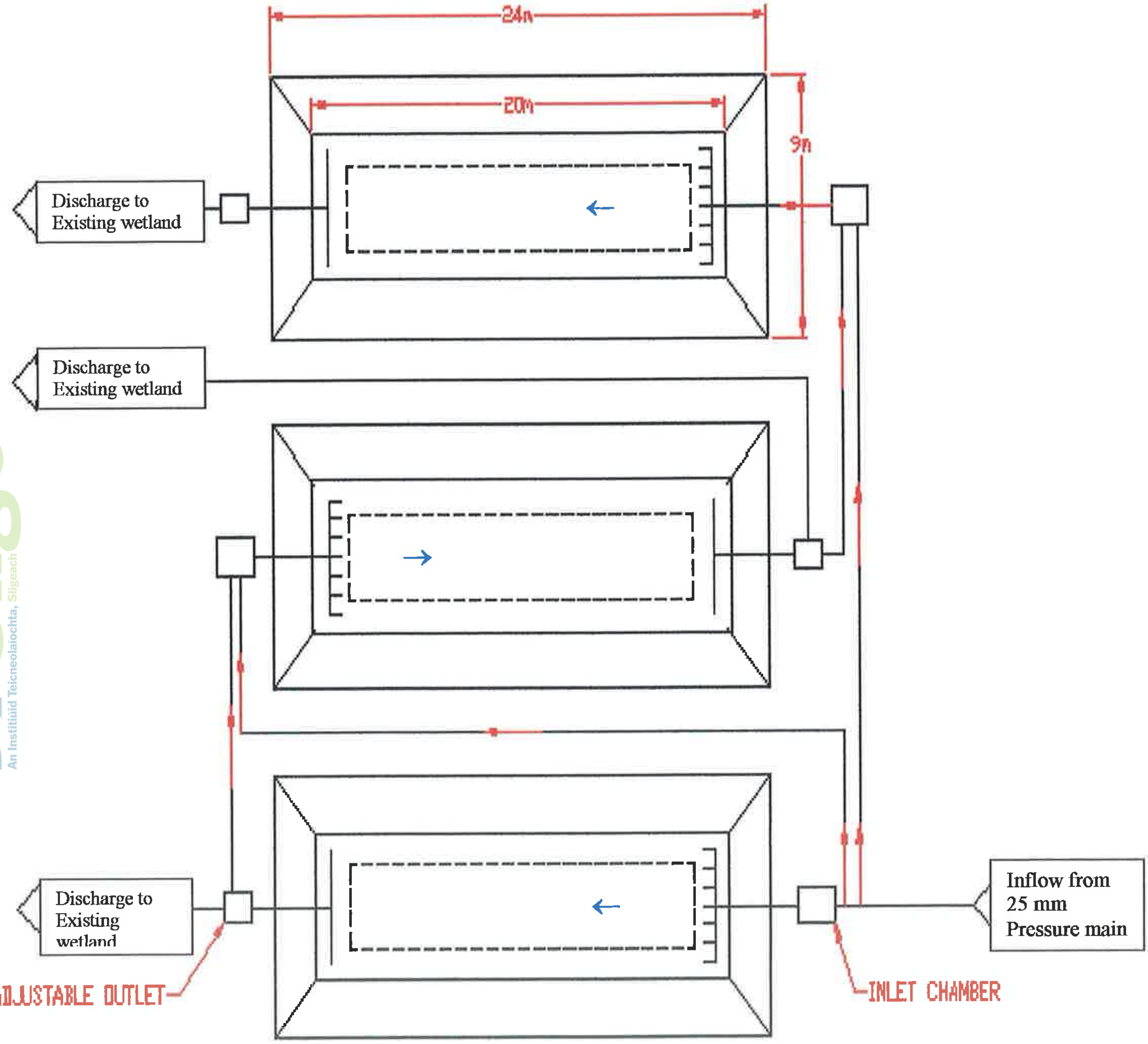
3.1.2 Construction of Pilot-Scale Wetland System - Design Overview

The potential for a wetland cover to be successfully established on pyritic Zn-Pb tailings is unknown; therefore, it is essential to conduct research trials over an extended time period. A pilot-scale research facility was constructed at the Institute of Technology in Sligo to commence these trials. The results from this facility are providing essential baseline data for the scaled-up field trials to be undertaken at Lisheen Mine. Figure 3.1 illustrates a schematic of the wetland pilot plant in Sligo. The approved Design Plan for the system, with cross sections and details, is attached in Appendix A. The research plant received full planning permission from Sligo Corporation and a discharge license from Sligo County Council.

Three wetland cells were constructed for the pilot-scale system. The first two cells were designed to model Lisheen's TMF (the TMF wetland) and proposed secondary treatment wetlands. The third was anticipated to act as an experimental control. The second cell was originally intended to evaluate the use of an aerobic wetland to treat drainage from the TMF wetland through its potential to remove various contaminants from mine drainage including sulphate, zinc, lead, and other metals. However, given the water quality discharging from the TMF wetland throughout the course of this experiment was within regulatory guidelines it was not necessary for the second cell to act as a treatment wetland and it was used as the Reference/Control wetland.

Many factors affect the ability of wetlands to treat AMD, including hydrology, metal and alkalinity concentrations and various wetland characteristics such as water depth, area, hydraulics, vegetative and microbial species and extent, and substrate. Because of the interrelationships among these many factors and their effects on wetlands treatment efficiencies, it is difficult to develop definitive treatment area design guidelines (Brodie, 1993). Therefore pilot-plant construction is essential for specific data collection.

Fig. 3.1 Schematic of wetland pilot plant constructed at the Institute of Technology, Sligo.

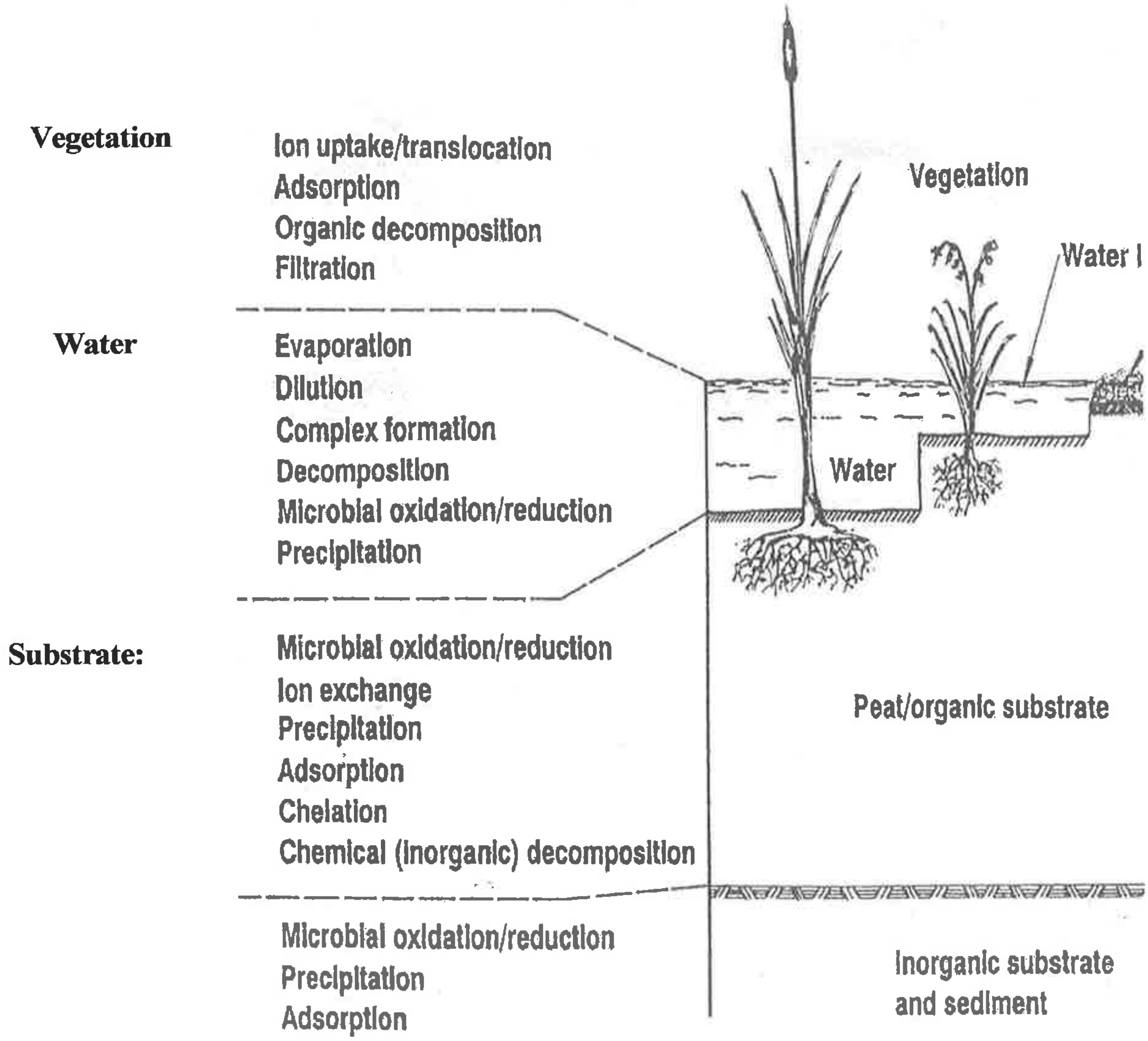


The current practice for the design of wetlands for the treatment of AMD is based on an empirical evaluation of the performance of successfully operating systems. Therefore, the available literature was reviewed in detail to make definitive judgements on the major design parameters for the pilot-scale wetland cells. Specific parameters have been selected from the literature based on good engineering practice as determined during pilot plant studies and larger field trials for wetlands treating AMD (Perry and Kleinmann, 1991; Brodie, 1991; Brodie *et al*, 1993; Reed *et al.*, 1995). Additional research, design and construction guidelines, and case studies for acid mine drainage wetland treatment systems are presented in Witthar (1993), Gross et al. (1993), Davison (1993), Hedin and Nairn (1993), Faulkner and Richardson (1990), Tarutis and Unz (1990), and Lan et al. (1990).

Because the Free Water Surface (FWS) wetland is widely used as an inexpensive method of treating AMD in the United States (Mitsch, 1992), this type of wetland was constructed in Sligo. A FWS aerobic wetland typically consists of basins or channels, with a natural or constructed subsurface barrier to prevent seepage, a layer of soil or another suitable medium to support the emergent wetland vegetation, and water at a relatively shallow depth flowing over the soil surface (see Design Plan in Appendx A). In FWS systems, oxygen for oxidation of mine wastes is supplied from the root zone of the emergent vegetation and from floating algae (Reed *et al.*, 1995). Floating algae remove carbon dioxide from the water column and thereby raise the pH. The net effect of the pH rise and interaction of metals from mine waste is physical-chemical precipitation of metals in the soil and mud of the wetland (Reed *et al.*, 1995).

The main metal removal processes in wetlands are facilitated by the vegetative, water column, and substrate components of the system. These processes are outlined in Figure 3.2. Vegetative processes include direct filtration of particulate matter, adsorption and cation exchange, direct uptake of heavy metals, providing organic material and attachment sites for bacteria, and oxygenation of the substrate (Hammer and Bastion, 1989; Kleinmann, 1990; Reed *et al.*, 1995). The main processes facilitating metal removal by water include dilution, evaporation, complex formation, precipitation, neutralisation and microbially-catalysed oxidation and hydrolysis, (Reed *et al.*, 1995). The main metal-removing processes in the substrate include adsorption and cation

Figure 3.2 Processes of metal removal that may occur in a wetland (Kleinmann and Girts, 1987).



exchange, complex formation, physical filtration, providing physical support for plants, and providing attachment surfaces for microbial populations, including sulphate-reducing bacteria and metal-oxidising bacteria which precipitate metals as sulphides and oxides (Vile and Wieder, 1992; Reed *et al.*, 1995).

3.1.2.1 General Construction of Wetland Cells

The pilot-scale research plant was constructed on-campus at the Institute of Technology in Sligo on a fenced-off site covering approximately 0.2 hectares. The site was surrounded on two sides by naturally-occurring wetlands with well-established stands of *Typha latifolia* and *Phragmites australis*.

The construction of the wetland system included excavation of three trapazoidal channels, placement of a high density plastic liner, placement of the organic substrate, establishment of the wetland vegetation, and placement of the inlet and outlet works.

The native soil at the bottom of each cell was compacted to ensure adequate support for the cell liner and substrate material. The dikes and berms for the wetland cells were constructed in the same manner as those for lagoons and similar water impoundments. To ensure long-term cell stability dikes were sloped no steeper than 2:1 (Brodie, 1993).

The wetland cells were excavated at appropriate elevations to facilitate gravity flow through the system (see Section A-A[1] on Design Plan in Appendix A). Figures 3.3 and 3.4 illustrate the excavation and establishment of the wetland channels.

The following design parameters were selected based on the specific requirements of this research.

3.1.2.2 Liner

A 2 mm high quality Ethylene-propylene rubber (EPDM) liner was used to prevent seepage and protect groundwater. The polymer EPDM is an elastomer obtained by means of copolymerization of ethylene, propylene and a nonconjugated diene

Fig. 3.3 Excavation of the TMF Wetland and placement of protective sand layer over the walls and base of the cell.

Fig. 3.4 Placement of outflow pipe and outlet controls in wetland cell to facilitate gravity flow.

monomer, giving a polymer composed of saturated linear macromolecules with a paraffinic structure. It is this crosslinked molecular structure which gives EPDM the important property of negligible ageing over long periods of time despite exposure to the atmosphere, sunlight, UV-radiation, chemical pollution, water, and high-low temperatures. The strength and elasticity remains without shrinkage, melting, hardening or cracking, and the membrane remains flexible even with large temperature variations thus modelling the Lisheen liner. The EPDM liner was placed between twin layers of plastic construction sheeting for protection on the completed sand bottom of each cell. A smooth surface was provided within each cell using a sand layer and a plastic construction liner, the EPDM liner, which was prefabricated to the exact size, was spread over the cell, filled with water and anchored at the edges. Figures 3.5 and 3.6 illustrate the placement of the EPDM liner.

3.1.2.3 Aspect Ratio

The aspect ratio (L:W) selected for a wetland strongly influences the hydraulic regime and the resistance to flow in the system (Reed et. al., 1995). Early studies in the United States emphasised the importance of a long length-to-width ratio in constructed wetlands to insure plug flow hydraulics (Miller, 1985). A major problem with this approach is that resistance to flow increases as the length of the flow path increases; consequently aspect ratios from less than 1:1 up to about 4:1 are acceptable (Reed et. al., 1995).

An aspect ratio of 4:1 was selected for the pilot wetland cells which consist of three trapezoidal channels 24m long x 9m wide and approximately 1.5m deep. Each cell bottom measures 18m x 3m; while the approximate surface area of wetland measures 20m x 5m (100m^2) (see Design Plan in Appendix A).

3.1.2.4 Substrate Material

<u>TMF Wetland</u>

Given Lisheen Mine had not commenced production when the pilot plant was under construction, it was necessary to obtain tailings that were geochemically similar to place

Fig. 3.5 Laying plastic construction sheeting as a protective layer for the EPDM liner.

Fig. 3.6 Sealing the EPDM liner around outlet pipe to prevent seepage.

in the TMF wetland cell. Minorco Lisheen's (1995c) *Planning Study of the Tailings Management Facility Volume I - Technical Report* and associated *Appendices*, in addition to Lisheen's (1995a) *Environmental Impact Statement - Supporting Technical Reports - Closure Plan*, were reviewed to obtain information on the geochemistry of the Lisheen tailings and the predicted tailings porewater quality after mine closure. This information was used to ensure the tailings used in the pilot system adequately represented those to be produced by Lisheen.

According to these reports, the Lisheen orebody is underlain by Lower Carboniferous Limestones. The Lisheen deposit occurs as a series of stratiform sulphide lenses at the base of regionally dolomotised Waulsortian limestones in an oolite within the Ballysteen Formation, adjacent to major structures. The mineral assemblage consists of pyrite (FeS_2), marcasite (FeS_2), sphalerite (ZnS) and galena (PbS) with minor chalcopyrite, tennantite, silver, arsenopyrite, gersdorffite and various lead sulphosalt minerals. Zinc mineralization (sphalerite ZnS) is primarily associated with pyrite while Pb mineralization (galena PbS) is associated with marcasite. Lisheen's planning study predicted the geochemistry of the tailings to be generated by the mine and estimates 50 % will have "high pyrite" content with net acid generation potential while the remaining 50 % will be marginally acid consuming. The average annual geochemical composition of Lisheen's tailings in 2002 was 48 % pyrite, 22.2 % Fe, 0.46 % Pb and 1.83 % Zn (personal communication with Conor Spollen at Lisheen Mine). The tailings porewater and seepage water quality after mine closure was estimated in Lisheen's planning study to have a pH of between 7.5 and 8.5, a sulphate concentration of 430 mg/l, and Pb and Zn concentrations of 0.09 mg/l and 0.72 mg/l respectively.

Tailings produced from Zn-Pb mining activities at Silvermines were deposited in the Gortmore tailings impoundment between 1966 and 1982 (Arthurs, 1994). This tailings dam is located a few miles from Silvermines village in the Kilmastulla River valley in County Tipperary (see Figure 1.4) and covers approximately 59.3 ha (Dept. of ACRD, 2000) with 8.2 m high walls (Arthurs, 1994). At Silvermines Zn-Pb mineralization occurs as syngenetic stratiform orebodies at the base of the Waulsortian carbonates; as a fault bounded epigenetic stratabound orebodies in Basal Carboniferous secondary massive dolomites and as tectonically controlled vein or breccia zones in the Upper Old Red Sandstones (Grennan, 1973). The estimated mineral composition of

Silvermines tailings is 60 % to 65 % dolomite and calcite, 30 % to 35 % pyrite, < 4 % sphalerite, galena, Pb, Zn, Ag and Cd sulphosalts, and < 5 % silica, barite and clays (Arthurs, 1994). The Fe concentration of Silvermines tailings ranges from 1.44 % to 1.84 %, the Pb concentration from 1.16 to 1.46 % and the Zn concentration from 0.7 to 1.24 % (as outlined in detail in Chapter Five). These tailings have the potential to be acid producing (Arthurs, 1994).

Silvermines tailings are similar geochemically to those that will be produced at Lisheen due to their high pyrite content, high concentrations of Fe, Pb and Zn and their potential for producing acid. Therefore, approximately 20 m^3 (approximately 40 tonnes) of these tailings were excavated from Silvermines tailings dam by dredging an existing channel on the surface of the tailings. These tailings were transported to Sligo in covered trucks and placed to a depth of 0.20 m covering 100 m^2 in the TMF wetland cell above the EDPM liner. Figure 3.7 illustrates the placement of these tailings in the TMF wetland cell of the pilot wetland plant at Sligo. The selected volume and depth parameters are similar to those selected by Sistani *et al.* (1999) who constructed nine wetland cells, each with a surface area of 112 m^2, to investigate the growth of wetlands on coal mine spoil. Each of these cells received approximately 27 tonnes of mine spoil or topsoil which was evenly spread in a 0.15 m layer on the cell bottom. Also, several investigators have observed that pyrite oxidation is limited to a shallow surface zone, suggesting that the rate of AMD formation may be limited by diffusion of atmospheric oxygen into coal mine spoil (Erickson *et al.*, 1982). For example Erickson *et al.* (1982) cite a study performed by Good *et al.* (1970) who found a pyrite oxidation zone 0.25 m thick on the surface of a coal refuse pile.

A layer of 0.2 m of Bord na Mona *sphagnum imbricatum* peat was then spread over the tailings in the TMF cell and saturated. This peat was harvested from a raised bog, 3 m to 6 m deep, in Counties Offaly and Kildare. The pH of the peat was within the range 3.8 to 4.3, its conductivity measured < 200 mS/m, and it had an organic matter content of > 95 % (personal communication with Pat Byrne, Quality Manager at Bord na Mona). The limestone layer proposed by Lisheen was purposely excluded to determine the necessity of such a step. Given the availability of peat at Lisheen mine, it was considered appropriate to use this material as organic cover. Figure 3.8 illustrates the peat layer covering the tailings in the TMF wetland.

Fig. 3.7 TMF Wetland with pyritic tailings in place.

Fig. 3.8 Peat cover over the tailings in the TMF Wetland in March, 1998 with initial planting of wetland macrophytes.

An important part of the pilot-scale investigation was to investigate the potential for modifying the closure plan in an environmentally sound fashion. Therefore, the pilot system investigated the implications of eliminating elements of the plan that may be inefficient and irrelevant in terms of environmental protection. The objective of the limestone cover layer is to reduce oxygen infiltration into the pyritic tailings, and to buffer any acid generated by pyrite oxidation. This research hypothsises that the peat will adequately perform this function. Eliminating the limestone layer will save quarrying approximately 128,000 m^3 of limestone for Lisheen's TMF in addition to eliminating the expenditure of energy necessary to crush and mill the limestone.

Reference/Control Wetland

The second cell models the proposed secondary treatment wetland at Lisheen designed to treat run-off from the TMF if necessary. Therefore, it was constructed as a conventional treatment wetland. Most constructed wetlands include 0.15-0.45 m of a composted organic substrate in which the emergent plants can root (U.S. Bureau of Mines, 1994). The substrate material in the treatment pilot cells consists of approximately 0.4 m of wetland soil mixed with slow release fertiliser to supplement its organic content. This wetland was used as the reference wetland. Measurements made in the potentially stressed TMF wetland were compared to this reference wetland to assess ecosystem health in the former.

3.1.2.5 Vegetation/Planting

Bands of different wetland species were planted identically in each of the three wetland cells in line with observations of wetland plant patterns made at Silvermines wetlands (Silvermines wetlands are discussed below in Section 3.3.4). These plants were taken from the natural wetland areas at the college surrounding the research facility. In addition, a small number of *Juncus effusus* plants were taken from an abandoned mine at Ballisodare, Co. Sligo where wetland plants have colonised mine drainage seeps. The planting layout consisted of 1.5 m of *Juncus effusus* transplanted from Ballisodare, and, 7.5 m of *Typha latifolia*, 7.5 m of *Phragmites australis*, and 3.5 m of *Juncus effusus* transplanted from natural wetlands.

Rushes and rhizomes were planted by hand along rows. Each row was 0.75 m apart. Each plant was placed 0.75 m to 1.0 m apart along the row. Plants in subsequent rows were staggered. The planting density was approximately 112 plants per 100 m^2. The use of individual root/rhizome material was used. Other wetland species introduced with the root ball of these plants also colonised the cells.

Inorganic fertilisers are particularly valuable to assist rapid establishment and therefore as proposed in the closure plan, a quantity of slow-release fertilizer was applied near the rhizome or shoot planting site. In spring 1998, 8 Kg of a slow release fertilizer (14.0 N-5.7 P-10.8 K) was spread over the surface area (100 m^2) of the TMF wetland. This is equivalent to 800 kg/ha and similar to fertilizer application rates recommended by Bradshaw and Chadwick (1980) for revegetation of mine tailings. At the same time 4 Kg of the same fertiliser was spread over 100 m^2 of the Control (equivalent to 400 kg/ha). Less fertiliser was used in the Control given this was seeded with natural wetland soils which have a higher nutrient content than the peat substrate. In spring 1999, 4 kg and 2 kg of slow release fertiliser was spread in the TMF and Control wetlands respectively (equivalent to 400 kg/ha and 200 kg/ha respectively).

3.1.2.6 Hydraulics

Critical to the design of the wetland cells is ensuring that the wetland operates within hydraulic thresholds or limits. The performance of any constructed wetland system is dependant upon the system hydrology in addition to other factors. Precipitation, infiltration, evapotranspiration, hydraulic loading rate, and water depth can all effect the performance of the system not only by altering the residence time, but also by either concentrating or diluting the inflow.

Inlet Structures/Outlet Structures

The inlet distribution system for each wetland cell consisted of perforated piping (3 m long) in rock-lined trenches perpendicular to the flow direction. Flow guages were installed on all of the inlet pipes to control flow through the system. The outlet device for each cell consisted of an effluent manifold laid in a rock-filled trench leading into an outlet pipe with an adjustable level to control the water depth in each cell (see Design Plan for details). The effluent manifold for the system is a 150 mm perforated plastic pipe leading into a 100 mm adjustable outlet pipe in an outlet chamber. This chamber facilitated outlet flow control and sampling.

The cells were designed to operate in parallel or in series if it was necessary to investigate the impact of successive treatments on mine drainage. Drainage flows from one cell to another through plastic piping. During the course of this experiment the TMF wetland and the Control operated independently, given the effluent from the TMF wetland did not require secondary treatment.

Hydraulic Loading

The entire pilot plant was fed by mains water supplied under pressure from I.T. Sligo facilities and by rainwater. Inflows to the wetland cells were monitored continuously by means of four flow guages. The first was positioned on the mains line from the college and gave a reading of the entire flow entering the system. The second, third and fourth were positioned on the influent pipes to each wetland cell after the flow had been split to obtain individual flows for each wetland. These guages incorporated valves to adjust the inflow to each wetland if required.

The minimum design flow for each cell was 5 m^3/d. This corresponds to a surface hydraulic loading on the system of 0.05 $m^3/day/m^2$ or 500 m^3/ha -day. This also corresponds to a hydraulic loading of 0.05 m/day as recommended by Mitsch (1992) for wetlands treating AMD. Sikora, Behrends and Brodie (1995) outline a range of 0.009 to 0.27 m/day for the hydraulic loading of wetland systems treating AMD. The cells were designed to carry the hydraulic load with an additional 1.0 m freeboard to accommodate storm events.

Water Depth

Flow through the wetland cells must overcome the frictional resistance imposed by the vegetation and litter layer in the FWS wetland. The energy to overcome this resistance was provided by the head differential between the inlet and outlet of the wetland. This head was provided in each cell by sloping the bottom of the wetland (1 percent slope) and using an adjustable outlet control to set whatever depth of water was required.

The water depth in a FWS wetland can range from a few centimetres to 0.8 m or more, depending on the purpose of the wetland (Reed *et al.*, 1995). In line with the hydraulic loading of this system, the water depth was set initially at 0.05 m in each wetland cell. Water depth is critical to ensure adequate oxygen distribution within the wetland system.

3.1.2.7 Final Discharge of Wetland Drainage

The influent drainage to the wetlands was dispersed through the pilot-scale wetland cells prior to being discharged into an existing well-established body of wetlands on site. The drainage from the wetland on site discharges to an existing tidal stream and ultimately, under licence, into Sligo Harbour.

3.1.2.8 Start Up and Acclimation Period

The first stage of the pilot-scale study was devoted to construction of the experimental facilities and the establishment of the wetland vegetation. There was a start up and acclimation period of 16 months. This was to ensure adequate plant growth and colonisation prior to the extensive ecological sampling event in summer 1999.

Figures 3.9 through 3.12 illustrate the growth rate in wetland plants in the TMF wetland between June and September, 1998. Figures 3.13 and 3.14 illustrate plants rooting directly into the tailings substrate in 1998. Figures 3.15 and 3.16 illustrate the growth rate in wetland plants in the Control between June and September, 1998. The ecological data associated with plant growth in these wetlands are presented in Chapter Four.

Fig. 3.9 *Juncus effuses* and *Typha latifolia* growth in TMF Wetland three months after initial planting.

Fig. 3.10 *Juncus effuses* and *Typha latifolia* growth in TMF Wetland six months after initial planting.

Fig. 3.11 Sparse cover growth in *Phragmites australis* region of TMF Wetland three months after initial planting.

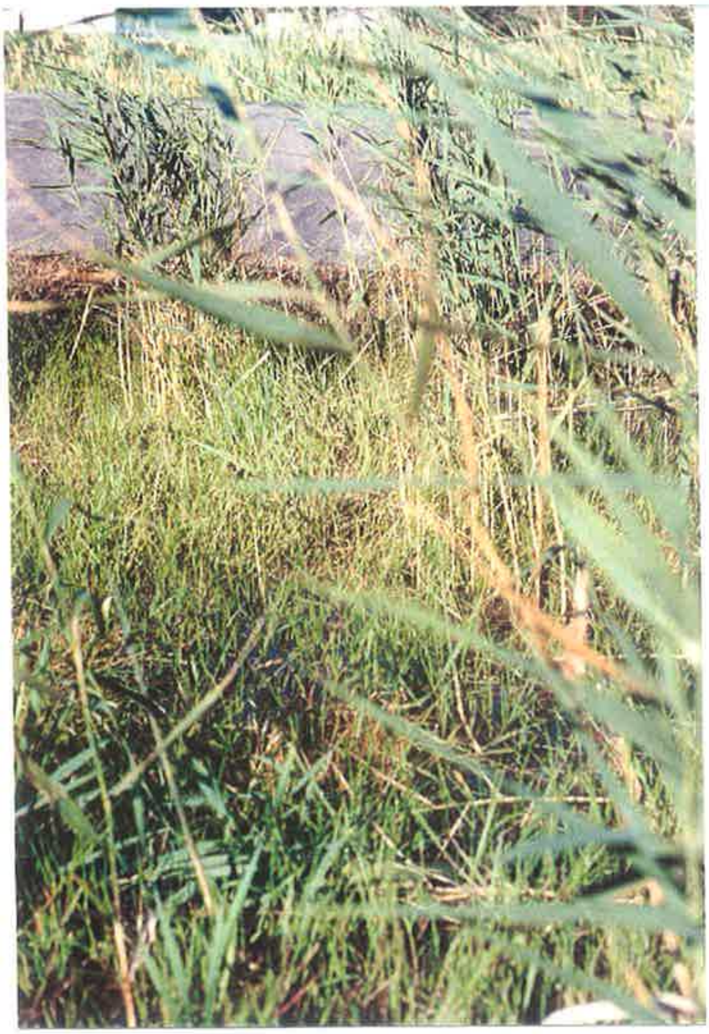


Fig. 3.12
Enhanced growth of *Phragmites australis* and grass cover in TMF Wetland six months after initial planting.

Fig. 3.13 Exposed mine tailings in TMF Wetland five months after planting.

Figure 3.14
New shoots of *Typha latifolia* growing in exposed tailings in TMF Wetland, six months after initial planting.

Fig. 3.15 Growth of wetland cover in Control Wetland three months after initial planting.

Fig. 3.16 Growth of wetland cover in Control Wetland five months after initial planting.

3.2 ECOLOGICAL SAMPLING AND ANALYSIS

The main field ecology study was conducted in July, August, and September 1999. In the TMF and Control wetlands respectively, thirty and twenty-five 1 m^2 quadrats were randomly selected for identification/enumeration of wetland biota, community composition, diversity analysis, and growth studies for productivity and biomass. Every plant occurring in each quadrat was counted and identified. Flora identification was carried out *in situ* and verified on return to the laboratory with the aid of reference to the identification keys in 'New Flora of the British Isles' by Stace (1995) published by Cambridge University Press.

Vegetative data including stem length, longest leaf length, maximum width of longest leaf and basal width were noted in each quadrat for *Typha latifolia, Phragmites australis*, and *Juncus effusus* to determine ecotypic variation in plants, within and between wetland cells (Cox, 1990). This facilitated a comparative analysis between wetland communities. Similarily, reproductive data also was listed including no. of flowering stalks, height of tallest flowering stalk, length of longest inflorescense and inflorescense thickness to determine ecotypic variation in plants within and between wetland cells (Cox, 1990).

Raw data including the diameter and area covered by each species were noted *in-situ* and modified to determine densities, frequencies, coverage and importance values for each wetland species. These data were used to generate Relative Abundance Curves, Dominance-Density Curves and Species Importance Curves for both wetlands as outlined in Brower, Zar and von Ende (1990). This facilitated a comparative analysis of the physiognomic aspects of the vegetation between the wetland cells.

Margalef's and Simpson's diversity indices, and the Shannon Diversity Index were calculated for each wetland as outlined in Brower, Zar and von Ende (1990). Diversity indices are based upon the concept that the structure of normal communities may be changed by perturbations in the environment and the degree of change in community structure may be used to assess the intensity of the environmental stress. Unpolluted environments are generally characterised by a large number of species, with no single species making up the majority of the community. Maximum diversity is obtained when a large number of species occur in relatively low numbers in a community (Brower, Zar and von Ende, 1990). Calculating diversity indices facilitated a comparison of differences in community structure between wetlands.

The following indices of community similarity for both wetlands were calculated: Jacard Coefficient, Sorensen Coefficient, Proportional Similarity, Bray and Curtis Index, Morisita's Index, and Horn's Index as outlined in Brower, Zar and von Ende (1990). These indices were used to establish the degree of community similarity between wetlands.

3.2.1 Biomass Determinations

Typha latifolia and *Phragmites australis* were separated into root, rhizome and stem material, whereas, *Juncus effusus* was separated into root and aerial stem tissues. Plant material from the TMF wetland was chopped and washed in a 10 % nitric acid wash to remove any soil or tailings material from plants and then rinsed in ultra pure water. Plant material from the Control was washed in ultra pure water to remove gross soil contamination (Levy *et al.*, 1992; Jackson *et al.*, 1993). Plant material was weighed and dried for 24 hours at a temperature of 105 °C for biomass determinations as outlined in Brower, Zar and Von Ende (1990).

3.3 PHYSICO-CHEMICAL, SEDIMENT AND BIOTIC SAMPLING METHODOLOGY

It was essential to establish a statistically credible sampling methodology to collect representational data from the wetland cells. Given heavy metals are the chief contaminants of concern, Data Quality Objectives (DQOs) were prepared in a structured way to plan data collection and analysis efforts for metals determinations. This approach was developed by the U.S.EPA to help define specific questions that an environmental project is intended to answer, identify the decisions that will be made when using the resulting data, and define the allowable risk of decision errors in specific and quantifiable terms (Keith, 1996).

The number of required samples was calculated on the basis of DQOs using a series of Mircosoft Windows-based computer programmes called *DQO-PRO* developed by U.S.EPA and outlined in detail in the American Chemical Society's 'Principles of Environmental Sampling' (Keith, 1996). These programmes calculate how many environmental and Quality Control (QC) samples are needed to analyse for specific objectives (e.g., the number of samples needed for various methods based on standard deviations or relative standard deviations of the sampling and analysis measurement systems used).

The DQO selected for this research was to obtain sufficient samples such that the average concentration of an analyte falls within a tolerable error of +/- 10% with 95% confidence. The standard deviations for ICP-AES (the analytical method used for metals analysis in this research) for the determination of Cd, Fe, Mn, Pb and Zn using U.S.EPA Method 6010 are 16 %, 15 %, 6.7 %, 32 % and 45 % respectively (Waste Policy Institute, 1998). Using the *DQO-PRO* programs and taking the standard deviation for Zn analysis on ICP-AES (given this has the highest S.D. value) the average concentration calculated from 81 samples falls within a tolerable error of +/- 10% with 95% confidence. The same statistical confidence would be obtained with 13 samples for Cd, 12 for Fe, 10 for Mn and 42 for Pb. Given Zn is an analyte of primary concern in this research, the target sample size selected was 90.

Physico-chemical, sediment and biotic sampling was conducted during the 1999 field ecology work. Seasonal physico-chemical sampling was conducted throughout 1999 and 2000 to determine temporal variations in water chemistry. Additional extensive sediment sampling was conducted in summer, 2000 to determine temporal variations in total metals in sediments and to determine metal speciation through sequential extractions. The specifics of these sampling protocols are outlined below.

3.3.1 Numbers of Samples taken in Summer 1999 Sampling Event

3.3.1.1 Water Matrix

- D.O., conductivity, pH, temperature and water depth measurements were taken in triplicate in each quadrat of both cells during field ecology work.

- Triplicate water samples were taken for Cd, Fe, Mn, Pb and Zn determinations in each quadrat of both cells during field ecology work. Overall, 165 water samples from Year 1 were analysed for total metals concentrations. Sample collection, preservation, and techniques for metals analysis are outlined for all matrices in Section 3.5.

3.3.1.2 Sediment Matrix

- Triplicate sediment cores were taken per quadrant to investigate the thickness of substrate in each wetland, particularly the peat layer covering the tailings in the TMF wetland.

- Total Cd, Fe, Mn, Pb and Zn concentrations were determined in 30 and 25 cores in the TMF and Control wetland respectively.

- Organic matter determinations were made for 14 cores in each wetland.

3.3.1.3 Biotic Matrix

- Triplicate plant samples of each dominant macrophyte species (*Typha latifolia, Phragmites australis, Juncus effusus*) were taken in each quadrat of both wetlands for Cd, Fe, Mn, Pb and Zn determinations in root, rhizome and stem tissues. In some quadrats fewer samples were taken due to the lack of plant material. Overall, a total of 409 plant samples from both wetlands were analysed for metals.

3.3.2 Numbers of Samples taken for Seasonal Sampling throughout 1999 and 2000

3.3.2.1 Water Matrix

- Between May 1999 and June 2000 weekly measurements of hydraulic flow rates and water depth at the top, middle and end of both wetland cells were measured in addition to obtaining daily rainfall records from Sligo Airport.

- Between May 1999 and June 2000 weekly measurements of D.O., conductivity, pH, temperature and water depth were taken in triplicate at the top, middle and end of both wetlands.

- Weekly measurements of alkalinity, acidity and hardness were undertaken as part of a separate project in spring 2000[1]. Duplicate samples were analysed from the top, middle and end of both wetlands. Overall, 18 samples were analysed for each parameter.

- Sulphate concentrations were taken in Cells 1 and 2 in summer 1999 and 2000. Overall, 70 samples were analysed in 1999 and 42 in 2000.

- Between May 1999 and June 2000 monthly measurements of Cd, Fe, Mn, Pb and Zn concentrations in flows entering and exiting each wetland, and in the top, middle and end of both wetlands were taken in duplicate in both wetlands. Overall, 160 samples were analysed for total metals.

3.3.3 Numbers of Sediment Samples taken in Summer 2000

- Duplicate sediment cores were taken at 5 equidistant locations across the width of the TMF wetland at the 6 m, 12 m and 18 m locations along the length of the wetland in summer 2000 for total metals and metal extraction determinations. Duplicate sediment cores were taken at 5 equidistant locations across the width of the Control wetland at the 10 m wetland centre line. Overall, 87 samples were analysed for total Cd, Fe, Mn, Pb and Zn determinations and 242 samples were analysed for extractable metals, in the substrates of the TMF and Control wetlands, the peat and tailings matrices. Sample collection, preparation, and analysis techniques for metals extractions are outlined in Section 3.5.

[1] Sampling and analysis for alkalinity, acidity and hardness was undertaken as part of a separate project by Sarah Dolan from the Institute of Technology, Sligo.

3.3.4 Sampling Silvermines Wetland in Summer 2000

The Gortmore tailings dam in Silvermines remained unrehabilitated after mine closure in 1982 until a major dust blow in 1985 precipitated the commencement of work on the surface of the dam to establish a self-sustaining grass over (Dept. of AFRD, 2000). In 1999, it was estimated that somewhere between 10 % and 25 % of the surface of this dam had poor or no grass cover, with most of the embankment wall having no cover (Dept. AFRD, 2000). Grass failure may be due to a number of factors that include the generation of acid at the surface due to the high pyrite content of some of the tailings, salinity, nutrient deficiencies, surface water-logging and water shortage in dry periods (Dept. AFRD, 2000). This tailings dam has been the subject of a major interagency review to examine potential remediation options (Dept. AFRD, 2000) to prevent the impact of acid-generation on the rehabilitated surface.

During the course of this research work prior to 1999, five separate wetlands (W1 to W5) were identified adjacent to the Gortmore tailings impoundment at Silvermines. Drainage from the tailings dam flows through these prior to its final discharge into the Kilmastulla River. Therefore, an investigation was initiated to examine if these wetlands are acting as treatment wetlands. Figure 3.17 is a schematic outlining the location of these wetlands around the wall of the tailings dam.

The largest and most well defined of these wetlands is wetland 1 (W1), which covers approximately 3,100 m^2, and consequently attention was focused on a detailed examination of the water and sediment quality of this wetland. Wetlands 2, 3 and 4 (W2, W3, and W4) are deep sedimentation ponds. These four wetlands were initially excavated by the mining company in the 1970s as sedimentation ponds. Wetland 5 (W5) is comprised of a channel leading from W4 with marsh-like wetlands extending from either side. This wetland is located around the base of the tailings wall for approximately 450 m. Figures 3.18 and 3.19 illustrate drainage high in Fe and other metals entering W1 and finally discharging into the Kilmastulla River after travelling through W2, W3, and W4.

Figures 3.20 and 3.21 illustrate wetland 1 in late spring, 1997 and mid summer, 1998. The banding of wetland vegetation with alternating water depths is obvious. The

Fig. 3.17 Locations of Wetlands 1, 2, 3, 4 and 5 around the Gortmore tailings dam at Silvermines.

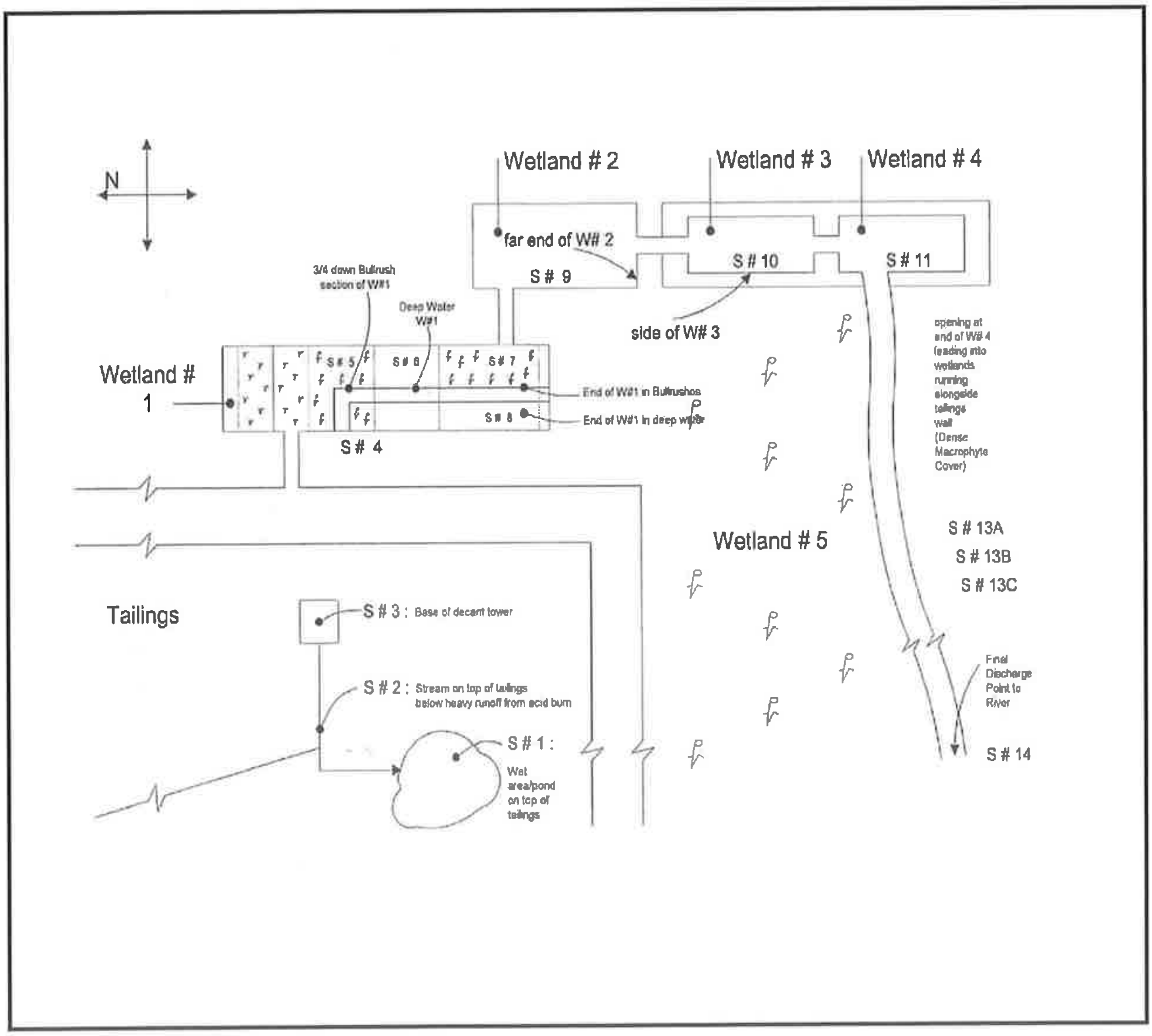


Fig. 3.18 Drainage with high concentrations of heavy metals entering Wetland 1 at Silvermines.

Fig. 3.19 Drainage discharging into the Kilmastulla River following passage through Wetlands 1, 2, 3, and 4 at Silvermines.

Fig. 3.20 *Typha* spp. and *Salix* spp. in Wetland 1 at Silvermines in late spring.

Fig. 3.21 Overview of Wetland 1 at Silvermines showing distinctive banding of wetland species in summer.

physico-chemical and sediment sampling carried out in this wetland in May 2000 included the following (sample collection, preparation and analysis techniques are outlined in Section 3.5):

- Measurements of D.O., conductivity, pH, and temperature were taken in triplicate at five locations along the length of Silvermines wetland 1.Sulphate concentrations were measured in 15 water samples taken along the length of this wetland.

- Water samples were taken in triplicate at five locations along the length of this wetland. Overall, 15 samples were analysed for Cd, Fe, Mn, Pb and Zn concentrations in flows in this wetland.

- Sediment grab samples were taken at seven locations in duplicate along the upper end of this wetland and analysed for total and extractable metals. Overall, 28 samples were tested for total Cd, Fe, Mn, Pb and Zn concentrations and 75 samples for metal extractions.

3.4 PHYSICO-CHEMICAL ANALYTICAL METHODS

Over the course of the study, a number of physico/chemical parameters were measured in the field, or samples taken for laboratory analysis, to investigate relationships between these parameters and wetland health.

3.4.1 Water Chemistry

All water chemistry analysis methods adhered to "Standard Methods for the Examination of Water and Wastewater 20th Edition, 1998" by Clesceri, Greenberg and Eaton.

3.4.1.1 pH and Temperature

pH and temperature were measured *in-situ* with a Delta OHM pH meter, model number HD8602 with a temperature probe. The pH meter was calibrated using certified buffer standards of pH 4 and 7. Standard Methods, Section 4500H.B., 4-94-102 outlines the procedure followed for the use of the instrument and the determinations.

3.4.1.2 Conductivity

Conductivity measurements are used to establish the degree of mineralisation to assess the effect of the total concentration of ions on chemical equilibria, and potential physiological effect on plants. Conductivity was determined *in-situ* using a Delta OHM conductivity meter, model number HD9213-R1. Standard Methods, Section 2510B., 2-60-61 outlines the procedure followed for the use of the instrument and the determinations.

3.4.1.3 Dissolved Oxygen and Temperature

Both these parameters were measured *in situ*. Dissolved oxygen was determined by using a manually calibrated Syland digital temperature/D.O. meter with an oxygen electrode, model number 4000. Standard Methods, Section 4500 O.G., 4-158-161 outlines the procedure followed for the use of the instrument and the determinations.

3.4.1.4 Hardness

Total hardness comprises the calcium and magnesium concentrations and is expressed as mg $CaCO_3$ /l. It was determined using the EDTA titrimetric method as per Section 2340C., 2-54 of Standard Methods.

3.4.1.5 Acidity

Acidity, expressed as mg $CaCO_3$/1 was determined for samples within 24 hours of collection. Bottles were filled completely, capped tightly, with agitation and prolonged exposure to air avoided. Methodology and calculations as per Section 2310B., 2-24 of Standard Methods.

3.4.1.6 Alkalinity

Alkalinity values were determined for samples within 24 hours of collection. Samples were collected as outlined in Section 4.4.1.5 above. Methodology and calculations as per Section 2340B., 2-26 of Standard Methods.

3.4.1.7 Determination of Sulphate by Ion Chromatography

The principle of ion chromatography is that anions are separated on the basis of their affinities for a low capacity, strongly basic anion exchanger. The separated anions are detected by a conductivity detector and identified on the basis of their retention times compared with those of certified standards.

Water samples for sulfate analysis ($\geq$ 100 mls) were collected in acid-washed polyethylene bottles and stored at 4 ^{o}C prior to analysis.

The ion chromatography system used in this analysis comprised a Metrohm 752 Pump Unit, a 709 IC Pump, a 733 IC Separation Center, a 732 IC Detector, a 750 autosampler and IC – Metrodata software package. The system also consisted of a Metrostep Dual 2 Anion column with 20 µl loop.

A certified sulphate IC standard was used to prepare 1.0, 10.0, and 20.0 mg/l calibration standards and a 10.0 mg/l quality control standard. Dilutions of water samples from Silvermines wetlands were necessary in order to fall within the standard range and avoid interference. Dilutions of water samples from the TMF and Control wetlands were unnecessary.

Lisheen Mine's EHS Department Standard Operating Procedure for conducting metals analysis using IC were followed. These are based on Clesceri et al. (1998)

Standard Methods for the Examination of Water and Wastewater published by the American Public Health Association.

All sampling equipment and laboratory glassware were washed with a 10 % nitric acid wash and rinsed twice with ultra pure water.

To ensure quality control objectives were met, 10 % of an analytical sample run consisted of blanks including equipment blanks, field blanks, method blanks, instrument blanks, and calibration blanks.

3.5 METALS ANALYSIS IN WATER, SEDIMENT AND BIOTIC MATRICES

3.5.1 Sample Collection and Preparation

Water samples for metals analysis were taken using the 'grab sample' technique with acid-washed polyethylene bottles. Samples were acidified to pH circa 2.0 using analar grade nitric acid and checking the pH with a pH meter, then stored at 4 °C prior to analysis.

Soil cores were collected with a plastic corer (6 cm inside diameter) carefully driven through the peat and tailings substrate of the TMF wetland and the wetland substrate of the Control wetland. Samples were removed into plastic trays, doubled bagged in plastic ziplock bags and refrigerated prior to analysis. Sediment cores were measured in the laboratory to quantify the depth of peat covering the tailings substrate. A 1 cm rind was removed from the length of the cores of the TMF wetland to prevent sample contamination with tailings slime. Samples weighing 0.5 g were taken along the centroid of each core for total metals determination. Sediment, peat and tailings samples were homogenised by pulverising with a marble pestle and mortar to ensure they passed through a sieve with a mesh size of 2 mm. All samples and standards were weighed using a BOSCH SAE200 digital balance accurate to four decimal places.

Samples for extraction were air dried upon collection and subsamples weighing 1.0 g taken from the oxic sediments.

Sediment samples from Silvermines were taken with a plastic scoop and air-dried prior to analysis. Subsamples of 0.5 g were selected for total metals analysis and subsamples of 1.0 g for extracted metals.

Root, rhizome and stem material dried for plant biomass determinations was prepared for microwave digestion by placing a sample in a blender and grinding. From this homogenised material, a 0.5 g subsample was taken. The blender was acid washed and rinsed with deionised water between samples and an equipment blank taken for every batch of 10 samples to ensure any metal contamination from the blender would be detected.

3.5.2 Sample Digestion

The instrument used for digestion was OI Analytical's Analytical Microwave Systems™ (AMS) Model 7195, which included an analytical microwave oven with 950 wattage output, exhaust model, pressure control system, and WinWave™ software.

Microwave energy heats microwave-absorbing reagents containing a sample inside a pressurized, microwave-transparent container. Closed, high-pressure Teflon® vessels allow higher temperatures to be achieved, thus increasing the speed of digestion.

The United States Environmental Protection Agency Method 3052 (Microwave assisted acid digestion of siliceous and organically based matrices (U.S. EPA, 1995b) was consulted in addition to the American Chemical Society's Microwave Enhanced Chemistry (Kingston and Haswell, 1998) and Davidson *et al.* (1998) to obtain a digestion procedure suitable for the wetland sediments and tailings substrate. The digestion method outlined by Davidson *et al.* (1998) for material from a trial pit on an industrially contaminated site was followed with one modification. Davidson *et al.* determined total metal concentrations by digestion with aqua regia; vessels containing

1 g of ground soil and 20 ml of acid were heated at full power to a pressure of 120 psi, for 10 minutes. Given the microwave model-type used by these researchers had 633 wattage output and the model used in this research work has 950 wattage output, the power requirement was reduced from 100 % to 75 % over the duration of the digestion.

To 1.0 g of homogenised sediment or tailings material, 20 mls of aqua regia prepared using aristar grade HNO_3 and HCL were added. Aqua regia digestion also was used for digesting sediment and soil matrices by Stoughton and Marcus (2000), Obarska-Pempkowiak and Klimkowska (1999) and Ladd, Marcus, and Cherry (1998). The microwave digestion procedure for 12 vessels containing sediment or tailings matrices, a QC sample (sediment standard) and a blank was as follows:

Stage	Power (%)	Pressure (psi)	Dwell Time (min)	Max. Time (min)
1	75	120	9	10

U.S. EPA Method 3051 (EPA SW-846) was used for the digestion of plant matrices (U.S. EPA, 1995b). To 0.5 g of homogenised plant material, 5 mls of aristar grade HNO_3 and 2 mls of ultra pure H_2O were added. The H_2O replaced 2 mls of H_2O_2 given the latter acts as a bleaching agent and may introduce interferences into the ICP-AES analysis. The microwave digestion procedure for 12 vessels containing plant tissues, a QC sample (plant standard) and a blank was as follows:

Stage	Power (%)	Pressure (psi)	Dwell Time (min)	Max. Time (min)
1	30	20	2	5
2	30	40	5	6
3	30	60	2	3
4	30	80	2	3
5	50	100	2	3
6	60	120	2	3
7	70	140	15	16

Following digestion samples were made up to the mark with ultra pure water in 50 ml volumetrics, transferred to polyethylene containers and refrigerated for ICP-AES analysis.

All microwave apparatus, glassware and polyethylene containers were washed between runs with detergent, followed by soaking in 10% analar grade nitric acid for thirty minutes, followed by rinsing with ultra pure water.

Blank and duplicate samples were digested and comprised 10 % of the analysis.

3.5.3 Standard Reference Materials

To verify the digestion and analysis methods used for metals determination in sediment and plant matrices, the standard reference materials outlined below were used. A reference standard was analysed in each run of the microwave digester and ICP-AES.

3.5.3.1 Sediment Standard

The National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1944 was used to verify the method used for the determination of heavy metals in sediments. The sample is a mixture of marine sediment collected near urban areas in New York and New Jersey. Certified metal concentrations are as follows:

Metal	Certified Value $mg.kg^{-1}$	95 % Confidence Interval $mg.kg^{-1}$
Cd	8.8	$\pm$ 1.4
Fe	35,300	$\pm$ 1,600
Mn	505	$\pm$ 25
Pb	330	$\pm$ 48
Zn	656	$\pm$ 75

The concentrations of Cd (7.8 mg/kg), Fe (34,000 mg/kg), and Zn (591 mg/kg) determined in the sediment standard in ICP-AES analysis fell within the certified ranges (N=17) whereas Mn varied by 22 % and Pb by 2 % (275 $\pm$10 mg/kg).

3.5.3.2 Plant Standard

The Commission of the European Communities Bureau of Reference (BCR) certified reference material No. 61 was used to verify the method used for the determination of heavy metals in plant materials. The sample consisted of cleaned, dried, ground and homogenised *Platihypnidium riparioides* (aquatic moss) with heavy metal levels considered to be typical for certain polluted areas. Certified metal concentrations are as follows:

Metal	Certified Value $\mu g.g^{-1}$	95 % Confidence Interval $\mu g.g^{-1}$
Cd	1.07	$\pm$0.08
Mn	3,771	$\pm$78
Pb	64.4	$\pm$3.5
Zn	566	$\pm$13

The concentration of Cd (1.13 mg/kg) determined in the aquatic plant standard in ICP-AES analysis fell within the certified range (N=25) whereas Mn varied by 5 % (3,495 mg/kg), Pb by 8 % (56 mg/kg) and Zn by 1 % (548 mg/kg).

3.5.4 Inductively Coupled Plasma-Atomic Emission Spectroscopy

The determination of metals in water, sediment and plant matrices were made using Inductively Coupled Plasma-Atomic Emission Spetroscopy (ICP-AES) (U.S. EPA Method 6010 for metals). The instrument used was a Liberty Series II ICP, SPS-5 autosampler, with ultrasonic nebulizer, Kt water cooler and Plasma 96 software package.

An ICP source consists of a flowing stream of argon gas ionized by an applied radio frequency field. This field is inductively coupled to the ionized gas by a water-cooled coil surrounding a quartz torch that supports and confines the plasma. A sample aerosol is generated in an appropriate nebulizer and spray chamber and is carried into the plasma through an injector tube located within the torch. The sample aerosol is injected directly into the ICP, subjecting the constituent atoms to temperatures of about 6,000 to 8,000 °K. The high temperature of the plasma excites atomic emission efficiently. Ionisation of a high percentage of atoms produces ionic emission spectra. Quantification is achieved using comparisons with certified standards.

Lisheen Mine's EHS Department Standard Operating Procedure for conducting metals analysis using ICP-AES were followed. This is based on Clesceri *et al.* (1998) Standard methods for the examination of water and wastewater published by the American Public Health Association.

Digested samples were stored in disposable test tubes with caps for analysis. A wavelength calibration was carried out at the beginning of every sample run and re-calibration occurred following the analysis of every 15 samples. Each analysis run included 10 % calibration standards, Q.C. spikes and procedural blanks as required for quality assurance. Certified Multi Element I ICP Standard was used to prepare calibration standards for Cd, Fe, Mn, Pb and Zn. Quality Control standards were prepared and checked after each batch of 10 test samples. Reagent grade chemicals were used throughout and standard solutions were treated in the same way as the samples. The wavelengths used to determine the individual metal concentrations are given below. Standards used to calibrate the instrument are also outlined. Samples were diluted into these standard ranges using ultra pure water.

Metal	**λ**	**Calibration Standards (mg/l)**	**Quality Control Standards (mg/l)**
Cadmium	228.802	0.02, 0.1, 0.2	0.1
Iron	238.204	0.5, 2.5, 5.0	0.1
Manganese	257.610	0.05, 0.25, 0.5	0.1
Lead	220.353	0.5, 2.5, 5.0	0.1
Zinc	213.856	0.5, 2.5, 5.0	0.1

3.6 ADDITIONAL SEDIMENT ANALYSIS

3.6.1 Organic Content

The organic content of the sediments was determined by drying 14 sediment cores from each wetland at 103 to 105 °C, in line with Section 2540B of Standard Methods and then extracting 2 g of sample from the cores and ashing these in a muffle furnace at 500 °C for 3.5 hours. This determines loss on ignition (LOI) values in line with Section 2540E of Standard Methods.

3.6.2 Sediment Extractions

The readily extractable metal forms and those more mobile under certain environmental circumstances were determined by identifying the speciation of Cd, Fe, Mn, Pb, and Zn in the wetland sediments through sequential extractions to distinguish among ion-exchangeable metals, a reducible fraction (typically hydrous oxides of iron and manganese), an oxidizable fraction (sulfides plus organic matter), and a residual fraction. A comprehensive discussion of the importance of speciation to metal mobility in water, soil and plant matrices occurs in Section 2.5 and Section 2.6 of Chapter Two.

The sequential extraction procedure recommended by the Bureau Commun de Référence (BCR) of the Commission of the European Communities (Davidson *et al.*, 1998; Marin *et al.*, 1997; Ure *et al.*, 1993) was used to quantify the metal species in the sediments of the TMF, Control and Silvermines wetlands. In addition to wetland sediments this extraction procedure was carried out on peat and tailings matrices, sediment standards and on blanks. The extraction procedure is as follows:

Step 1 – Ion Exchangeable Metals and Metals Co-precipitated with Carbonates

- 40 mls of acetic acid (0.11 mol/l CH_3COOH) was added to 1 g of dry sediment in a 250 ml polyethylene bottle (all chemicals used in the extractions were aristar grade). The bottle was then shaken for 16 hr (overnight) at ambient temperature (approx. 20 °C) on a mechanical shaker at a speed of 30 rpm. The supernatant was separated from the solid residue by centrifugation at 8000 rpm for 25 min and decanted into an acid-washed polyethylene container and stored at 4 °C for analysis. The residue was washed with 20 ml of ultra-pure water by shaking for 15 min, centrifuged and the washings stored for analysis to measure trace element losses.

Step 2 – Metals Bound to Iron/Manganese Oxyhydroxides

- 40 ml of hydroxylammonium chloride (0.1 mol/l $NH_2OH.HCL$, adjusted to pH 2 with nitric acid) was added to the residue from step 1. The extraction procedure is repeated as described above and the extracts and washings stored.

Step 3 - Metals Bound to Organic Matter and Sulfides

- 10 ml of hydrogen peroxide (8.8 mol/l H_2O_2) was carefully added, to avoid losses due to violent reaction with organic matter, to the residue of step 2. The bottle was covered and the contents digested at room temperature for 1 hr with occasional manual shaking. Digestion was continued by heating the bottle to 85 °C in a water bath for 1 hr. The cover was removed and the solution reduced to a small volume. (It was anticipated that the solution would reduce to a volume of 2-3 ml, however, in this experiment the volume of the sample did not reduce significantly.) A second aliquot of 10 ml of hydrogen peroxide was added and the bottle again covered, heated at 85 °C for 1 hr, and the solution reduced. A 50 ml volume of ammonium acetate (1 mol/l CH_3COONH_4, adjusted to pH 2 with nitric acid) was then added to the cool and moist residue. The extraction of supernatant was conducted as described above.

Step 4 – Residual Metals held within Crystalline Matrix

- The remaining solid residue underwent microwave digestion as outlined in Section 3.5.2 using aqua regia.

For sediment standards, the sum of the four fractions (ΣExt1→Ext4) of the sequential extraction procedure did not differ significantly ($P>0.05$) from the concentration of the direct total metal determination for Cd, Fe, Mn and Zn. There was a significant difference for Pb ($P=0.03$) but the average value for the sum of the extractions was 219 mg/kg and the average for the total digestion was 273 mg/kg.

3.7 STATISTICAL ANALYSIS

All statistical analysis was carried out using SPSS for Windows Release 10.0. Descriptive statistics were carried out to calculate mean, minimum, maximum, median, standard deviation and variance values for all data sets. An independent samples t-test was conducted to compare ecological parameters between the TMF and Control wetlands. Comparisons of mean metal concentrations in water, sediment and biotic matrices between these wetlands were carried out using one-way analysis of variance (ANOVA). Each variable was tested for normality prior to ANOVA analysis using Shapiro-Wilk's and Kologorov-Smirov Lilliefors tests for normality. Each variable also was tested for homogeneity of variance using the Levene statistic. Variables were log transformed prior to ANOVA analysis when they did not exhibit normality. If required the ANOVA analysis was followed by Bonferroni's multiple comparison test to denote significant differences between individual regions in the wetlands, or by Tukey's Honestly Significant Difference (HSD) test for the calculation of Least Significant Difference at a significance level of 0.05 to denote significant differences between the plant tissues. The paired-samples t-test was conducted to investigate significant differences between metal concentrations in the TMF wetland sediments in 1999 and 2000. The Kruskal-Wallis test, a nonparametric alternative to the one-way ANOVA, was conducted to compare mean metal concentrations in each of the four fractions extracted from Silvermines tailings and sediments from the TMF and Silvermines wetlands. Correlation analysis was conducted for a range of parameters using Pearson and Spearman rank coefficients. The least-squares linear regression lines and Rsq values were calculated for each significant bivariate correlation.

CHAPTER FOUR

RESULTS
ECOLOGICAL INDICATORS

4.1 RESULTS – ECOLOGICAL INDICATORS

An extensive field ecology study was carried out on the wetland cells in the pilot system throughout summer, 1999. The objective of this study was to obtain ecological data to compare indicators of ecosystem health or degradation between the TMF and Reference/Control wetlands. The study consisted of extensive plot sampling to facilitate this comparison of wetland communities including vegetative analysis (species composition, coverage, density, frequency, importance values, ecotypic variation), species diversity indices, community similarity indices and, an analysis of production.

Aims of the field ecology study were as follows:

- To identify, enumerate and compare the composition of plant species in the TMF and Control wetlands.
- To compare community composition, vegetation cover, distribution, density, dominance and importance values for each species in the TMF and Control wetlands.
- To produce Relative Abundance Curves, Dominance-Density Curves and Species Importance Curves for both wetlands.
- To investigate any vegetative and reproductive ecotypic variation in *Typha latifolia*, *Phragmites australis*, and *Juncus effusus* species between the TMF and Control wetlands.
- To calculate and compare the following indices of floral diversity for each wetland Margalef's Index, Simpson's Index, and the Shannon Diversity Index.
- To calculate the following indices of community similarity for both wetlands: Jacard Coefficient, Sorensen Coefficient, Proportional Similarity, Bray and Curtis Index, Morisita's Index, and Horn's Index.
- To calculate and compare biomass values for *Typha latifolia*, *Phragmites australis*, and *Juncus effusus* species between wetlands.

- To produce performance curves for *Typha latifolia*, *Phragmites australis*, and *Juncus effusus* species for each wetland.

- To investigate any evidence of the presence of aquatic and other fauna in both wetlands.

4.2 ECOLOGICAL MEASUREMENTS IN TMF AND CONTROL WETLANDS, SUMMER 1999

During summer 1999, extensive quadrat sampling was conducted in the pilot plant wetland facility. Figures 4.1 and 4.2 illustrate the locations of thirty and twenty-five, 1 m^2 quadrats sampled in the TMF and Control wetlands respectively. These quadrats were selected randomly in each of three regions where *Typha latifolia, Phragmites australis*, or *Juncus effusus* was initially planted. These regions correspond to the top (near point of water inflow), middle and end sections of each wetland. The initial planting regime for all species in both wetlands was identical.

4.2.1 Analysis of Communities

4.2.1.1 Community Structure – Species Composition and Vegetation Analysis

By summer, 1999 (16 months after planting), the TMF wetland had an extensive cover of emergent vegetation. Figure 4.3 illustrates the overall growth in this wetland in May, 1999 and Figures 4.4, 4.5, and 4.6 illustrate growth in the *Typha, Phragmites,* and *Juncus* sections respectively during the plot sampling in July and August, 1999. As anticipated an extensive wetland cover was established in the Control wetland during the first (1998) and subsequent growing seasons.

A complete list of plant species identified in the TMF and Control wetlands during the field ecology study is outlined in Table 4.1. This table includes those species observed and counted during the quadrat sampling procedure and species observed in the wetlands but not counted in quadrats. Some plants were identified to species level, some to genera (e.g. *Potamogeton*) and some to family level (e.g. *Gramineae* and *Bryophytes*) given that the identification of species composition was for comparative purposes only.

Fig. 4.1 Spatial layout of quadrats and plant regions in TMF Wetland during field ecology study, Summer 1999.

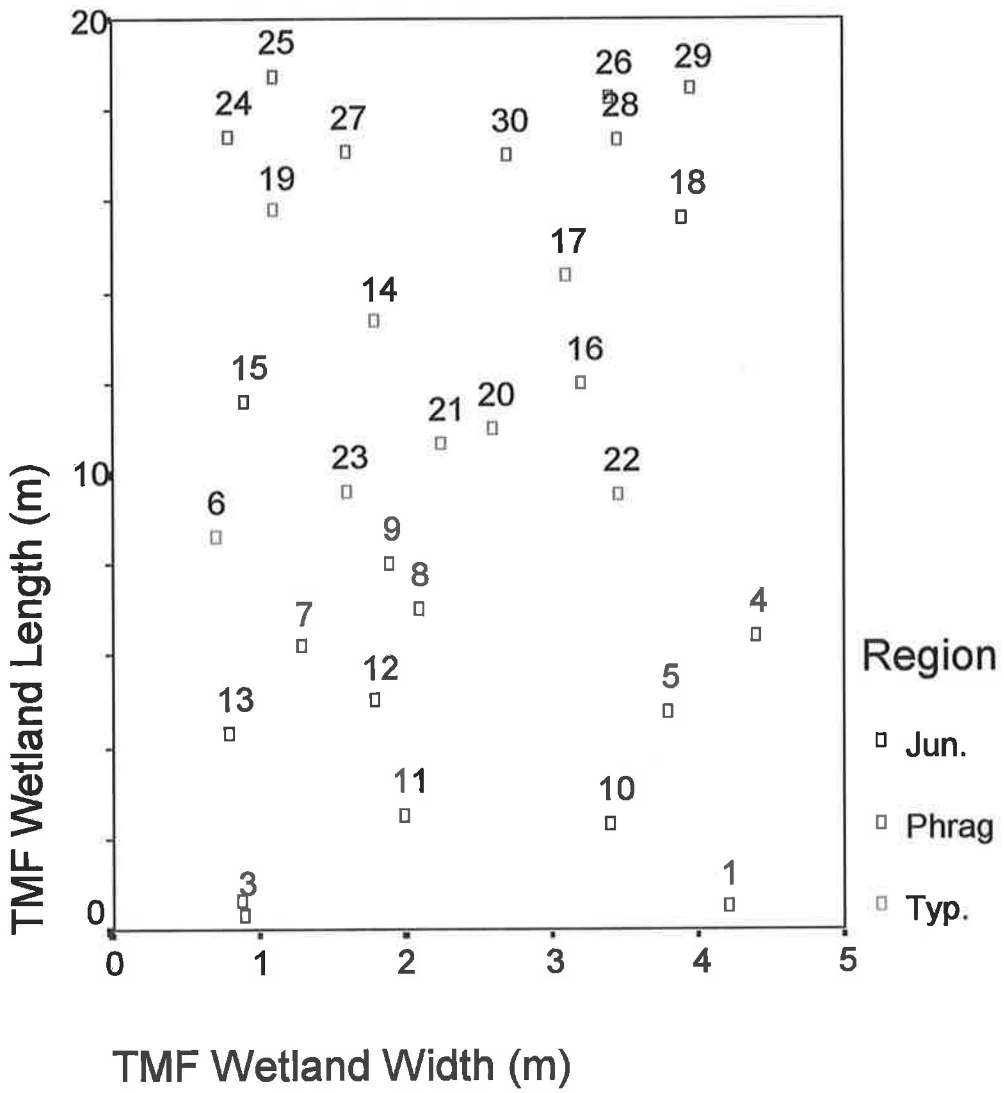


Fig. 4.2 Spatial layout of quadrants and plant regions in Reference/Control Wetland during field ecology study, Summer 1999.

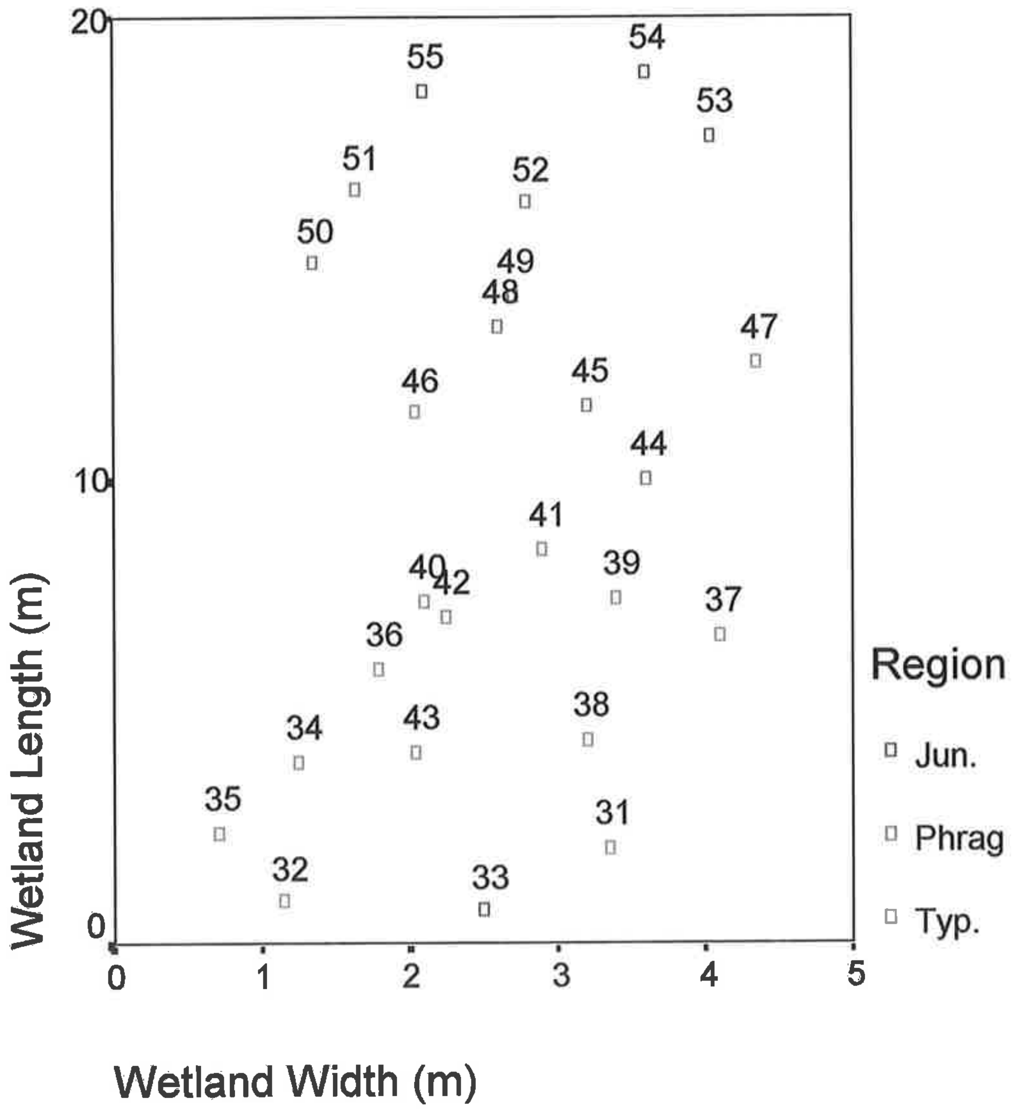


Fig. 4.3 Cover of emergent vegetation in TMF Wetland in May, 1999.

Fig. 4.4 Growth in *Typha* region of TMF Wetland during plot sampling in July, 1999.

Fig. 4.5 Growth in *Phragmites* region in TMF wetland during plot sampling in July, 1999.

Fig. 4.6 Growth in *Juncus* region of TMF Wetland during plot sampling in Aug 1999.

Table 4.1 Plant species identified in the TMF and Control wetlands during the field ecology study in summer, 1999.

Scientific Name	Common Name	Present in TMF Wetland	Present in Control Wetland
Observed and Counted during Quadrant Sampling			
Typha latifolia L.	Cattail/Greater reedmace	√	√
Phragmites australis L.	Common reed	√	√
Juncus effusus L.	Soft rush	√	√
Juncus acutiflorus Ehrh.	Sharp-flowered rush	√	√
Scirpus maritimus L.	Sea club-rush	√	√
Equisetaceae: *Equisetum fluviatile* L. *Equisetum palustre* L.	Horsetail family: Water horsetail Marsh horsetail	 √ √	 √ √
Onagraceae: *Epilobium hirsutum* L. *Epilobium palustre* L.	Willowherb family: Great willowherb Marsh willowherb	 √ √	 √ √
Iris pseudacorus L.	Yellow iris/Flag iris	√	
Mentha aquatica L.	Water mint		√
Potamogetonaceae: *Potamogeton* L.	Pondweed family: Pondweeds	 √	 √
Gramineae: *Agrostis -* *Agrostis stolonifera* L.	Grass family: Bents - Creeping Bent	√ √ √	√ √ √
Bryophytes: *Sphagnum rubellum* Wils. *Brachythecium rutabulum* Hedw.	Mosses: Moss Moss	√ √ √	√ √ √
Observed in Wetlands but Not Counted during Quadrant Sampling			
Juncus articulatus L.	Jointed rush	√	√
Juncus inflexus L.	Hard rush	√	
Juncus squarrosus L.	Heath rush	√	
Eriophorum angustifolium (L.) Honck.	Common cotton grass	√	
Lythrum salicaria L.	Purple loosestrife		√
Salix L.	Willow	√	

As outlined in Table 4.1, the species identified and counted during the plot sampling in the TMF wetland are extremely similar to those identified in the Control. The exceptions include *Iris pseudacorus* which was counted only in plots in the TMF wetland and *Mentha aquatica* which was counted only in the Control.

As expected *Typha latifolia* spread quickly in both wetlands because it colonizes by rhizomes, although this occurred more rapidly and over a wider area in the Control wetland. *Phragmites australis* did not establish itself as quickly, even though it also spreads by rhizomes. *Juncus effusus* established itself to a much greater extent in the TMF wetland than in the Control.

A variety of indigenous wetland vegetation became established in both wetlands including *Juncus acutiflorus, Scirpus maritimus, Equisetaceae* and *Onagraceae*. This was anticipated given the species initially planted were taken from natural tidal wetland stands with rootballs of wetland soils. A significant cover of grass species, *Gramineae* including *Agrostis stolonifera*, was established in both wetlands.

Tables 4.2 and 4.3 quantify these observations in terms of relative densities (RD_i), relative frequencies (Rf_i), relative coverage (RC_i), and importance values (IV_i) for each species in the TMF and Control wetlands respectively. In comparative studies it is important to obtain data on the number of individuals relative to other populations. Abundance (n) is the number of individuals in a given area, and density (D) is that number expressed per unit area. Relative density (RD) is the total number of individuals of a species expressed as a proportion of the total number of individuals of all species (Brower *et al.*, 1990). Densities for all species were evaluated using stem (or clump) counts with the exception of *Potamogeton*, *Gramineae* and *Bryophytes* where a density of 1 or 0 was allocated for their presence or absence in any plot.

Frequency (f) is the number of times a given event occurs. The relative frequency (Rf) of a species is the frequency of that species divided by the sum of the frequencies of all species in the community (Brower *et al.*, 1990). The coverage (C) is the proportion of ground occupied by the perpendicular projection to the ground from the outline of the aerial parts of a plant. In the wetland cells coverage was estimated by converting diameters and circumferences of plants to circular coverage areas, calculating basal

Table 4.2 Summary of data from quadrat sampling in TMF Wetland, Summer 1999.

Total No. of Quadrats (k) = 30
Quadrat Area = 1 m^2
Total Quadrat Area = 30 m^2

Species (i)	No. of Individuals (n_i)	Density (D_i) $D_i = n_i /A$	Relative Density (RD_i) $RD_i = n_i/\Sigma n$	Present in how many quadrats? (j_i)	Frequency (f_i) $f_i = j_i/k$	Relative Frequency (Rf_i) $Rf_i = f_i/\Sigma f$	Coverage (C_i) $C_i = a_i/A$	Relative Coverage (RC_i) $RC_i = C_i/\Sigma C$	Importance Value (IV_i) $IV_i = (RD_i + Rf_i + RC_i)$	Importance % (IV%) IV% = $IV_i/3$
Typha latifolia	339	11.30	0.43	28	0.93	0.17	0.045	0.091	0.69	23%
Phragites australis	247	8.23	0.31	14	0.47	0.09	0.015	0.03	0.43	14%
Juncus effusus	41	1.37	0.05	17	0.517	0.11	0.072	0.145	0.31	10%
Juncus acutiflorus	20	0.67	0.03	11	0.37	0.07	0.004	0.008	0.11	4%
Scirpus maritimus	21	0.70	0.03	9	0.30	0.06	0.0003	0.001	0.09	3%
Equisetaceae	25	0.83	0.03	11	0.37	0.07	0.0001		0.10	3%
Onagraceae	41	1.37	0.05	18	0.60	0.11	0.0001		0.16	5%
Iris pseudacorus	15	0.50	0.02	3	0.10	0.02	0.0004	0.001	0.04	1%
Potamogeton	20	0.67	0.03	20	0.67	0.12	0.06	0.121	0.28	9%
Gramineae	29	0.97	0.04	29	0.97	0.18	0.298	0.600	0.82	27%
Bryophytes	2	0.07	0.003	2	0.07	0.013	0.002	0.004	0.02	1%
Totals	Σn=800	ΣD=26.68	ΣRD=1.0		Σf=5.42	ΣRf=1.0	ΣC=0.497	ΣRC=1.0		

Table 4.3 Summary of data from quadrat sampling in Control Wetland, Summer 1999.

Total No. of Quadrats (k) = 25
Quadrat Area = 1 m^2
Total Quadrat Area = 25 m^2

Species (i)	**No. of Individuals (n_i)**	**Density (D_i) $D_i = n_i/A$**	**Relative Density (RD_i) $RD_i = n_i/\Sigma n$**	**Present in how many quadrats? (j_i)**	**Frequency (f_i) $f_i = j_i/k$**	**Relative Frequency (Rf_i) $Rf_i = f_i/\Sigma f$**	**Coverage (C_i) $C_i = a_i/A$**	**Relative Coverage (RC_i) $RC_i = C_i/\Sigma C$**	**Importance Value (IV_i) $IV_i = (RD_i + Rf_i + RC_i)$**	**Importance % (IV%) IV% = $IV_i/3$**
Typha latifolia	495	19.80	0.45	25	1	0.16	0.081	0.125	0.74	25%
Phragites australis	358	14.32	0.33	11	0.44	0.07	0.03	0.046	0.45	15%
Juncus effusus	12	0.48	0.01	6	0.24	0.04	0.02	0.031	0.08	3%
Juncus acutiflorus	26	1.04	0.02	14	0.56	0.09	0.001	0.002	0.11	4%
Scirpus maritimus	58	2.32	0.05	21	0.84	0.13	0.02	0.031	0.21	7%
Equisetaceae	13	0.52	0.01	7	0.28	0.05			0.06	2%
Onagraceae	78	3.12	0.07	19	0.76	0.12	0.0002	0.0003	0.19	6%
Mentha aquatica	5	0.20	0.01	1	0.04	0.01			0.02	1%
Potamogeton	22	0.88	0.02	22	0.88	0.14	0.178	0.275	0.44	15%
Gramineae	24	0.96	0.02	24	0.96	0.15	0.318	0.491	0.66	22%
Bryophytes	7	0.28	0.01	7	0.28	0.05			0.06	2%
Totals	$\Sigma n = 1098$	$\Sigma D = 43.92$	$\Sigma RD = 1.0$		$\Sigma f = 6.28$	$\Sigma Rf = 1.0$	$\Sigma C = 0.648$	$\Sigma RC = 1.0$		

coverage for clumps, or in the case of *Potamogeton, Gramineae* and *Bryophytes*, estimating coverage by visual estimation. The relative coverage (RC) of a species is the proportion of its coverage compared to that of all species in the community (Brower *et al.*, 1990).

The importance value (IV) or the importance percentage (IV%) gives an overall estimate of the influence or importance of a plant species in a community. Importance values were calculated as the sum of RD_i, Rf_i and RC_i and importance percentages were calculated by dividing this value by three (Brower *et al.*, 1990). Although this estimate has an advantage of using more than one measure of influence, it has the disadvantage of giving equal weight to each and yielding similar values for different combinations of the three relative values. For the purposes of this research IV and IV% estimates were useful for comparing differences in floral composition and diversity between wetlands.

From Tables 4.2 and 4.3 it is obvious that *Gramineae* and *Typha latifolia* are the dominant species in both wetlands. *Gramineae* has IV% values of 27% and 22% for the TMF and Control wetlands respectively. *Typha latifolia* has RD values of 0.43 and 0.45, Rf values of 0.17 and 0.16, RC values of 0.091 and 0.125, and IV% values of 23% and 25% in the TMF and Control wetlands respectively. These values are very similar for both wetlands. Likewise, *Phragmites australis*, the next most dominant species has similar values for RD (0.31 and 0.33), Rf (0.09 and 0.07), RC (0.03 and 0.05), and IV% (14% and 15%) in the TMF and Control wetlands respectively. There is, however, a substantial difference in the degree of dominance exerted by *Juncus effusus* in the TMF wetland in comparison to the Control as reflected in the Rf values (0.11 and 0.04), the RC values (0.145 and 0.031) and the IV values (10% and 3%) for each wetland. The remaining species identified in both wetlands (*Juncus acutiflorus, Scirpus maritmus, Equisetaeae, Onagraceae, Potamogeton and Bryophytes*) have relatively similar IV% values for each wetland. Overall, Tables 4.2 and 4.3 indicate similar IV% values for the majority of species and this shows similar vegetative diversity for both wetlands.

[Tables B.1 to B.6 in Appendix B outline relative densities, relative frequencies, relative coverage, and importance values for each species in each region (*Typha*, *Phragmites* and *Juncus*) of both wetlands. A comparison of regional vegetative diversity between wetlands indicated the same similarity as for the overall wetlands.]

To further investigate diversity patterns in these wetlands these data were ranked to produce Relative Abundance Curves, Dominance-Density Curves, and Species Importance Curves for both wetlands as illustrated in Figures 4.7 and 4.8. These curves were prepared using density/abundance, coverage, frequency and importance values for both wetlands as outlined in Brower *et al.* (1990). (Ranking data is presented in Appendix B.) Species are ranked in a sequence from 1 to i, where i is the total number of species being considered. The most abundant species (or the one with the greatest coverage, frequency or importance values) is assigned rank 1and so on with the least abundant receiving rank i. Then growth analysis parameters, abundance or coverage etc., are plotted on a logarithmic scale against the corresponding species rank as in Figures 4.7 and 4.8. A community with a high degree of diversity will tend to have more species and more even abundance in each species than will a community of low diversity. Communities with low species diversity and/or a high degree of dominance tend to have very steep curves on these graphs. Those with high species diversity and/or low dominance assume a more horizontal aspect.

Species diversity has been considered an important community characteristic in detecting polluted waters (Brower et al., 1990). The curves in Figures 4.7 and 4.8 do not have steep slopes but assume a more horizontal aspect thus indicating that both wetlands have high species diversity and low dominance. In addition to illustrating the individual curves for each wetland Figures 4.7 and 4.8 also show the curves for both wetlands on a single graph for comparison purposes. These graphs illustrate the similarity in floral diversity between the TMF and Control wetlands graphically. Calculated indices of species diversity are outlined below in Section 4.1.2.

4.1.1.2 Community Structure – Ecotypic Variation

Ecotypes are local populations of a plant that differ in genetically based adaptions and responses to environmental conditions (Cox, 1990). The characteristics showing ecotypic variation can either be morphological or physiological. Morphological differences may involve almost any feature of form and structure, vegetative or

Fig. 4.7 Relative Abundance Curves/Species Importance Curves for TMF and Control Wetlands.

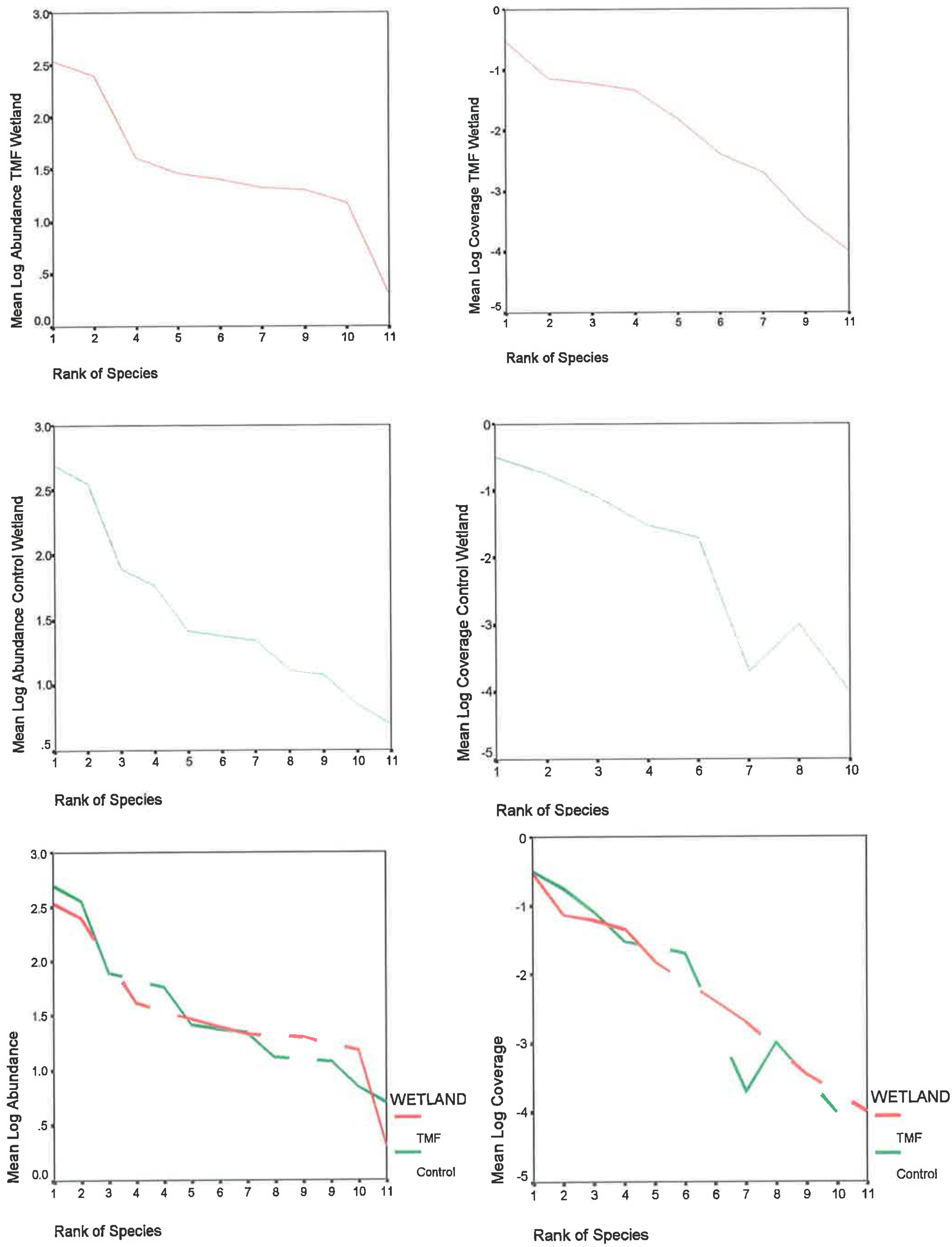
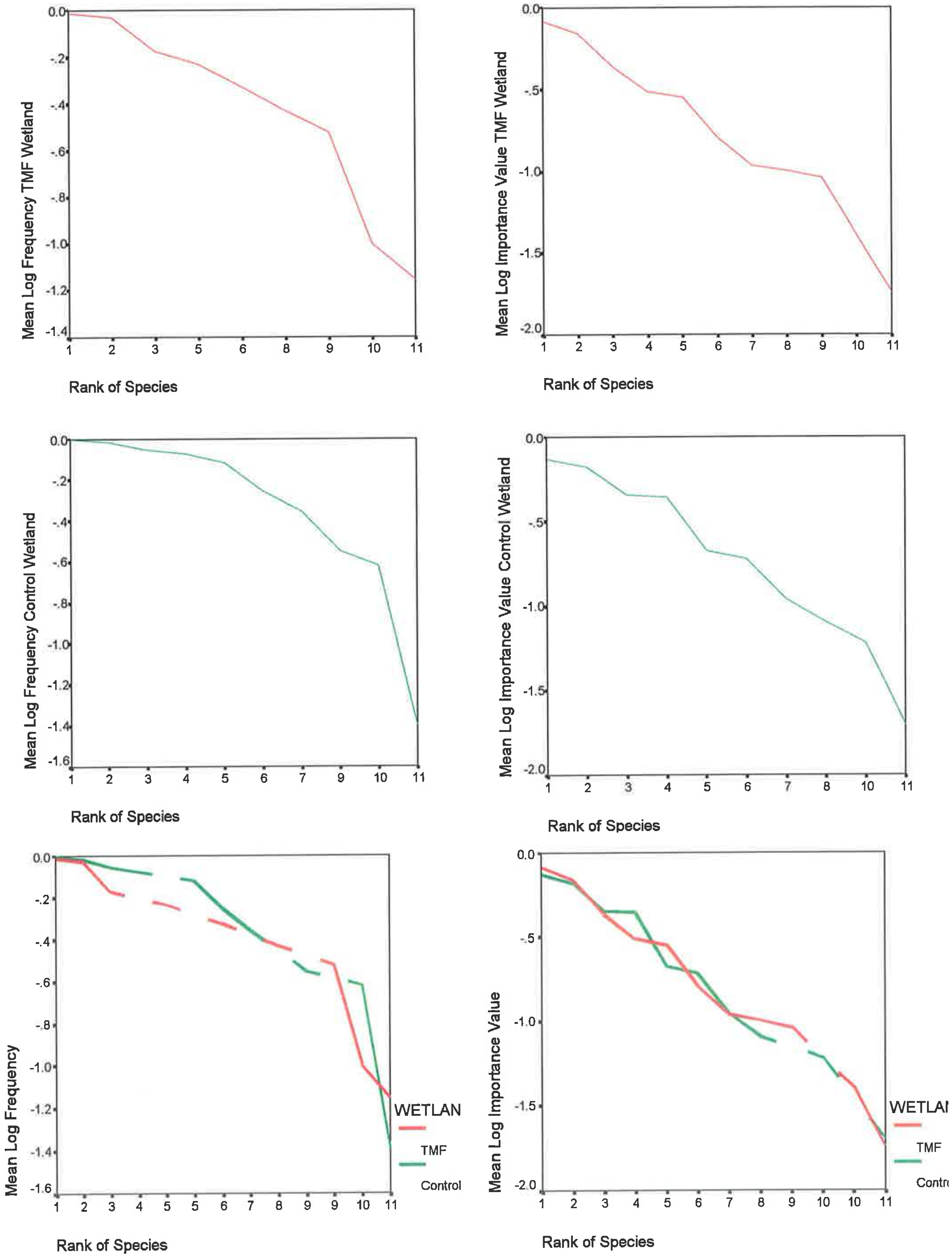


Fig. 4.8 Dominance-Density Curves/Species Importance Curves for TMF and Control Wetlands.



reproductive. Physiological differences are varied and may involve germination, photosynthesis, respiration, growth rate, or allocation of photosynthate to various plant components and structures (Cox, 1990).

Ecotypic variation in emergent species was investigated between the TMF and Reference/Control wetlands to determine if morphological differences occurred in the plants of the TMF wetland as a result of degraded environmental conditions. This work focused on morphology because of the time constraints and specialised equipment required for physiological studies.

A range of data for each quadrat sampled in summer 1999, including vegetative and reproductive data to determine ecotypic variation in *Typha, Phragmites,* and *Juncus* species between wetlands are outlined in Tables 4.4 and 4.5. These tables also outline percentages of *Typha* per quadrat infested by *Lepidoptera* in both wetlands. The infestation was discovered during the 1999 field ecology study. Some plants, particularly *Typha* are subject to damage by lepidopterous insects.

As determined from the data in Tables 4.4 and 4.5, descriptive statistics comparing stem densities in quadrants for *Typha, Phragmites,* and *Juncus* species between wetlands are as follows:

	Typha Density		***Phrag. Density***		***Juncus Density***	
	TMF	Control	TMF	Control	TMF	Control
Mean	12	20	15	14	3	< 1
Minimum	2	9	0	0	1	0
Maximum	40	38	31	88	5	3
Std. Deviation	9	6	11	26	1	1

These values indicate lower mean densities of *Typha* in the TMF wetland than in the control, similar mean densities of *Phragmites* between wetlands, and higher mean densities of *Juncus* in the TMF wetland.

Also, as determined from the data in Tables 4.4 and 4.5, descriptive statistics comparing ecotypic variation in vegetative data for *Typha, Phragmites,* and *Juncus* species between wetlands are outlined in Table 4.6. Figure 4.9 illustrates differences

Table 4.4 Vegetative and reproductive data for *Typha, Phragmites,* and *Juncus* species obtained for each quadrat in TMF Wetland, Summer 1999.

					Plant Density			Typha latifolia						Phragmites australis					Junc.	Total Biomass		
Region	Quadrant No.	Species Richness	Total Cover	Total Density	Typha Density	Phragmite Density	Juncus Density	Stem Length	Leaf Width	Infested	No. Flowers	Flower Length	Flower Width	Stem Length	Leaf Length	Leaf Width	Flower Length	Flower Width	Juncus Stem Length	Typha Total Biomass	Phragmite Total Biomass	Juncus Total Biomass
J.	1	5	0.2	17	8		3	114	1.0	0	1	26	3						70	278.71		502.62
J.	2	6	0.3	34	23		3	115	1.3	0.26	1	15	3						73	269.15		335.48
J.	3	4	0.02	25	14		4	124	1.4	0.31	6	15	3						75	735.64		246.38
T.	4	4	0.6	19	16		1	112	1.1	0.13	1	19	3.3						95	672.08		159.68
T.	5	5	0.98	21	16		2	124	1.4	0.31	2	15	3						103	285.47		369.12
T.	6	6	0.50	29	20			134	1.4	0.42	5	14	3.1							356.84		
T.	7	5	0.75	21	13			162	1.3	0	0									232.7		
T.	8	5	0.55	26	19			128	1.4	0.32	5	14	2.9							302.1		
T.	9	5	0.50	20	16			129	1.4	0.33	4	13	2.6							190.74		
T.	10	4	0.40	30	26			119	1.2	0	2	11	2.9							694.2		184.56
T.	11	6	0.45	27	18			105	1.2	0.06	2	15	3.0						45	326.63		184.56
T.	12	4	0.75	19	11			129	1.5	0.18	0								90	204.23		184.56
T.	13	6	0.85	25	19			127	1.9	0.05	2	17	2.9						20	603.84		184.56
P.	14	6	0.78	28	3	21		78	1.1	0	0			86	22	1.7	14	3		70.48	55.08	
P.	15	9	0.50	44	2	31		98	1.6	0	0			97	20	1.4	15	4	72	46.99	95.98	184.56
P.	16	4	0.70	17		12				0	0			103	25	1.8	22	5			62.21	
P.	17	5	0.6	39	7	25		103	1.3	0	1	17	3.2	103	17	2.2	17	5		164.45	98.88	
P.	18	4	0.3	39	7	30		104	1.0	0	3	10	2.5	83	12	1.5	12	3		164.45	60.57	
P.	19	4	0.3	61	40	16		65	0.8	0	1	8	2.8	94	15	1.5	15	5		939.72	38.32	
P.	20	7	0.5	39	9	22		111	1.2	0	4	13	3.1	91	14	1.8	14	5		211.44	50.56	
P.	21	7	0.75	29	3	21		71	0.9	0	0			95	23	1.7	16	5		70.48	94.06	
P.	22	7	0.55	41	6	25		105	1.4	0	1	12	2.8	105	20	1.6	18	5		140.96	74.28	
P.	23	7	0.50	43	10	23		125	1.5	0.20	2	17	3.0	106	22	1.8	16	7		234.93	97.13	
J.	24	6	0.30	22	8	6	3	70	0.9	0	0			100	26	2.3	16	9	101	187.94	19.94	569.3
J.	25	6	0.46	13	5	0	3	72	1.0	0	0								110	117.47		987.81
J.	26	5	0.30	8	2	0	5	76	0.8	0	0								93	46.99		644.8
J.	27	6	0.30	26	12	5	4	91	1.1	0	2	14	3.4	117	22	1.9	16	7	97	281.92	16.62	236.6
J.	28	5	0.45	13		3	4			0	0			92	21	1.6	16	6	89		9.97	1438.1
J.	29	4	0.25	7	3		2	133	1.4	0	2	14	3.1						105	70.48		539.94
J.	30	6	0.25	17	3	7	2	116	0.9	0	0			86	18	1.5	15	6	82	70.48	23.27	385.76

Table 4.5 Vegetative and reproductive data for *Typha, Phragmites,* and *Juncus* species obtained for each quadrat in Control Wetland, Summer 1999.

				Plant Density				Typha latifolia						Phragmites australis					Junc.	Total Biomass		
	Quadrant No.	Species Richness	Total Cover	Total Density	Typha Density	Phragmites Density	Juncus Density	Stem Length	Leaf Width	Infested	No. Flowers	Flower Length	Flower Width	Stem Length	Leaf Length	Leaf Width	Flower Length	Flower Width	Juncus Stem Length	Typha Total Biomass	Phragmites Total Biomass	Juncus Total Biomass
J.	31	6	0.9	27	17	0	2	121	1.2	0.06	6	11	2.7						75	555.56		271.2
J.	32	8	0.8	21	9	0	1	99	1.1	0	1	14	2.5						94	159.03		118.17
J.	33	7	0.45	24	14	0	3	85	0.9	0	1	11	2.5						89	405.3		367.43
T.	34	8	0.88	35	21	0	0	141	1.4	0.38	12	10	2.8							437.93		
T.	35	7	0.95	41	26	0	0	134	1.4	0.12	8	12	2.8							952.12		
T.	36	6	0.75	30	18	0	0	167	1.7	0.11	5	14	3.0							690.3		
T.	37	6	0.85	32	24	0	0	149	1.6	0.08	5	13	2.7							636		
T.	38	5	0.50	42	21	0	0	157	1.7	0.10	4	12	2.9							529.83		
T.	39	4	0.80	35	28	0	0	159	1.5	0.25	10	11	2.9							851.76		
T.	40	4	0.95	32	27	0	0	171	1.7	0.15	3	15	3.0							1326.81		
T.	41	6	0.75	45	38	2	0	160	1.7	0.05	2	13	3.0	143	17	1.3	14	6		853.48	8.26	
T.	42	4	0.80	29	24	0	0	166	1.7	0.08	3	16	2.8							581.52		
T.	43	7	0.80	30	18	0	0	150	1.8	0.22	6	12	2.7							450.9		
P.	44	6	0.95	43	23	13	0	180	1.9	0.13	3	12	2.5	136	22	1.7	15	6		665.85	65.52	
P.	45	7	0.70	48	20	19	0	136	1.2	0	2	9	2.3	128	20	1.6	16	8		579.0	60.23	
P.	46	5	0.55	21	15	3	0	153	1.5	0	0			135	22	1.8	19	9		327.3	14.82	
P.	47	8	0.55	36	15	5	0	123	1.1	0.13	2	14	3.1	141	21	1.9	14	7		513.63	25.45	
P.	48	6	0.50	75	15	51	0	165	1.6	0	1	17	3.0	152	20	1.6	16	7		434.25	191.25	
P.	49	5	0.55	79	25	45	0	155	1.9	0.08	15	13	3.0	144	19	1.6	15	7		723.75	227.25	
P.	50	7	0.40	77	18	49	0	128	1.8	0.22	8	13	2.6	143	18	1.6	18	10		521.1	207.76	
P.	51	6	0.65	107	21	80	0	154	1.5	0.14	9	14	2.5	146	19	1.6	17	8.5		607.95	260.8	
P.	52	8	0.45	117	20	88	0	142	1.6	0	7	15	2.8	135	16	1.2	13	5		579.0	230.56	
P.	53	6	1.0	17	11	0	1	127	1.3	0	4	13	3.1						85	318.45		85.63
J.	54	8	1.0	31	13	5	2	110	1.1	0	1	9	3.2	110	17	1.4	17	7	121	376.35	20.65	496.6
J.	55	7	0.9	26	14	0	3	142	1.7	0.07	3	15	2.2						93	405.3		311.46

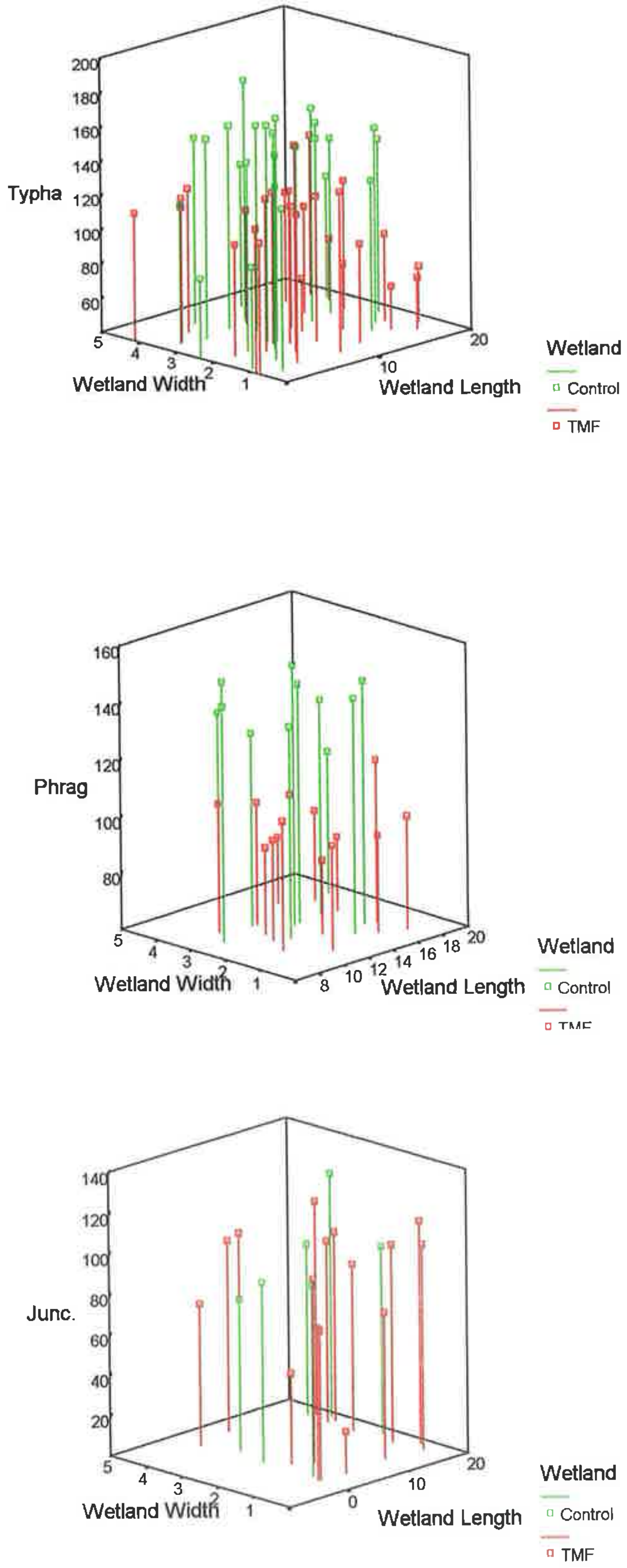
Table 4.6 Comparison in ecotypic variation in vegetative data between wetlands.

Typha latifolia		TMF Wetland (m)	Control Wetland (m)
Typha Stem Length	Mean	109	143
	Minimum	65	85
	Maximum	162	180
	Std Dev.	24	23
	Variance	566	534
Typha Leaf Width	Mean	1.2	1.5
	Minimum	.8	.9
	Maximum	1.9	1.9
	Std Dev.	.3	.3
	Variance	.1	.1
% of Plot Infested	Mean	9	9
	Minimum	0	0
	Maximum	42	38
	Std Dev.	13	10
	Variance	2	1

Phragmites australis		TMF Wetland (m)	Control Wetland (m)
Phrag. Stem Length	Mean	97	138
	Minimum	83	110
	Maximum	117	152
	Std Dev.	9	11
	Variance	88	126
Phrag. Leaf Length	Mean	20	19
	Minimum	12	16
	Maximum	26	22
	Std Dev.	4	2
	Variance	17	4
Leaf Width	Mean	1.7	1.6
	Minimum	1.4	1.2
	Maximum	2.3	1.9
	Std Dev.	.3	.2
	Variance	.1	.0

Juncus effusus		TMF Wetland (m)	Control Wetland (m)
Juncus Stem Length	Mean	83	93
	Minimum	20	75
	Maximum	110	121
	Std Dev.	24	15
	Variance	555	238

Fig. 4.9 Three-dimensional comparisons between Typha, Phrag and Juncus stem lengths between wetlands.



between wetlands in stem lengths for each plant species three-dimensionally. For the three species the mean stem length is higher in the Control than in the TMF wetland. *Typha* leaf width (1.2 and 1.5 cm) and *Phragmites* leaf length (12 and 16 cm) are also higher in the Control. The mean percentage of *Typha* stems infested per quadrat by *Lepidoptera* in both wetlands is 9%, indicating that *Typha* stems in the TMF wetlands were not more or less susceptible to infestation than in the Control.

As determined from the data in Tables 4.4 and 4.5, descriptive statistics comparing ecotypic variation in reproductive data for *Typha* and *Phragmites* species between wetlands are as follows:

	Typha		***Phragmites***	
	TMF	Control	TMF	Control
No. of Flowers				
Mean	2	5	4	6
Minimum	0	0	0	0
Maximum	6	15	15	36
Std. Deviation	2	4		
Flower Length (cm)				
Mean	15	13	16	16
Minimum	8	9	12	13
Maximum	26	17	22	19
Std. Deviation	4	2	2	2
Flower Width (cm)				
Mean	3.0	2.8	5	7
Minimum	2.5	2.2	3	5
Maximum	3.4	3.2	9	10
Std. Deviation	0.2	0.3	2	1

These values indicate lower mean numbers of *Typha* flowers in the TMF wetland than in the Control, however mean *Typha* flower lengths and flower widths are higher in the TMF than in the Control. There are also lower mean numbers of *Phragmites* flowers in the TMF wetland but again mean flower lengths and flower widths are similar in both wetlands. Overall, these data indicate greater densities and numbers of flowers of *Typha* and *Phragmites* in the Control than in the TMF wetland.

The data in Tables 4.4 and 4.5 also yield the following descriptive statistics:

	Species Richness		*Total Cover*		*Total Density*	
	TMF	Control	TMF	Control	TMF	Control
Mean	5	6	49%	74%	27	44
Minimum	4	4	2%	40%	7	17
Maximum	9	8	98%	100%	61	117
Std. Deviation	1	1	22%	19%	12	26

These values indicate similar mean values for species richness between wetlands even though mean total density and total cover is much higher in the Control. Overall, vegetative and reproductive data used to determine vegetative ecotypic variation between both wetlands shows greater vegetative success for *Typha* and *Phragmites* in the Control wetland and for *Juncus* in the TMF wetland. However, according to Mitsch (1992) vegetation success, which has been the primary indicator of the success of restored wetlands, should be measured more by the success of the original objective of the wetland than by the success of individual species (Mitsch, 1992). In the case of the TMF wetland, sustainability is the original objective and species richness and diversity were selected as important indicators of wetland sustainability as indicated by Brower *et al*. (1990), UNEP/IUCN/WWF as cited by Burton (1992), Bagatto and Shorthouse (1999) and Stoughton and Marcus (2000). Given values for species richness were similar for both wetlands, further calculations were conducted to compare species diversity between wetlands.

4.2.2 Measures of Species Diversity

A community is said to have a high species diversity if many equally, or nearly equally, abundant species are present. High species diversity indicates a highly complex community for a greater variety of species allows for a larger array of species interactions (Brower *et al.*, 1990). To investigate differences in species diversity between the TMF and the Control wetlands the following indices of diversity were calculated: Margalef's Index, Simpson's Index, and the Shannon Diversity Index. These indices calculate diversity using a variety of techniques ranging from simple measures incorporating species richness to more complex measures based on information theory and the concept of uncertainty as outlined in

Brower *et al.* (1990). Summarized calculations for these indices are outlined below. (Appendix B outlines these calculations in detail.)

4.2.2.1 Margalef's Index

Margalef's Index (D_a) is the simplest measure of species diversity and is based on species richness (Brower *et al.*, 1990). It is calculated as:

$D_a = (s-1) / \text{Log } N$

Where: s = No. of species and N = No. of individuals

Calculated values of D_a for each region in the TMF and Control wetlands are:

	TMF Wetland **D_a**	Control Wetland **D_a**
Total Cell	3.790	3.288
Typha Region	4.252	3.143
Phragmites Region	3.488	3.582
Juncus Region	3.532	4.263

These results show the similarity in D_a values for each wetland region in the TMF and Control wetlands in addition to the overall D_a for each wetland. In a study conducted by Pritchard (2000), values of 0.7 and 1.0 for D_a were obtained for two wetland sites in Florida, U.S., which had been stressed by lead acid. These values were the lowest obtained in this study which also evaluated a reference forest wetland and reference pond which had values of 1.7 and 3.0 for D_a respectively. Other wetland areas had D_a values ranging from 1.8 to 3.2 respectively (Pritchard, 2000).

4.2.2.2 Simpson's Index

Simpson's index considers not only the number of species and the total number of individuals but also the proportion of the total that occurs in each species. The quantity *l* is a measure of dominance. A community with high diversity will have low dominance (Brower *et al.*, 1990).

Simpson's Dominance (*l*) is calculated as:

$$l = \frac{\sum n_i (n_i - 1)}{N (n - 1)} \qquad \text{Inverse of l: } d_s = 1 / l$$

Simpson Diversity (D_s) is calculated as:

$$D_s = 1 - \frac{\sum n_i (n_i - 1)}{N (n - 1)}$$

Calculated values of D_s and d_s for each region in the TMF and Control wetlands are:

	TMF Wetland		Control Wetland	
	D_s	**d_s**	**D_s**	**d_s**
Total Cell	0.715	3.509	0.682	3.135
Typha Region	0.470	1.888	0.493	1.972
Phragmites Region	0.589	2.439	0.586	2.415
Juncus Region	0.758	4.132	0.708	3.425

These results show that D_s and d_s for each wetland region in the TMF and Control wetlands in addition to the overall D_s and d_s values for each wetland are very similar. Pritchard's 2000 study reported D_s values of 0.115 and 0.504 for for two wetland sites in Florida, U.S., which had been stressed by lead acid. The reference wetlands in this study had D_s values of 0.558 and 0.691. Other wetland areas had D_s values ranging from 0.347 and 0.871 (Pritchard, 2000).

4.2.2.3 Shannon Diversity Index

The Shannon Diversity Index (H^1) is based on information theory and is related to the concept of uncertainty. High diversity is associated with high uncertainty in predicting the identity of a randomly picked individual and low diversity with low uncertainty (Brower *et al.*, 1990). H^1 was calculated to express the diversity in abundance and the diversity of coverage between the TMF and Control wetlands. It was calculated as:

$$H^1 = -\sum p_i \log p_I$$

Where: $p_i = n_i / N$ for Shannon Diversity Index of plant abundance
$p_i = c_i / C$ for Shannon Diversity Index of plant coverage

Calculated values of H^1 for plant abundance and plant coverage in the TMF and Control wetlands are:

	TMF Wetland **H^1_1**	Control Wetland **H^1_2**
H^1 of plant abundance	0.764	0.877
H^1 of plant coverage	0.580	0.539

While H^1 values for both wetlands appear similar it was important to conduct a statistical comparison of these indices.

Comparing Indices of Shannon Diversity

To compare the Indices of Shannon Diversity (H^1_1 and H^1_2) calculated for the TMF and Control wetlands to determine if the wetlands are equally diverse it was necessary to compute the variance (s^2) of H^1 for each collection where:

$$s^2 = \frac{\sum f_i \log^2 f_i - (\sum f_i \log f_i)^2/n}{n^2}$$

and

$$H^1 = -\sum p_i \log p_i \quad \text{is equivalent to} \quad H^1 = \frac{n \log n - \sum f_i \log f_i}{n}$$

Where n denotes sample size and f_i the number of observations in each category i, therefore $p_i = f_i / n$.

The t test and degrees of freedom (v) used to compare Shannon diversity indices were:

$$t = \frac{H^1_1 - H^1_2}{\sqrt{s^2_1 + s^2_2}} \qquad v = \frac{(s^2_1 + s^2_2)^2}{\frac{(s^2_1)^2}{n_1} + \frac{(s^2_2)^2}{n_2}}$$

(a) Comparing Diversity of Plant Abundance between TMF and Control Wetlands

The null hypothesis is:

H_O : The diversity of plant abundance in the TMF wetland is the same as the diversity of plant abundance in the Control.

	$\sum f_i$	$\sum f_i \log f_i$	$\sum f_i \log^2 f_i$	H^1	s^2
TMF Wetland	800	1756.4	4033.8	$H^1_1 = 0.708$	$s^2_1 = 0.00027764$
Control Wetland	1098	2634.3	6563.7	$H^1_2 = 0.641$	$s^2_2 = 0.00020213$

$$t = \frac{H^1{}_1 - H^1{}_2}{\sqrt{s^2{}_1 + s^2{}_2}} = 3.059$$

$$v = \frac{(s^2{}_1 + s^2{}_2)^2}{\frac{(s^2{}_1)^2}{n_1} + \frac{(s^2{}_2)^2}{n_2}} = 1{,}722$$

Computed $t = 3.0594$

$v = 1{,}722$

From t tables: $t_{0.001\,(2)\,1722} = 3.098$
$t_{0.05\,(2)\,1722} = 1.96$

Therefore, while the computed t is smaller than the t from the statistical tables at the 0.01 significance level, the Ho is rejected at the 0.05 significance level leading to the conclusion that the Control wetland has greater diversity of plant abundance than the TMF wetland.

(b) Comparing Diversity of Plant Coverage between TMF and Control Wetlands

The null hypothesis is:

Ho : The diversity of plant coverage in the TMF wetland is the same as the diversity of plant coverage in the Control.

	Σf_i	$\Sigma f_i \log f_i$	$\Sigma f_i \log^2 f_i$	H^1	s^2
TMF Wetland	0.4967	- 0.4178	0.4434	$H^1{}_1 = 0.5371$	$s^2{}_1 = 0.3728$
Control Wetland	0.6482	- 0.4970	0.4719	$H^1{}_2 = 0.8929$	$s^2{}_2 = 0.2161$

$$t = \frac{H^1{}_1 - H^1{}_2}{\sqrt{s^2{}_1 + s^2{}_2}} = -0.4636$$

$$v = \frac{(s^2{}_1 + s^2{}_2)^2}{\frac{(s^2{}_1)^2}{n_1} + \frac{(s^2{}_2)^2}{n_2}} = 0.986$$

Computed $t = -0.4636$

$v = 0.986$

From t tables: $t_{0.05\,(2)\,1} = 12.706$

Therefore, the Ho is accepted at the 0.05 significance level leading to the conclusion that the diversity of plant coverage in the TMF wetland is the same as the diversity of plant coverage in the Control.

4.2.2.4 Conclusions Regarding Species Diversity

Based on Margalef's Index, Simpson's Index, and the Shannon Diversity Index of plant coverage, the diversity of both the TMF and Control wetlands is very similar. When tested statistically, the Shannon Diversity Index of plant abundance indicates the Control has greater diversity than the TMF wetland at the 0.05 significance level but not at the 0.01 significance level. When the relative abundance curves in Figures 4.7 and 4.8 (graphical representations of diversity) are considered, the similarity of diversity between wetlands is again apparent. Overall, both wetland communities appear to exhibit a high degree of similarity in regard to floral diversity.

4.2.3 Measures of Community Similarity

Following the tabulation of species composition in the TMF and Control wetlands a range of indices were calculated to investigate the similarity between both communities. A large number of quantitative measures of community similarity have been proposed, given these indices do not necessarily express the same quantitative measures of similarity. From these the following indices of community similarity were calculated as outlined in Brower *et al.*, (1990): the Jacard Coefficient, the Sorensen Coefficient, Proportional Similarity, the Bray and Curtis Index, Morisita's Index, and Horn's Index. Summarised calculations for these indices are outlined below. (Appendix B outlines these calculations in detail.)

4.2.3.1 Coefficient of Community

Jacard Coefficient

The Jacard Coefficient is calculated as:

$$CC_J = \frac{c}{s_1 + s_2 - c} = 0.77$$

Where s_1 and s_2 are the number of species in each community and c is the number of species common to both communities. The CC_J indicates 77% similarity between the communities.

Sorensen Quotient of Similarity

Using similar values for s_1, s_2 and c, the Sorensen Quotient of Similarity is calculated as:

$$CC_S = \frac{2c}{s_1 + s_2} = 0.87$$

The CC_S indicates 87% similarity between the communities. Both the CC_J and CC_S indicate a high percentage of similarity between the TMF and Control wetlands.

4.2.3.2 Proportional Similarity

The index of proportional similarity takes into consideration the percentage abundance of the various species in each wetland and is calculated as:

$$P.S. = 1 - \Sigma \mid p_i - q_i \mid / 2 \quad = 0.903$$

The P.S. indicates 90% proportional similarity in plant abundance between the TMF and Control wetland communities.

4.2.3.3 Bray and Curtis Index

The Bray and Curtis Index for measuring differences in species abundance between wetlands is calculated as:

$$I_{BC} = 1 - \frac{\sum | x_i - y_i |}{\sum (x_i + y_i)} = 0.775$$

Values for I_{BC} range from 0 when two communities are vastly different to 1.0 when the two are identical in species composition and abundance. Therefore, the calculated I_{BC} value of 0.78 indicates a high degree of similarity between the wetlands.

4.2.3.4 Dominance Indices - Morisita's Index of Community Similarity

Morisita's index of community similarity is based on Simpson's Index of Dominance (l). Simpson's Indices of Dominance for communities 1 and 2 are:

$$l_1 = \frac{\sum x_i (x_i - 1)}{N_1 (N_1 - 1)} = 0.285 \qquad l_2 = \frac{\sum y_i (y_i - 1)}{N_2 (N_2 - 1)} = 0.319$$

The Morrisita index of community similarity is calculated as:

$$I_M = \frac{2 \sum x_i y_i}{(l_1 + l_2) N_1 N_2} = 0.984$$

Values for I_M range from 0 when two communities have no similarity to approximately 1.0 when the two are identical. The calculated value for I_M indicates an extremely high level of similarity between wetlands.

4.2.3.5 Information Theoretic Index – Horn's Index of Community Similarity

To calculate Horn's index of community similarity ("community overlap") (Ro) the Shannon diversity index (H^1) for each community is first calculated.

TMF Wetland $\quad H^1{}_1 = 0.764$

Control Wetland $\quad H^1{}_2 = 0.877$

Then:

$$H^1{}_3 = [N \log N - \sum (x_i + y_i) \log (x_i + y_i)] / N = 0.690$$

Where, $\quad N = N_1 + N_2$

Then:

$$H^1_4 = \frac{(N \log N - \Sigma x_i \log x_i - \Sigma y_i \log y_i)}{N} = 0.975$$

Then:

$$H^1_5 = (N_1 H^1_1 + N_2 H^1_2) / N = 0.669$$

Horn's Index of Community Similarity is calculated as:

$$Ro = \frac{H^1_4 - H^1_3}{H^1_4 - H^1_5} = 0.93$$

Horn's index Ro is 0 when the two communities have no species in common and is a maximum of 1.0 when the species are identical in both communities. Therefore, the calculated value for Ro indicates an extremely high level of community similarity.

Overall, all of the indices of community similarity calculated indicate a high degree of similarity between the TMF and Control wetlands.

4.2.4 Analysis of Production

During the summer 1999 field ecology event, three plants from each quadrat sampled in the TMF and Control wetlands were harvested for biomass determinations. The species of plant harvested depended on the region being sampled. For example, three *Typha* plants were sampled in each quadrat in the *Typha* Region and three clumps of *Phragmites* were sampled in each quadrat of the *Phragmites* Region. If three samples were not available (e.g. in the *Juncus* Region) a plant from either of the other two species was harvested. Tables 4.4 and 4.5 outline the total biomass (aerial tissues) values for each plant species in each quadrat for both wetlands. (Complete biomass data is presented in Appendix B.) These values were determined by multiplying the average plant biomass obtained for a particular species in that quadrat by the number of stems of that species in the quadrat.

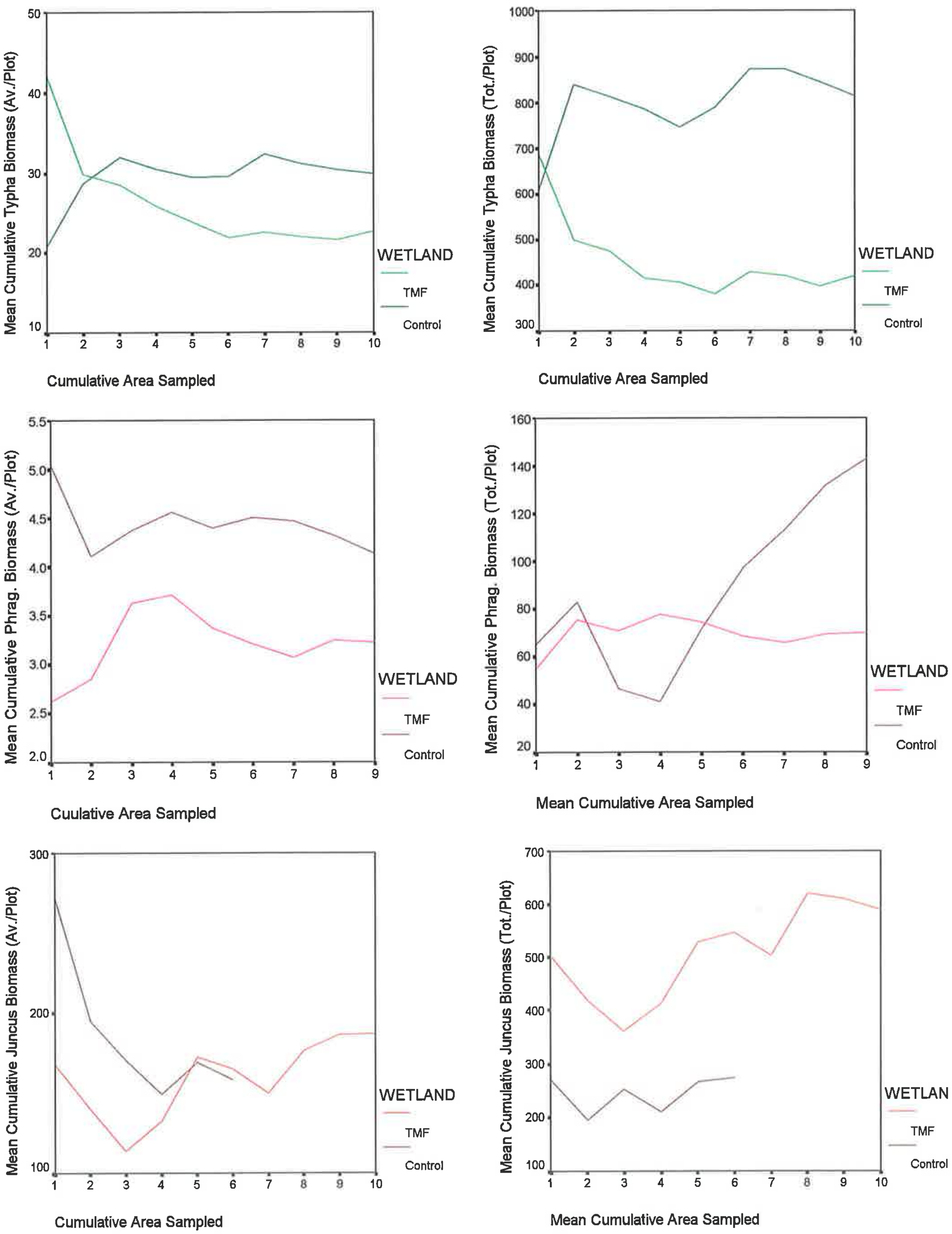
As determined from the data in Tables 4.4 and 4.5, descriptive statistics comparing Biomass data for *Typha* and *Phragmites* and *Juncus* species between wetlands are as follows:

		TMF Wetland g/m^2	Control Wetland g/m^2
***Typha* Biomass**	Mean	284.70	579.30
	Minimum	46.99	159.03
	Maximum	939.72	1326.81
	Std Dev.	233.25	238.92
Relative Biomass $RB_i = B_i / \Sigma B$		0.51	0.84
***Phragmites* Biomass**	Mean	56.92	119.32
	Minimum	9.97	8.26
	Maximum	98.88	260.80
	Std Dev.	32.04	102.58
Relative Biomass $RB_i = B_i / \Sigma B$		0.05	0.08
***Juncus* Biomass**	Mean	431.67	275.08
	Minimum	159.68	85.63
	Maximum	1438.08	496.60
	Std Dev.	341.89	154.56
Relative Biomass $RB_i = B_i / \Sigma B$		0.44	0.08

From these statistics it is obvious that mean total biomass values per quadrat for *Typha* and *Phragmites* are higher in the Control than in the TMF wetland whereas mean values for *Juncus* are higher in the TMF wetland. Relative biomass values are much closer between wetlands for *Phragmites*.

These results are illustrated in the performance curves outlined in Figure 4.10. The biomass data in Tables 4.4 and 4.5 were used to plot these curves. Mean cumulative biomass (average/quadrat and total/quadrat) for each species was plotted as a function of the cumulative area sampled. These curves emphasise the higher biomass values for *Typha* and *Phragmites* in the Control wetland and the higher values for *Juncus* in the TMF wetland. These results were expected given the higher abundance values for *Typha* and *Phragmites* in the Control and for *Juncus* in the TMF wetland. The productivity results for *Typha* and *Phragmites* were expected in the Control given it was initially seeded with wetland soils with higher levels of nutrients than the peat in the TMF wetland. Although slow release fertiliser was applied to the TMF wetland, it took longer for an extensive cover to be established on this wetland than on the Control. The rapid establishment of *Typha* in the Control possibly impeded the growth and coverage of *Juncus* in this wetland.

Fig. 4.10 Performance Curves for *Typha, Phragmites* and *Juncus* mean biomass.



An independent samples t-test was conducted to compare mean biomass values for *Typha*, *Phragmites*, and *Juncus* species in the TMF and Control wetlands. Each variable was tested for normality prior to analysis using Shapiro-Wilk's and Kologorov-Smirov Lilliefors tests for normality. Each variable also was tested for homogeneity of variance using the Levene statistic. Variables were log transformed prior to analysis when they did not exhibit normality. The results of the analysis are as follows:

	t-test for Equality of Means t	df	Sig. (2-tailed)
Log *Typha* Biomass	-5.121	51	.000
Log *Phragmites* Biomass	-.943	23	.355
Log *Juncus* Biomass	1.250	21	.225

The independent samples t-test indicated a significant difference in mean *Typha* biomass values between the wetlands at the 0.01 significance level. However, there was no significant difference between the wetlands in mean biomass values for *Phragmites* and *Juncus* at a significance level of 0.05.

4.3 WETLAND VEGETATION AND FAUNA

The aims of this research include an assessment of the feasibility of creating a diverse wetland ecosystem (as found in nature) over pyritic tailings, which will attract and provide the habitat for fauna of various types. While the data obtained in the 1999 field floral ecology study indicate that mean total density and cover is higher in the Control than in the TMF wetland, it is clear that individual species success is not the primary indicator of ecosystem health. Instead, species richness and diversity were considered more robust indicators of ecosystem health. A variety of wetland cover types, including dense stands of emergent vegetation in association with areas of open water, are likely to produce more diversity and higher quality faunal habitat as determined by Nelson *et al.* (2000). Research conducted by these authors suggest the presence of open water in wetlands, in addition to a lack of dense emergent vegetation that allows for light penetration to water, enhances habitat quality as measured by invertebrate taxa richness and abundance.

During the main ecological field study in 1999 and during all of the seasonal sampling events, evidence of the presence of aquatic and other fauna was noted. Frogspawn and young frogs were observed in the TMF wetland in summer and spring of 1999 and 2000. Frogspawn was not observed in the Control. The frogspawn in the TMF wetland was observed in an area of open water in this wetland. The water profile in the TMF wetland is deeper than in the Control wetland (see Chapter Five for a complete hydrological assessment of wetlands). Figures 4.11 and 4.12 illustrate cover and water depth variations in the TMF wetland during the summer, 1999 sampling event.

In addition, as illustrated in Figure 4.13, a birds nest was observed amongst the rushes in the *Typha* region of the TMF wetland in August, 1999.

4.3 SUMMARY

The main findings of the investigation assessing ecological indicators of ecosystem health and sustainability in the pilot plant wetlands are as follows:

- After two growing seasons, following an identical initial planting regime, the composition of plant species in the TMF and Control wetlands was identified and enumerated using quadrat sampling. Of the 17 species identified 15 occurred in both wetlands. The exceptions include *Iris pseudacorus* which was found only in the TMF wetland and *Mentha aquatica* which was found only in the Control.

- Relative densities, relative frequencies, relative coverage, and importance values were calculated for each species. *Gramineae* and *Typha latifolia* are the dominant species in both the TMF and Control wetlands. *Phragmites australis* is the next most dominant species in both wetlands. There is, however, a substantial difference in the degree of dominance exerted by *Juncus effusus* in the TMF wetland in comparison to the Control. Overall, IV values and Relative Abundance Curves indicate that both wetlands have high species diversity and low dominance.

- Vegetative and reproductive data were used to determine ecotypic variation in *Typha, Phragmites,* and *Juncus* species between both wetlands. There were lower mean densities of *Typha* in the TMF wetland than in the Control, similar mean

Fig 4.11 Cover and water depth at top end (*Typha* Region) of TMF Wetland, Summer, 1999.

Fig. 4.12 Cover and water depth in lower end (*Phragmites* Region) of TMF Wetland, Summer 1999.

Fig. 4.13 Birds nest made from *Typha* leaves observed in the *Typha* Region of the TMF Wetland, Summer 1999.

densities of *Phragmites* between wetlands, and higher mean densities of *Juncus* in the TMF wetland. Overall, field data including reproductive data indicate greater vegetative success for *Typha* and *Phragmites* in the Control than in the TMF wetland.

- Vegetative data also indicated similar mean values for species richness between wetlands even though mean total density and total cover is much higher in the Control. In the case of the TMF wetland, species richness and diversity are important indicators of wetland sustainability given high species diversity indicates a highly complex community with a larger array of species interactions. Margalef's and Simpson's Indices for individual wetland regions are very similar. A comparison of Shannon Diversity indices between wetlands indicates the Control wetland has greater diversity of plant abundance than the TMF wetland, however, the diversity of plant coverage in the TMF wetland is the same as the diversity of plant coverage in the Control.

- A range of indices including the Jacard Coefficient, the Sorensen Coefficient, Proportional Similarity, the Bray and Curtis Index, Morisita's Index, and Horn's Index. were calculated to investigate the similarity between both communities. These indicate a high level of similarity between both wetlands.

- Mean total biomass values per quadrant for *Typha latifolia* and *Phragmites australis* were higher in the Control than in the TMF wetland whereas mean values for *Juncus effusus* were higher in the TMF wetland. These results are to be expected given the higher abundance values for *Typha* and *Phragmites* in the Control.

- A variety of wetland cover types, including dense stands of emergent vegetation in addition to areas of open water, exist in the TMF wetland and are likely to produce more diversity and higher quality wildlife habitat. Evidence of the presence of aquatic and other wildlife was noted in the TMF wetland that was not observed in the Control.

A detailed correlation analyses was carried out on the ecological, hydrological, physiochemical and geochemical data produced during this study to determine what significant relationships exist between ecological health and environmental variables. This analyses is outlined in detail in Chapter Eight.

CHAPTER FIVE

RESULTS
HYDROLOGICAL AND PHYSICO-CHEMICAL INDICATORS

5.1 RESULTS – HYDROLOGICAL INDICATORS

Creating the appropriate hydrological conditions for the establishment of a wetland ecosystem is a prerequisite for success. Hydrologic conditions in natural wetlands are dependant on climate, seasonal patterns in streamflow and the potential for groundwater impacts. In the pilot plant, hydrologic conditions are dependant on rainfall and inflows from mains water. Both wetlands were initially flooded and then fed by an uninterrupted stream of mains water that was continuously measured by individual flow guages located at the inflow point to each wetland. Rain data was collected throughout the experiment. A hydrologic analysis of the wetlands was conducted as a basis for subsequent regression analysis to investigate the relationships between hydrology and ecological health, and between hydrology and water and soil chemistry.

Aims of the hydrological analysis were as follows:

- To establish the hydrologic loading on the TMF and Control wetlands during the course of the experiment.
- To establish the pattern of depth over time, called the hydroperiod, within each wetland and to identify seasonal episodes of drought or flooding.

5.1.1 Hydrologic Inflows and Surface Hydraulic Loadings to TMF and Control Wetlands

A surface hydraulic loading range of 0.05 to 0.10 $m^3/day/m^2$ was selected as the design range for the Free-Water-Surface wetlands constructed in the pilot plant. This was based on design data from the literature for constructed wetlands. Mitsch (1992) recommends a hydrologic loading of 0.05 $m^3/day/m^2$ for marsh-type wetlands used to treat mine drainage. This design loading corresponds to a design flow of 5 to 10

m^3/day and a surface depth of 0.05 to 0.10 m. The wetlands were designed to carry the hydraulic load with an additional 1.0 m freeboard to accommodate storm events.

Once the wetland cells were constructed they were flooded to a mean depth of approximately 0.05 m and the flow guages and outlet structures adjusted to obtain a constant flow-rate of between 5 to 10 m/day. Fluctuations in the daily surface hydraulic flow-rate occurred due to rainfall additions and very occasional site vandalism (when flow guages or outlet chambers were adjusted).

Table 5.1 outlines cumulative flows into the TMF and Control Wetland in 1999 and 2000, as registered on the flow guages, for the months during which intensive water chemistry sampling was conducted in 1999 and 2000. This Table also outlines mean daily inflows to both wetlands during these months. These are illustrated graphically in Figure 5.1. Based on these data the mean surface hydraulic loadings from mains water for the TMF and Control wetlands were 0.103 $m^3/day/m^2$ and 0.101 $m^3/day/m^2$ respectfully.

A one-way analysis of variance (ANOVA) was conducted to compare the means of this inflow data for the TMF and Control wetlands. This data was tested for normality prior to ANOVA analysis using Shapiro-Wilk's and Kologorov-Smirov Lilliefors tests for normality. This data also was tested for homogeneity of variance using the Levene statistic. The null hypothesis (H_o) in this analysis proposes that the population means for both wetlands are the same. The ANOVA analysis determined there was no significant difference between the wetlands in influent flow-rates ($p=0.742$).

Given both systems had equal surface areas, both also received equal hydraulic loadings from rainfall. Therefore, both systems received equal hydrologic inflows during the course of the experiment.

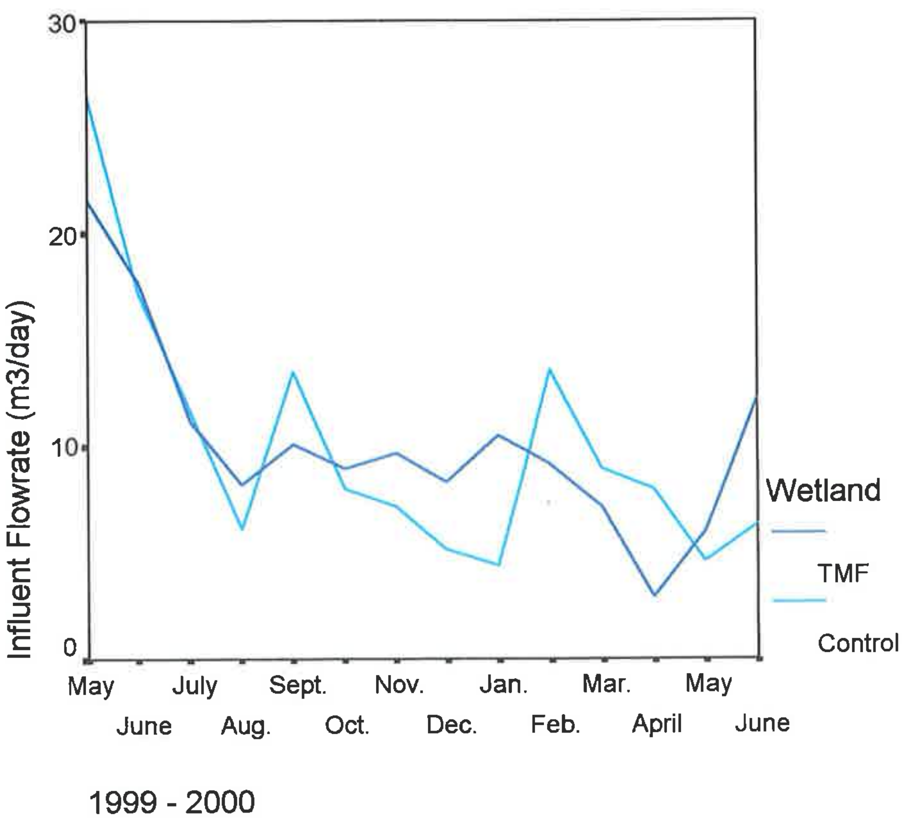
5.1.2 Hydroperiod for TMF and Control Wetlands

The hydroperiod for a wetland is the pattern of depth over time and includes the frequency of flooding and seasonal patterns. The accumulation of water in the TMF wetland is clear from a review of the mean water depth profiles through each wetland

Table 5.1 Cumulative flows and mean monthly inflows for TMF and Control Wetlands, 1999-2000.

	Cumulative Flow (m3)		Mean Monthly Inflows (m3/day)	
	TMF Wetland	Control Wetland	TMF Wetland	Control Wetland
1999				
May	464.97	996.78	21.69	26.52
June	900.04	1426.61	17.72	17.21
July	1330.4	1915.35	11.15	11.63
August	1662.57	2273.53	8.29	6.13
September	1700.75	2336.72	10.17	13.54
October	1974.02	2679.51	9.00	8.01
November	2250.11	2929.78	9.70	7.18
December	2711.42	3044.46	8.31	5.18
2000				
January	2711.42	3159.4	10.58	4.40
February	3034.01	3687.59	9.23	13.65
March	3231.11	4100.51	7.22	8.99
April	3321.72	4360.26	2.95	8.04
May	3534.66	4437.92	5.99	4.60
June	3811.37	4676.12	12.3	6.36
August	4466.23	4809.22		

Fig. 5.1 Monthly inflow toTMF and Control Wetlands during 1999 –2000.



as outlined in Table 5.2 and Figure 5.2. The water depth in the TMF wetland increases significantly across its length from 0.05 m to 0.10 m to 0.17 m, whereas the water depth through the Control remains consistently at 0.06 m. Although the design plans called for a bed gradient of 1%, it is possible the TMF wetland was constructed with a steeper gradient causing higher water levels to accumulate at the bottom end of this wetland. Also, it is possible that the outlet drainage manifold was not flush with the base of the wetland causing water to collect until reaching the level of the manifold.

Overall, an increase in water depth along the length of the TMF wetland was maintained throughout the experiment whereas the water depth in the Control remained at the same level along its length. Figures 5.3 and 5.4 illustrate the water depth in both wetlands three-dimensionally. These distinctive patterns in water depth are examined in detail in Chapter Eight to establish whether correlations exist between wetland hydrology, ecology and physico-chemical parameters. While unintentional, the increased pattern in water depth in the TMF wetland facilitated a beneficial examination of the impact of varying water depths on the establishment of a sustainable ecosystem.

Mean seasonal water flow-rates and corresponding water depth profiles for both wetlands are outlined in Table 5.3, Figures 5.5a and b, and Figures 5.6a and b. The disparity in inflow and outflow from the TMF wetland can be explained by the addition of rainfall to the system. There is a significant increase in the mean daily outflow from the TMF wetland in spring from rainfall (18.05 m^3/day) and this corresponds to a significant increase in the water depth at the end of the wetland. The average hydrologic retention times (HRT) in the TMF wetland was 1.2 days. The recommended HRT for marsh-type wetlands used to treat mine drainage is 1 day (Mitsch, 1992).

Table 5.3 indicates that mean daily outflows for the Control wetlands were consistently lower than inflows. However, Figure 5.6 illustrates how closely inflow and outflow values resemble each other for this wetland. The reduced outflow in the Control can be explained by the enhanced transpiration from the denser vegetation mass in this wetland. Evapotranspiration slows water flow and increases contact times in wetlands (Kadlec, 1989). Also, the impact of a rain event on a vegetation flow-

Table 5.2 Descriptive statistics for water depth in TMF and Control Wetland regions, 1999-2000

Water Depth (m)

		TMF Wetland	Control Wetland
Region 1 Typha	**Mean**	**.05**	**.06**
	Minimum	.02	.04
	Maximum	.09	.07
	Median	.05	.06
	Std Dev.	.02	.01
	Variance	.00	.00
Region 2 Phrag.	**Mean**	**.10**	**.06**
	Minimum	.07	.04
	Maximum	.13	.09
	Median	.10	.06
	Std Dev.	.02	.02
	Variance	.00	.00
Region 3 Juncus	**Mean**	**.17**	**.06**
	Minimum	.11	.03
	Maximum	.28	.10
	Median	.15	.06
	Std Dev.	.06	.02
	Variance	.00	.00

Figure 5.2 Mean seasonal water depth in TMF and Control Wetlands, 1999-2000.

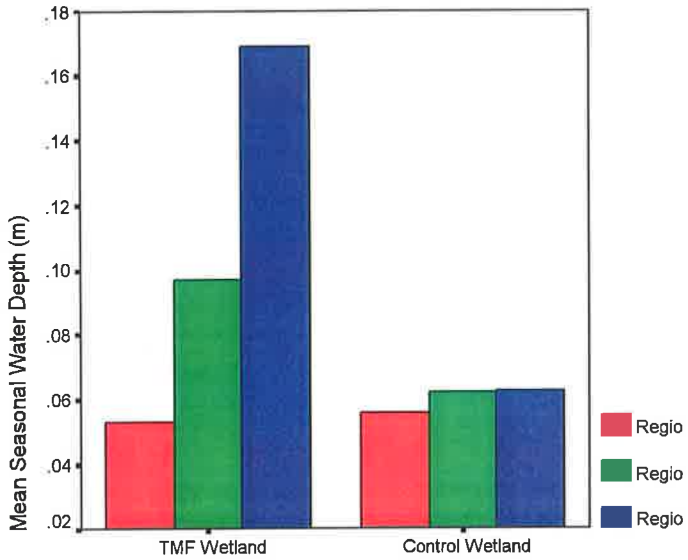


Figure 5.3 Three-dimensional water depth profile in TMF Wetland in Summer 1999.

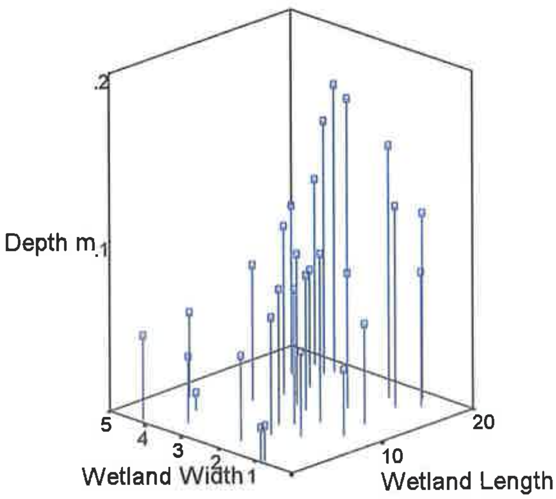


Fig. 5.4 Three-dimensional water depth profile in Control Wetland in Summer 1999.

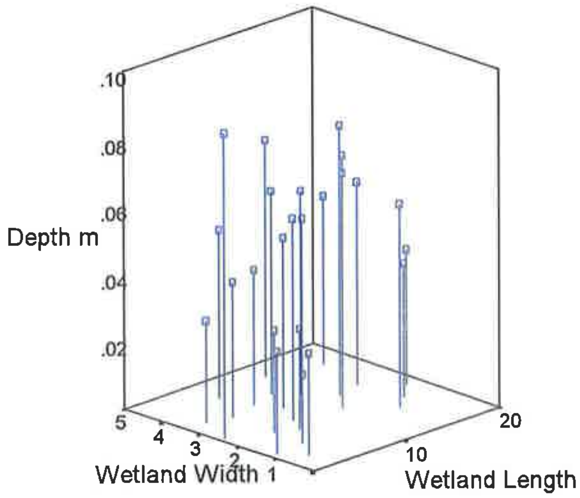


Table 5.3 Seasonal flowrates and corresponding water depths in TMF and Control Wetlands.

Wetland	Season	Mean Inflow (m3/day)	Mean Outflow (m3/day)	Wetland Region		
				Typha (*Top*)	Phragmites (*Middle*)	Juncus (*End*)
TMF	Winter	9.11	9.62	0.04	0.10	0.17
	Spring	9.75	18.05	0.06	0.12	0.27
	Summer	11.41	12.33	0.04	0.09	0.12
Control	Winter	7.82	6.78	0.06	0.06	0.07
	Spring	10.17	7.81	0.06	0.07	0.09
	Summer	8.01	7.43	0.06	0.06	0.04

Fig. 5.5a Inflow and outflow streams in TMF Wetland, 1999-2000.

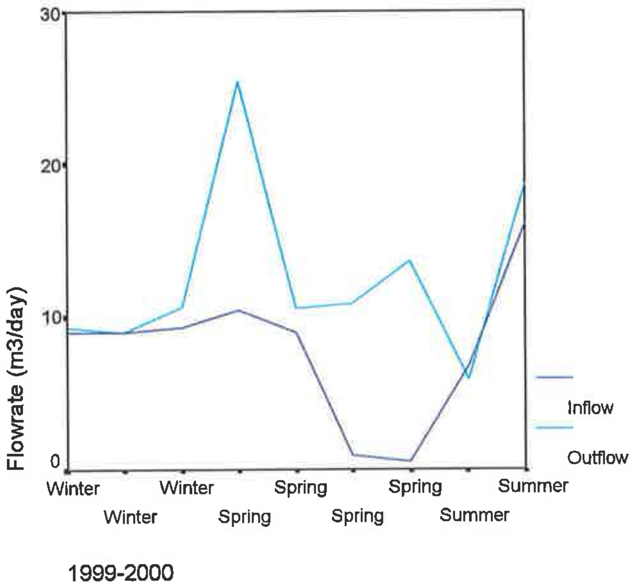


Fig. 5.5b Seasonal depth profiles in TMF Wetland, 1999-2000.

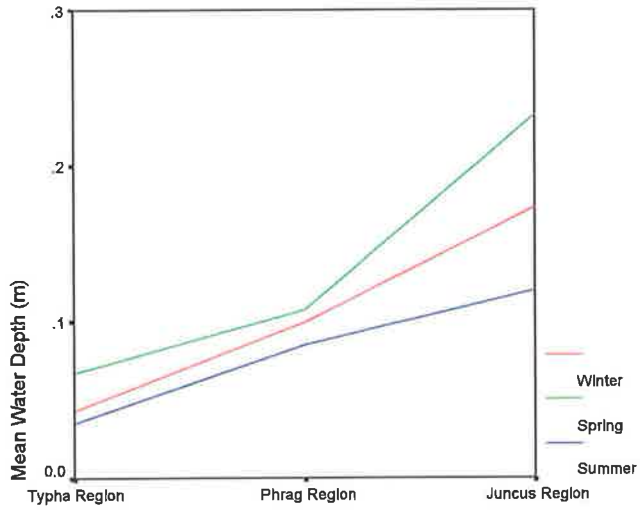


Fig. 5.6a Inflow and outflow streams in Control Wetland, 1999-2000.

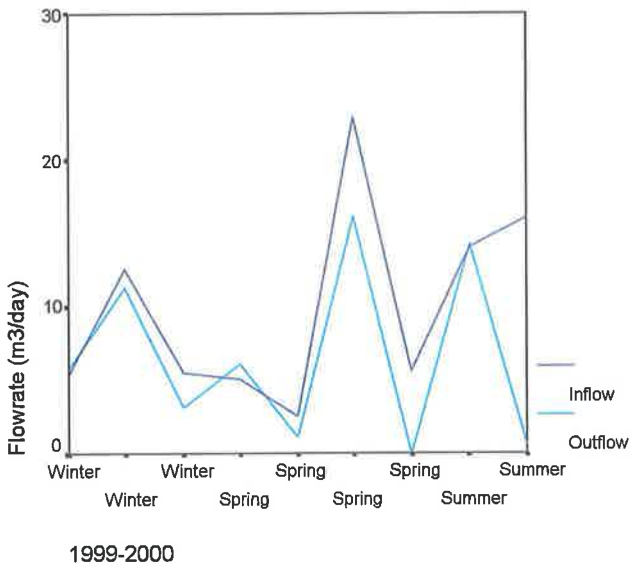
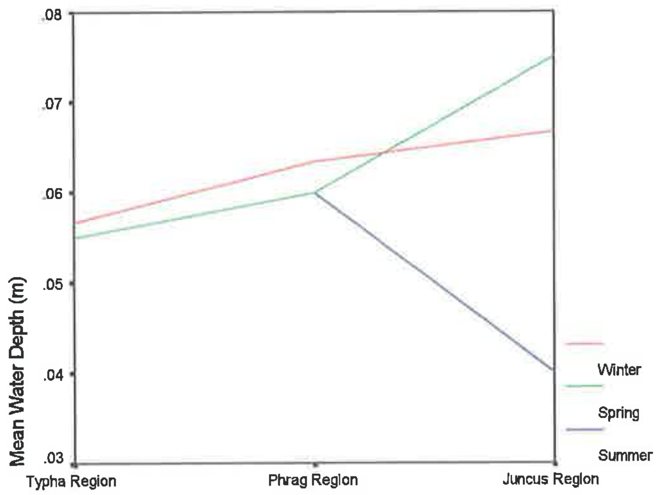


Fig. 5.6b Seasonal depth profiles in Control Wetland, 1999-2000.



controlled wetland is mitigated because of a surge damping mechanism (Kadlec, 1989). Linacre (1976) cites several studies of small vegetated wetlands with enhanced evapotranspiration for what amounts to be potted plants and calls this the "clothesline effect". Very small wetlands will react strongly to the surrounding microclimate (Kadlec, 1989).

5.2 RESULTS – PHYSICO-CHEMICAL INDICATORS

In the pilot system extensive physico-chemical sampling of the water column was conducted during the field ecology study conducted in summer 1999, and seasonally throughout 1999 and 2000. This facilitated a complete characterisation of the water chemistry of the TMF and Reference/Control wetlands throughout the experiment.

Aims of the physico-chemical analysis were as follows:

- To characterise the overall water chemistry of the TMF and Control wetlands in 1999 and 2000.
- To compare mean physico-chemical parameters between the wetlands in summer 1999.
- To compare mean metal concentrations between the wetlands in summer 1999.
- To compare seasonal physico-chemical parameters between the wetlands throughout 1999 and 2000.
- To compare seasonal metal concentrations between the wetlands throughout 1999 and 2000.
- To compare mean physico-chemical parameters and metal concentrations in Silvermines wetland with the TMF and Control wetlands in 2000.
- To compare mean sulphate concentrations between the TMF and Control wetlands in 1999 and 2000, and to compare these with Silvermines wetland in 2000.

5.2.1 Water Column Sampling in TMF and Control Wetlands, Summer 1999

Throughout summer, 1999, extensive water chemistry sampling and analysis was conducted in the pilot plant wetland facility. Figures 4.1 and 4.2 illustrate the locations of 30 and 25 quadrants sampled in the TMF and Control wetlands respectively. The water chemistry of influent and effluent samples taken during this sampling programme in summer 1999 met the E.U. standards for potable water abstractions. This data is included later in this chapter as part of the seasonal water column sampling analyses, and is outlined fully in Section 5.2.2.5.

5.2.1.1 Physico-chemical Parameters in TMF and Control Wetlands, Summer 1999

In each quadrat, water depth, pH, conductivity, dissolved oxygen (D.O.) and temperature were measured in triplicate on-site. Descriptive statistics for the mean physico-chemical parameters over the entire area of each wetland are outlined in Tables 5.4a through 5.4d. Mean values for each of the three wetland regions are outlined in Tables 5.5a through 5.5d. Water chemistry parameters measured in each quadrat during summer, 1999 are outlined in Appendix C.

These results indicate the general water chemistry of both wetlands is similar and reflects that of natural wetland ecosystems. The mean pH of the water column in the TMF wetland was 7.44 and the pH range was 5.59 to 8.49, whilst that of the Control was 7.20 with a range of 6.72 to 8.00. These mean values conform to the standards specified for salmonid and cyprinid waters under the EC Freshwater Fish Directive which require a pH range of 6.0 to 9.0.

An examination of the pH values within the regions of the TMF wetland (Table 5.5) shows the lower pH value of 5.59 occurring in the *Typha latifolia* (top) section of the TMF wetland. Figure 5.7a compares the spatial variation in pH in both wetlands three-dimensionally and illustrates that this is a single outlier value in Quadrant 11. A review of the field notes indicates that 50 % of the quadrat had no standing water. Under non-flooded, oxidised conditions changes can occur in soil pH, redox potential and metal mobility (Gambrell, 1994) which can effect water chemistry. While this single outlier value does not significantly impact the water chemistry of the wetland cell it points to the potential impact of sediment oxidation processes on water chemistry which are further investigated in Chapters Six and Eight.

Mean conductivity measurements in both wetlands reflect pH measurements. The mean conductivity of the water column in the TMF wetland was 0.26 mS/cm with a

Table 5.4a –5.4d Descriptive statistics for physico/chemical parameters in wetland cells, 1999.

pH of Water Column

	TMF Wetland	Control Wetland
Mean	**7.44**	**7.20**
Minimum	5.59	6.72
Maximum	8.49	8.00
Median	7.48	7.15
Std Dev.	.60	.27
Variance	.36	.07

Conductivity (mS/cm)

	TMF Wetland	Control Wetland
Mean	**.26**	**.23**
Minimum	.15	.16
Maximum	.46	.26
Median	.26	.23
Std Dev.	.05	.02
Variance	.00	.00

Dissolved Oxygen (mg/l O2)

	TMF Wetland	Control Wetland
Mean	**6.19**	**7.54**
Minimum	.90	3.30
Maximum	13.10	12.60
Median	5.60	7.30
Std Dev.	2.95	2.81
Variance	8.70	7.91

Temperature (oC)

	TMF Wetland	Control Wetland
Mean	**17.48**	**13.83**
Minimum	14.00	10.10
Maximum	19.90	15.90
Median	17.70	14.10
Std Dev.	1.29	1.11
Variance	1.67	1.23

Fig. 5.7a Spatial variations in pH in wetland cells, 1999.

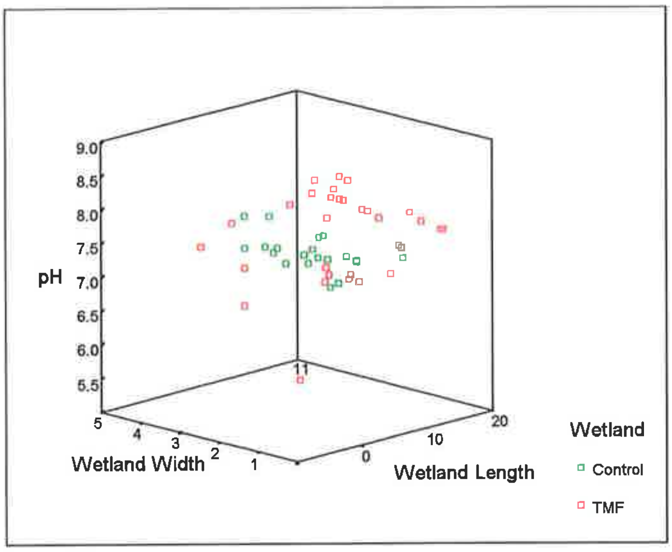


Fig. 5.7b Spatial variations in conductivity in wetland cells, 1999.

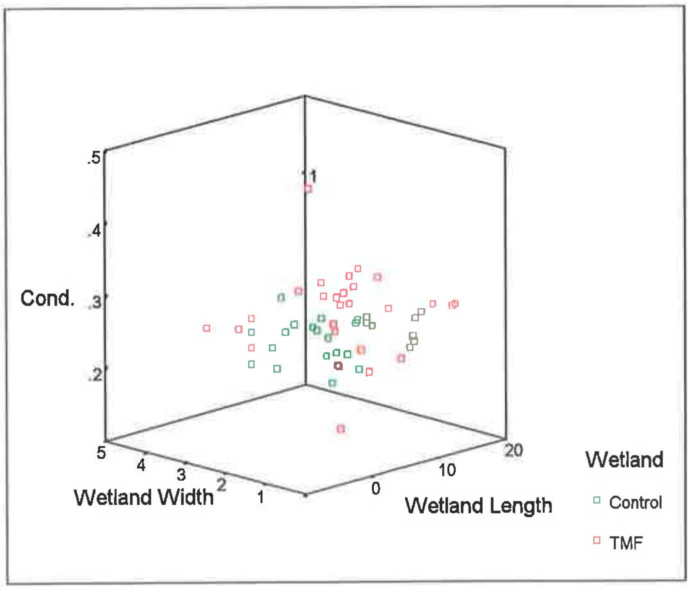


Table 5.5a –5.5d Descriptive statistics for physico/chemical parameters in regions of wetland cells, 1999.

Water depth in wetland regions (m)

		TMF Wetland	Control Wetland
Typha Region	**Mean**	**.05**	**.04**
	Min.	.01	.02
	Max.	.08	.07
	Median	.05	.04
	Std Dev.	.02	.02
	Variance	.00	.00
Phrag. Region	**Mean**	**.09**	**.06**
	Min.	.06	.04
	Max.	.12	.08
	Median	.08	.06
	Std Dev.	.02	.01
	Variance	.00	.00
Juncus Region	**Mean**	**.09**	**.05**
	Min.	.02	.03
	Max.	.17	.09
	Median	.08	.05
	Std Dev.	.06	.02
	Variance	.00	.00

D.O. of water column in wetland regions (mg/l O2)

		TMF Wetland	Control Wetland
Typha Region	**Mean**	**6.87**	**9.09**
	Min.	.90	5.60
	Max.	13.10	12.60
	Median	7.00	8.40
	Std Dev.	3.23	2.19
	Variance	10.43	4.81
Phrag. Region	**Mean**	**4.87**	**4.64**
	Min.	2.90	3.30
	Max.	7.03	5.40
	Median	5.20	4.90
	Std Dev.	1.20	.74
	Variance	1.43	.54
Juncus Region	**Mean**	**6.94**	**7.60**
	Min.	1.73	4.30
	Max.	13.10	11.40
	Median	5.40	7.35
	Std Dev.	3.59	3.06
	Variance	12.86	9.36

pH of water column in wetland regions

		TMF Wetland	Control Wetland
Typha Region	**Mean**	**7.08**	**7.26**
	Min.	5.59	6.88
	Max.	8.49	7.90
	Median	7.16	7.25
	Std Dev.	.67	.22
	Variance	.45	.05
Phrag. Region	**Mean**	**7.86**	**7.01**
	Min.	7.48	6.88
	Max.	8.12	7.12
	Median	7.94	7.06
	Std Dev.	.18	.11
	Variance	.03	.01
Juncus Region	**Mean**	**7.58**	**7.45**
	Min.	7.28	6.72
	Max.	7.94	8.00
	Median	7.63	7.53
	Std Dev.	.19	.54
	Variance	.04	.30

Conductivity of water column in Wetland Regions (mS/cm)

		TMF Wetland	Control Wetland
Typha Region	**Mean**	**.26**	**.23**
	Min.	.15	.20
	Max.	.46	.26
	Median	.24	.23
	Std Dev.	.07	.02
	Variance	.00	.00
Phrag. Region	**Mean**	**.27**	**.24**
	Min.	.25	.22
	Max.	.30	.26
	Median	.27	.24
	Std Dev.	.01	.01
	Variance	.00	.00
Juncus Region	**Mean**	**.24**	**.20**
	Min.	.15	.16
	Max.	.29	.21
	Median	.26	.21
	Std Dev.	.05	.02
	Variance	.00	.00

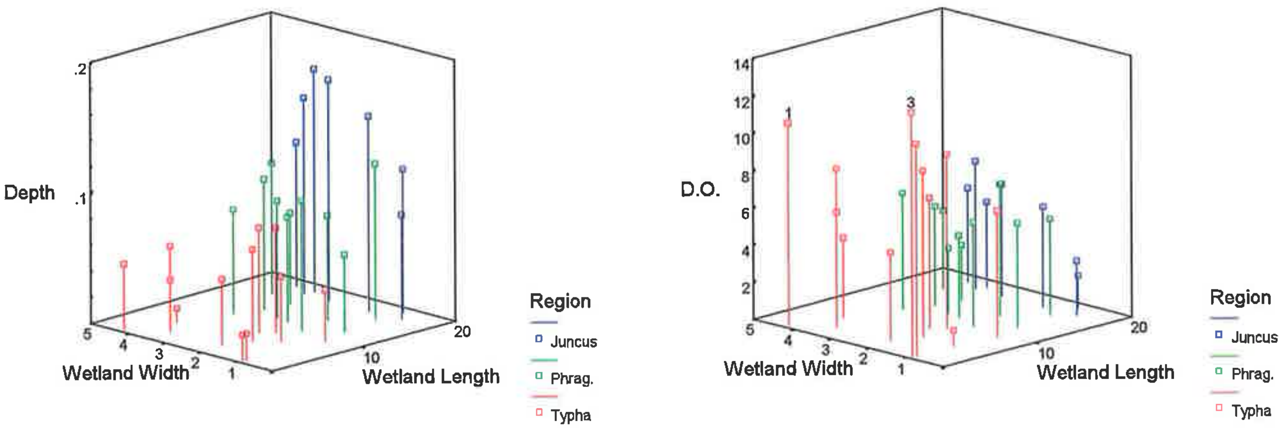
range of 0.15 mS/cm to 0.46 mS/cm, whereas that of the Control was 0.23 mS/cm with a range of 0.16 mS/cm to 0.26 mS/cm. Again, these mean values fall within reported ranges of 0.01 to 0.3 mS/cm for conductivity in surface waters (Kadlec and Knight, 1996).

A review of the conductivity values within the regions of the TMF wetland (Table 5.5) shows the higher value of 0.46 mS/cm occurring in the *Typha latifolia* region. Again, Figure 5.7b illustrates this as a single outlier value in Quadrant 11 that does not significantly impact the water chemistry. However, it indicates higher concentrations of ions in this quadrat, possibly sulphates. Under non-flooded conditions metal sulphides in wetland sediments are oxidised leading to increased sulphate concentrations. These processes are also further investigated in Chapter Eight.

Variations in D.O. occurred throughout the 1999 summer sampling event in both wetlands. These variations can be attributed to temperature fluctuations and biological activity. Mean D.O. concentrations were 6.19 mg/L O_2 for the TMF wetland with a range of 0.9 mg/L O_2 to 13.10 mg/L O_2, and 7.54 mg/L O_2 for the Control with a range of 3.30 mg/L O_2 to 12.60 mg/L O_2. Table 5.5 indicates higher D.O. levels in the Control particularly in the *Typha latifolia* region of this wetland. The variation in mean D.O. levels between wetlands may be explained by the influence of higher plant densities in the Control which influence D.O. levels through photosynthesis. Photosynthetic processes cause a rise in D.O. during daylight hours (Csuros, 1994).

Diurnal D.O. can change considerably over a 24 hour period during the summer with undersaturation occurring at dawn and saturation or supersaturation occurring in late afternoon with rising temperatures. In still waters, pockets of high and low D.O. can occur depending on the water depth and the rates of biological processes. In the TMF wetland, the extreme value of 0.9 mg/L O_2 was recorded in Quadrant 13 where 95% of the peat substrate had no cover of standing water. The remaining 5% where the reading was taken consisted of saturated peat and can be associated with anoxic conditions. Figure 5.8 illustrates the variation in D.O. concentration and water depth within the TMF Wetland. Generally, higher levels of D.O. were measured in the

Figure 5.8 Comparisons between water depth (m) and D.O. (mg/L O_2) in TMF Wetland regions, 1999.



Tables 5.6a – 5.6d One-way ANOVA to compare physico-chemical parameters in wetlands in 1999.

pH	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	3.268	1	3.268	21.962	0
Within Groups	18.302	123	0.149		
Total	21.569	124			

Conductivity	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1.18E-02	1	1.18E-02	13.675	0
Within Groups	0.115	134	8.60E-04		
Total	0.127	135			

D.O., Logdo	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.387	1	0.387	7.302	0.008
Within Groups	6.204	117	5.30E-02		
Total	6.591	118			

Depth	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1.44E-02	1	1.44E-02	16.801	0
Within Groups	0.114	133	8.58E-04		
Total	0.128	134			

Typha latifolia region where mean water depth is 0.05 m compared to the other two regions where mean water depth is 0.09 m and 0.13 m respectively.

5.2.1.1 ANOVA to Compare Physico-chemical Parameters in Wetlands, 1999

A one-way analysis of variance (ANOVA) was conducted to compare the means of physico-chemical parameters measured in the TMF and Control wetlands in summer, 1999. Each variable was tested for normality prior to ANOVA analysis using Shapiro-Wilk's and Kologorov-Smirov Lilliefors tests for normality. Each variable also was tested for homogeneity of variance using the Levene statistic. Variables were log transformed prior to ANOVA analysis when they did not exhibit normality.

The null hypothesis (H_o) in this analysis proposes that the population means for both wetlands are the same. As outlined in Tables 5.6a through d, there was a significant difference between the wetlands in pH ($p<0.001$), conductivity ($p<0.001$), D.O. ($p<0.05$) and depth ($p<0.001$). This was anticipated for depth (see Section 5.1) and D.O. (given the time difference in sampling the wetlands) but unexpected for pH and conductivity. A closer examination of the ANOVA analysis reveals the 95% confidence interval for the mean pH is 7.41 to 7.63 for the TMF wetland and 7.12 to 7.27 for the Control. Similarly, the 95% confidence interval for the mean conductivity is 0.241 to 0.258 for the TMF wetland and 0.226 to 0.236 for the Control. While the ANOVA analysis indicates the means for pH and conductivity between the wetlands varies significantly, the actual values within the TMF wetland are well within normal values for natural wetlands.

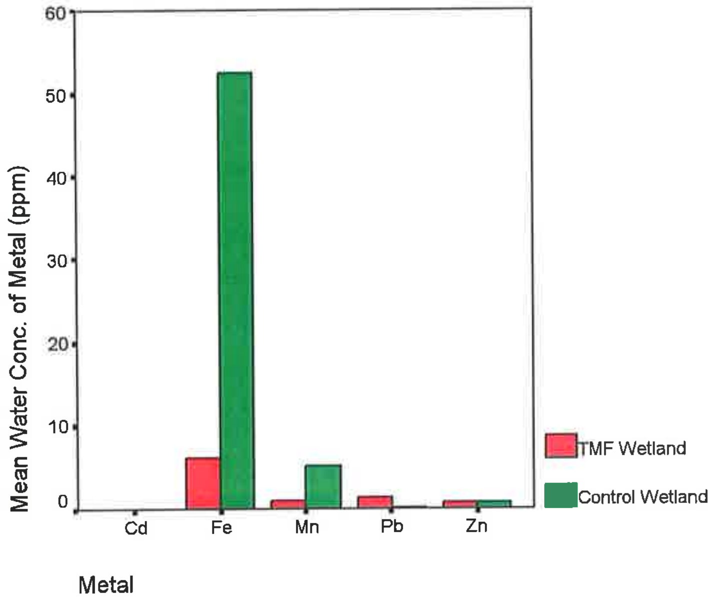
5.2.1.3 Metal Concentrations in TMF and Control Wetlands, Summer, 1999

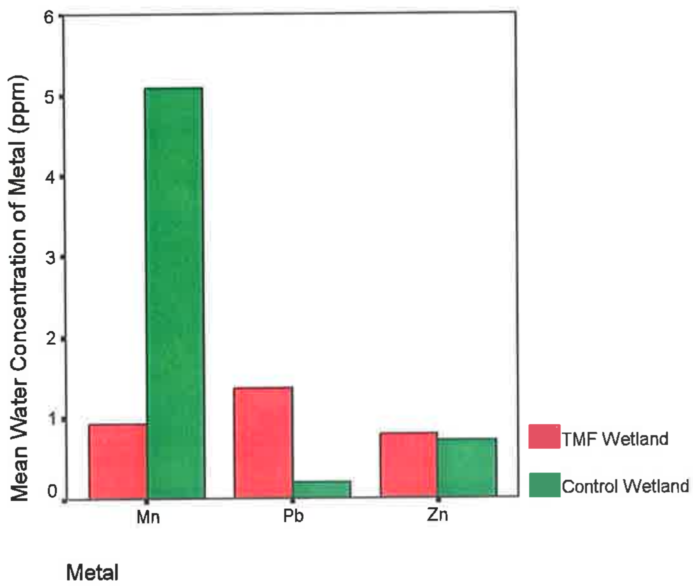
During the sampling programme in summer 1999, triplicate water samples were taken in each quadrat and analysed for metals including Cd, Fe, Mn, Pb and Zn. Descriptive statistics for mean metals concentrations over the entire area of each wetland are outlined in Table 5.7. Figures 5.9a and 5.9b illustrate the differences in overall mean metal concentrations between the TMF and Control wetlands. Boxplots illustrating the median, interquartile range (25^{th}–75^{th} percentile), outliers and extreme values for each

Table 5.7 Descriptive statistics for metal concentrations in wetlands, Summer 1999.

		TMF Wetland (ppm)	Control Wetland (ppm)
Cd	**Mean**	**.002**	**.003**
	Min.	<.001	<.001
	Max.	.013	.013
	Median	.000	.002
	Std Dev.	.004	.003
	Variance	.000	.000
Fe	**Mean**	**6.076**	**35.314**
	Min.	.190	6.988
	Max.	51.370	74.389
	Median	1.045	32.089
	Std Dev.	12.910	19.460
	Variance	166.661	378.692
Mn	**Mean**	**.944**	**2.392**
	Min.	.065	.131
	Max.	7.326	6.145
	Median	.201	1.963
	Std Dev.	1.926	2.025
	Variance	3.708	4.102
Pb	**Mean**	**1.364**	**.204**
	Min.	<.05	.050
	Max.	18.211	.473
	Median	.038	.171
	Std Dev.	3.955	.119
	Variance	15.644	.014
Zn	**Mean**	**.787**	**.708**
	Min.	<.05	.077
	Max.	7.473	2.289
	Median	.084	.440
	Std Dev.	1.969	.573
	Variance	3.877	.328

Fig 5.9a –5.9b Mean metal concentrations in water column, Summer 1999.





metal are presented in Figure 5.10. Metal concentrations in the water column of each quadrat sampled during summer 1999 are outlined in Appendix D.

Mean Cd values for the water column in the TMF and Control wetlands are similar (0.002 mg/l and 0.003 mg/l respectively) and fall within the acceptable range for E.U. standards for potable water abstractions. Table 5.8 outlines these regulatory standards for metal concentrations in surface waters and examples of various metal concentrations in Acid Mine Drainage (AMD) from the literature.

Mean Fe and Mn concentrations in the water column of the TMF (6.07 mg/l and 0.944 mg/l) and Control (35.31 mg/l and 2.39 mg/l) wetlands are higher than E.U. standards for potable water extraction. Reported metal concentrations in river water impacted by AMD vary widely from 3.8 mg/l to 700.0 mg/l for Fe, and 0.29 to 200 mg/l for Mn (see Table 5.8). Given Fe and Mn values are higher in the Control, concentrations in the TMF wetland do not indicate the presence of AMD.

A review of the influent water quality data to both systems (Section 5.2.2.5 and Table 5.16) indicates mean seasonal Fe concentrations of 0.159 mg/l and 0.172 mg/l, and Mn concentrations of 0.023 mg/l and 0.044 mg/l in inflows to the TMF and Control wetlands respectively. The enhanced Fe and Mn concentrations in the water column of both wetlands are impacted by the wetland sediment in each system. The TMF wetland was seeded with peat and root ball material from natural wetlands, whereas the Control was seeded only with natural wetland soil. Natural wetland sediments have higher concentrations of Fe and Mn than peat. A full assessment of the metal concentrations in all these soils is outlined in Chapter Six.

A review of the Fe and Mn data show samples exhibiting higher metals levels in the TMF wetland were taken in quadrats with shallower water depths. This pattern is illustrated three-dimensionally in Figure 5.11. For each metal, elevated values consistently occur in Quadrats 10 and 13 which are located in the *Typha latifolia* (top) region. Extreme and outlier values were not removed from the data set prior to calculating mean values in the interests of identifying the worst case scenario for water quality from breakthrough metals from the tailings substrate. (A complete

Fig. 5.10 Mean Cd, Pb, Zn, Fe and Mn concentrations in water column of wetlands, Summer 1999. (Outliers are designated with O and extreme values with *. Numbers indicate position in data set.)

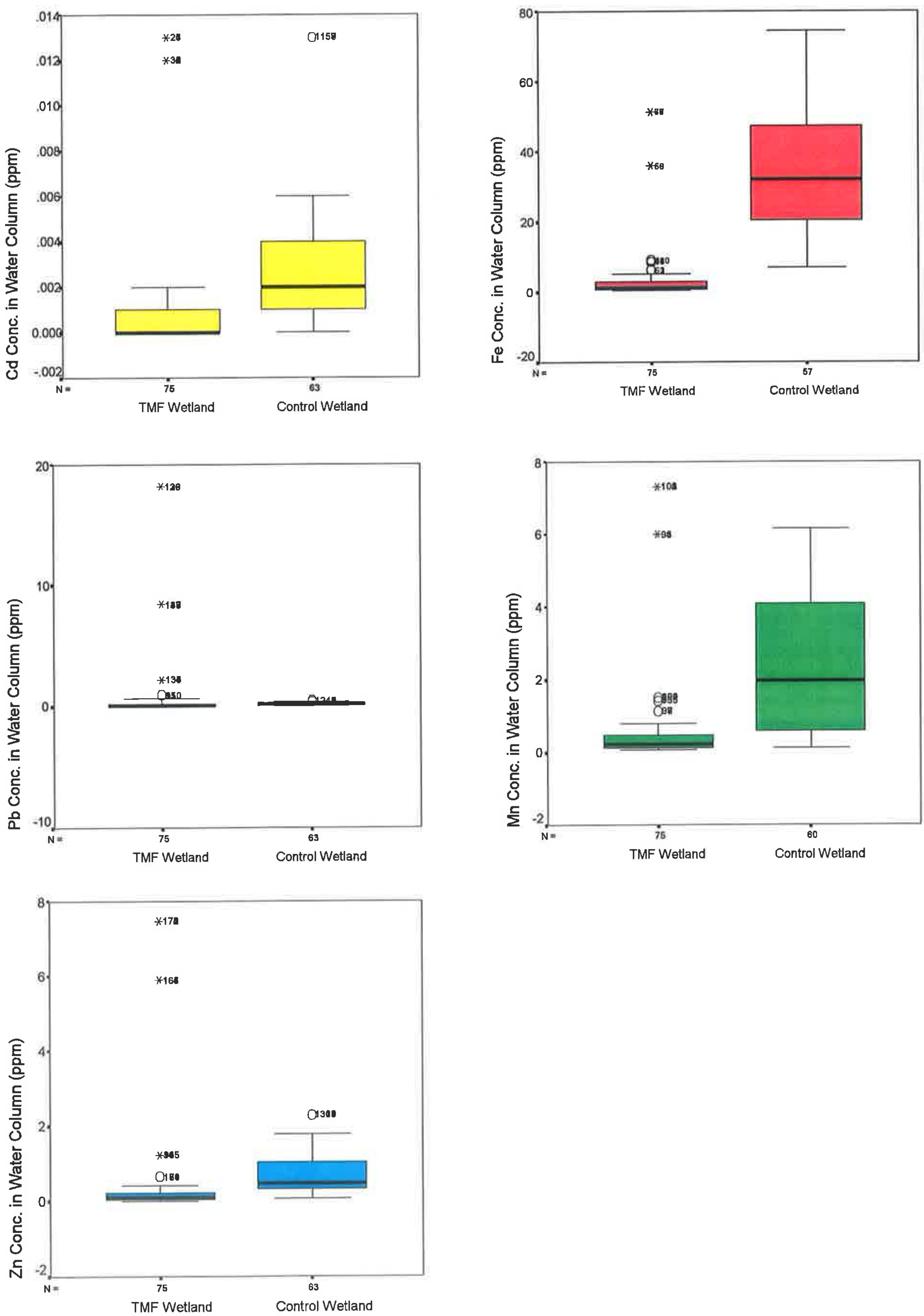
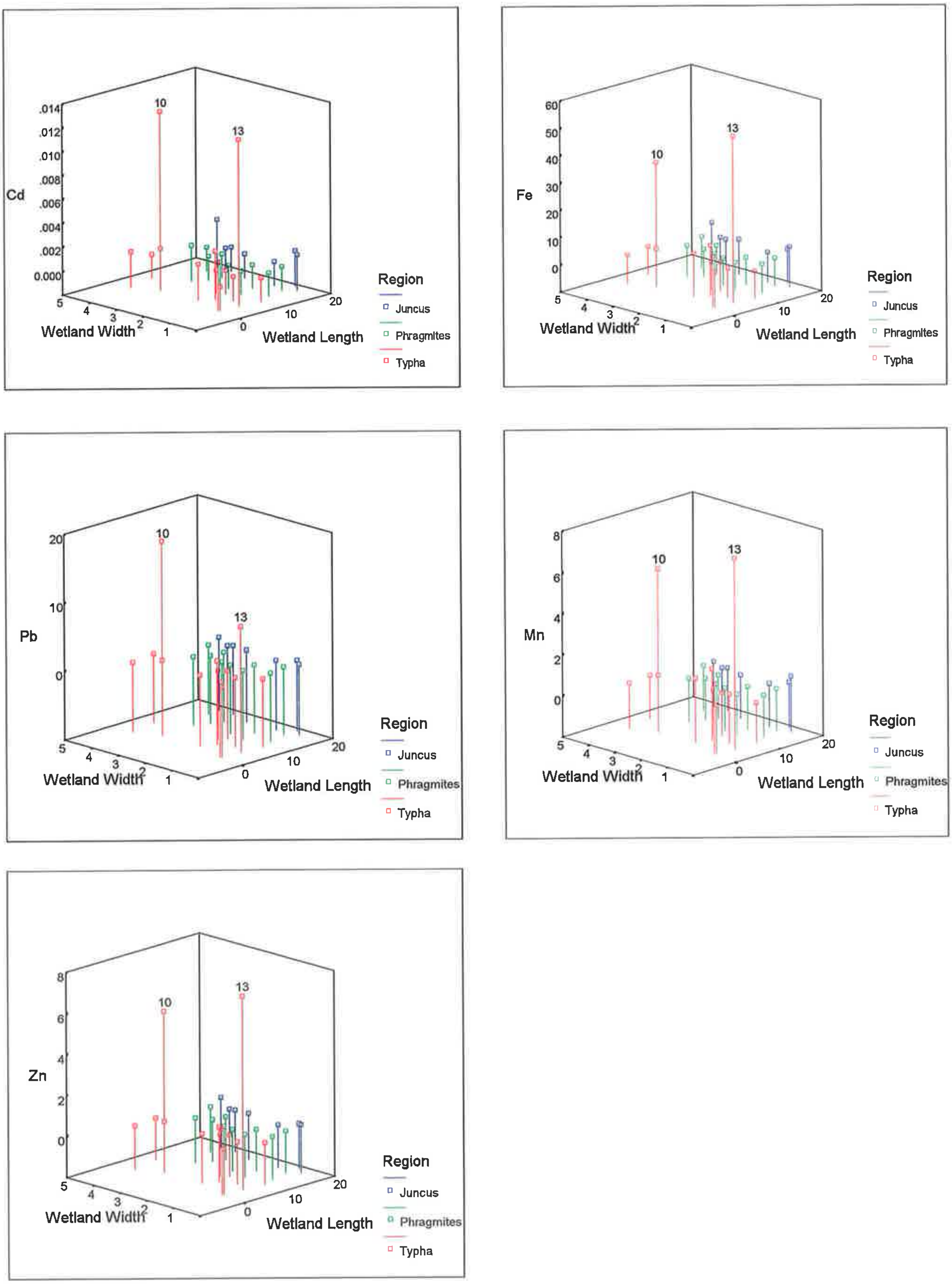


Table 5.8 **National and international standards for metal concentrations in water, and metal concentrations in AMD and wetlands impacted by AMD.**

	National & International Standards for Water (mg/l)				
	Cd	**Fe**	**Mn**	**Pb**	**Zn**
Surface Water Abstraction					
→ Directive 75/440/EEC					
A1 Treatment					
Guide	0.001	0.1	0.05	-	0.5
Maximum Admissible Concentration	0.005	0.3	-	0.05	3.00
→ Irish Standard S.I. No.294 of 1989	0.005	0.2	0.05	0.05	3.00
→ Irish Water Quality Regulations, 2001 S.I. No.12 of 2001				0.005[a] 0.010[b]	0.008[c] 0.050[d] 0.100[b]
Drinking Waters					
→ Directive 80/778/EEC					
Guide	-	0.05	0.02	-	0.10
Maximum Admissible Concentration	0.005	0.2	0.05	0.05	-
→ Irish Standard S.I. No.81 of 1988	0.005	0.20	0.05	0.05	1.0
Freshwater Fish					
→ EC Directive 78/659/EEC					
Salmonid					
Guide	-	-	-	-	-
Maximum Admissible Concentration	-	-	-	-	0.30[b]
Cyprinid					
Guide	-	-	-	-	-
Maximum Admissible Concentration	-	-	-	-	1.0[b]
→ Irish Salmonid Standards S.I. No. 293 of 1988	-	-	-	-	0.30[b]
British Environmental Water Quality Standards 1998 (Gray, 1999)	0.005	1.0	-	0.010[b]	0.075[b]
United States U.S. EPA Water Quality Regulations U.S. EPA 40CFR Part 131 (57 FR 60848)					
→ Acute					
Total	0.004			0.082	0.120
Dissolved	0.003			0.041	0.102
→ Chronic					
Total	0.001			0.003[b]	0.110[b]
Dissolved	0.001			0.0008[b]	0.094[b]
Metal Concentrations in River Waters					
→ U.S.A.	0.00002	0.055	0.006	0.0002	0.010
→ Mississippi River	0.0001	0.005	0.010	0.0002	0.010
→ Rhine River	0.0055	0.035	0.005	0.057	0.330
→ South Africa (AMD Impacted)	0.052	550	200	0.290	26
(Salomons & Förstner, 1984)					
Metal Concentrations in Wetlands impacted by AMD (Wójcik & Wójcik, 2000)	0.007 → 0.01	3.8 → 6.0	0.26 → 0.29	1.24 → 8.71	0.30 → 0.53
Dissolved metals in waters associated with mine drainage (Wildeman & Laudon, 1989)	0.01 → 0.3	2 → 700	1.0 → 120	0.01 → 0.5	0.3 → 400
Tennessee Valley Authority Acid Drainage Wetlands (Brodie, Hammer and Tomljanovich, 1989)					
AMD Inflow	-	11 → 170	4.9 → 24	-	-
Wetland Outflow	-	0.5 → 17.0	3.8 → 3.5	-	-
AMD (Wenerick et al., 1989)	-	440.8	76.4	-	-
AMD (Wieder, 1993)	-	119	19	-	-
AMD Impacted Watershed (Soucek et al, 2000a and 2000b)	-	5.78 → 17.09	1.27 → 3.29	-	-

a Standard based on ≤100mg/l $CaCO_3$ water hardness
b Standard based on >100mg/l $CaCO_3$ water hardness
c Standard based on ≤10mg/l $CaCO_3$ water hardness
d Standard based on ≤50mg/l $CaCO_3$ water hardness

Fig 5.11 Spatial concentrations of Cd, Pb, Zn, Fe and Mn in TMF wetland regions during Summer, 1999.



analysis of the correlations between metal concentrations in the water column and water depth occurs in Chapter Eight.)

Mean Pb and Zn concentrations in the TMF (1.364 mg/l and 0.787 mg/l) and Control (0.204 mg/l and 0.708 mg/l) also are higher than those required under the most recent (2001) Irish water quality regulations (see Table 5.8). Concentrations of these metals in river water impacted by AMD also vary widely from 0.29 mg/l to 8.71 mg/l for Pb, and 0.53 mg/l to 400 mg/l for Zn (see Table 5.8). A review of the boxplots in Fig. 5.10, however, shows extreme data values in the TMF wetland that disproportionately affect overall mean metal values within the cell.

Figure 5.11 shows these values occur again in Quadrants 10 and 13. Field notes indicate that 75% of Quadrant 10 and 95% of Quadrant 13 had no standing water over the peat substrate. Laboratory notes on sediment cores indicate a thin covering of 0.04 m of peat over tailings in Quadrant 10 (N.B. substrate layer was subjected to compression during core sampling). Quadrant 13 had a covering of 0.09 m of peat. Other quadrants had ≤ 0.09 m peat covering tailings but were covered with standing water.

Metal levels in the water column are reduced significantly in the middle and end sections of the TMF wetland. Table 5.9 and Figure 5.12 outline these reductions in metal profiles through the wetland. Importantly, mean metal concentrations in the outflows from the TMF and Control wetlands in summer 1999 meet the most recent Irish water quality regulations and fall within the acceptable range for E.U. standards for potable water abstractions. Metal concentrations in the outflows from the TMF and Control wetlands in summer, 1999 were: Cd <0.001 mg/l and <0.001 mg/l; Fe 0.034 mg/l and 0.313 mg/l; Mn 0.004 mg/l and 0.110 mg/l; Pb 0.007 mg/l and 0.005 mg/l; and Zn 0.017 mg/l and 0.009 mg/l respectively. (A comprehensive analysis of seasonal metal concentrations in wetland outflows follows in Section *5.2.2.5*.)

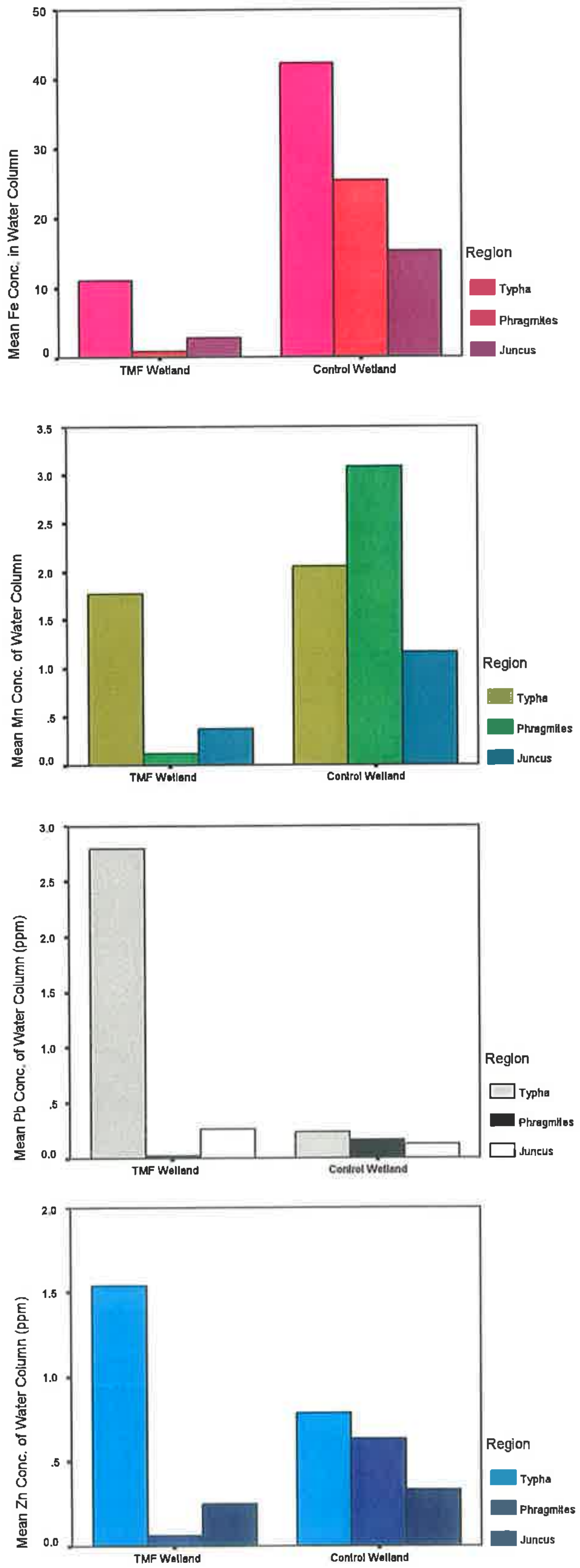
5.2.1.2 ANOVA to Compare Metal Concentrations in Wetlands, 1999

A one-way ANOVA was conducted to compare the means of metal concentrations in the water column of the TMF and Control wetlands in summer, 1999. Again each

Table 5.9 Metal concentrations in wetland regions during Summer 1999.

Metal	Region		TMF Wetland	Control Wetland
Cd	Typha	**Mean**	**.003**	**.003**
		Min.	.000	.001
		Max.	.013	.013
	Phrag.	**Mean**	**.000**	**.002**
		Min.	.000	.001
		Max.	.001	.004
	Juncus	**Mean**	**.001**	**.001**
		Min.	.000	.000
		Max.	.002	.002
Fe	Typha	**Mean**	**11.130**	**42.346**
		Min.	.375	8.943
		Max.	51.370	74.389
	Phrag.	**Mean**	**.896**	**25.519**
		Min.	.190	8.943
		Max.	2.219	37.097
	Juncus	**Mean**	**2.919**	**15.313**
		Min.	.416	6.988
		Max.	9.021	27.764
Mn	Typha	**Mean**	**1.776**	**2.056**
		Min.	.065	.144
		Max.	7.326	5.462
	Phrag.	**Mean**	**.120**	**3.094**
		Min.	.066	.131
		Max.	.225	6.145
	Juncus	**Mean**	.375	1.160
		Min.	.119	.287
		Max.	**1.420**	**2.883**
Pb	Typha	**Mean**	**2.790**	**.229**
		Min.	.000	.050
		Max.	18.211	.473
	Phrag.	**Mean**	**.031**	**.171**
		Min.	.000	.060
		Max.	.114	.267
	Juncus	**Mean**	**.258**	**.123**
		Min.	.005	.083
		Max.	.942	.197
Zn	Typha	**Mean**	**1.539**	**.783**
		Min.	.022	.198
		Max.	7.473	2.289
	Phrag.	**Mean**	**.060**	**.632**
		Min.	.000	.209
		Max.	.197	1.128
	Juncus	**Mean**	**.247**	**.329**
		Min.	.013	.077
		Max.	1.234	.713

Fig. 5.12 Metal profiles through wetland regions, Summer 1999.



variable was tested for normality and homogeneity of variance prior to ANOVA analysis. Variables were log transformed when they did not exhibit normality.

Figure 5.13 compares metal concentrations in each quadrant for the TMF and Control wetlands. Cd, Pb and Zn concentrations are generally similar in both wetlands except for the breakthrough values in Quadrats 10 and 13. Fe and Mn concentrations are higher in the Control. This evaluation is supported by the ANOVA analysis, the results of which are outlined in Table 5.10.

There was no significant difference in mean Cd ($p=0.651$) and Pb ($p=0.465$) concentrations between the wetlands. There was a significant difference in Fe ($p<0.001$) and Mn ($p<0.001$) concentrations due to higher values in the Control attributed to the impact from natural wetland sediments. Mean Zn concentrations did not differ between wetlands at a significance level of 0.001 but differed at a significance level of 0.05. The Kruskal-Wallis test, a non-parametric alternative to one-way ANOVA, was performed to check this statistic and confirmed a significant difference in mean zinc concentrations between wetlands ($H=15.753$, $p<0.001$).

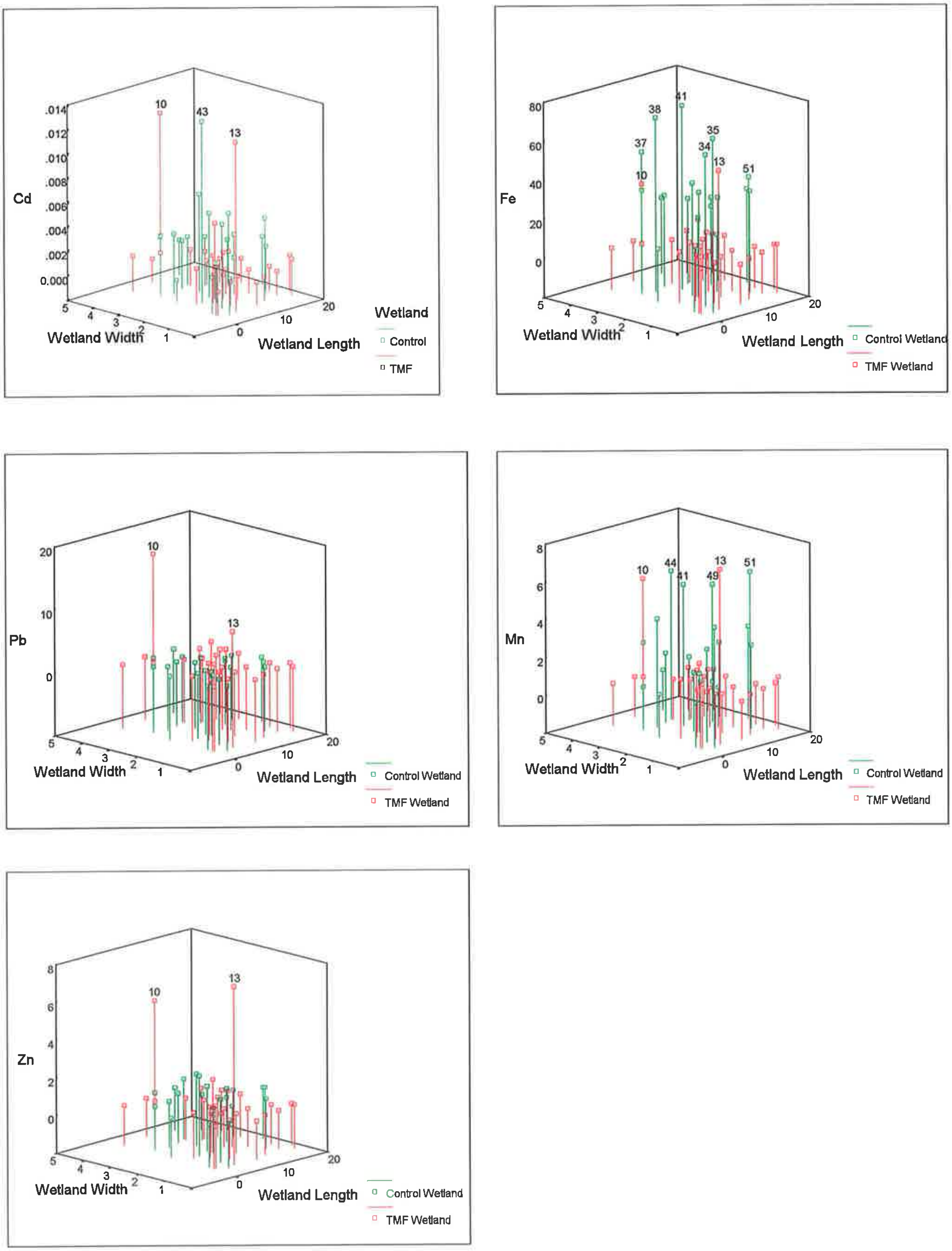
5.2.2 Seasonal Water Column Sampling in TMF and Control Wetlands, 1999-2000

Throughout 1999 and 2000, seasonal water chemistry sampling and analysis was conducted in the pilot plant wetland facility. In each region, *Typha latifolia* (top), *Phragmites australis* (middle), and *Juncus effusus* (end), water depth, pH, conductivity, D.O., temperature, total metals, and sulphate were measured in triplicate across the width of the wetland. Wetland inflows and outflows also were sampled in triplicate for pH, conductivity, D.O. temperature, total metals and sulphate.

5.2.2.1 Seasonal Physico-chemical Parameters in TMF and Control Wetlands

Descriptive statistics for the mean physico-chemical parameters over the entire area of each wetland are outlined in Tables 5.11a through 5.11e. Descriptive statistics for the mean physico-chemical parameters in wetland inflows and outflows are outlined in

Fig 5.13 Spatial concentrations of Cd, Pb, Zn, Fe and Mn in TMF and Control wetlands during summer, 1999.



Tables 5.10a – 5.10e One-way ANOVA to compare metal concentrations in wetlands, 1999.

Water Concentration of Cd

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2.40E-02	1	2.40E-02	0.208	0.651
Within Groups	4.14	36	0.115		
Total	4.164	37			

Water Concentration of Fe

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	19.464	1	19.464	88.692	0
Within Groups	12.289	56	0.219		
Total	31.753	57			

Water Concentration of Mn

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	4.735	1	4.735	15.613	0
Within Groups	17.285	57	0.303		
Total	22.02	58			

Water Concentration of Pb

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.25	1	0.25	0.542	0.465
Within Groups	24.391	53	0.46		
Total	24.64	54			

Water Concentration of Zn

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	4.844	1	4.844	12.765	0.001
Within Groups	21.628	57	0.379		
Total	26.472	58			

Table 5.11a – 5.11e Descriptive statistics for seasonal physico/chemical parameters in wetlands, 1999-2000.

pH of Water Column

	TMF Wetland	Control Wetland
Mean	7.18	7.07
Minimum	5.81	5.62
Maximum	8.64	8.30
Median	7.23	7.21
Std Dev.	.65	.63
Variance	.42	.39

Conductivity (mS/cm)

	TMF Wetland	Control Wetland
Mean	.245	.245
Minimum	.160	.150
Maximum	.320	.350
Median	.255	.239
Std Dev.	.042	.054
Variance	.002	.003

Dissolved Oxygen (mg/l as O_2)

	TMF Wetland	Control Wetland
Mean	7.72	7.45
Minimum	2.76	4.13
Maximum	11.80	12.10
Median	7.20	7.20
Std Dev.	2.41	1.93
Variance	5.80	3.73

Temperature (°C)

	TMF Wetland	Wetland Control
Mean	9	9
Minimum	5	5
Maximum	18	18
Median	8	9
Std Dev.	4	3
Variance	13	9

pH of Sediment

	TMF Wetland	Control Wetland
Mean	6.71	6.40
Minimum	5.89	5.72
Maximum	7.44	7.31
Median	6.71	6.33
Std Dev.	.45	.46
Variance	.20	.21

Table 5.12a – 5.12d Descriptive statistics for physico/chemical parameters of influent and effluent streams for wetlands, 1999-2000.

pH

		TMF	Control
Inflow	Mean	7.34	7.48
	Minimum	5.85	6.81
	Maximum	8.58	8.38
	Std Dev.	.72	.48
	Variance	.53	.23
Outflow	Mean	7.28	7.31
	Minimum	6.00	6.40
	Maximum	8.22	8.52
	Std Dev.	.68	.62
	Variance	.46	.38

Conductivity (mS/cm)

		TMF	Control
Inflow	Mean	.248	.244
	Minimum	.180	.207
	Maximum	.293	.291
	Std Dev.	.045	.027
	Variance	.002	.001
Outflow	Mean	.247	.264
	Minimum	.180	.213
	Maximum	.300	.330
	Std Dev.	.037	.047
	Variance	.001	.002

Dissolved Oxygen (mg/l as O_2)

		TMF	Control
Inflow	Mean	10.21	10.22
	Minimum	7.80	8.63
	Maximum	12.30	11.66
	Std Dev.	1.52	1.01
	Variance	2.32	1.03
Outflow	Mean	9.07	9.79
	Minimum	8.30	6.80
	Maximum	10.46	14.10
	Std Dev.	.82	2.26
	Variance	.67	5.10

Temperature (°C)

		TMF	Control
Inflow	Mean	9	9
	Minimum	7	6
	Maximum	18	17
	Std Dev.	4	3
	Variance	13	10
Outflow	Mean	9	9
	Minimum	6	6
	Maximum	16	16
	Std Dev.	3	3
	Variance	9	9

Tables 5.12a through 5.12d. Seasonal water chemistry parameters measured throughout 1999 and 2000 are outlined in Appendix C.

Overall, these results indicate that the seasonal water chemistry of both wetlands is similar and reflects that of natural wetland ecosystems. The mean seasonal pH of the water column in the TMF wetland was 7.18 and the pH range was 5.81 to 8.64, whilst that of the Control was 7.07 with a range of 5.62 to 8.30. Similarly mean seasonal inflow pH values for the TMF and Control wetlands were 7.34 and 7.48 respectively, whilst mean outflow values were 7.28 and 7.31. These mean values conform to the E.C. standards specified for salmonid and cyprinid waters. Similar mean acidity values of 14.11 mg/L $CaCO_3$ and 15.67 mg/L $CaCO_3$ for the water column were determined for the TMF and Control wetlands respectively. In addition, similar alkalinity values of 14.25 mg/L $CaCO_3$ and 13.83 mg/L $CaCO_3$, and hardness values of 123.88 mg/L $CaCO_3$ and 133.33 mg/L $CaCO_3$ were determined for the TMF and Control wetlands respectively.

Seasonal conductivity measurements in both wetlands reflect pH measurements. The mean seasonal conductivity of the water column in the TMF wetland was 0.25 mS/cm with a range of 0.16 mS/cm to 0.32 mS/cm, and that of the Control was 0.25 mS/cm with a range of 0.15 mS/cm to 0.35 mS/cm. Similarly mean seasonal inflow values for conductivity in the TMF and Control wetlands were 0.25 mS/cm and 0.24 mS/cm respectively, whilst mean outflow values were 0.25 mS/cm and 0.26 mS/cm. These mean values fall within reported ranges for conductivity in surface waters.

As expected for natural systems seasonal variations in D.O. occurred throughout 1999 and 2000 in both wetlands. These variations can be attributed to temperature fluctuations, biological activity and variations in the time of sampling. Mean seasonal D.O. concentrations were 7.72 mg/L O_2 for the TMF wetland with a range of 2.76 to 11.80 mg/L O_2, and 7.45 mg/L O_2 for the Control with a range of 4.13 mg/L O_2 to 12.10 mg/L O_2. Mean seasonal inflow values for D.O. in the TMF and Control wetlands were 10.21 mg/L O_2 and 10.22 mg/L O_2 respectively, whilst mean outflow values were 9.07 mg/L O_2 and 9.79 mg/L O_2.

Figures 5.14a through 5.14c depict the mean seasonal pH, conductivity, and D.O. profiles through both wetlands and indicate that pH and conductivity in the TMF wetland is not adversely impacted by the acid-generating potential or sulphate concentration of the tailings substrate. Figure 5.15a through 5.15c illustrate the similarity in seasonal pH, conductivity and D.O. levels in both wetlands.

Figure 5.16 illustrates mean sediment pH profiles in the TMF and Control wetlands. The mean seasonal pH of the sediment in the TMF wetland was 6.71 with a pH range of 5.89 to 7.44, whilst that of the Control was 6.40 with a range of 5.72 to 7.31. This similarity is surprising given the TMF wetland has a peat substrate and low pH is often associated with peat sediments.

Figure 5.17 illustrates the similarity in seasonal temperature fluctuations in both wetlands.

5.2.2.2 ANOVA to Compare Seasonal Physico-chemical Parameters in Wetlands

A one-way ANOVA was conducted to compare the means of seasonal physico-chemical parameters in the TMF and Control wetlands. Each variable was tested for normality and homogeneity of variance prior to ANOVA analysis and log transformed when necessary.

As outlined in Table 5.13 there was no significant difference between the wetlands for seasonal mean values of pH of water ($p=0.427$), conductivity ($p=0.985$), D.O. ($p=0.612$), pH of sediment ($p=0.101$) and temperature ($p=0.858$). Therefore, with regard to seasonal physio-chemical parameters, the water chemistry of the TMF wetland is statistically indistinguishable from that of the Reference/Control wetland.

5.2.2.3 Seasonal Metal Concentrations in TMF and Control Wetlands

Descriptive statistics for seasonal mean metals concentrations in the water column over the entire area of each wetland are outlined in Table 5.14. Boxplots illustrating the median, interquartile range (25^{th}–75^{th} percentile), outliers and extreme values for

Fig. 5.14a – 5.14c Profiles of mean seasonal physico-chemical parameters through wetlands, 1999-2000.

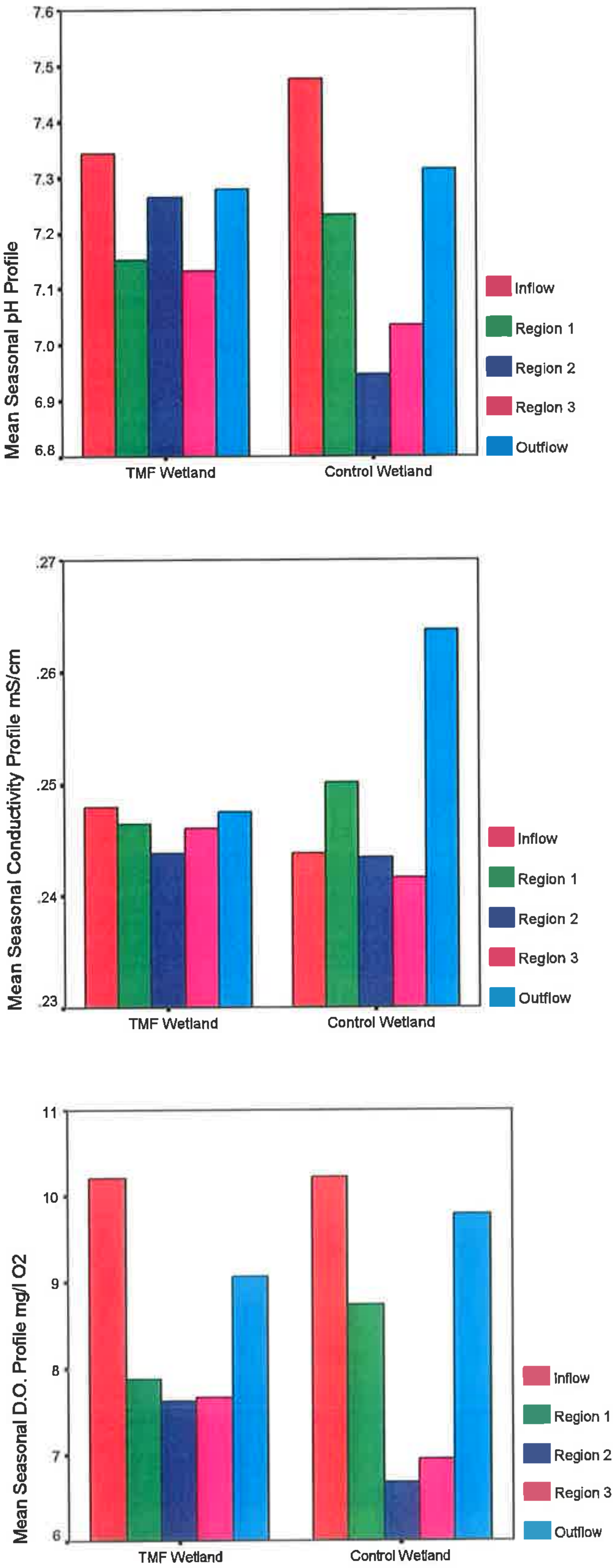


Fig. 5.15a – 5.15c Seasonal effects on physico-chemical parameters in wetlands, 1999 – 2000.

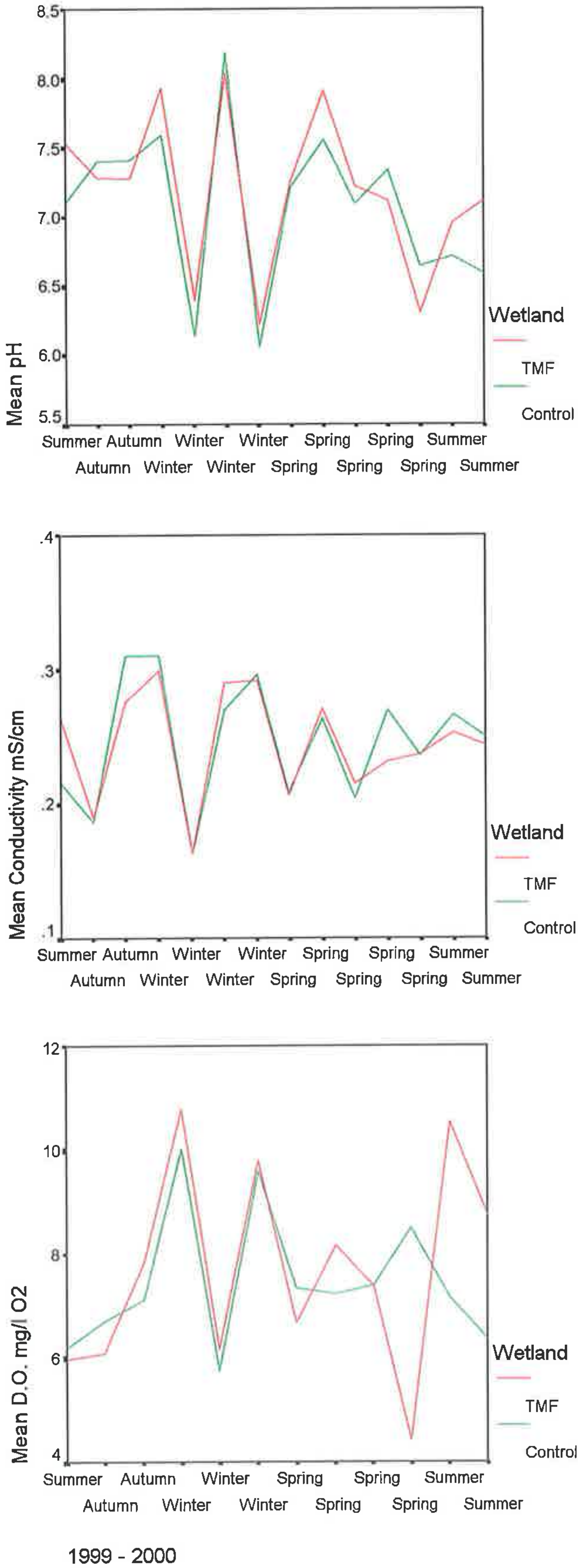


Fig 5.16 Mean sediment pH, 1999-2000.

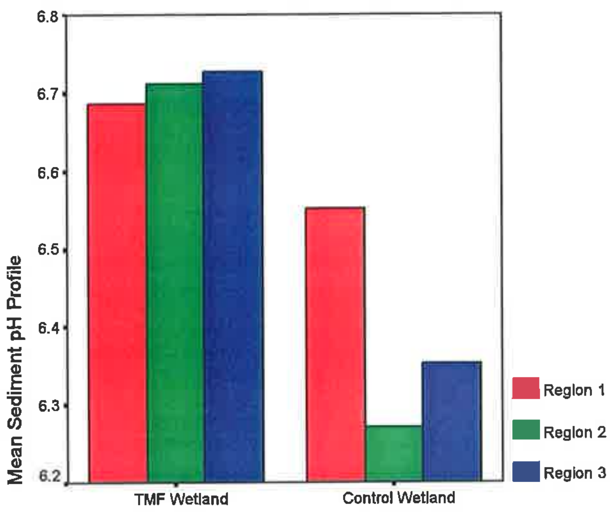


Fig. 5.17 Seasonal temperatures in wetlands.

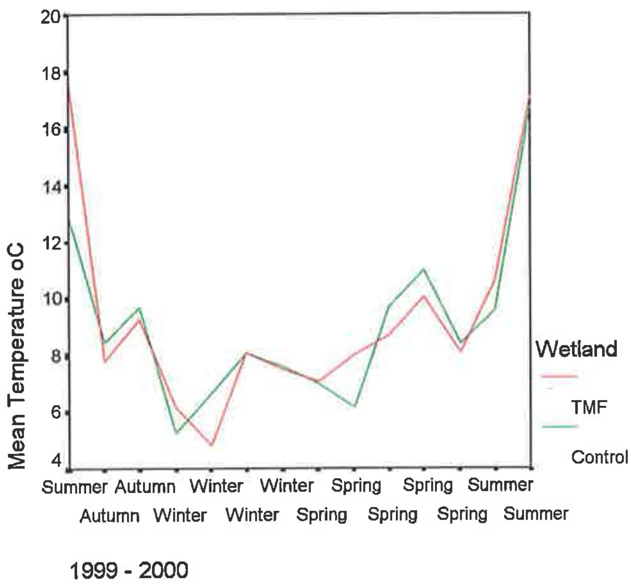


Table 5.13 One-way ANOVA to compare mean seasonal physico-chemical parameters between TMF and Control Wetlands.

		Sum of Squares	df	Mean Square	F	Sig.
pH water	Between Groups	.259	1	.259	.636	.427
	Within Groups	33.327	82	.406		
	Total	33.585	83			
D.O.	Between Groups	1.237	1	1.237	.260	.612
	Within Groups	333.440	70	4.763		
	Total	334.678	71			
Cond.	Between Groups	7.920E-07	1	7.920E-07	.000	.985
	Within Groups	.179	78	2.292E-03		
	Total	.179	79			
pH sediment	Between Groups	.594	1	.594	2.918	.101
	Within Groups	4.886	24	.204		
	Total	5.480	25			
Temp.	Between Groups	6.595E-04	1	6.595E-04	.032	.858
	Within Groups	1.668	82	2.034E-02		
	Total	1.668	83			

Table 5.14 Descriptive statistics for seasonal metal concentrations in wetlands, 1999-2000.

		TMF Wetland ppm	Control Wetland ppm
Cd	Mean	**.001**	**.001**
	Minimum	<0.001	<0.001
	Maximum	.003	.008
	Std Dev.	.001	.002
	Variance	.000	.000
Fe	Mean	**2.275**	**11.294**
	Minimum	<0.50	<0.50
	Maximum	13.761	99.983
	Std Dev.	4.466	23.699
	Variance	19.948	561.652
Mn	Mean	**.177**	**.662**
	Minimum	<0.05	<0.05
	Maximum	1.743	7.285
	Std Dev.	.381	1.559
	Variance	.145	2.429
Pb	Mean	**.320**	**.061**
	Minimum	<0.05	<0.05
	Maximum	2.925	.509
	Std Dev.	.761	.122
	Variance	.579	.015
Zn	Mean	**.207**	**.202**
	Minimum	<0.05	<0.05
	Maximum	1.485	2.085
	Std Dev.	.366	.442
	Variance	.134	.195

Table 5.15 One-way ANOVA to compare metal concentrations in wetlands, 1999-2000.

		Sum of Squares	df	F	Sig.
Cd	Between Groups	2.06E-02	1	0.258	0.618
	Within Groups	1.359	17		
	Total	1.38	18		
Fe	Between Groups	3.255	1	4.287	0.044
	Within Groups	32.646	43		
	Total	35.901	44		
Mn	Between Groups	2.124	1	3.371	0.073
	Within Groups	27.092	43		
	Total	29.216	44		
Pb	Between Groups	0.906	1	1.058	0.311
	Within Groups	29.134	34		
	Total	30.04	35		
Zn	Between Groups	1.23E-02	1	0.029	0.865
	Within Groups	16.702	40		
	Total	16.714	41		

each metal are presented in Figure 5.18. Seasonal metal concentrations in the water column throughout 1999 and 2000 are outlined in Appendix C.

Mean seasonal Cd concentrations for the TMF and Control wetlands are equal at 0.001 mg/l and fall within the acceptable range for E.U. standards for potable water abstractions (see Table 5.8).

Mean seasonal concentrations of Fe and Mn in the TMF (2.275 mg/l and 0.177 mg/l) and Control (11.294 mg/l and 0.662 mg/l) wetlands are higher than E.U. standards for potable water extraction but lower than reported metal concentrations in river water impacted by AMD (see Table 5.8). As in the summer 1999 sampling programme, Fe and Mn values are higher in the Control and the boxplots indicate higher extreme values for Fe and Mn in this wetland; therefore, Fe and Mn values do not indicate the presence of AMD in the TMF wetland.

Mean Pb and Zn concentrations in the TMF (0.320 mg/l and 0.207 mg/l) and Control (0.061 mg/l and 0.202 mg/l) wetlands also are higher than those required under Irish water quality regulations (see Table 5.8). However, these concentrations are lower than water impacted by AMD (see Table 5.8) and the boxplots indicate extreme data values in the TMF wetland that disproportionately affect overall mean metal values within the cell.

Figures 5.19 and 5.21 illustrate mean seasonal Cd, Pb, and Zn, and, Fe and Mn, profiles through the TMF and Control wetlands. These charts indicate that the seasonal extreme metal values for all metals in the TMF wetland occur in the *Typha latifolia* (top) region of this cell, as occurred during the 1999 summer sampling event.

Figures 5.20 and 5.22 illustrate seasonal variations in metals concentrations during 1999 and 2000. Cd concentrations follow the same general seasonal pattern of peaks and troughs for both wetlands with concentrations remaining relatively low. Pb levels again follow the same general seasonal pattern of peaks and troughs for both wetlands with concentrations in the TMF wetland being higher during peak episodes. The seasonal pattern of Zn concentrations in the TMF wetland appears to mimic that of lead, while Zn concentrations in the Control rise during the summer months. Fe and

Fig. 5.18 Mean seasonal Cd, Pb Zn, Fe and Mn conc.s in water column of wetlands, 1999-2000. (Outliers are designated with O and extreme values with *. Numbers indicate position in data set.)

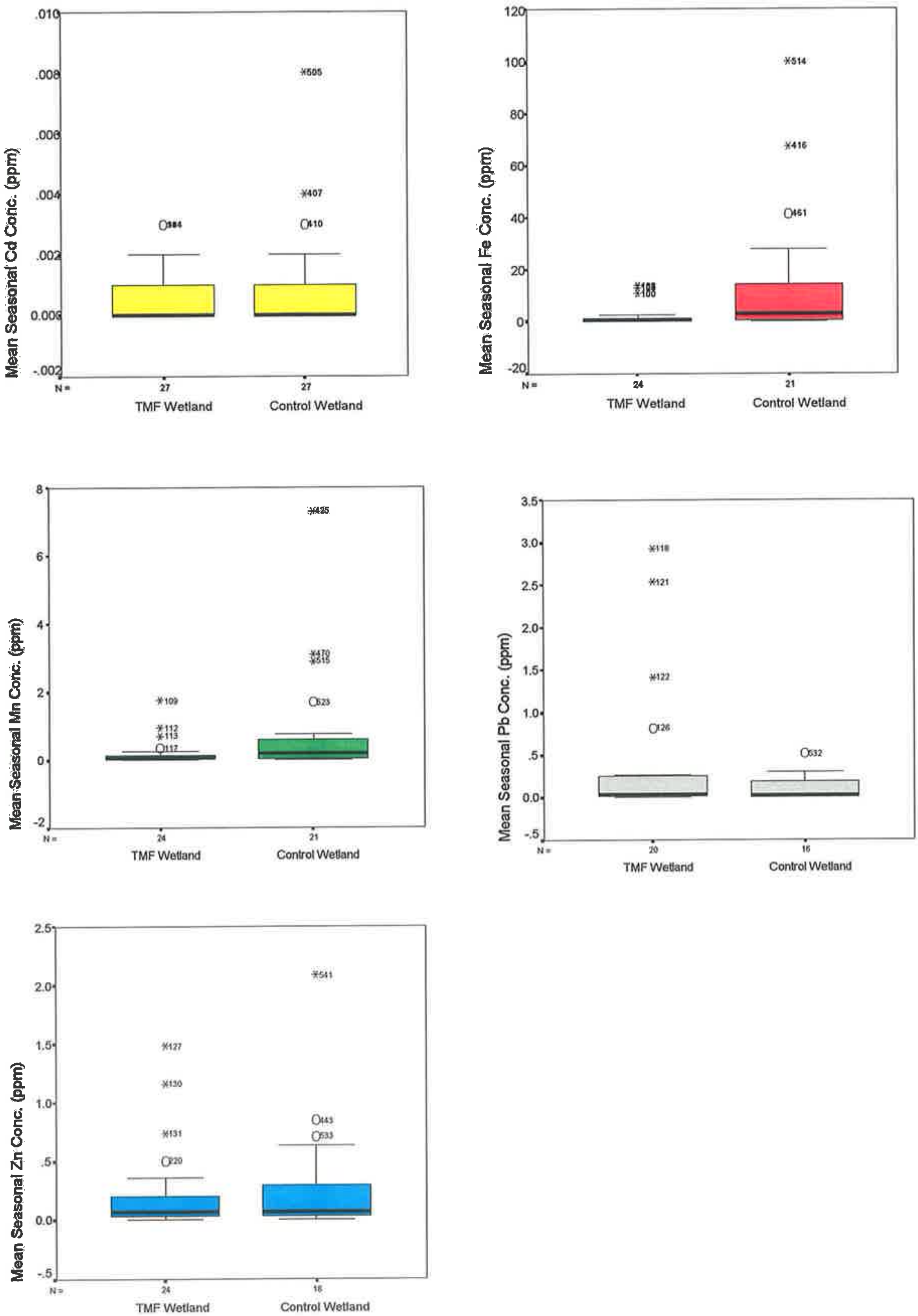


Fig. 5.19 Mean seasonal Cd, Pb and Zn profiles in wetlands.

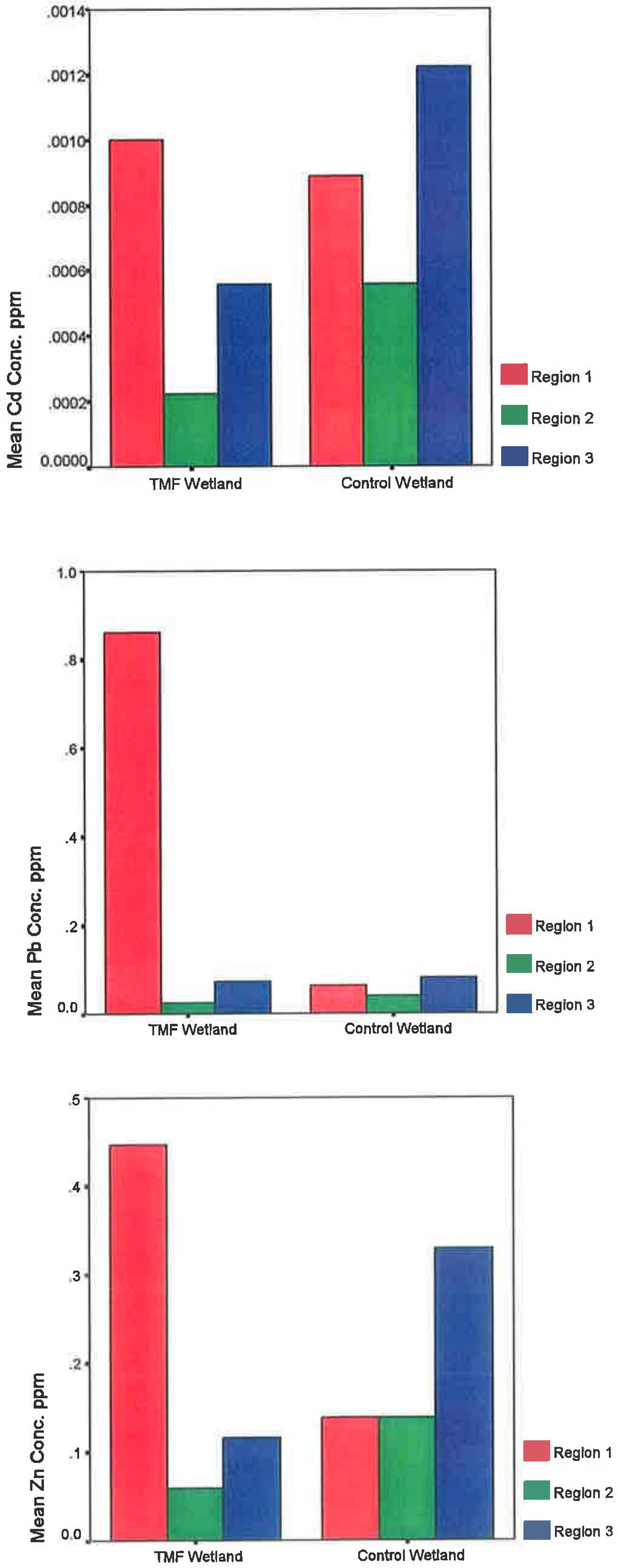


Fig. 5.20 Seasonal effects in Cd, Pb and Zn concs. in wetlands.

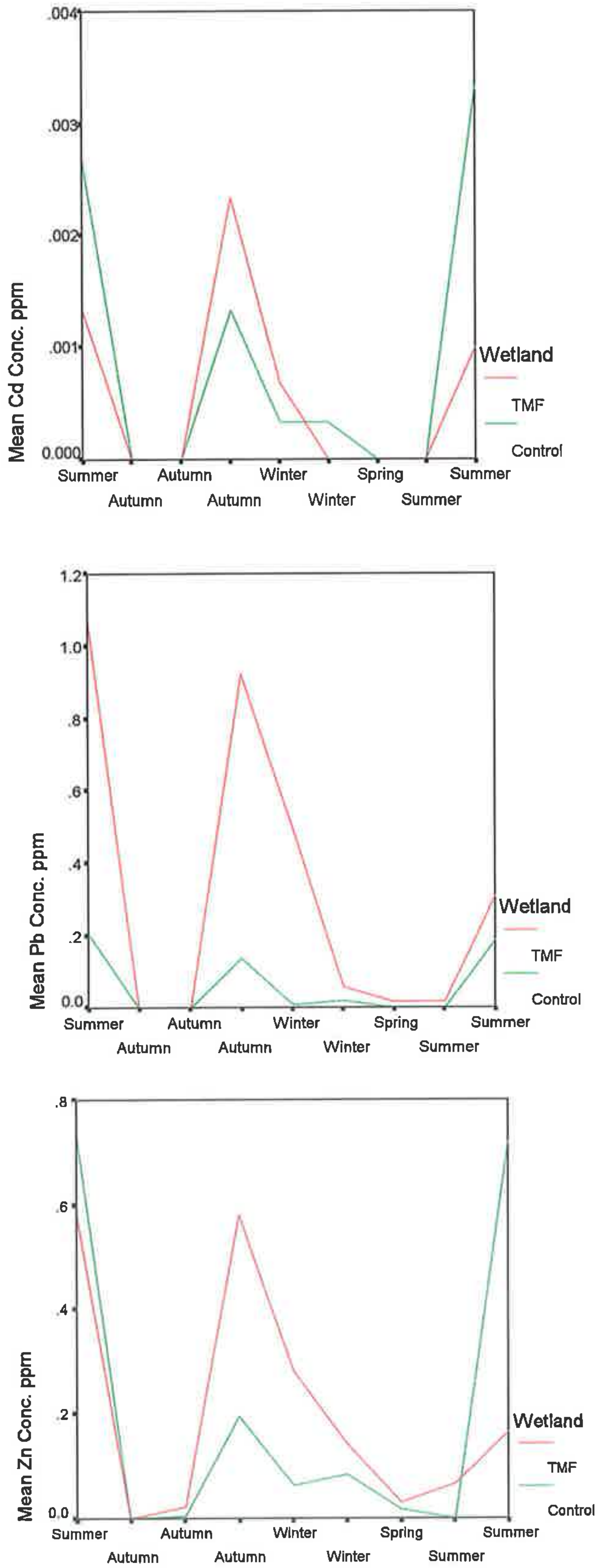


Fig. 5.21 Mean seasonal Fe and Mn profiles in wetlands.

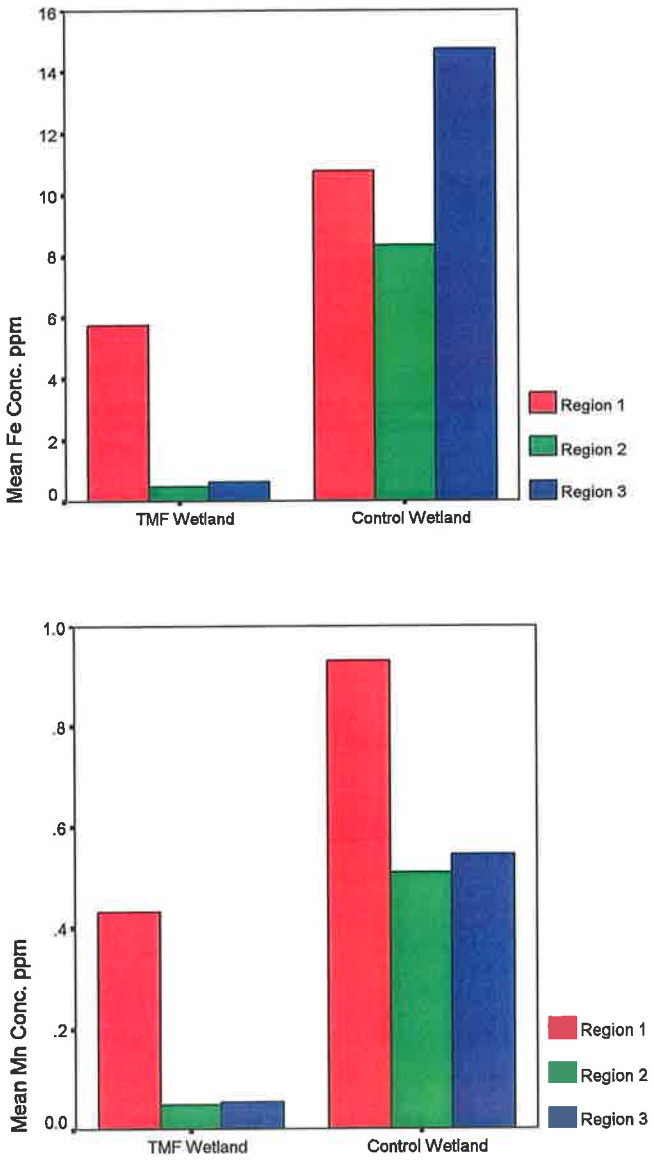
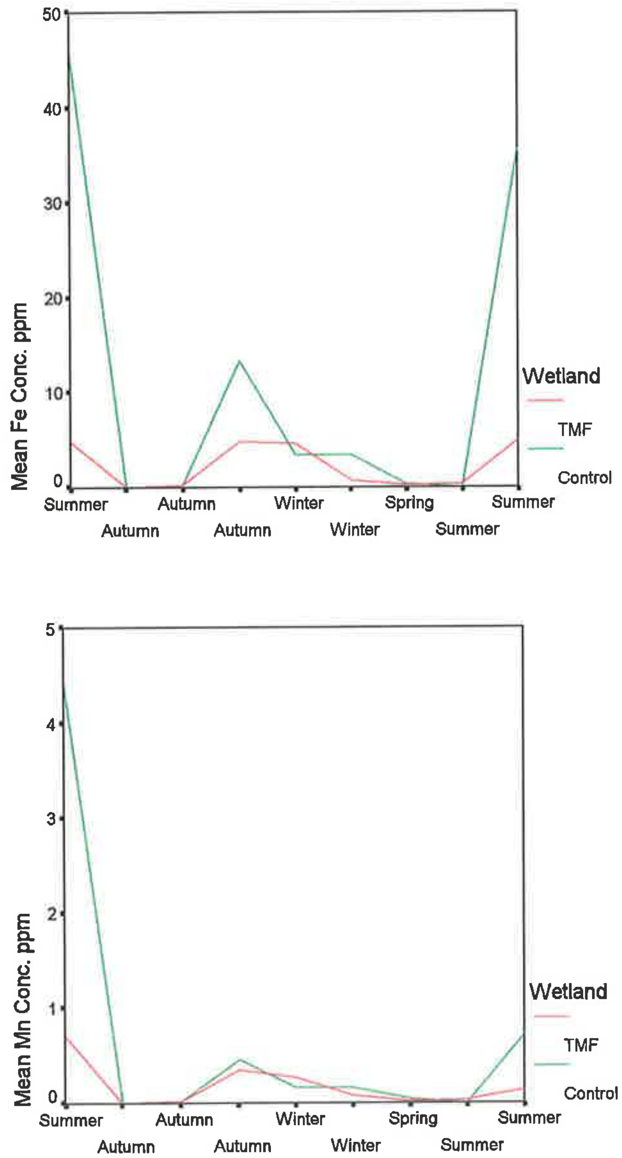


Fig. 5.22 Seasonal effects in Fe and Mn concs. in wetlands.



Mn concentrations peak during the summer months in the Control wetland, but follow the same general pattern for both wetlands during autumn, winter and spring. The increased Cd, Fe, Mn and Zn concentrations in the water column of the Control during summer may be related to shallower water depths in this wetland (see Fig. 5.6b).

5.2.2.4 ANOVA to Compare Seasonal Metal Concentrations in Wetlands

A one-way ANOVA was conducted to compare the seasonal means of metal concentrations in the water column of the TMF and Control wetlands. Again each variable was tested for normality and homogeneity of variance prior to ANOVA analysis and log transformed where necessary. The results of this analysis are outlined in Table 5.15.

There was no significant difference in mean seasonal Cd ($p=0.618$), Mn ($p=0.073$), Pb ($p=0.311$), and Zn ($p=0.865$) concentrations between the wetlands. Mean seasonal Fe concentrations did not differ at a significance level of 0.001 but differed at a significance level of 0.05 due to higher levels in the Control. From these results we can infer no enhanced seasonal toxicity from metals in the TMF wetland in comparison to the Reference/Control wetlands.

5.2.2.5 Seasonal Metal Concentrations in Wetland Inflows and Outflows

Descriptive statistics for seasonal mean metals concentrations in inflowing and outflowing streams for each wetland are outlined in Table 5.16.

As expected mean seasonal metal concentrations for inflowing streams (mains water) to both wetlands meet the most recent E.U. water quality regulations for metals. Mean seasonal metal concentrations for outflows from the TMF wetland also meet these regulatory requirements and fall within the acceptable range for E.U. standards for potable water abstractions (Cd<0.001 mg/l, Fe=0.145 mg/l, Mn=0.02 mg/l, Pb=0.003 mg/l and Zn=0.043 mg/l). Mean seasonal Fe (1.820 mg/l) and Mn (0.283 mg/l) concentrations in outflows from the Control are higher than for the TMF wetland.

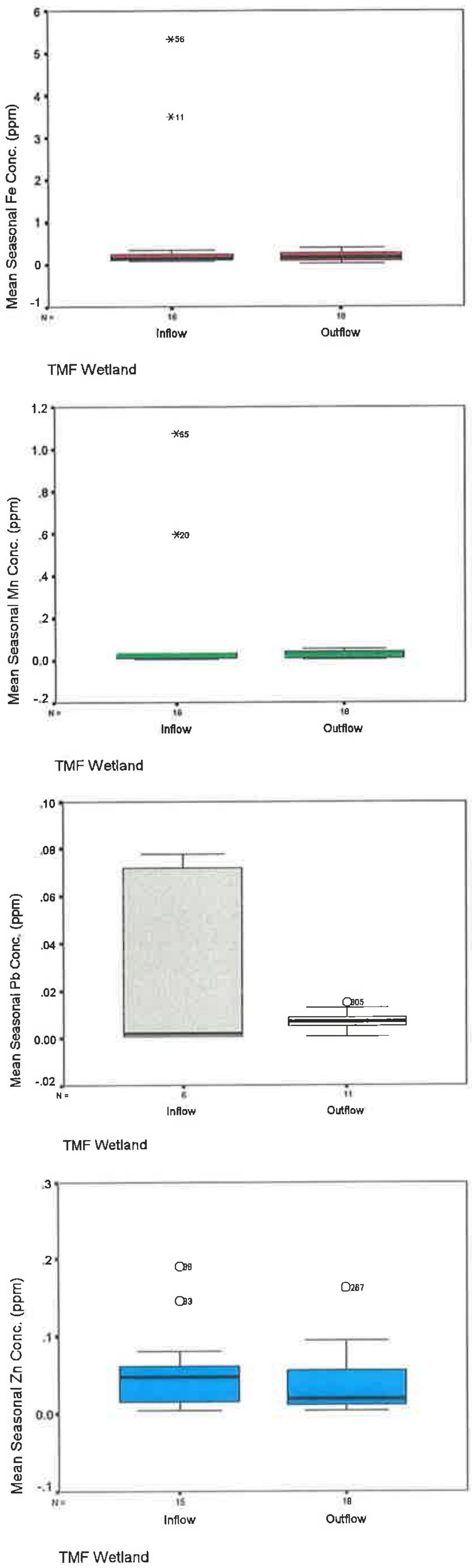
Table 5.16 Statistics for seasonal metal concs. in wetlands influent and effluent.

		TMF Wet.		Control Wet.	
		Inflow	Outflow	Inflow	Outflow
Cd	Mean	**<.001**	**<.001**	**<.001**	**<.001**
	Min.	<.001	<.001	<.001	<.001
	Max.	.001	.001	.001	.001
	SD	.000	.000	.000	.000
	Var.	.000	.000	.000	.000
Fe	Mean	**.159**	**.145**	**.172**	**1.820**
	Min.	.078	.034	.098	.095
	Max.	.342	.287	.440	14.402
	SD	.078	.088	.121	4.144
	Var.	.006	.008	.015	17.170
Mn	Mean	**.023**	**.020**	**.044**	**.283**
	Min.	.007	.004	.008	.003
	Max.	.035	.054	.191	1.830
	SD	.012	.015	.049	.529
	Var.	.000	.000	.002	.280
Pb	Mean	**.001**	**.003**	**.002**	**.020**
	Min.	.000	.000	.000	.000
	Max.	.002	.011	.016	.267
	SD	.001	.004	.004	.067
	Var.	.000	.000	.000	.004
Zn	Mean	**.039**	**.043**	**.041**	**.048**
	Min.	.005	.004	.000	.000
	Max.	.081	.163	.238	.267
	SD	.026	.045	.066	.066
	Var.	.001	.002	.004	.004

Table 5.17 One-way ANOVA to compare metal concs. in TMF inflow/outflow

		Sum of Squares	df	F	Sig.
Fe	Between Groups	0.266	1	1.4	0.245
	Within Groups	6.074	32		
	Total	6.339	33		
Mn	Between Groups	0.525	1	2.127	0.154
	Within Groups	7.898	32		
	Total	8.423	33		
Pb	Between Groups	4.30E-03	1	0.012	0.913
	Within Groups	5.25	15		
	Total	5.255	16		
Zn	Between Groups	0.203	1	0.974	0.331
	Within Groups	6.477	31		
	Total	6.681	32		

Fig. 5.23 Mean seasonal Fe, Mn, Pb and Zn Concs. in TMF Wetland inflow/outflow streams.



Again, this indicates the impact of the natural wetland sediments on the water chemistry of this wetland

Boxplots comparing mean seasonal metal data for inflows and outflows from the TMF wetland are presented in Figure 5.23. A boxplot for Cd is not included because concentrations of this metal were too small. Table 5.17 outlines the results of the one-way ANOVA analysis conducted to compare these flows. There was no significant difference in mean seasonal Fe ($p=0.245$), Mn ($p=0.154$), Pb ($p=0.913$), and Zn ($p=0.331$) concentrations between inflows and outflows from the TMF wetland. Cd concentrations were too low to conduct an ANOVA analysis but the data also indicate no significant difference in concentrations between flows. These results indicate that throughout the seasonal sampling analysis, the tailings in the TMF wetland did not adversely impact the final water quality of the outflows from this wetland.

5.2.3 Comparison with Silvermines Wetland Water Quality, 2000

Descriptive statistics for the mean physico-chemical parameters in the Silvermines wetland (W1, see Section 3.3.4) during summer 2000 are outlined in Table 5.18. The mean pH of the water column in Silvermines (6.71) is slightly lower than the seasonal mean for the TMF and Control wetlands, but conforms to the EU standards specified for salmonid and cyprinid waters which require a pH range of 6.0 to 9.0.

The mean conductivity of 1.34 mS/cm (1340 μS/cm), however, is substantially higher than seasonal mean conductivity measurements taken in both wetlands in the pilot plant. Previous experiments by McCabe and Otte (2000) measured the conductivity of porewater samples taken from Silvermines tailings at approximately 3000 μmol/cm indicating their high salt content ($MgSO_4$). The conductivity measured in Silvermines wetlands compares with values of 1160 μmhos/cm to 1720 μmhos/cm measured in rivers impacted by AMD (Soucek et al., 2000a).

Variations in D.O. in the Silvermines wetland can be attributed to water depth and temperature fluctuations and biological activity.

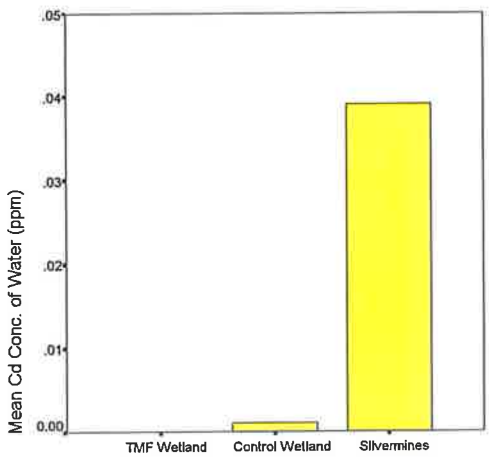
Table 5.18 Descriptive statistics for physico-chemical parameters in Silvermines wetlands in 2000.

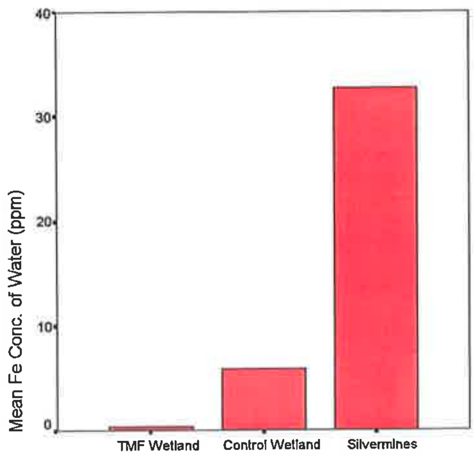
	pH of Water	Conductivity (mS/cm)	D.O. (mg/L O2)
Mean	**6.71**	**1.34**	**3.75**
Minimum	6.19	.89	1.67
Maximum	7.16	2.27	8.67
Std Dev.	.32	.60	3.17
Variance	.10	.36	10.06

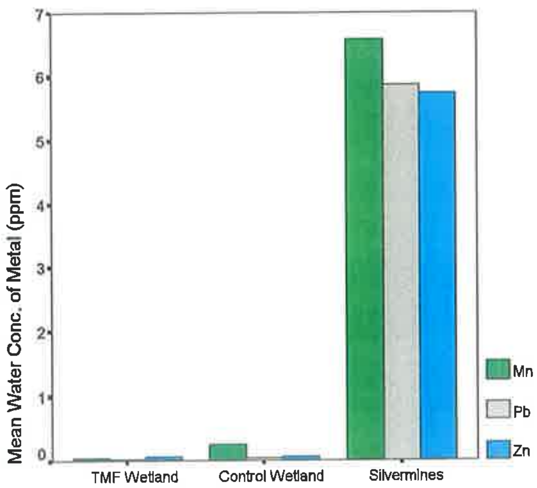
Table 5.19 Descriptive statistics for metal concs. of water column in Silvermines wetlands in 2000.

	Cd (ppm)	Fe (ppm)	Mn (ppm)	Pb (ppm)	Zn (ppm)
Mean	**.039**	**32.749**	**6.590**	**5.864**	**5.752**
Minimum	.001	6.484	3.098	.007	1.633
Maximum	.061	45.881	8.159	8.853	8.664
Std Dev.	.028	19.398	2.090	3.854	2.760
Variance	.001	376.272	4.369	14.857	7.615

Fig. 5.24 Comparison of mean metal concentrations in water of TMF, Control and Silvermines wetlands in 2000.







Descriptive statistics for the mean metal concentrations in the water column of Silvermines wetland during summer, 2000 are outlined in Table 5.19. Mean total metal concentrations of this water during this sampling programme exceed water quality regulations particularly in regard to Pb and Zn concentrations. However, water exiting this wetland flows into a series of wetlands which act as treatment processes prior to being discharged into the Kilmastulla River, and preliminary sampling data from this research indicate metal levels have been reduced upon discharge to this river.

Figure 5.24 illustrates that mean metal concentrations, for all 5 metals, are substantially higher in the Silvermines wetland than those measured in the TMF wetland during summer, 2000. Silvermines wetland was originally built as a settlement pond for drainage from the Gortmore tailings dam including drainage from the decant tower. Its sediments are likely to consist of tailings particles. This wetland continues to act as a treatment wetland for drainage from the Gortmore tailings dam.

5.2.4 Sulphate Concentrations in Wetlands, 1999 and 2000

Descriptive statistics for sulphate concentrations in the water column of the TMF and Control wetlands in summer, 1999 are outlined in Table 5.20. Mean values for each of the three wetland regions are outlined in Table 5.21. Figures 5.25 and 5.26 illustrate these results graphically.

Mean sulphate concentrations for the TMF and Control wetlands are similar (5.45 mg/l and 5.10 mg/l respectively) and fall well below the acceptable E.U. maximum standard for potable water abstractions of 250 mg/l. Concentrations within each wetland region differ minimally. Table 5.22 and Figure 5.27 outline mean sulphate concentrations in inflows and outflows from each wetland in summer, 1999. These values are similar for both wetlands and also fall well beneath the E.U. maximum.

Descriptive statistics for sulphate concentrations in the water column of the TMF and Control wetlands in summer, 2000 are outlined in Table 5.23. Table 5.24 outlines mean sulphate concentrations in inflows and outflows from each wetland during this event. Figures 5.28 and 5.29 illustrate this data graphically. As for 1999, mean

Table 5.20 Mean sulphate conc. in wetlands, 1999.

	TMF Wetland	Control Wetland
Mean	**5.45**	**5.10**
Minimum	2.97	2.99
Maximum	10.57	8.06
Median	5.26	5.00
Std Dev.	1.74	1.09
Variance	3.02	1.18

Table 5.21 Mean sulphate conc. in regions, 1999.

	TMF			Control		
	Typha	Phrag.	Juncus	Typha	Phrag.	Juncus
Mean	**6.23**	**4.75**	**5.02**	**4.92**	**4.98**	**5.57**
Min.	3.67	2.97	3.06	4.35	2.99	3.06
Max.	10.57	6.39	6.36	6.57	6.43	8.06
Med.	5.46	4.53	5.24	4.62	5.12	5.39
S.D.	2.07	1.31	1.05	.68	1.01	1.65
Var.	4.28	1.73	1.11	.46	1.01	2.71

Fig. 5.25 Mean sulphate conc. in wetlands, 1999.

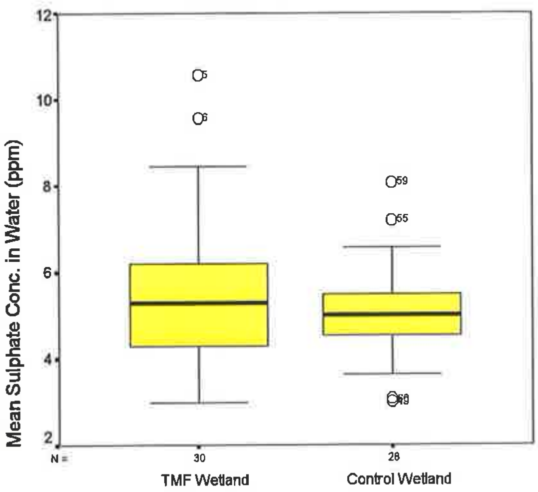


Fig. 5.26 Mean sulphate conc. in regions, 1999.

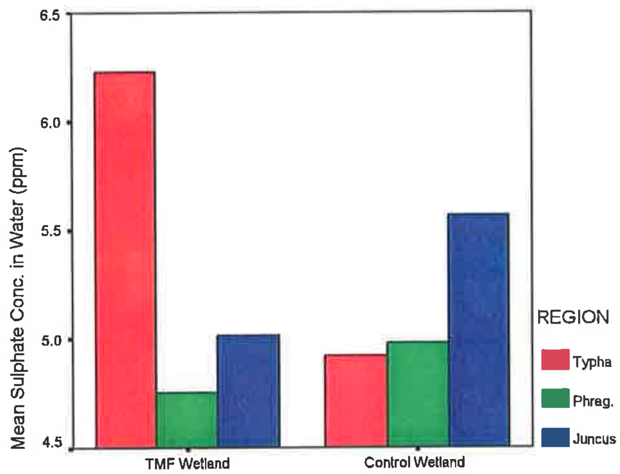


Table 5.22 Mean sulphate concs. in influent and effluent streams to wetlands, 1999.

	TMF Wetland		Control Wetland	
	Inflow	Outflow	Inflow	Outflow
Mean	**5.156**	**5.130**	**3.781**	**5.220**
Min.	4.766	4.938	2.582	4.027
Max.	5.713	5.349	4.551	6.640
Med.	4.990	5.104	4.209	4.994
SD.	.495	.207	1.052	1.321
Var.	.245	.043	1.107	1.745

Fig. 5.27 Mean sulphate concs. in influent and effluent streams, 1999.

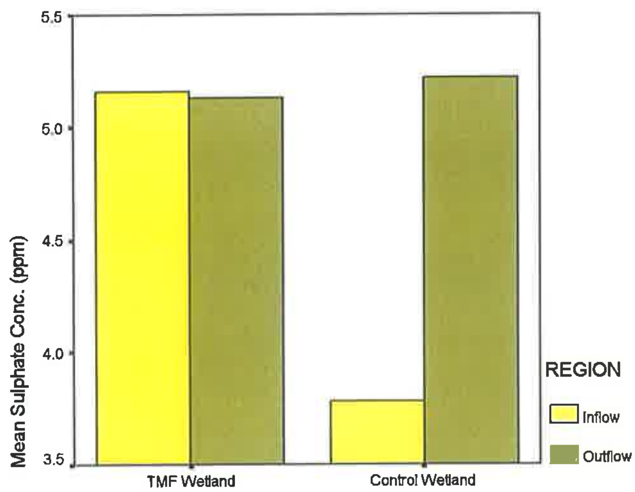


Table 5.23 Mean sulphate conc. in wetlands, 2000.

	TMF Wetland	Control Wetland
Mean	**6.505**	**6.035**
Minimum	5.265	4.666
Maximum	7.932	11.506
Median	6.663	5.180
Std Dev.	1.064	2.202
Variance	1.133	4.851

Table 5.24 Mean sulphate concs. in influent and effluent streams, 2000.

	TMF Wetland		Control Wetland	
	Inflow	Outflow	Inflow	Outflow
Mean	**6.663**	**7.573**	**7.487**	**4.949**
Min.	6.417	7.337	5.445	4.723
Max.	6.909	7.932	11.506	5.180
Med.	6.663	7.450	5.509	4.944
SD	.348	.316	3.481	.229
Var.	.121	.100	12.117	.052

Fig. 5.28 Mean sulphate conc. in wetlands, 2000.

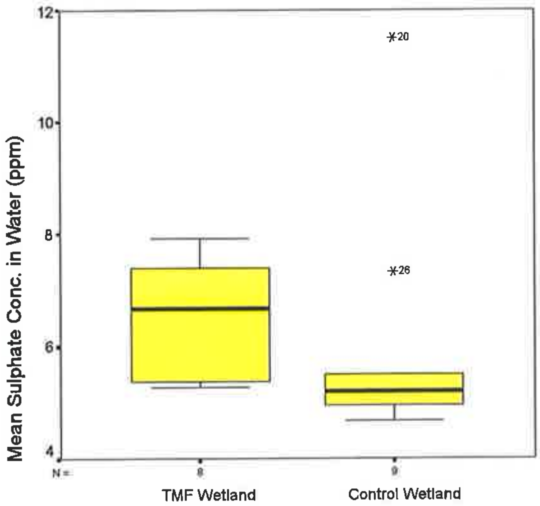


Fig. 5.29 Mean sulphate concs. in influent and effluent streams, 2000.

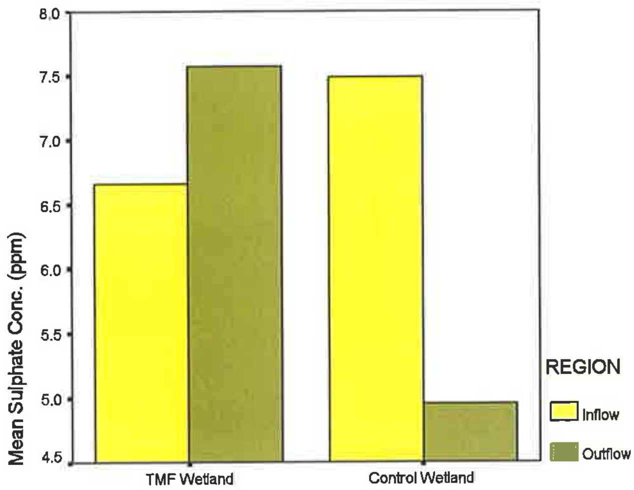
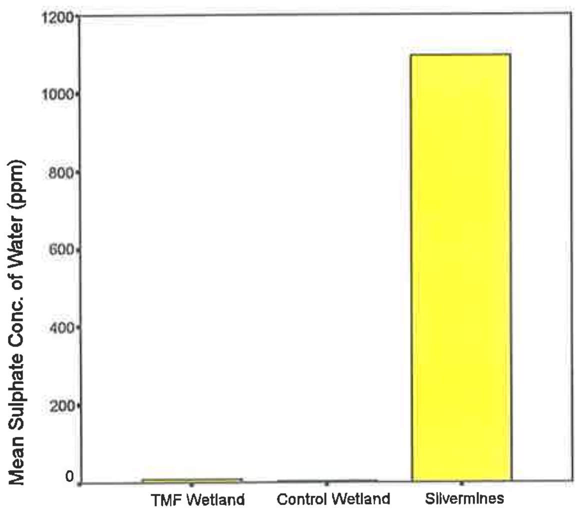


Table 5.25 Mean sulphate conc. in Silvermines wetlands, 2000.

	Silvermines
Mean	**1097.411**
Minimum	583.633
Maximum	1306.367
Std Dev.	218.750
Variance	47851.627

Fig. 5.30 Comparison of mean sulphate concs. in TMF, Control and Silvermines wetlands, 2000.



sulphate concentrations in the water column and outflows from both wetlands in summer 2000 fall well below the E.U. maximum.

By comparison, the mean sulphate concentration in the Silvermines wetland in summer 2000 measured 1097.41 mg/l which is substantially higher than that measured in either the TMF or Control wetlands (see Table 5.25 and Figure 5.30). This corresponds to the high conductivity values measured at Silvermines. Sulphate concentrations in waters associated with mining range from 900 mg/l to 4000 mg/l (Wildeman and Laudon, 1989).

5.2.4.1 ANOVA to Compare Sulphate Concentrations in Wetlands

A one-way ANOVA was conducted to compare the means of sulphate concentrations in the water column of the TMF and Control wetlands in 1999 and 2000. Again each variable was tested for normality and homogeneity of variance prior to ANOVA analysis and log transformed where necessary. The results of this analysis are outlined in Tables 5.26, 5.27 and 5.28.

There was no significant difference in mean sulphate concentrations between both wetlands in 1999 ($p=0.538$) and in 2000 ($p=0.376$). Mean sulphate concentrations in the TMF wetland between 1999 and 2000 did not differ at a significance level of 0.001 but differed at a significance level of 0.05. This result is academic given the maximum sulphate concentrations in the TMF wetland are so low.

5.3 SUMMARY

The main findings of the assessment of hydrological and physico-chemical indicators of ecosystem health and sustainability in the pilot wetlands were as follows:

- Mean surface hydraulic loadings for the TMF and Control wetlands were 0.103 and 0.101 $m^3/day/m^2$ during the course of the experiment. The water depth in the TMF wetland increased significantly across its length from 0.05 m to 0.10 m to 0.17 m, whereas the water depth through the Control remained consistently at 0.06 m. While unintentional, the increased pattern in water depth in the TMF wetland facilitated a beneficial examination of the impact of varying water depths on the establishment of a sustainable ecosystem.

Table 5.26 One-way ANOVA to compare mean sulphate concentrations between TMF and Control wetlands, 1999.

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	5.060E-03	1	5.060E-03	.383	.538
Within Groups	.739	56	1.320E-02		
Total	.744	57			

Table 5.27 One-way ANOVA to compare mean sulphate concentrations between TMF and Control wetlands, 2000.

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	9.144E-03	1	9.144E-03	.832	.376
Within Groups	.165	15	1.099E-02		
Total	.174	16			

Table 5.28 One-way ANOVA to compare mean sulphate concentrations in TMF Wetlands between 1999 and 2000.

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	3.673E-02	1	3.673E-02	11.324	.004
Within Groups	4.866E-02	15	3.244E-03		
Total	8.539E-02	16			

- During summer 1999, water depth, pH, conductivity, D.O. and temperature were measured in triplicate in each of 30 and 25 quadrats in the TMF and Control wetlands. Results indicate that the general water chemistry of both wetlands was similar and reflected that of natural wetland ecosystems. Cd values for the TMF and Control wetlands were similar and fell within the acceptable range for E.U. standards for potable water abstractions. Mean Fe and Mn concentrations were lower in the TMF wetland than in the Control and did not indicate the presence of AMD. Mean Pb and Zn concentrations in the both wetlands were higher than regulatory requirements, however lower than metal concentrations in river water impacted by AMD.

- Elevated metal concentrations occurred consistently in Quadrats 10 and 13 in the top region of the TMF wetland and disproportionately affected overall mean metal values within this wetland. Field notes indicated a substantial portion of both quadrats had no standing water over the peat substrate. Outflows from the TMF wetland met the most recent Irish and E.U. water quality regulations.

- Seasonal physio-chemical analysis of the water column in both wetlands conducted throughout 1999 and 2000 indicated no significant difference between the wetlands for mean values of water and sediment pH, conductivity, D.O., and temperature. Mean seasonal Cd concentrations for both wetlands were equal and fell within the acceptable range for E.U. standards for potable water abstractions. Mean seasonal concentrations of Fe and Mn were lower in the TMF wetland than in the Control, higher than E.U. standards, but lower than metal concentrations in river water impacted by AMD. Mean seasonal Pb and Zn concentrations were higher in the TMF wetland than in the Control but lower than water impacted by AMD. ANOVA analysis indicates no significant difference in mean seasonal Cd, Mn, Pb, and Zn concentrations between the wetlands.

- Mean seasonal metal concentrations for outflows from the TMF wetland also met the most recent E.U. water quality regulations for all metals and ANOVA analysis indicated no significant difference in mean seasonal metal concentrations between inflows and outflows from the TMF wetland. From these results we can infer no enhanced seasonal toxicity from metals in the water column of the TMF wetland in comparison to the Control and no adverse impact on the final water quality of the outflows from the TMF wetland.

- The mean pH of the water column in the Silvermines wetland was slightly lower than the seasonal mean for the TMF and Control wetlands but conformed to E.U. standards. The mean conductivity of the water column was substantially higher than seasonal mean conductivity measurements taken in both wetlands in the pilot plant. Mean metal concentrations in the water column were substantially higher in Silvermines wetland than those measured in the TMF wetland.

- Mean sulphate concentrations for the TMF and Control wetlands were statistically similar and fall well below the acceptable E.U. maximum standard for potable water abstractions. By comparison, the mean sulphate concentration in the

Silvermines wetland was substantially higher and closer to Sulphate concentrations in waters associated with mining.

This hydrological and physico-chemical analysis of the wetlands water column forms the basis for the subsequent regression analyses conducted in Chapter Eight to investigate whether correlations exist between hydrology, water and soil chemistry and ecological health, that affect the potential sustainability of the TMF wetland.

CHAPTER SIX

RESULTS
SEDIMENT INDICATORS

6.1 RESULTS – SEDIMENT INDICATORS

In the pilot system a combination of total metal analyses and metal extractions, in addition to the use of geochemical regression models to estimate free-metal ion concentrations, were carried out on sediment samples to evaluate metal speciation and bioavailability in the pilot wetlands. This facilitated an investigation of the potential for mobilisation of metals under changing environmental conditions at the tailings-sediment interface and the interface between sediments and the water column in the TMF wetland.

Aims of the sediment geochemical analysis were as follows:

- To investigate sediment geochemistry to assess metal mobility for the TMF, Control and Silvermines wetlands in 1999 and 2000.
- To compare total metal concentrations between the TMF and Control wetlands sediments in summer 1999.
- To compare total metal concentrations between the TMF and Control wetlands sediments in summer 2000.
- To compare regional differences in total metal concentrations in the TMF wetland in summer 1999 and 2000.
- To compare temporal variability in total metals concentrations in the TMF wetland between 1999 and 2000.
- To compare total metal concentrations in Silvermines wetland with the TMF and Control wetlands in 2000.
- To compare metal extractions from the TMF, Control and Silvermines wetlands sediments in summer 2000.
- To compare total metals and metal extractions from the three wetlands with Silvermines tailings, Bord na Mona peat and a sediment standard.

- To estimate potentially bioavailable metals and free-metal ion concentrations in the porewater of the TMF, Control and Silvermines wetlands sediments in 2000.

6.1.1 Sediment Sampling in TMF and Control Wetlands, Summer 1999

During the summer, 1999 sampling programme, triplicate sediment cores were taken in each of the 30 and 25 quadrats sampled in the TMF and Control wetlands respectively. Figures 4.1 and 4.2 illustrate the locations of each quadrant. The substrate material in the TMF wetland was a combination of Bord na Mona peat, natural wetland sediments from the rootball of transplanted rhizomes and litter from decaying wetland vegetation. The substrate material in the Reference/Control wetland consisted of natural wetland sediments and a litter layer from wetland vegetation. Measurements of each core sampled in the TMF wetland were taken to estimate the thickness of wetland substrate over tailings. The cores from both wetlands were oven-dried and subsamples tested to determine organic content (through loss on ignition). Total Cd, Fe, Mn, Pb and Zn concentrations were determined for each quadrat in both wetlands.

6.1.1.1 Total Metal Concentrations in Sediments of Wetlands, 1999

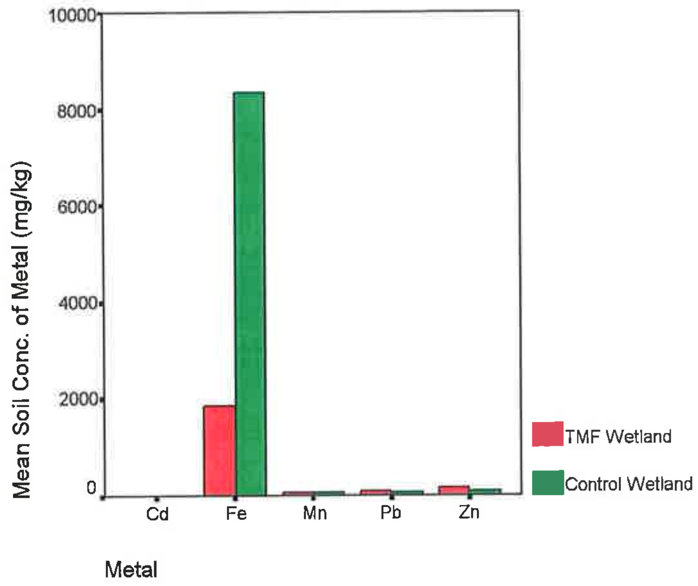
Descriptive statistics for mean total metals concentrations over the entire area of each wetland are outlined in Table 6.1, and Figures 6.1a and 6.1b illustrate the differences in mean metal concentrations between the TMF and Control wetlands. Boxplots illustrating the median, interquartile range (25^{th}–75^{th} percentile), outliers and extreme values for each metal are presented in Figure 6.2. Metal concentrations in the sediments of each quadrat sampled in summer 1999 are outlined in Appendix D. Table 6.2 outlines the range of metal concentrations in agricultural soils, natural wetland sediments and riverine sediments impacted by acid mine drainage (AMD) from the literature.

Mean total Cd values for the TMF and Control wetlands are similar (0.506 mg/kg and 0.436 mg/kg respectively) and fall within the recently published range for Irish agricultural soils of 0.39 mg/kg (50^{th} percentile) and 1.48 mg/kg (95^{th} percentile) (see

Table 6.1 Descriptive statistics for total metals in wetland sediments, summer 1999.

		TMF Wetland mg/kg	Control Wetland mg/kg
Cd	**Mean**	**.506**	**.436**
	Min.	.100	.000
	Max.	3.007	.695
	Median	.393	.428
	Std Dev.	.488	.150
	Variance	.238	.022
Fe	**Mean**	**1869.034**	**8335.839**
	Min.	404.037	4570.170
	Max.	16650.46	11298.20
	Median	1364.495	8854.822
	Std Dev.	2712.970	1975.222
	Variance	7360208	3901503
Mn	**Mean**	**60.422**	**68.941**
	Min.	11.021	17.005
	Max.	186.447	163.861
	Median	46.827	68.676
	Std Dev.	43.672	37.532
	Variance	1907.237	1408.623
Pb	**Mean**	**98.305**	**65.162**
	Min.	11.990	9.752
	Max.	1011.628	138.395
	Median	54.747	55.866
	Std Dev.	170.388	37.725
	Variance	29032.21	1423.144
Zn	**Mean**	**158.003**	**100.013**
	Min.	23.828	26.316
	Max.	1192.161	478.450
	Median	108.322	68.608
	Std Dev.	202.889	118.537
	Variance	41163.98	14051.02

Fig. 6.1a and 6.1b Total metal concs. in wetland sediments, 1999.



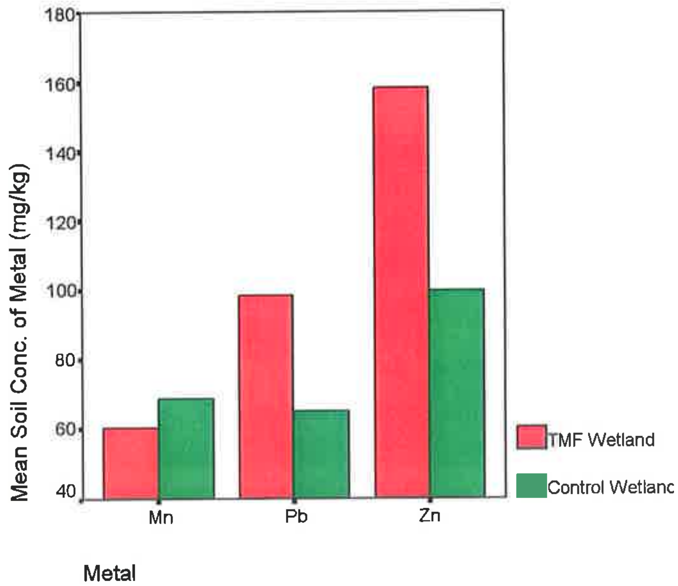


Fig. 6.2 Boxplots of Cd, Fe, Mn, Pb and Zn concentrations (mg/kg) in wetland sediments, 1999. (Outliers are designated with O and extreme values with *. Numbers indicate position in data set.)

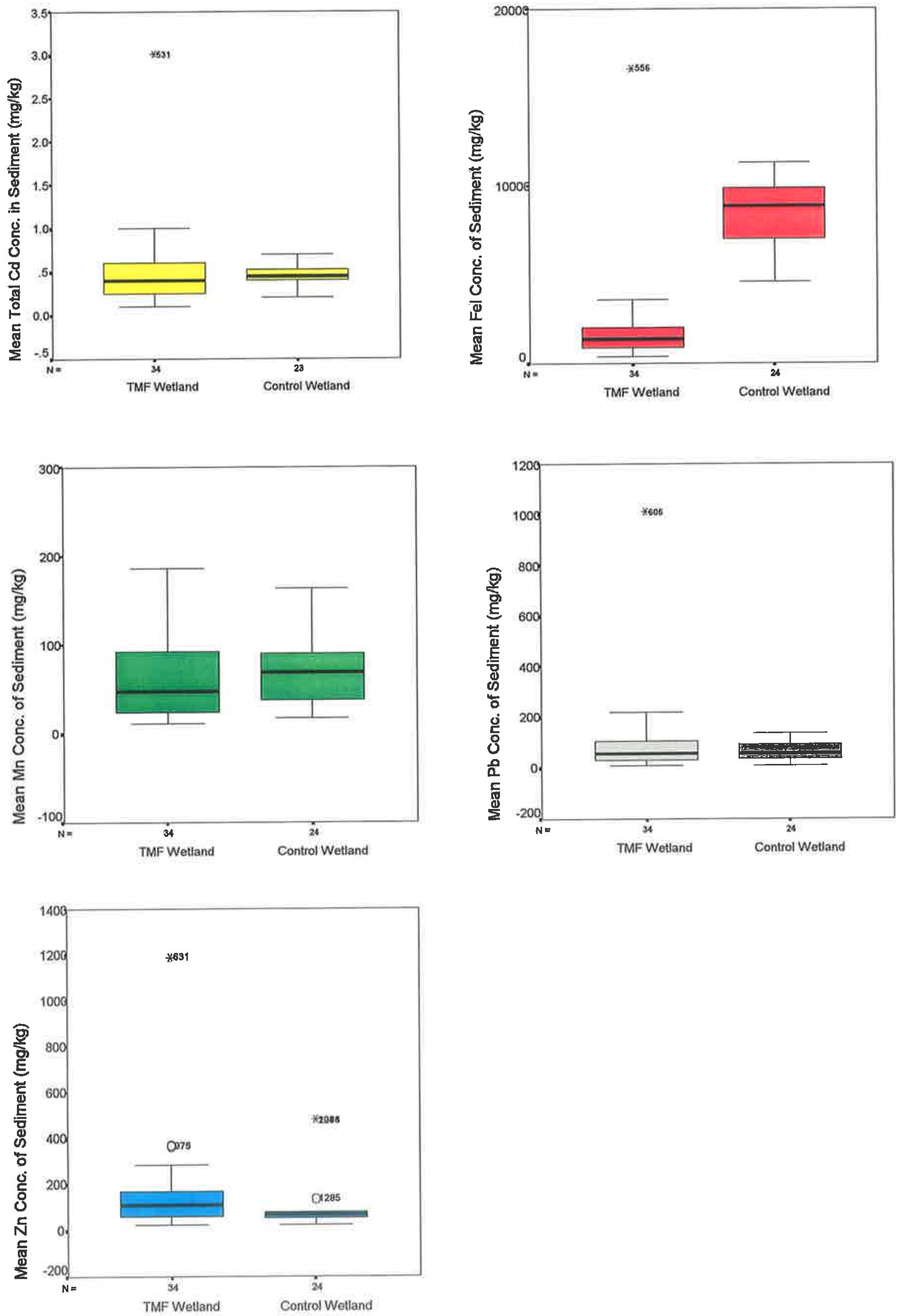


Table 6.2 Range of total metal concentrations in agricultural soils, natural wetland sediments, and riverine sediments impacted by AMD from the literature.

	Total Metals (mg/kg)				
	Cd	**Fe**	**Mn**	**Pb**	**Zn**
(Kerbata-Pendias & Pendias, 1992) M.A.C. in Agricultural Soils				20-500	70-400
(McGrath & McCormack, 1999) Irish Agricultural Soils	0.39[a] (1.48)[b]			26.5[a] (59.3)[b]	43.7[a] (134.1)[b]
(Dept. of Agriculture, Food & Rural Development, 2000)					
Agricultural Soils near Silvermines	1.11			780	365
Gortmore TMF	20.21			11694	7046
(Salomons & Förstner, 1984)					
Soils	0.62	32,000	760	29.2	59.8
Rhine Sediments	0.3	32,300	960	30	115
Iacustrine Sediments	0.4	43,400	760	34	118
Marine Sediments					
- Surface		25,900	1,230		
- Reduced		21,120	580		
(Ginn & Pastorok, 1992) Sediment Management Standards for Puget Sound in Fjord-like estuary, State of Washington, U.S.A. 3 Superfund sites					
- Sediment Quality Standard	5.1			450	410
- Sediment Cleanup Standard	6.7			530	960
(Soucek et al., 2000b) AMD impacted watershed, Virginia, U.S.A.					
- Upstream		25,900	956		48.9
- AMD Impacted		23,100 → 86,100	111 → 779		45.0 → 80.6
(Martin, 2000) River Lahn Sediments (Trib. to River Rhine)					
→ 0 – 5cm	0.6			41.9	121
→ 5 – 15cm	0.3			33.4	93.6
(Levy et al., 1992) Mountain meadows near Leadville, Colorado, U.S.A. contaminated with metals from mining					
- Control	-	15,300	1,230	-	-
- Contaminated meadows	3 → 110	9,500 → 60,000	630 → 8,760	46 → 49,000	44 → 12,000
(Stoughton & Marcus, 2000) Floodplain soils contaminated by tailings in Yellowstone National Park, U.S.A.					
- Background		50,000		13	69
- Tailings		117,000 → 261,000		71 → 672	120
- Floodplain soils (0-20cm)		24,000 → 93,000		8 → 270	50 → 598
(Basta & Gradwohl, 2000) Soils from Pb & Zn mining and smelting operations in U.S.A.	7.5 → 296			249 → 3,180	1,300 → 23,970
(Emerson et al., 1999) River receiving AMD from pyrite mines Virginia, U.S.A.					
- Control		142,082			
- AMD impacted river		135,045			
(Obarska-Pompkowiak & Klimkowska, 1998) Constructed wetland system to treat sewage in Poland	1.0 → 2.5		116 → 148	31 → 45	62 → 98
(Lau & Chu, 2000b) Coastal wetland in Hong Kong, China	5.81 → 7.47				149 → 229
(Sparling & Lowe, 1998) Constructed wetland ponds in Maryland, U.S.A.					
- Control	0.53 → 1.06	18,100	240	32	42.4
- Acidified soil	0.1 → 1.03	17,200	195	29	45.3
(Sistani, Mays & Taylor, 1999) Wetlands constructed on top of coal mine spoil					
- Topsoil		400	639		7.3
- A1 soil		362	372		5.1
- Mn soil		467	220		14.2
(Wójcik & Wójcik, 2000)					
- Vicinity of natural wetlands in Poland	3			100	200
- Wetlands treating mine waters in Poland				13,400	44,600
- River sediments in Gdansk				15 (Max 414)	
(Odum et al., 2000)					
- Natural artic lakes				20	
- Peatlands, N.C., U.S.A.				12.8	
- European bogs (Glooschenko, 1986)				3.8 → 32	16 → 68
- Wetland sediments (Gardner, 1978)				25 → 42	80 → 162
- Steel City swamps, Florida (Ton & Delfino, 2000) receiving wetland					
- Background				9	
- Wetland receiving Pb drainage				10.6 → 940	
- Asami, Japan					
- Unpolluted topsoil				30	
- Polluted soil				237	
- Lakes near metal mining				3,700	
- Norwegian Fjord receiving waste				11,400	

M.A.C. = Maximum Admissible Concentration
[a] 50% and [b] 95% of agricultural soils have values less than this

Table 6.2). The mean total Cd concentrations in sediments from both wetlands also fall within the range determined for the Rhine River in Germany (0.3 mg/kg to 0.6 mg/kg); fall below values for constructed wetlands in the U.S. (0.53 mg/kg to 1.06 mg/kg); and are well below Cd levels for soils contaminated from mining activities in the U.S. (3.0 to 296 mg/kg).

Mean total Fe concentration in the TMF wetland (1,869 mg/kg) is substantially lower than the control (8,336 mg/kg). This is due to fact that the control was seeded with soils from natural wetlands whereas the TMF was seeded with a peat substrate which contained very low levels of metals. The Fe values in the wetlands compare favourably with those found in natural systems not impacted by AMD (32,300 mg/kg in the Rhine River; 18,100 mg/kg, 25,900 mg/kg, and 50,000 mg/kg in wetlands in the U.S. as outlined in Table 6.2). The difference in Fe concentrations in the TMF and Control wetland sediments explains the difference detected in Fe concentrations in the water column for both wetlands in 1999.

The TMF and Control wetlands were found to have similar concentrations of total Mn (60.422 mg/kg and 68.941 mg/kg respectively) and these values are much lower than those outlined in Table 6.2 for uncontaminated soils (760 mg/kg to 1,230 mg/kg) and wetland sediments (116 mg/kg to 956 mg/kg). Increasing Mn values by 22 %[1] yields mean concentrations of 73.71 mg/kg and 84.11 mg/kg for the TMF and Control wetland which remain below those reported for natural systems.

Mean total Pb concentrations in the TMF (98.305 mg/kg) and Control (65.162 mg/kg) wetland sediments are higher than the range for Irish agricultural soils of 26.5 mg/kg (50^{th} percentile) and 59.3 mg/kg (95^{th} percentile) outlined in Table 6.2. However, these values fall within the lower end of the range reported by Kabata-Pendias and Pendias (1992) for maximum admissible concentrations (M.A.C.) in agricultural soils (20-500 mg/kg) and substantially lower than the mean concentration reported for agricultural soils near Silvermines in Co. Tipperary (780 mg/kg) (see Table 6.2). The Pb concentration in the TMF wetland sediment is also substantially lower than the

[1] The increase of 22% accounts for the discrepancy in Mn concentrations detected during analysis for the sediment standard (SRM 1944) and those specified in the standard certification as discussed in Chapter Three.

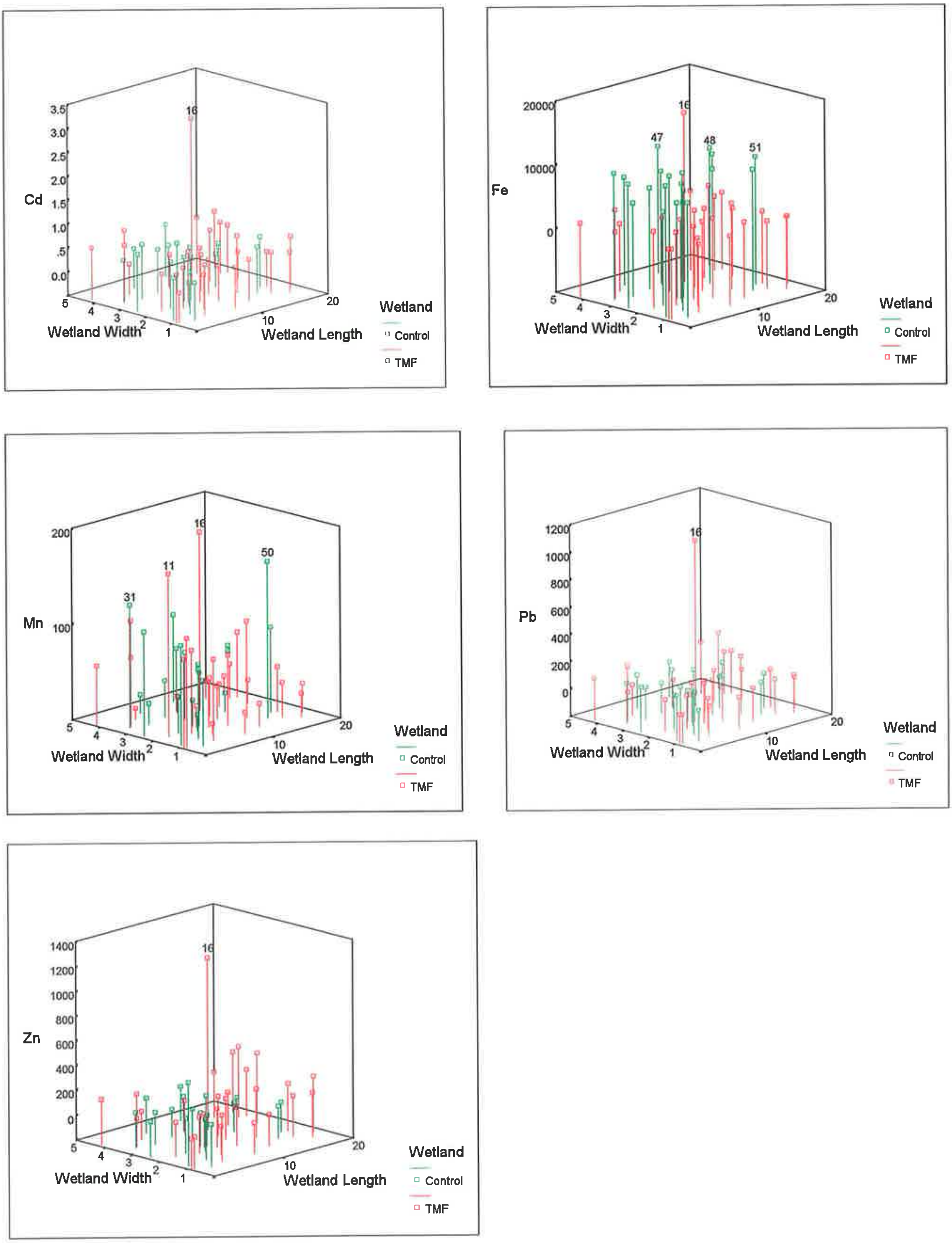
sediment quality standard (450 mg/kg) and sediment cleanup standard (530 mg/kg) established for heavily contaminated sediments in Puget Sound in the State of Washington in the U.S (see Table 6.2). The sediment quality standards are intended to provide a regulatory goal for the state by identifying surface sediments that have no adverse-effects on biological resources. They are based on a biological effects-based approach that uses the lowest apparent effects threshold values of biological indicators.

The mean Zn concentration in the TMF wetland (158.003 mg/kg) is higher than the range for Irish agricultural soils of 43.7 mg/kg (50^{th} percentile) and 134.1 mg/kg (95^{th} percentile) while the value for the Control (100.013 mg/kg) falls within this range (see Table 6.2). As was the case with Pb, the mean value for Zn falls within the lower end of the range for MACs in agricultural soils (70-400 mg/kg) and below mean Zn concentrations reported for soils near Silvermines (365 g/kg). It also is well below the sediment quality standard (410 mg/kg) and cleanup standard (960 mg/kg) set for Puget Sound in the U.S. and falls within the range (80-162 mg/kg) reported by Gardner for wetland sediments as cited in Odum *et al.*, 2000 (see Table 6.2).

Further, the boxplots in Figure 6.2 indicate there is an extreme data point in the TMF wetland that disproportionately affects overall mean metal values within the cell. Extreme and outlier values were not removed from the data set prior to calculating mean values in the interests of identifying the worst case scenario for sediment quality from breakthrough metals from the tailings substrate. This extreme value consistently occurs in Quadrat 16 located in the *Phragmites australis* (middle) region for each metal. This pattern is illustrated three-dimensionally in Figure 6.3 which compares metal concentrations in each quadrat for the TMF and Control wetlands. Cd, Mn, Pb and Zn concentrations are generally similar in both wetlands except for the breakthrough value in Quadrat 16. Fe concentrations are generally higher in the Control.

Field notes indicate quadrat 16 had a water depth of 0.10 m over the peat substrate with no adverse levels in the physico-chemical parameters of the water column

Fig. 6.3 Comparison in total Cd, Fe, Mn, Pb and Zn concs. (mg/kg) in wetland sediments, 1999.



including metals concentrations. Laboratory notes indicate the sediment core used for total metals analysis from Quadrat 16 had a peat layer of 0.08 m over tailings (N.B. substrate layer was subject to compression during core sampling).

6.1.1.2 ANOVA to Compare Metal Concentrations in Wetland Sediments, 1999

A one-way analysis of variance (ANOVA) was conducted to compare metal concentrations in the sediments of the TMF and Control wetlands in summer, 1999. Each variable was tested for normality prior to ANOVA analysis using Shapiro-Wilk's and Kologorov-Smirov Lilliefors tests for normality. Each variable also was tested for homogeneity of variance using the Levene statistic. Variables were log transformed prior to ANOVA analysis when they did not exhibit normality.

The null hypothesis (H_o) in this analysis proposes that the population means for sediment metals in both wetlands are the same. F values and observed significance levels for each metal are as follows:

Metal	F	P
Cd	0.430	0.515
Fe	143.717	0
Mn	1.362	0.248
Pb	0.065	0.800
Zn	3.259	0.076

The results of the ANOVA analysis indicate no significant difference in mean total Cd, Mn, Pb and Zn concentrations in the sediments of the TMF and Control wetlands at a significance level of 0.05. There was a significant difference ($p<0.001$) in mean total Fe concentration due to higher concentrations in the Control.

6.1.1.3 Metal Concentrations in Sediments of Wetland Regions, 1999

The impact of the extreme data in Quadrant 16 on mean values in the *Phragmites* region of the TMF wetland is obvious from Table 6.3 which outlines descriptive statistics for sediment metals in the three regions of each wetland. The maximum

Table 6.3 Descriptive statistics for total metals (mg/kg) concentrations of sediments from wetland regions in summer sampling event, 1999.

		TMF Wetland			Control Wetland		
		Typha mg/kg	Phragmites mg/kg	Juncus mg/kg	Typha mg/kg	Phragmites mg/kg	Juncus mg/kg
Cd	**Mean**	**.448**	**.669**	**.425**	**.422**	**.433**	**.545**
	Min.	.130	.198	.100	.000	.198	.395
	Max.	.994	3.007	.690	.653	.595	.695
	Std Dev.	.237	.843	.199	.155	.138	.212
Fe	**Mean**	**1193.396**	**3264.048**	**1399.322**	**7536.669**	**9312.740**	**10022.426**
	Min.	404.037	462.644	633.413	4570.170	7196.098	9414.266
	Max.	2484.803	16650.461	2504.536	10630.585	11298.202	10630.585
	Std Dev.	604.341	4802.158	559.977	2020.907	1395.748	860.067
Mn	**Mean**	**68.239**	**55.466**	**55.690**	**59.379**	**76.302**	**106.438**
	Min.	11.021	16.845	17.847	17.005	19.557	103.895
	Max.	168.951	186.447	113.505	127.676	163.861	108.981
	Std Dev.	46.086	53.024	32.958	34.183	42.543	3.596
Pb	**Mean**	**52.797**	**173.250**	**83.957**	**53.442**	**68.470**	**133.970**
	Min.	16.119	11.990	16.119	9.752	31.312	129.545
	Max.	108.925	1011.628	213.666	138.395	118.839	138.395
	Std Dev.	35.477	302.370	58.957	34.588	28.438	6.258
Zn	**Mean**	**76.681**	**223.301**	**194.749**	**97.468**	**59.357**	**280.453**
	Min.	23.828	57.570	39.602	26.316	32.892	82.456
	Max.	174.553	1192.161	368.584	478.450	79.435	478.450
	Std Dev.	49.312	343.226	112.040	112.541	15.518	280.010

values for Cd, Fe, Pb and Zn are much higher in the *Phragmites* region than in others. Profiles of mean metal concentrations in the wetland regions are illustrated graphically in Figure 6.4.

A one-way ANOVA was conducted to compare mean sediment metals in the three regions of the TMF wetland followed by Bonferroni's multiple comparison test to denote significant differences between individual regions. The results indicate no significant difference between regions for Cd (p=0.753), Fe (p=0.139), Mn (p=0.798) and Pb (p=0.314) at a significance level of 0.05 whereas the difference in Zn concentrations between the TMF regions was significant (p=0.01). Bonferroni's test indicated a significant difference between the *Typha* and *Juncus* regions (p=0.041), relatively small similarity between regions *Typha* and *Phragmites* (p=0.061), and substantial similarity between regions *Phragmites* and *Juncus* (p=1.00).

Overall, the results for mean total metal concentrations in the sediments of the TMF wetland in 1999 in comparison to the Control, indicate no significant adverse mobilisation of metals into the peat substrate from the tailings.

6.1.2 Sediment Sampling in TMF and Control Wetlands, Summer 2000

During summer, 2000, sediment cores were taken across the width (x dimension) of the TMF wetland at 0.5 m, 1.5 m, 2.5 m, 3.5 m and 4.5 m, in three locations at 6 m, 12 m and 18 m (y dimension) corresponding to the different regions along the length of the cell. Similarily, equidistant sediment samples were taken across the width of the Control at one location 10 m along the length of the cell. Analyses for total Cd, Fe, Mn, Pb and Zn concentrations, were conducted on each sample in duplicate.

6.1.2.3 Total Metal Concentrations in Sediments of Wetlands, 2000

Descriptive statistics for mean total metals concentrations in summer, 2000 over the entire area of each wetland as outlined in Table 6.4 and Figures 6.5a and 6.5b illustrate the differences between the TMF and Control wetlands. Boxplots illustrating the median, interquartile range (25^{th}–75^{th} percentile), outliers and extreme values for

Fig. 6.4 Profiles of total Cd, Fe, Mn, Pb and Zn (mg/kg) in wetland sediments through regions, 1999.

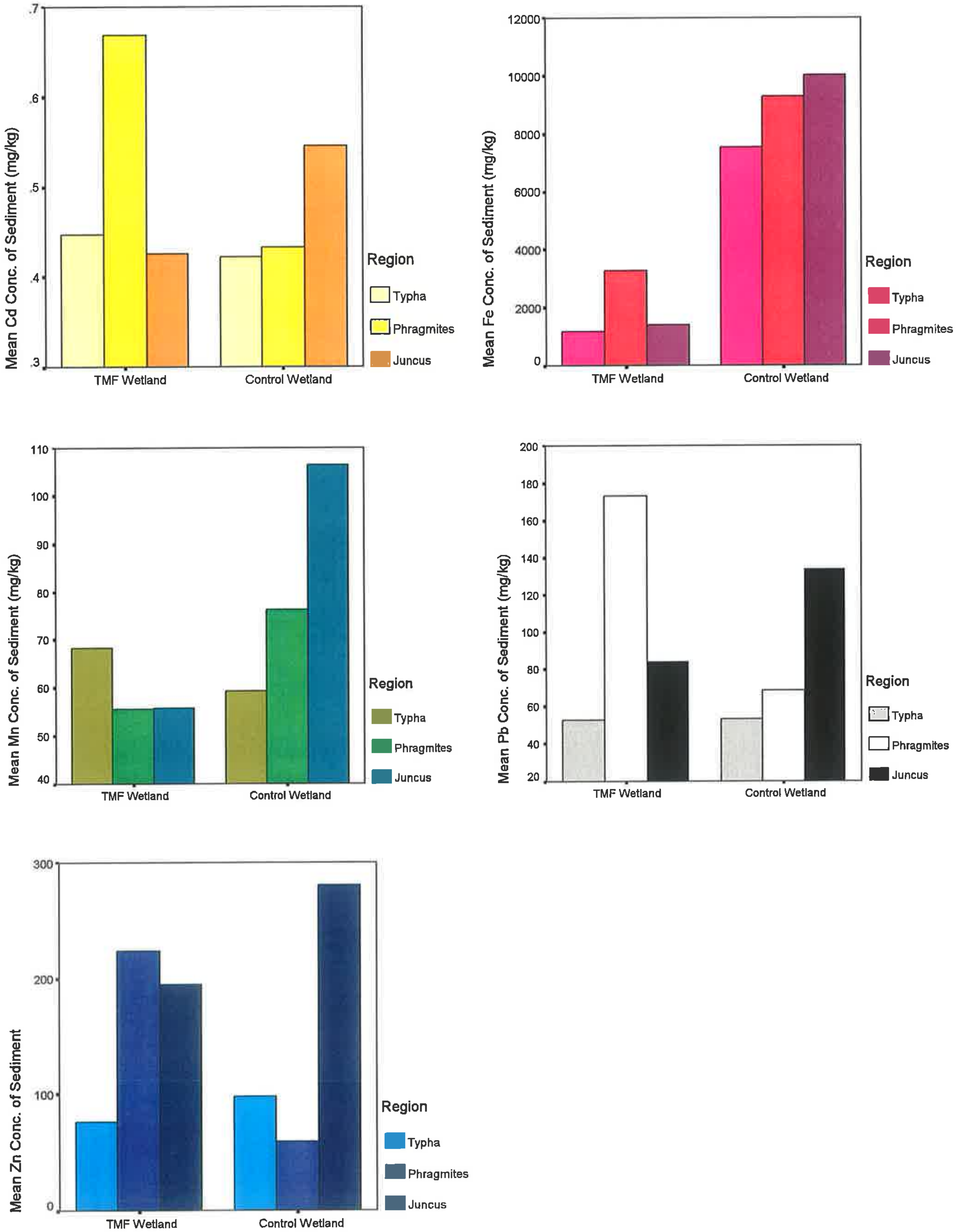
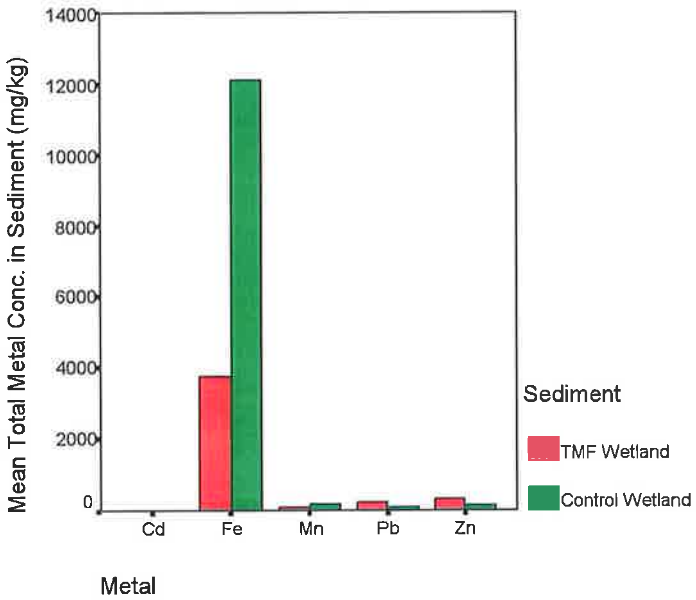
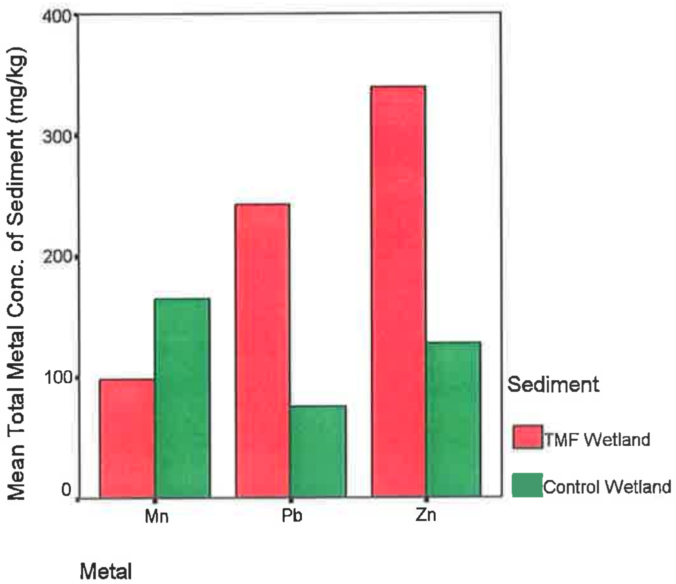


Table 6.4 Descriptive statistics for total metals in wetland sediments, 2000.

		TMF Wetland mg/kg	Control Wetland mg/kg
Cd	**Mean**	**.657**	**.488**
	Minimum	.000	.000
	Maximum	2.470	1.309
	Median	.366	.416
	Std Dev.	.728	.339
	Variance	.530	.115
Fe	**Mean**	**3748.914**	**12085.163**
	Minimum	630.340	10699.523
	Maximum	12618.726	13964.145
	Median	2784.355	11908.470
	Std Dev.	3460.590	956.233
	Variance	11975682.3	914381.752
Mn	**Mean**	**98.036**	**163.986**
	Minimum	13.261	97.653
	Maximum	256.094	219.704
	Median	77.999	186.302
	Std Dev.	69.314	45.695
	Variance	4804.373	2088.007
Pb	**Mean**	**241.927**	**74.972**
	Minimum	5.083	45.404
	Maximum	884.623	130.222
	Median	142.802	67.270
	Std Dev.	253.745	30.300
	Variance	64386.515	918.088
Zn	**Mean**	**339.294**	**127.726**
	Minimum	8.010	37.199
	Maximum	1781.294	299.251
	Median	176.458	90.691
	Std Dev.	443.049	103.235
	Variance	196292.696	10657.485

Fig. 6.5a and 6.5b Mean total metal concs. in wetland sediments, 2000.





each metal are presented in Figure 6.6. Total metal concentrations for sediments in the TMF and Control wetlands are outlined in Appendix E.

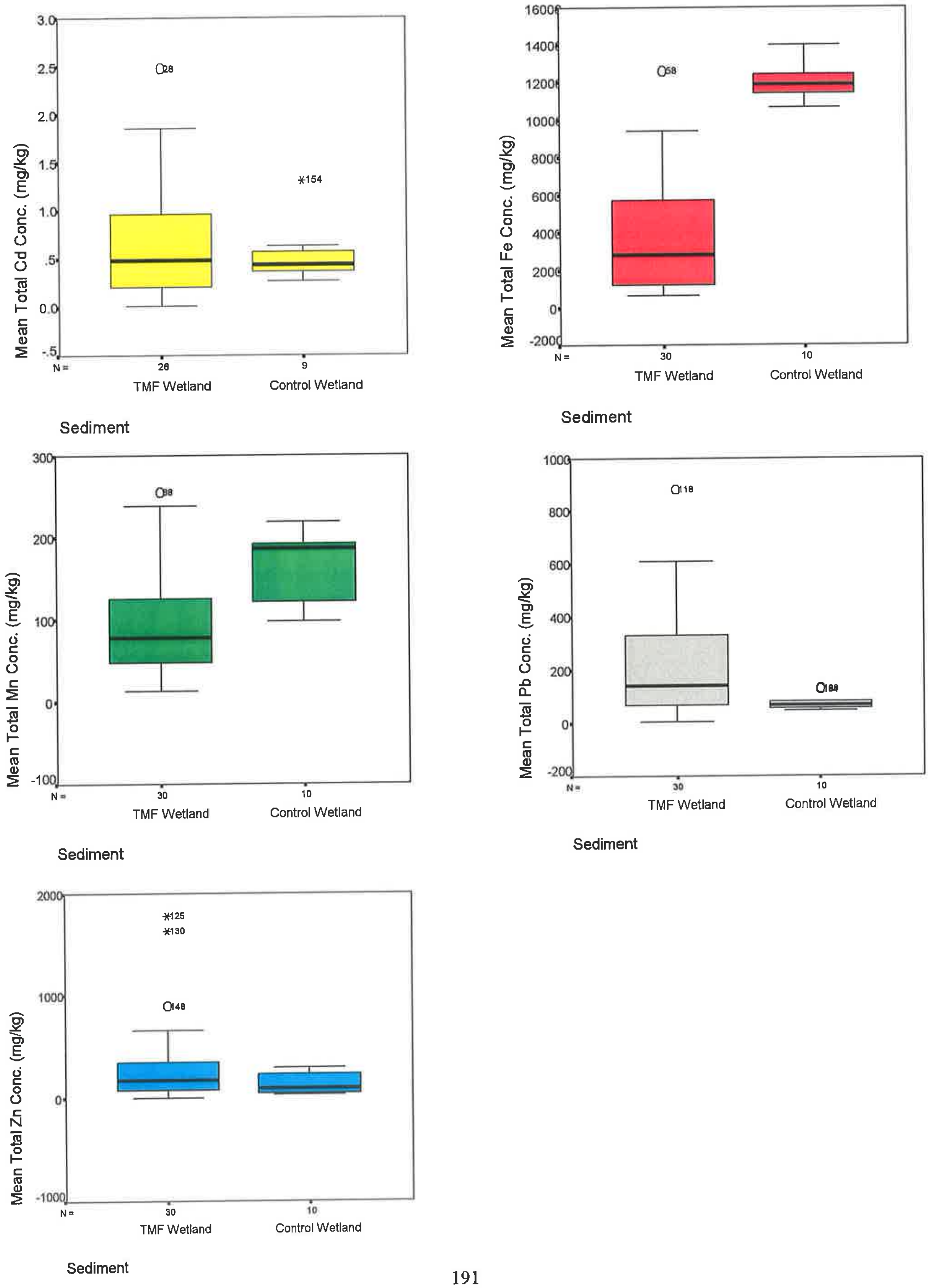
When Figures 6.1a and b are compared with Figures 6.5a and b they indicate the same general pattern of metal concentrations occurring between the TMF and Control wetlands in 1999 and 2000, although mean concentrations are higher in both wetlands for all metals in 2000.

Mean total Cd values for the TMF and Control wetlands in 2000 are similar (0.657 mg/kg and 0.488 mg/kg respectively, see Table 6.4) and fall within the range for Irish agricultural soils and below values for constructed wetlands (see Table 6.2).

Mean total Fe concentration in the TMF wetland (3,749 mg/kg) was substantially lower than the control (12,085 mg/kg). Again, these Fe values compare favourably with those found in natural systems not impacted by AMD (18,100 mg/kg to 50,000 mg/kg). Mean total Mn concentration also was lower in the TMF wetland (98.04 mg/kg) than in the Control (163.986 mg/kg) but these values are much lower than those outlined in Table 6.2 for uncontaminated soils (760 mg/kg to 1,230 mg/kg) or well within the range for wetland sediments (116 mg/kg to 956 mg/kg). Increasing Mn values by 22 % yields mean concentrations of 119.61 mg/kg and 200.06 mg/kg for the TMF and Control wetlands respectively which remain below those reported for natural systems. The differences in Fe and Mn concentrations in the TMF and Control wetland sediments follows the same pattern detected in the Fe and Mn concentrations in the water column for both wetlands seasonally.

Mean total Pb concentrations in the TMF (241.927 mg/kg) and Control (74.972 mg/kg) wetlands are higher than the range for Irish agricultural soils, however, they fall within the lower end of the range reported for MACs in agricultural soils (20-500 mg/kg) and substantially lower than the mean concentration reported for agricultural soils near Silvermines (780 mg/kg) (see Table 6.2). The Pb concentration in the TMF wetland sediment also is substantially lower than the sediment quality standard (450 mg/kg) and cleanup standard (530 mg/kg) established for contaminated sediments in Puget Sound. Soils contaminated with heavy metals from mining activities have exhibited Pb concentrations as high as 49,000 mg/kg and wetlands receiving Pb and

Fig. 6.6 Boxplots of total Cd, Fe, Mn, Pb and Zn concentrations in wetland sediments, 2000.
(Outliers are designated with O and extreme values with *. Numbers indicate position in data set.)



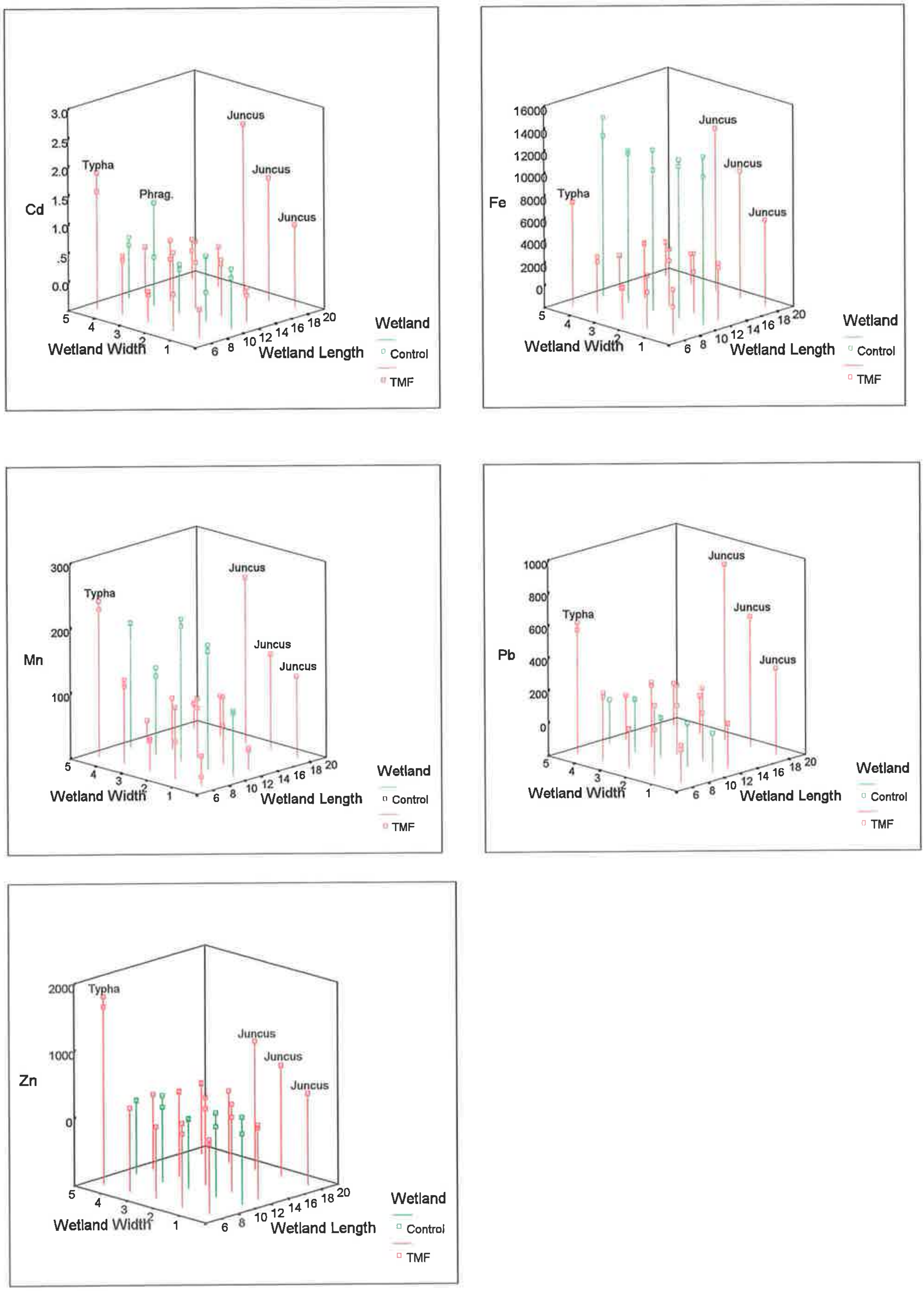
Zn wastewaters from mining activities for 400 years in Poland have exhibited sediment Pb concentrations of 13,400 mg/kg (see Table 6.2).

The mean Zn concentration in the TMF wetland (339.294 mg/kg) is higher than the range for Irish agricultural soils while the value for the Control (127.726 mg/kg) falls within this range (see Table 6.2). However, the mean TMF value for Zn falls within the range for MACs in agricultural soils (70-400 mg/kg) and below mean Zn concentrations reported for soils near Silvermines (365 g/kg). It also is below the sediment quality standard (410 mg/kg) and cleanup standard (960 mg/kg) set for Puget Sound. Soils and wetland sediments contaminated with heavy metals from mining activities have exhibited Zn concentrations as high as 23,970 mg/kg and 44,600 mg/kg (see Table 6.2).

Additionally, the boxplots in Figure 6.6 indicate extreme and outlier data points in the TMF wetland that disproportionately affect overall mean metal values within the cell. These outlier values consistently occur in the *Typha latifolia* (6 m line) and *Juncus effusus* (18 m line) regions for each metal. Field notes indicate no adverse levels in the physico-chemical parameters of the water column including metals concentrations at the 6 m or 18 m sampling line. This pattern is illustrated three-dimensionally in Figure 6.7 which compares metal concentrations in each location sampled in the TMF and Control wetlands. Cd, Pb and Zn concentrations are generally similar in both wetlands except for the breakthrough values. Fe and Mn concentrations are generally higher in the Control.

Laboratory notes indicate the sediment core with elevated metals values (x = 4.5m) from the 6 m line had a rind of tailings around it from the sampling corer. Similarly, the cores with elevated metals values (x = 0.5, 1.5 and 2.5 m) from the 18 m line had tailings rinds which may have contributed to the elevated metals levels in these samples. These samples were included in the overall data analyses to ensure the most conservative values for metal concentrations in the sediments of the TMF wetland were used for comparisons with the Reference wetland and with Silvermines wetland.

Fig. 6.7 Comparison of total Cd, Fe, Mn, Pb and Zn concs. (mg/kg) in wetland sediments, 2000.



6.1.2.4 ANOVA to Compare Metal Concentrations in Wetland Sediments, 2000

A one-way ANOVA was conducted to compare the means of metal concentrations in the TMF and Control wetlands in summer, 2000. Each variable was tested for normality and homogeneity of variance prior to ANOVA analysis and log transformed when necessary.

F values and observed significance levels for each metal are as follows:

Metal	**F**	**p**
Cd	2.9×10^{-5}	0.996
Fe	29.464	0
Mn	9.168	0.004
Pb	2.766	0.104
Zn	2.277	0.140

The results of the ANOVA analysis indicate no significant difference in mean total Cd, Pb and Zn concentrations in the sediments of the TMF and Control wetlands at a significance level of 0.05. There was a significant difference in mean total Fe concentration ($p<0.001$) and Mn concentration ($p<0.05$).

6.1.2.5 Metal Concentrations in Sediments of Wetland Regions, 2000

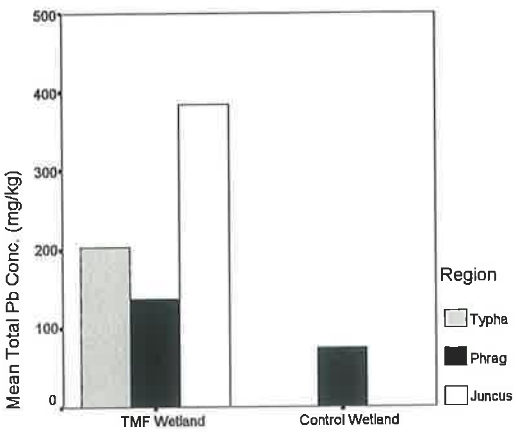
The impact of the outlier data in the TMF wetland on mean values in the *Typha* and *Juncus* regions is obvious from Table 6.5 which outlines descriptive statistics for sediment metals in the three regions of this wetland. The maximum values for Cd, Fe, Mn, Pb and Zn are much higher in these regions than in the *Phragmites* region. Profiles of mean total metal concentrations in the wetland regions are illustrated graphically in Figure 6.8.

A one-way ANOVA was conducted to compare mean sediment metals in the three regions of the TMF wetland followed by Bonferroni's multiple comparison test to denote significant differences between individual regions. The results indicated no

Table 6.5 Descriptive statistics for total metals in sediments in wetland regions, 2000.

		TMF Wetland			Control Wetland
		Typha mg/kg	Phrag. mg/kg	Juncus mg/kg	Phrag. mg/kg
Cd	**Mean**	**.546**	**.344**	**1.080**	**.488**
	Min.	.000	.000	.000	.000
	Max.	1.857	.685	2.470	1.309
	S.D.	.675	.202	.943	.339
Fe	**Mean**	**2882.985**	**2463.949**	**5899.806**	**12085.163**
	Min.	630.340	1178.067	656.355	10699.523
	Max.	7310.042	3319.173	12618.726	13964.145
	S.D	2466.371	832.238	4899.448	956.233
Mn	**Mean**	**104.382**	**63.282**	**126.445**	**163.986**
	Min.	13.261	33.911	38.795	97.653
	Max.	239.219	104.150	256.094	219.704
	S.D.	77.460	26.892	80.461	45.695
Pb	**Mean**	**203.776**	**138.078**	**383.926**	**74.972**
	Min.	5.083	75.363	29.412	45.404
	Max.	609.004	258.325	884.623	130.222
	S.D.	219.776	70.558	343.779	30.300
Zn	**Mean**	**441.983**	**171.714**	**404.184**	**127.726**
	Min.	8.010	54.386	49.833	37.199
	Max.	1781.294	291.584	897.471	299.251
	S.D.	673.823	90.685	350.198	103.235

Fig. 6.8d and e Profiles of total Pb and Zn in wetland sediments, 2000.



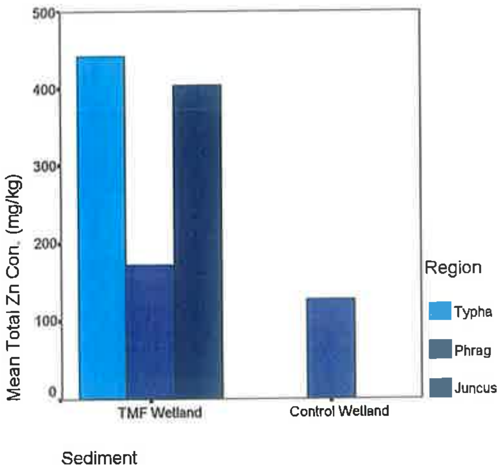
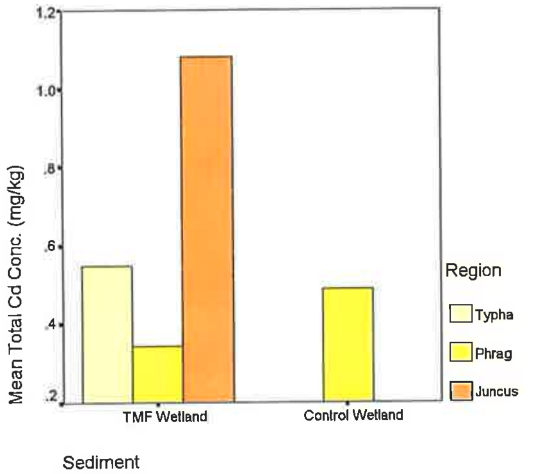
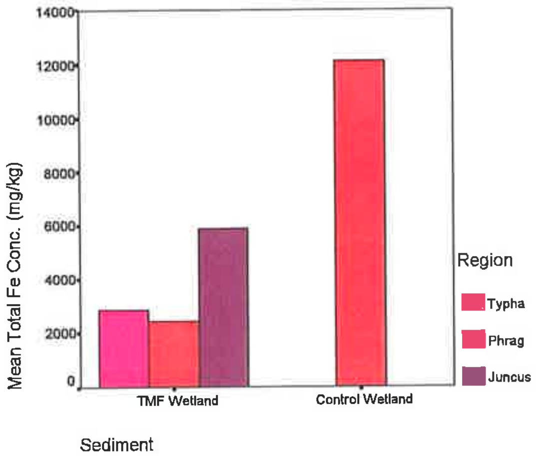
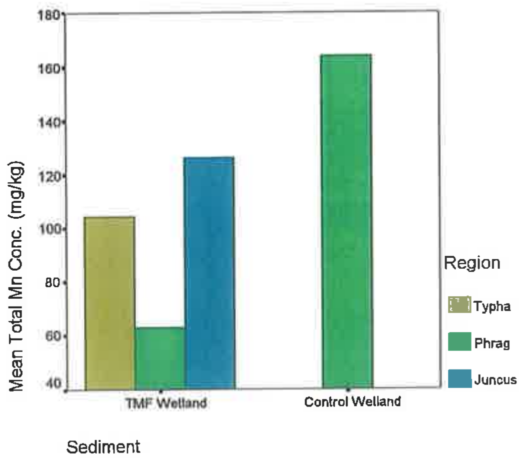


Fig. 6.8a, b and c Profiles of total Cd, Fe and Mn, 2000.







significant difference between each of the regions for Cd (p=0.190), Fe (p=0.436), Mn (p=0.199), Pb (p=0.402) and Zn (p=0.668) at a significance level of 0.05.

Overall, the results for mean total metal concentrations in the sediments of the TMF wetland in 2000 in comparison to the Control, indicate no significant adverse mobilisation of metals into the peat substrate from the tailings.

6.1.3 Comparison in Total Metal Concentrations of Wetland Sediments between 1999 and 2000

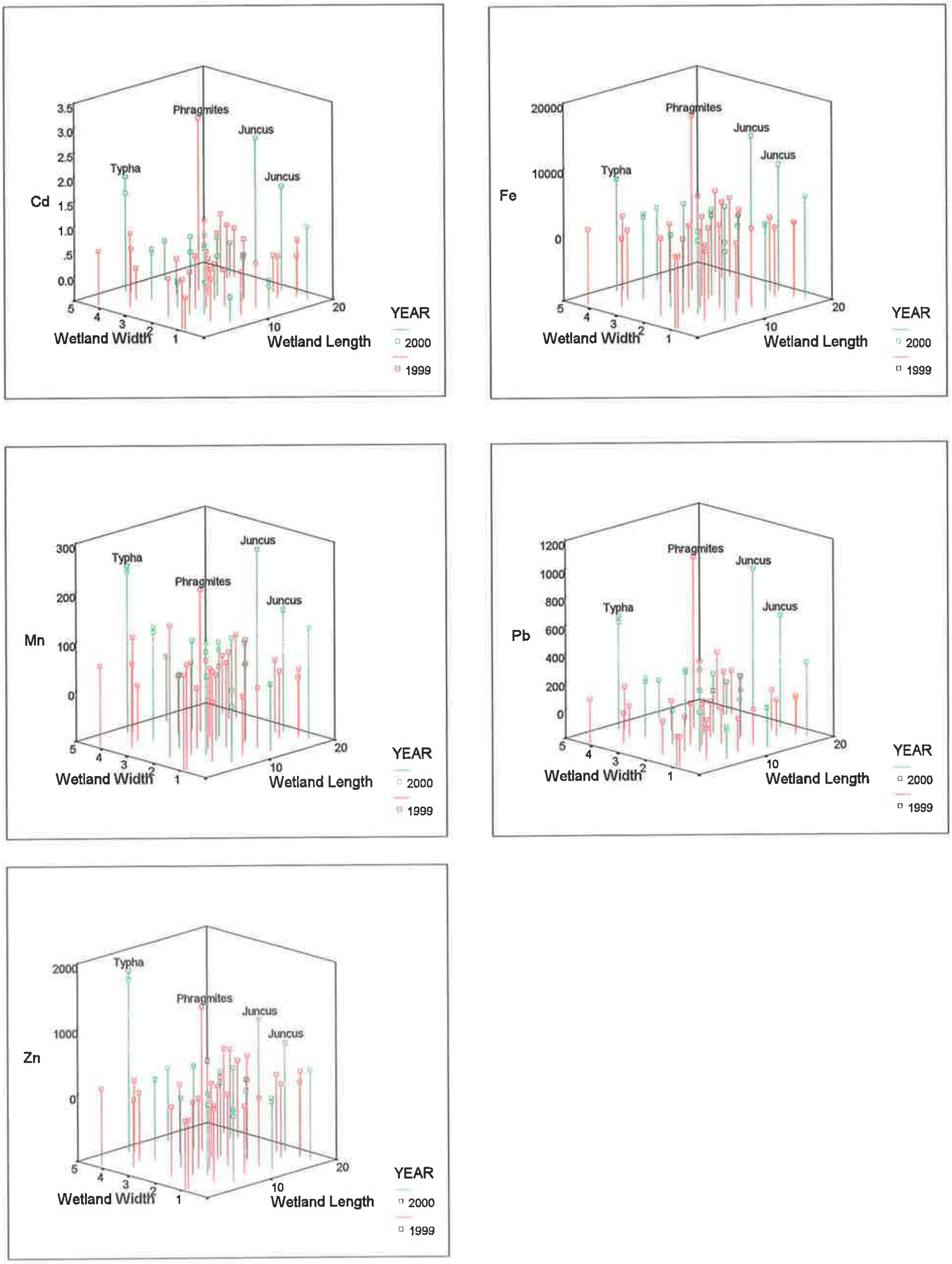
A comparison between mean total sediment metals in the TMF wetland in 1999 and 2000 was conducted in order to investigate the potential for metal accumulations, over time, due to metal mobilisation from the tailings.

Figure 6.9 illustrates comparative differences in metal concentrations in the TMF wetland sediments for both years. For all five metals, this figure shows that metal concentrations in the majority of samples are similar for both years with the consistent exceptions of extreme and outlier values. These values correspond to the extreme values identified in quadrant 16 in 1999, and in the 6 m and 18 m sampling lines in 2000.

The paired-samples t-test was conducted to test the hypothesis that there was no significant difference between metal concentrations in the TMF wetland sediments in 1999 and 2000. Metals data were log transformed to normalise the frequency distributions prior to this statistical analysis. The results were as follows:

Metal	t	p (2-tailed)
Cd	-1.222	0.230
Fe	3.444	0.002
Mn	2.957	0.006
Pb	3.198	0.003
Zn	2.811	0.008

Fig. 6.9 Comparisons of total Cd, Fe, Mn, Pb and Zn content between TMF wetland sediments in 1999 and 2000.



No difference was determined in sediment Cd concentrations (p=0.230) between 1999 an 2000, but differences were determined for Fe (p=0.002), Mn (p=0.006), Pb (p=0.003) and Zn (p=0.008) at a significance level of 0.05.

However, when the extreme data from 1999 and 2000 are eliminated from the data sets and the paired samples t-test repeated, the results are as follows:

Metal	**t**	**p (2-tailed)**
Cd	-2.617	0.015
Fe	2.057	0.051
Mn	1.494	0.148
Pb	1.743	0.094
Zn	1.415	0.170

These results indicate mean total Fe, Mn, Pb and Zn concentrations in the sediments of the TMF wetland do not differ from 1999 to 2000 at a significance level of 0.05. The result for Cd indicates a reduction in mean sediment concentration between 1999 and 2000. A similar one-way ANOVA analysis conducted on the sediments in the Control indicated no significant difference in mean Cd (p=0.438), Pb (p=0.255) and Zn (p=0.345) concentrations, but significant differences in Fe (p<0.001) and Mn (p<0.001) concentrations.

Overall, the results do not indicate substantial accumulation of metals in the peat substrate of the TMF wetland due to the presence of tailings.

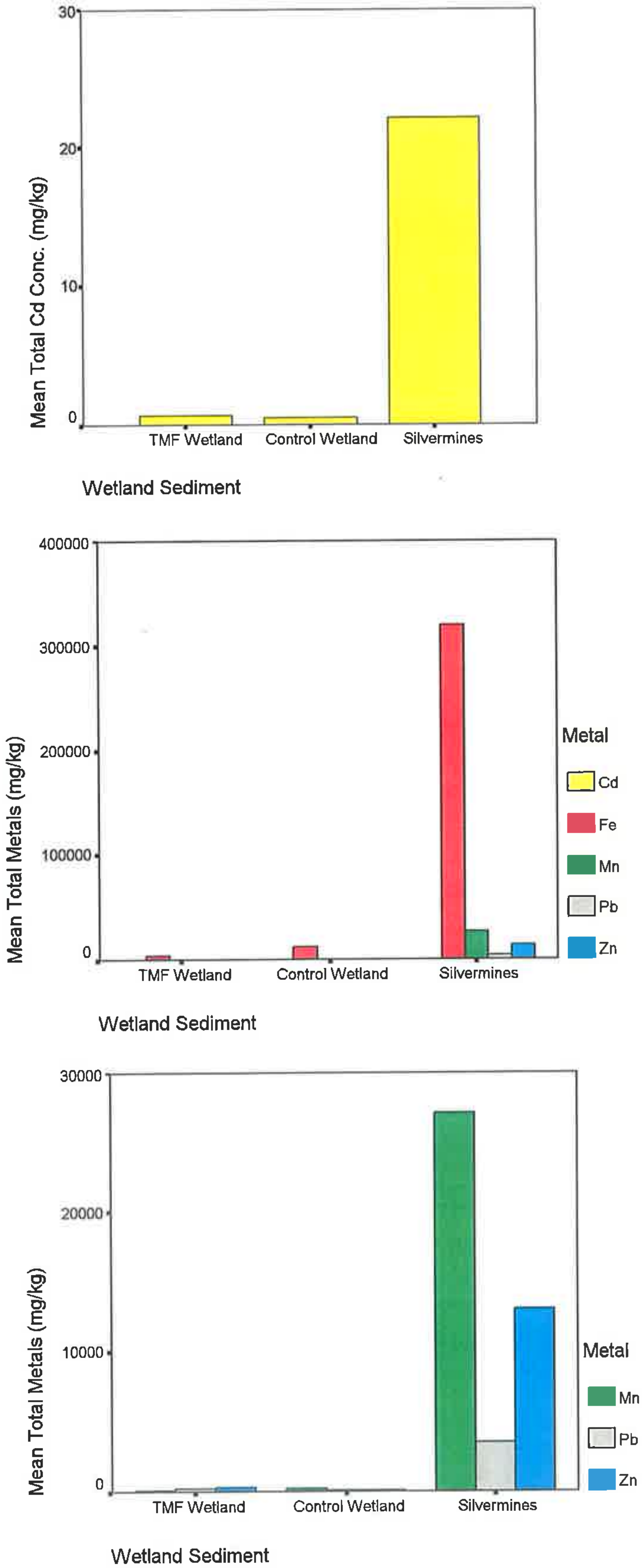
6.1.4 Comparisons with Silvermines Sediment Quality, 2000

Descriptive statistics for the mean metal concentrations in the sediment of Silvermines wetland during summer, 2000 are outlined in Table 6.6. Mean total metal concentrations for Cd (22.17 mg/kg), Fe (3.18 %), Mn (27,088 mg/kg), Pb (3,467 mg/kg) and Zn (12,981 mg/kg) greatly exceed values for uncontaminated soils and natural wetlands outlined in Table 6.2. Instead, they more closely approximate soils and wetland sediments contaminated with metals from mining in Colorado, Oklahoma, and Poland (levy *et al.*, 1992; Basta and Gradwohl, 2000; and Wojcik and

Table 6.6 Descriptive statistics on total metals in sediments at Silvermines in 2000.

		Total Metals mg/kg
Cd	**Mean**	**22.171**
	Minimum	5.005
	Maximum	68.643
	Median	14.778
	Std Dev.	18.940
Fe	**Mean**	**318959.684**
	Minimum	156313.417
	Maximum	416595.541
	Median	324905.833
	Std Dev.	75270.074
Mn	**Mean**	**27087.969**
	Minimum	450.736
	Maximum	71382.006
	Median	16004.673
	Std Dev.	28844.704
Pb	**Mean**	**3467.723**
	Minimum	1197.557
	Maximum	10681.603
	Median	2357.597
	Std Dev.	3121.812
Zn	**Mean**	**12981.573**
	Minimum	3753.974
	Maximum	24808.253
	Median	11367.529
	Std Dev.	7199.091

Fig. 6.10 Comparison of total metals in sediments in TMF, Control and Silvermines wetlands in 2000.



Wojcik, 2000). Mean concentrations in Silvermines wetland sediments sampled in summer 2000 are outlined in Appendix E.

Figure 6.10 illustrates that mean sediment concentrations, for all 5 metals, are substantially higher in Silvermines wetland than those measured in the TMF wetland during summer, 2000. This is significant given the Silvermines wetland is acting as a treatment wetland for runoff from the Silvermines tailings dam whereas the TMF wetland consists of a peat wetland growing on top of the tailings.

Sediment metal concentrations in Silvermines wetland were found to be similar to total metals values obtained for Silvermines tailings and for surface samples on the tailings dam at Silvermines as can be observed from the following:

	Cd (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Tailings[1]	29.5	183,693	1,883	11,638	12,436
Tailings[2]		144,316		14,645	7045
Tailings Dam[3]	20.21			11,694	7046

1. Values for Silvermines tailings from this study.
2. Values for Silvermines tailings from McCabe and Otte, 2000.
3. Values for surface samples from Silvermines tailings dam from Department of Agriculture, Food and Rural Development, 2000.

Table 6.7 outlines complete descriptive statistics for the mean total metal concentrations of Silvermines tailings, the Bord na Mona peat substrate prior to its use in the TMF wetland, and the standard reference sediment (SRM 1944 – a mixture of contaminated marine sediment collected near urban areas in New York and New Jersey) used for quality control checks in the laboratory analysis. Figure 6.11 emphasises the difference in metal concentrations between the tailings and Bord na Mona peat substrate.

In Figure 6.12 mean total metal concentrations in the TMF, Control and Silvermines wetlands have been added to those for Silvermines tailings, the Bord na Mona peat and the sediment standard for comparative purposes. This figure emphasises the

Table 6.7 Descriptive statistics on total metals in Silvermines tailings, peat and sediment standard.

		Tailings mg/kg	Peat mg/kg	Sed Standard mg/kg
Cd	**Mean**	**29.523**	**.030**	**7.416**
	Min.	29.456	.030	7.229
	Max.	29.589	.030	7.603
	Med.	29.523	.030	7.416
	S.D.	.094	.000	.264
Fe	**Mean**	**183693.12**	**214.88**	**28509.03**
	Min.	168363.21	188.89	28272.69
	Max.	199023.03	240.86	28745.36
	Med.	183693.12	214.88	28509.03
	S.D.	21679.77	36.75	334.23
Mn	**Mean**	**1883.156**	**4.815**	**329.186**
	Min.	1844.184	4.464	292.850
	Max.	1922.128	5.165	365.521
	Med.	1883.156	4.815	329.186
	S.D.	55.115	.496	51.386
Pb	**Mean**	**11638.370**	**1.926**	**273.005**
	Min.	11430.865	1.528	259.972
	Max.	11845.874	2.324	286.038
	Med.	11638.370	1.926	273.005
	S.D.	293.456	.563	18.431
Zn	**Mean**	**12436.239**	**67.204**	**590.685**
	Min.	11677.451	64.583	562.303
	Max.	13195.026	69.825	619.067
	Med.	12436.239	67.204	590.685
	S.D.	1073.088	3.707	40.138

Fig. 6.11 Comparison in total metals in sediments in Silvermines tailings, peat and sediment standard samples.

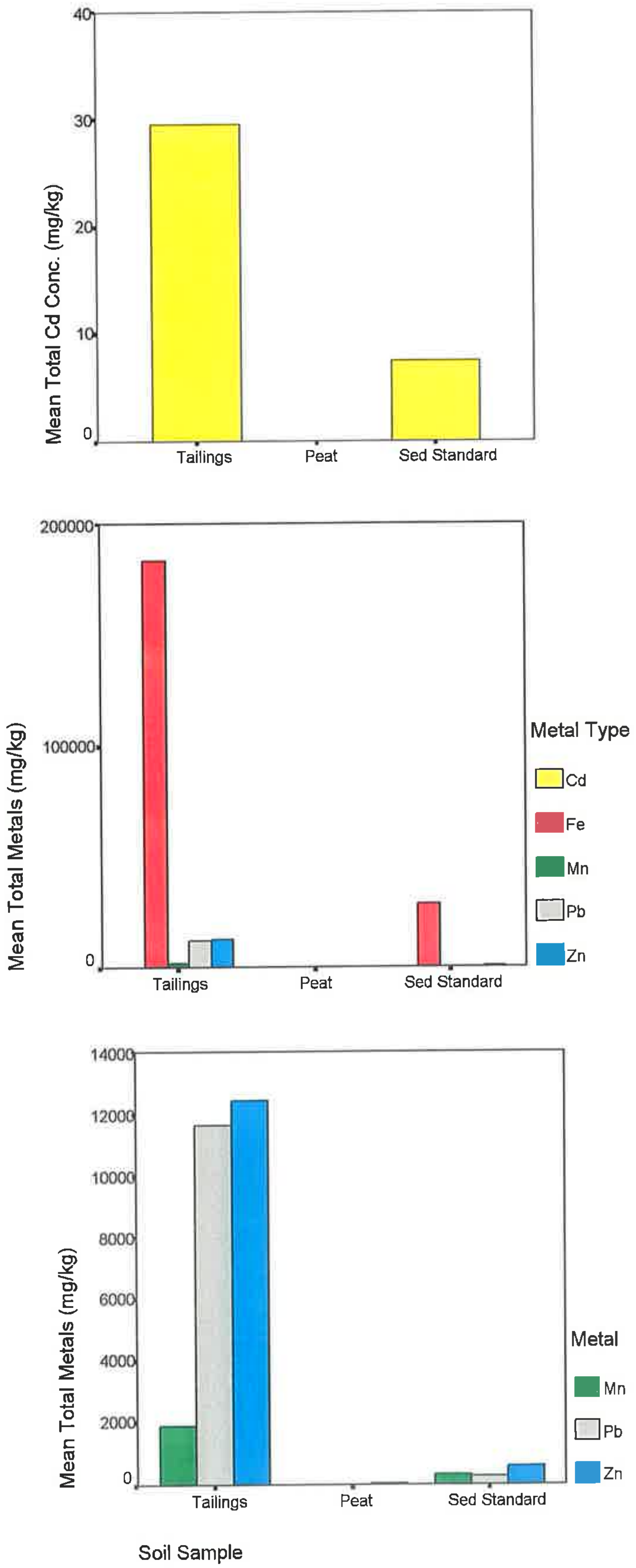
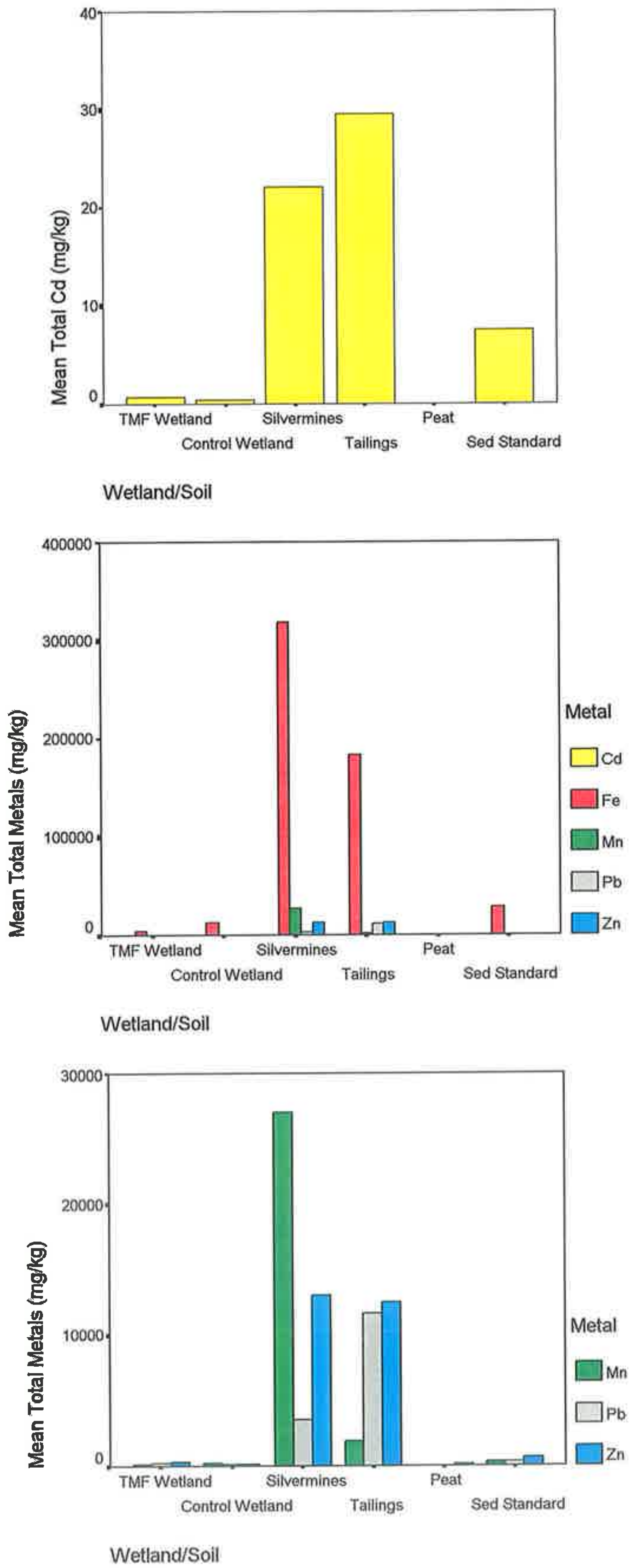


Fig. 6.12 Comparison of total metals in sediments in TMF, Control, and Silvermines wetlands and in Silvermines tailings, peat and sediment standard samples.



elevated metals concentrations in the sediments of Silvermines wetland in comparison to the TMF wetland.

6.1.5 Metal Speciation in TMF, Control and Silvermines Wetlands, 2000

In addition to assessing total metals concentrations in the sediments of the TMF, Control and Silvermines wetlands, a series of four sequential extractions also were carried out on these sediments to evaluate metal speciation and potential bioavailability in these systems. These extractions were used to quantify the ion-exchangeable fraction (including carbonates), the reducible fraction (typically hydrous oxides of Fe and Mn), the oxidisable fraction (including sulfides and organic matter) and the residual fraction. Metal extractions for all metals in sediments from the TMF, Refererence/Control and Silvermines wetlands sampled in summer, 2000 are outlined in Appendix F.

6.1.5.1 Cd Extractions

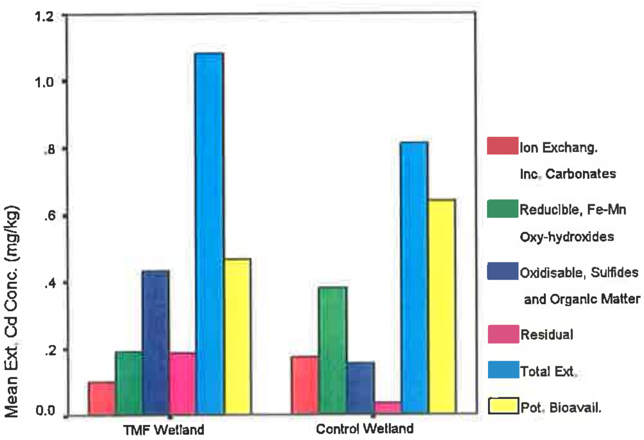
Table 6.8 outlines descriptive statistics for mean Cd extractions from the sediments of the TMF, Control and Silvermines wetlands sampled during summer, 2000. Table 6.9 outlines metal concentrations in extractions from natural wetlands and wetlands impacted by AMD from the literature.

The concentration of Cd extracted from the TMF wetland sediments in the ion-exchangeable and reducible fractions (0.099 mg/kg and 0.190 mg/kg) as outlined in Table 6.8 are well within ranges reported for Cd in these fractions in sediments from the St. Lawrence River in Canada (0.09 mg/kg to 1.51 mg/kg), constructed wetlands receiving urban runoff (0.46 mg/kg to 3.05 mg/kg), and uncontaminated soils (1.96 mg/kg to 8.78 mg/kg) as outlined in Table 6.9. The Cd concentration in the oxidisable fraction (0.431 mg/kg) is also within the range obtained for uncontaminated sediments in 38 lakes in Quebec, Canada (0.188 mg/kg to 0.980 mg/kg). The values of Cd in the Control sediments for all of these extractions also are well within the ranges reported for uncontaminated soils and sediments. However, the values obtained for Silvermines sediments in the ion-exchangeable and reducible fractions (4.779 mg/kg and 10.767 mg/kg respectively) are closer to ranges reported for soils contaminated

Table 6.8 Descriptive statistics for Cd extractions (mg/kg) from TMF, Control and Silvermines wetland sediments in 2000.

Cd		Wetland		
		TMF	Control	Silvermines
Ion Ex.	**Mean**	**.099**	**.173**	**4.779**
	Max.	.324	.633	8.420
	Min.	.000	.036	.020
	S.D.	.089	.184	2.650
Red.	**Mean**	**.190**	**.380**	**10.767**
	Max.	.634	.553	36.563
	Min.	.000	.155	1.039
	S.D.	.164	.134	11.158
Oxid.	**Mean**	**.431**	**.156**	**1.197**
	Max.	2.098	.614	5.276
	Min.	.000	.000	.202
	S.D.	.531	.201	1.604
Resid.	**Mean**	**.186**	**.037**	**1.506**
	Max.	1.522	.159	5.656
	Min.	.000	.000	.000
	S.D.	.375	.056	1.888
Total	**Mean**	**1.082**	**.811**	**19.681**
	Max.	4.400	1.348	55.690
	Min.	.025	.151	2.791
	S.D.	.955	.439	16.430

Fig. 6.13 Cd extracted from TMF, Control and Silvermines sediments in 2000.



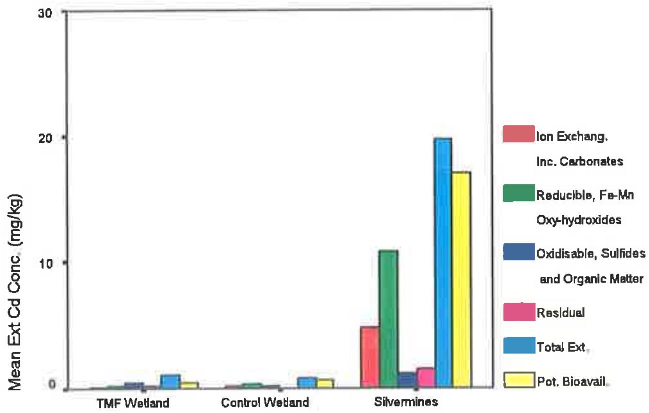
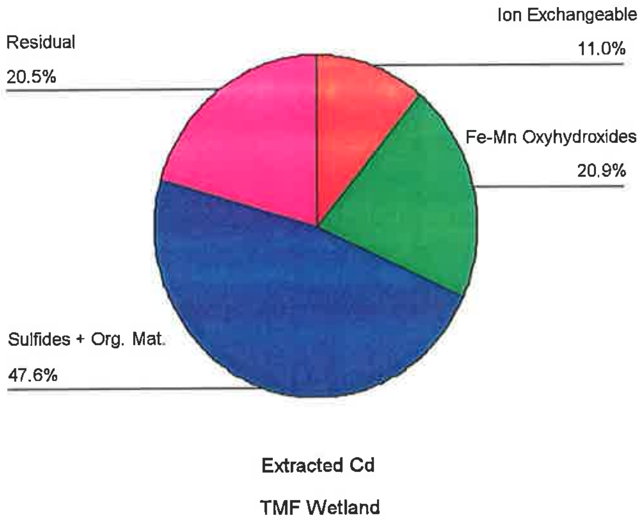
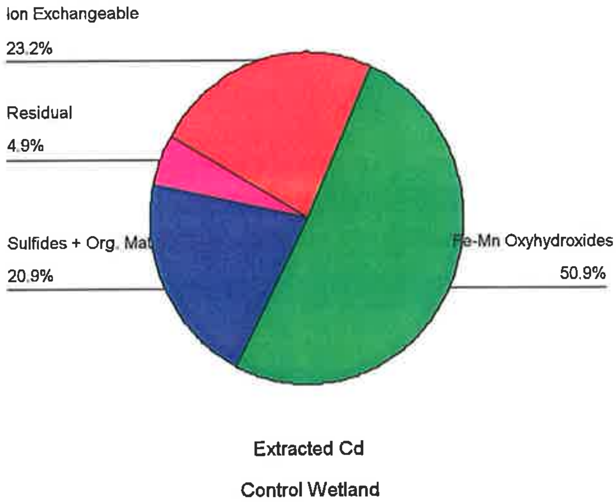


Fig. 6.14 (%) Cd ext. in different species in TMF, Control and Silvermines wetlands, 2000.





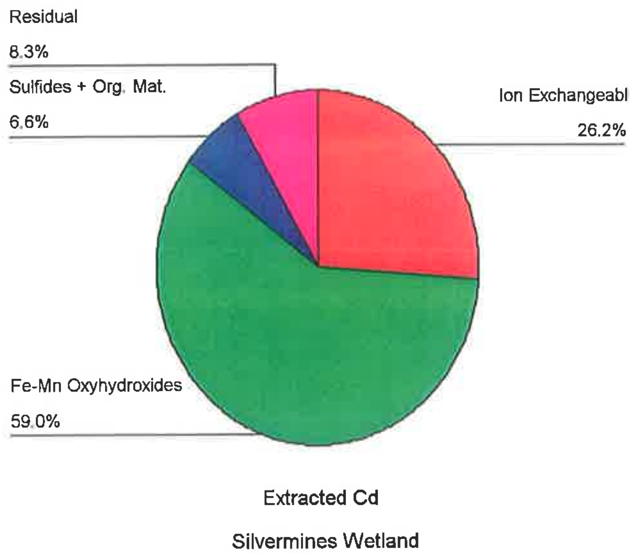


Table 6.9 Range of metal concentrations in extracted fractions from river sediments, natural wetlands, wetlands receiving AMD and contaminated soils from the literature.

	Ext 1	Ext 2	Ext 3	Ext 4	Ext 5
	Exchangeable (Water & Acid Soluble)	**Reducible (Fe-Mn Oxy-Hydroxides)**	**Oxidisable (Organic Matter & Sulphides)**	**Residual**	**Total**
	(µg/g)	**(µg/g)**	**(µg/g)**	**(µg/g)**	**(µg/g)**
St. Lawrence River, Canada (St. Cyr & Campbell, 2000) (Potentially bioavailable metals)					
→ Cd					
1990	0.09 → 1.44[a]				0.23 → 3.15
1991	0.10 → 1.51[a]				0.22 → 1.38
→ Fe					
1990		2,513 → 11,170[a]			
1991		1,731 → 14,521[a]			
→ Pb					
1990	4 → 24.3[a]				17.6 → 56.2
→ Zn					
1990	19.5 → 168[a]				70.9 → 362
1991	14.1 → 418[a]				59.2 → 552
Weser Estuary, Rhine River (Salomons & Förstner, 1984)					
→ Cd					
Weser Estuary	8%	77%	12%	3%	
Rhine River	27%	44%	17%	12%	
Sediments from the Mississippi River and Mobile River, U.S.A. (Gambrell, 1994)					
→ Cd					
Mississippi River	2.0 → 57.1				
Mobile River	1.3 → 20.6				
→ Pb					
Mississippi River	5.33 → 3.14				
Mobile River	0.11 → 0.28				
→ Zn					
Mississippi River	1.2 → 24.8				
Mobile River	0.7 → 7.9				
49 littoral sites and 38 lakes in Quebec, Canada (Tessier et al., 1993)					
→ Cd					
Subject to AMD			0.301 → 11.578		0.150 → 12.14
Control			0.188 → 0.980		0.214 → 1.011
→ Fe					
Subject to AMD		4,915 → 38,146			
Control		1,385 → 26,919			
Constructed wetlands receiving urban runoff, London, U.K. (Carapato & Purchase, 2000)					
→ Cd	0.46 → 3.051		0.820 → 3.252	1.691 → 7.271	2.723 → 11.405
→ Pb	4.247 → 18.657		44.779 → 251.622	12.507 → 160.869	50.309 → 384.5
Soils contaminated from Pb & Zn mining and smelting in Oklahoma, U.S.A. (Basta & Gradwohl, 2000)					
→ Cd	25	5	7		31
→ Pb	227	394	294		872
→ Zn	2,420	977	2,230		5,020
Mountain meadow near Leadville, Colorado, U.S.A. contaminated with metals from mining (Levy et al., 1992)					
→ Cd					
Control	1.96	8.78	0.048		
Contaminated Soil	2.0 → 14.5	10.7 → 125	1.5		
→ Pb					
Control	4.96	264	6.29		
Contaminated Soil	4.48 → 55.2	1,254 → 5,381	43.8 → 45.1		
→ Zn					
Control	13.65	126			
Contaminated Soil	801.6 → 974.4	3,757 → 16,285	199 → 2,433		

[a] Value includes Ext1 and Ext2 and is equivalent to potentially bioavailable metals.

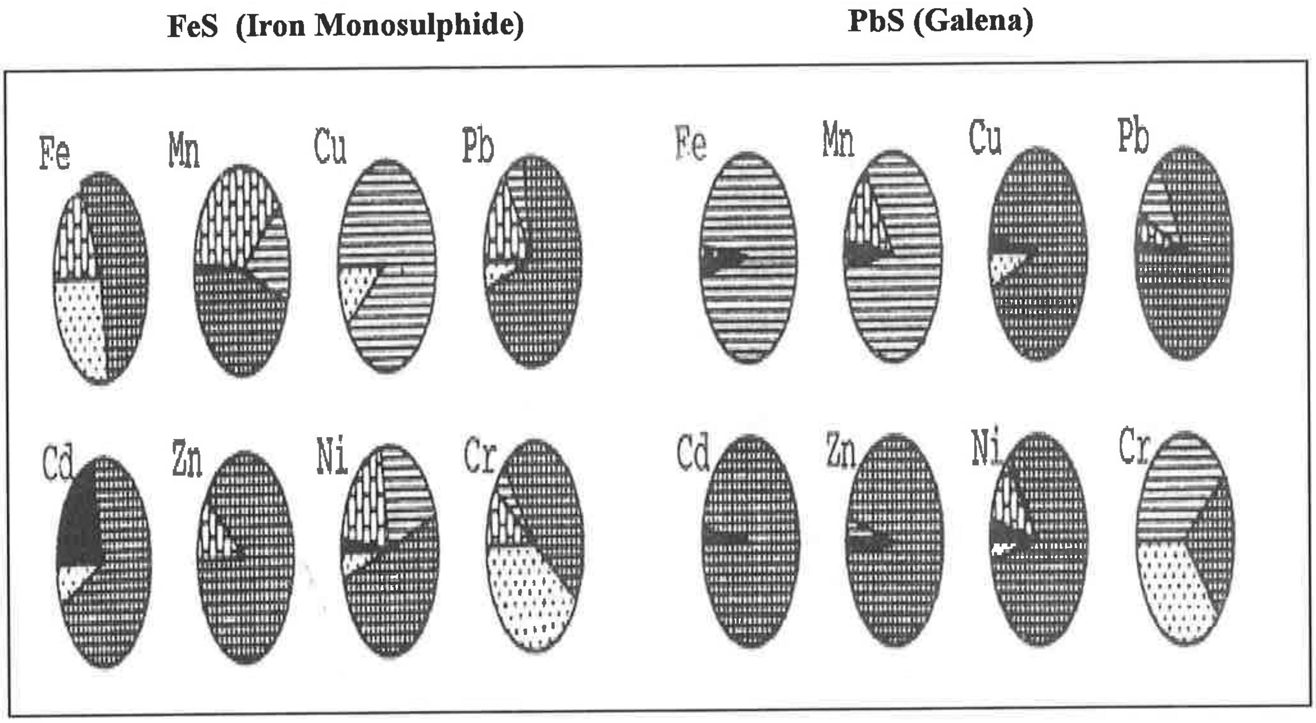
with metals from mining (2.0 mg/kg to 14.5 mg/kg and 10.7 mg/kg to 125 mg/kg respectively), although they are closer to the lower end of these ranges.

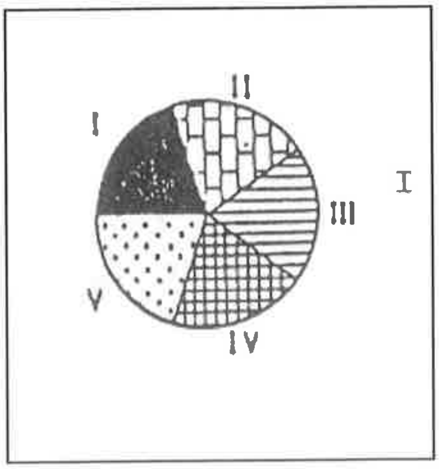
Figure 6.13a and b illustrate the differences in Cd extracted from the TMF, Control and Silvermines wetlands. In addition to Cd extracted in the four extractions, total Cd and potentially bioavailable Cd are outlined. The potentially bioavailable sediment-bound metal corresponds to the sum of the ion-exchangeable and reducible fractions (St-Cyr and Campbell, 2000, Gambrell, 1994). From Figure 6.13a it is obvious that mean total Cd concentration is higher in the TMF wetland than in the Control, but the mean potentially bioavailable fraction is higher in the Control. Figure 6.13b shows mean total and potentially bioavailable Cd are substantially higher in Silvermines wetland.

Figure 6.14 illustrates the % of Cd extracted in each of the four fractions in the sequential extraction process for the TMF, Control and Silvermines wetlands. The % of ion-exchangeable, reducible (Fe and Mn oxyhydroxides), oxidisable and residual Cd in the TMF sediments (11% : 20.9% : 47.6 % : 20.5 %) shows that Cd is enriched in the oxidisable fraction which includes that bound to sulfides and organic matter. The fact that the peat substrate in this system has an extremely high organic matter content, 94.5% (determined as % LOI), may have influenced this speciation. Additionally, an examination of Figure 6.15 which illustrates the results of extraction studies on individual minerals shows a similar pattern of enrichment for Cd (predominantly associated with sulfides and organic matter) for FeS (iron monosulphide) and PbS (galena). The estimated mineral composition of Silvermines tailings is 30-35% pyrite and <4% galena and other sulphosalts, although the proportions of various minerals will vary throughout the tailings pile and metal distribution will be heterogeneous (Arthurs, 1994). Therefore, the enrichment of Cd in the oxidisable fraction of the TMF wetland could also be due to the presence of sulphides in the sediments of this system.

The Control wetland has a much lower organic matter content (20.4%) and Figure 6.14 shows Cd is predominantly enriched in the reducible fraction (50.9%) of this wetland which includes that bound to Fe and Mn oxyhydroxides. This follows the general pattern reported for sediments in German estuarine and riverine environments

Fig. 6.15 Extraction studies on individual minerals and simple mixtures of compounds (from Rapin and Förstner, 1983).





I: Exchangeable (pH 7)
II: Carbonates + exchangeable (pH 5)
III: Fe-Mn oxides (reducible fraction)
IV: Organic matter + sulfides
V: Residual fraction

where most of the extractable Cd is associated with the reducible fraction (77% and 44% respectively) (see Table 6.9). Similarly, Cd is predominantly enriched in the reducible fraction (59%) in the sediments of Silvermines wetlands.

An examination of the enrichment of metals in different fractions for each wetland sediment and corresponding potentially bioavailable and free-metal ion concentrations in the sediments occurs in Section 6.1.6.

6.1.5.2 Fe Extractions

Table 6.10 outlines descriptive statistics for mean Fe extractions from the sediments of the TMF, Control and Silvermines wetlands sampled during summer, 2000.

The concentration of Fe extracted from the TMF wetland sediments in the ion-exchangeable, reducible, oxidisable and residual fractions (40.38 mg/kg, 481.61 mg/kg, 2349.65 mg/kg, and 74.66 mg/kg respectively) are well within ranges reported for Fe in the reducible fraction for uncontaminated sediments in lakes in Quebec, Canada (1,385 mg/kg to 26,919 mg/kg) and in the same fraction for sediments from the St. Lawrence River in Canada (1,731 mg/kg to 14,521 mg/kg) (see Table 6.9).

The values of Fe in the Control sediments for all of these extractions are higher than in the TMF wetland but also are well within the ranges reported for uncontaminated sediments. The concentrations obtained for Silvermines sediments in all fractions are much higher than for the TMF and Control wetlands and higher than values reported for the reducible fraction in sediments subject to AMD in Canada (4,915 mg/kg to 38,146 mg/kg). However, this Canadian study also cites a single value of 179,390 mg/kg for Fe oxyhydroxide at an uncontaminated site.

Figure 6.16a and b illustrate the differences in Fe extracted from the TMF, Control and Silvermines wetlands. From Figure 6.16a it is obvious that mean total Fe and potentially bioavailable Fe concentrations are higher in the Control than in the TMF wetland. Figure 6.16b illustrates mean total and potentially bioavailable Fe are substantially higher in Silvermines wetland.

Table 6.10 Descriptive statistics for Fe extractions (mg/kg) in sediments of TMF, Control and Silvermines wetlands in 2000.

Fe		Wetland TMF	Control	Silvermines
Ion Ex.	**Mean**	**40.38**	**181.36**	**1058.79**
	Max.	145.32	277.83	2918.10
	Min.	1.14	101.84	298.84
	S.D.	40.54	61.21	920.98
Red.	**Mean**	**481.61**	**3335.41**	**128927.75**
	Max.	1489.03	4291.22	201903.45
	Min.	88.27	2419.22	37931.28
	S.D.	388.50	609.24	47360.20
Oxid.	**Mean**	**2349.65**	**3751.98**	**56517.49**
	Max.	13535.57	4473.38	83114.00
	Min.	45.56	2756.35	27729.13
	S.D.	3338.78	618.62	18047.90
Resid.	**Mean**	**74.66**	**1247.28**	**82806.43**
	Max.	262.96	2079.64	207917.12
	Min.	.000	130.32	24338.51
	S.D.	61.35	586.61	48066.39
Total	**Mean**	**3071.32**	**8634.47**	**279030.10**
	Max.	15463.12	10653.01	374625.85
	Min.	274.08	7084.93	110414.01
	S.D.	3823.32	1111.01	66012.52

Fig. 6.16a and b Fe extracted from TMF, Control and Silvermines sediments in 2000.

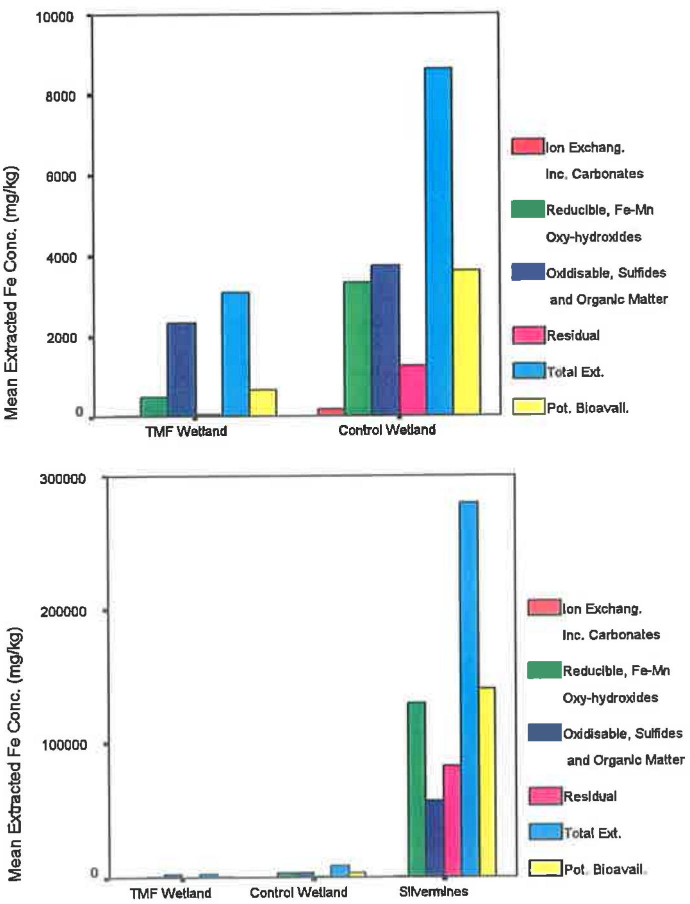
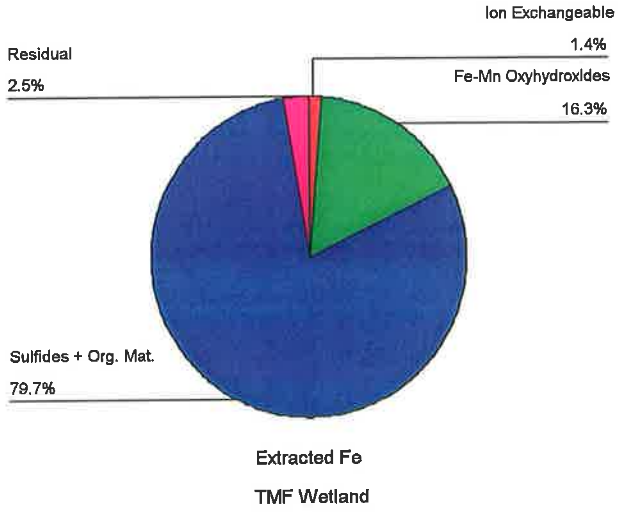
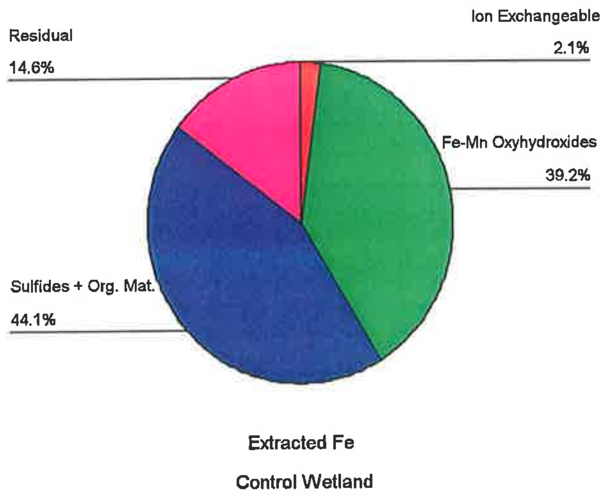


Fig. 6.17 (%) Fe ext. in different species in TMF, Control and Silvermines wetlands, 2000.





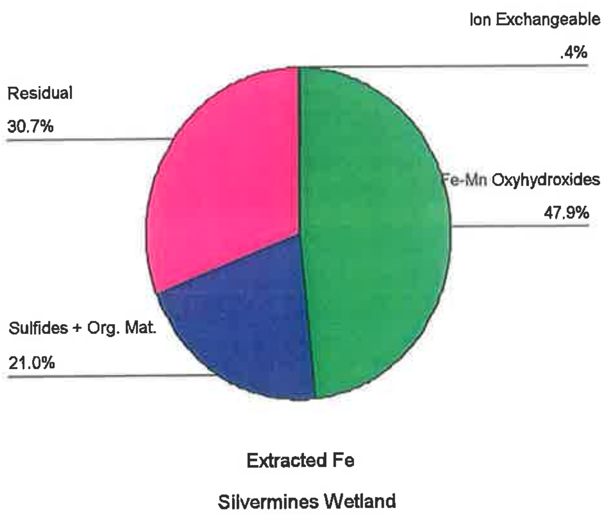


Figure 6.17 illustrates the % of Fe extracted in each of the four fractions in the sequential extraction process for the TMF, Control and Silvermines wetlands. This figure indicates Fe is substantially enriched in the oxidisable fraction (79.7% bound to sulfides and organic matter) of the TMF wetland, whereas in the Control, Fe is predominantly bound up in the reducible (39.2%) and oxidisable fractions (44.1%). The majority of extracted Fe in Silvermines wetland is also bound up in the reducible fraction (47.9%).

Again the fact that the peat substrate in the TMF system has an extremely high organic matter content may have influenced the speciation of Fe in this wetland. Additionally, Figure 6.15 shows Fe predominantly associated with the oxidisable fraction for FeS and with the reducible fraction for PbS. The enrichment of Fe in the oxidisable fraction of the TMF wetland also could be due to the presence of sulphides in the sediments of this system.

6.1.5.3 Mn Extractions

Table 6.11 outlines descriptive statistics for mean Mn extractions from the sediments of the TMF, Control and Silvermines wetlands sampled during summer, 2000.

The concentration of Mn extracted from the TMF wetland sediments in the ion-exchangeable, reducible, oxidisable and residual fractions (54.73 mg/kg, 31.70 mg/kg, 16.69 mg/kg, and 1.03 mg/kg respectively) are lower than in the Control with the exception of the oxidisable fraction. The concentrations obtained for Silvermines sediments in all fractions are substantially elevated in comparison to the TMF and Control wetlands.

Figure 6.18a and b illustrate the differences in Mn extracted from the three wetlands. From these figures it is obvious that mean total and potentially bioavailable Mn concentrations are lower in the TMF wetland than in the Control, and mean total and potentially bioavailable Mn are substantially higher in Silvermines wetland.

Figure 6.19 illustrates the % of Mn extracted in each of the four fractions for the three wetlands. The majority of Mn was extracted in the ion-exchangeable fraction

Table 6.11 Descriptive statistics for Mn extractions (mg/kg) in sediments of TMF, Control and Silvermines wetlands in 2000.

Mn		Wetland		
		TMF	Control	Silvermines
Ion Ex.	**Mean**	**54.73**	**109.63**	**3244.91**
	Max.	423.22	149.41	6616.74
	Min.	1.46	69.51	147.35
	S.D.	80.07	30.27	2542.97
Red.	**Mean**	**31.70**	**42.87**	**18198.42**
	Max.	132.53	63.07	73894.91
	Min.	.00	18.87	81.39
	S.D.	32.42	14.88	26813.34
Oxid.	**Mean**	**16.69**	**9.71**	**538.76**
	Max.	74.33	13.49	1790.17
	Min.	.00	7.20	48.25
	S.D.	19.04	2.14	624.34
Resid.	**Mean**	**1.03**	**4.58**	**100.71**
	Max.	17.85	6.48	592.05
	Min.	.00	1.02	34.74
	S.D.	3.20	1.68	148.51
Total	**Mean**	**123.78**	**180.39**	**23047.08**
	Max.	463.41	227.03	84641.94
	Min.	10.21	108.53	556.45
	S.D.	114.50	47.66	30330.92

Fig. 6.18a and b Mn extracted from TMF, Control and Silvermines sediments in 2000.

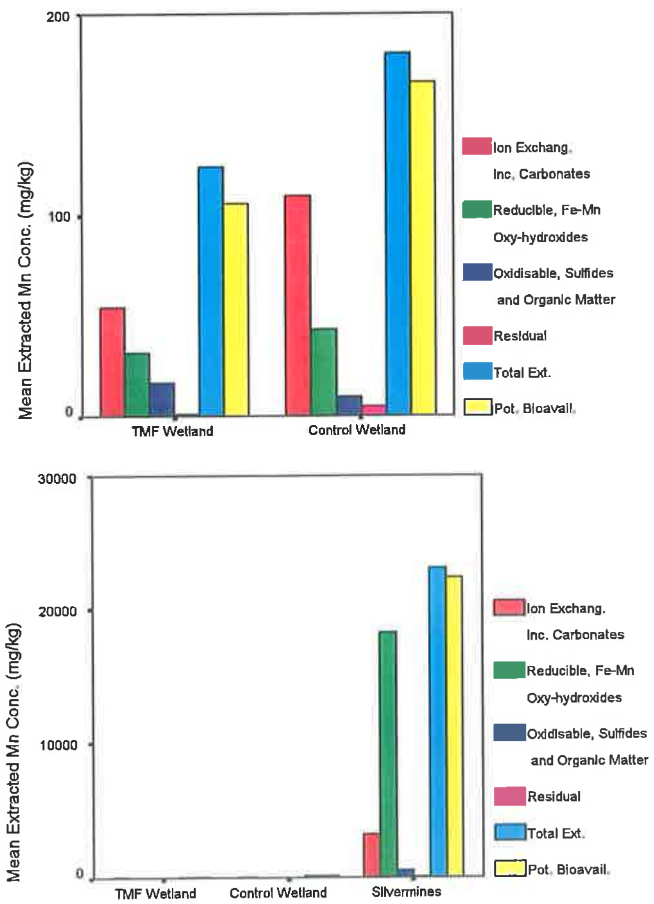
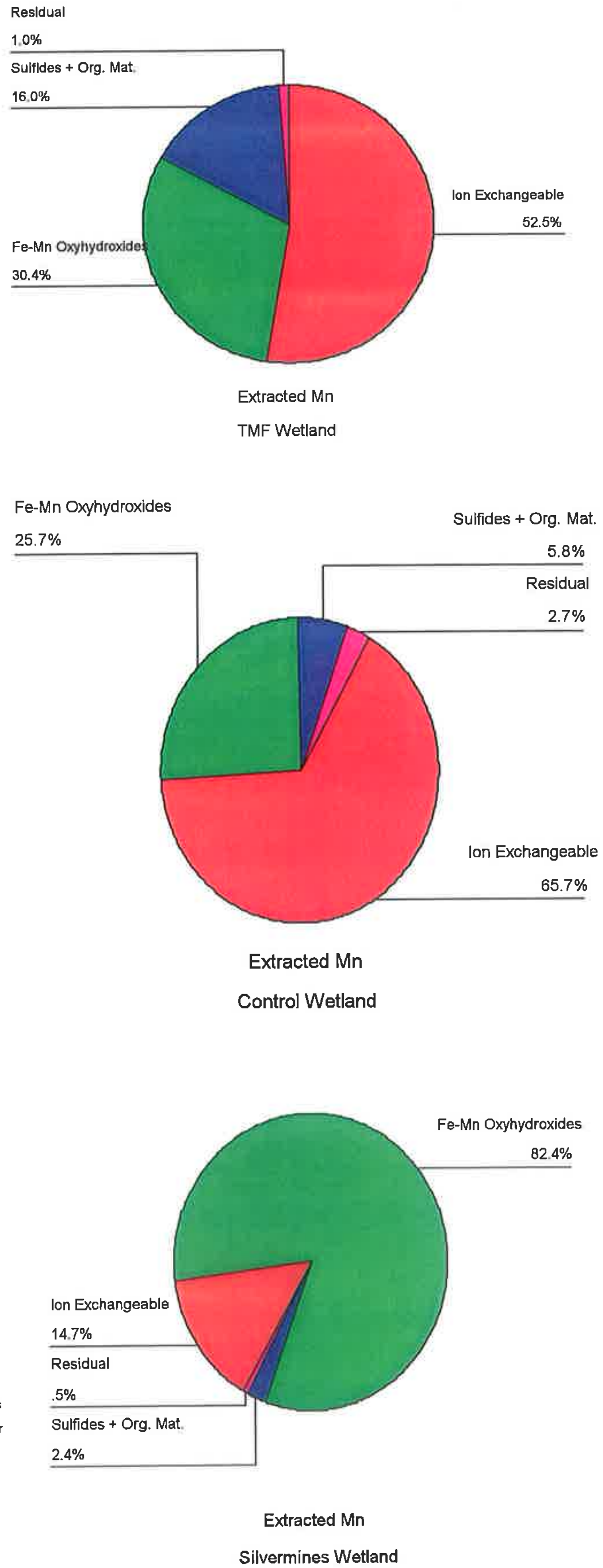


Fig. 6.19 (%) Mn ext. in different species in TMF, Control and Silvermines wetlands, 2000.



(including carbonates) for both the TMF wetland (52.5%) and the Control (65.7%). The majority of Mn was extracted in the reducible fraction (82.4%) for Silvermines. Figure 6.15 shows Mn predominantly associated with the exchangeable and reducible fractions of FeS and with the reducible fraction for PbS.

6.1.5.4 Pb Extractions

Table 6.12 outlines descriptive statistics for mean Pb extractions from the sediments of the TMF, Control and Silvermines wetlands sampled during summer, 2000.

The concentration of Pb extracted from TMF wetland sediments in the ion-exchangeable fraction (8.29 mg/kg) is within the range reported for Pb in this fraction in sediments from the St. Lawrence River in Canada (4.0 mg/kg to 24.3 mg/kg) and from constructed wetlands receiving urban runoff in the U.K. (4.247 mg/kg to 18.657 mg/kg) (see Table 6.9). The concentration of Pb extracted in the reducible fraction (48.48 mg/kg) is substantially below values outlined for uncontaminated soils (264 mg/kg) and for soils contaminated with metals from mining (394 mg/kg to 5,381 mg/kg) in the U.S. Regarding the oxidisable fraction, Pb concentrations (174.41 mg/kg) are within the range reported for constructed wetlands in the U.K. (44.78 mg/kg and 251.62 mg/kg) (Carapato and Purchase, 2000).

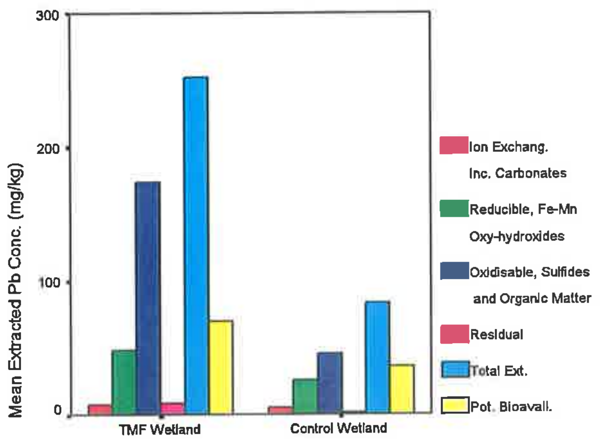
The values of Pb in the Control sediments for all of these extractions are also well within the ranges reported for uncontaminated soils and sediments. The values obtained for Pb extracted from Silvermines sediments in all fractions are higher than in the TMF and Control wetlands. The Pb concentration of the reducible fraction (2,119 mg/kg) is closer to the range reported for soils contaminated with metals from mining.

Figures 6.20a and b illustrate the differences in Pb extracted from the TMF, Control and Silvermines wetlands. From Figure 6.20a it is obvious that mean total Pb concentration is higher in the TMF wetland than in the Control, but the mean potentially bioavailable fraction is much closer between both wetlands. This is due to the high concentration of Pb extracted in the oxidisable fraction of the TMF wetland.

Table 6.12 Descriptive statistics for Pb extractions (mg/kg) in sediments of TMF, Control and Silvermines wetlands in 2000.

Pb		Wetland		
		TMF	Control	Silvermines
Ion Ex.	**Mean**	**8.29**	**5.59**	**234.51**
	Max.	48.15	9.27	2781.31
	Min.	.00	1.55	.001
	S.D.	11.72	2.91	734.30
Red.	**Mean**	**48.48**	**25.81**	**2118.74**
	Max.	309.73	45.23	6733.83
	Min.	.24	15.18	664.87
	S.D.	73.79	9.66	1928.50
Oxid.	**Mean**	**174.41**	**46.04**	**263.54**
	Max.	956.41	77.04	595.24
	Min.	5.69	28.42	82.97
	S.D.	232.99	15.29	171.29
Resid.	**Mean**	**8.70**	**1.97**	**274.816**
	Max.	67.60	3.84	533.51
	Min.	.00	.00	74.88
	S.D.	13.63	1.29	154.19
Total	**Mean**	**252.73**	**83.56**	**3095.18**
	Max.	1394.77	128.92	10337.84
	Min.	11.37	53.84	882.90
	S.D.	343.72	24.35	2801.35

Fig. 6.20a and b Pb extracted from TMF, Control and Silvermines sediments in 2000.



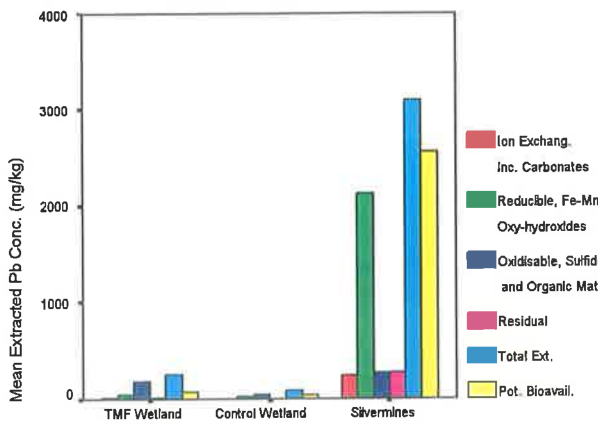


Fig. 6.21 (%) Pb ext. in different species in TMF, Control and Silvermines wetlands, 2000.

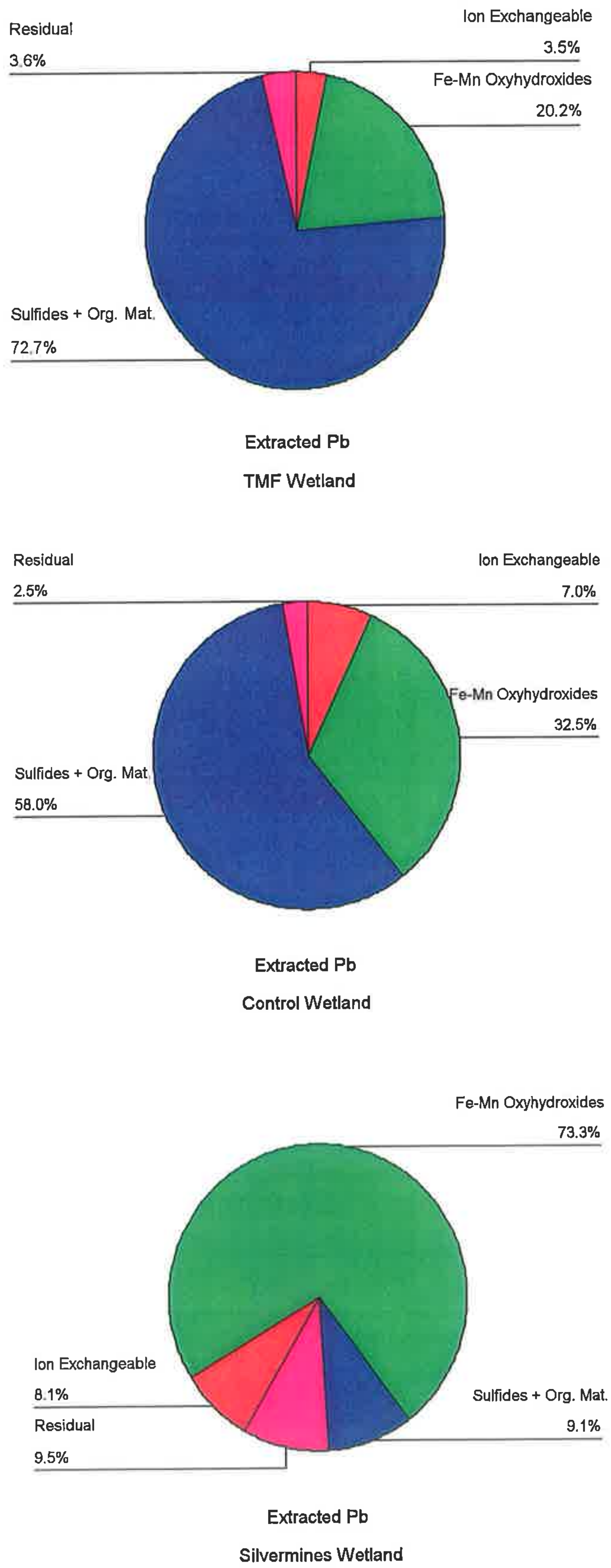


Figure 6.20b shows mean total and potentially bioavailable Pb are substantially higher in Silvermines wetland.

Figure 6.21 illustrates the % of Pb extracted in each of the four fractions for the three wetlands and shows that Pb is enriched in the oxidisable fraction of the TMF wetland (72.7%) and the Control (58%). The high organic content of the peat substrate in the TMF system is likely to have influenced this speciation. Sequential extractions conducted on sediments from wetlands in Florida determined the highest percentage of Pb was organically bound followed by that bound to the carbonate fraction (Ton, 1990). Additionally, an examination of Figure 6.15 shows a similar pattern of enrichment for Pb in the oxidisable fraction for FeS and PbS. The enrichment of Pb in the oxidisable fraction of the TMF and Control wetlands could also be due to the presence of sulphides in the sediments of these system.

Pb is predominantly enriched in the reducible fraction (73.3%) in the sediments of Silvermines wetlands.

6.1.5.5 Zn Extractions

Table 6.13 outlines descriptive statistics for mean Zn extractions from the sediments of the TMF, Control and Silvermines wetlands sampled during summer, 2000.

The concentration of Zn extracted from TMF wetland sediments in the ion-exchangeable fraction and reducible fractions (36.33 mg/kg and 84.72 mg/kg) are within the range outlined for Zn in these combined fractions in sediments from the St. Lawrence River in Canada (14.1 mg/kg to 418 mg/kg) and substantially below the range outlined for both fractions in soils contaminated from mining (802 mg/kg to 2,420 g/kg and 3,757 mg/kg to 16,285 mg/kg respectively) (see Table 6.9). Regarding the oxidisable fraction in the TMF, Zn concentration (316.10 mg/kg) is within the range reported for contaminated soils (199 mg/kg to 2,433 mg/kg) but at the lower end of this range.

The values of Zn in the Control sediments for all of these extractions are well within the ranges reported for uncontaminated soils and sediments. The values obtained for

Table 6.13 Descriptive statistics for Zn extractions (mg/kg) in sediments of TMF, Control and Silvermines wetlands in 2000.

Zn		Wetland		
		TMF	**Control**	**Silvermines**
Ion Ex.	**Mean**	**36.33**	**14.69**	**3021.29**
	Max.	172.39	72.34	7085.76
	Min.	.00	2.67	56.70
	S.D.	48.16	20.76	2627.45
Red.	**Mean**	**84.72**	**41.79**	**3107.37**
	Max.	621.58	74.85	8336.38
	Min.	.00	22.41	299.88
	S.D.	150.44	17.94	3056.60
Oxid.	**Mean**	**316.10**	**27.98**	**865.55**
	Max.	2493.08	59.48	1609.75
	Min.	.00	9.42	164.99
	S.D.	501.52	16.74	408.27
Resid.	**Mean**	**30.69**	**17.06**	**1125.13**
	Max.	160.50	28.11	2772.17
	Min.	.00	8.47	303.30
	S.D.	35.86	6.83	627.79
Total	**Mean**	**503.55**	**122.52**	**8785.12**
	Max.	2700.05	215.88	19313.30
	Min.	52.88	73.28	2455.87
	S.D.	617.29	39.79	5953.57

Fig. 6.22a and b Zn extracted from TMF, Control and Silvermines sediments in 2000.

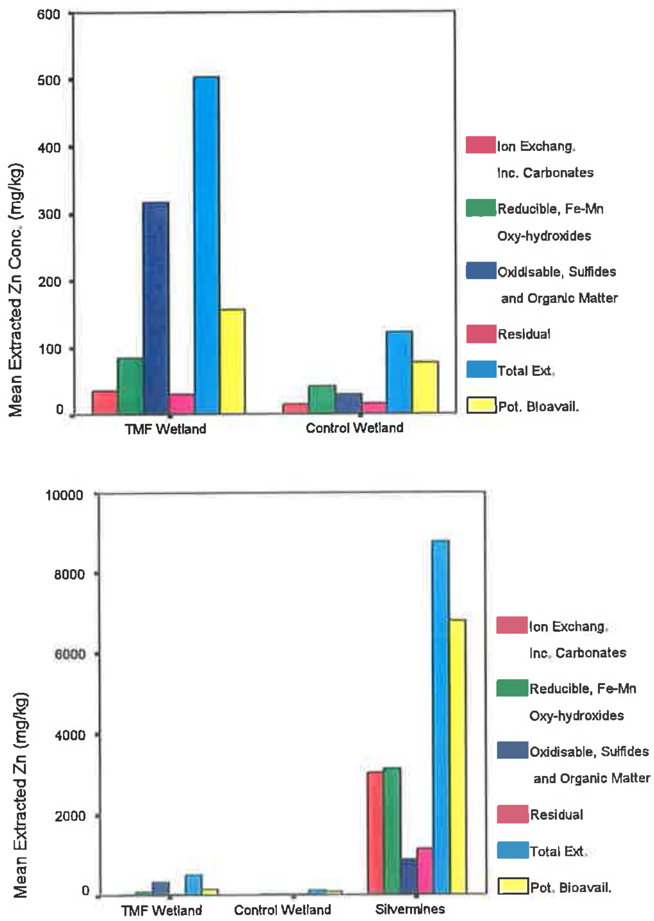
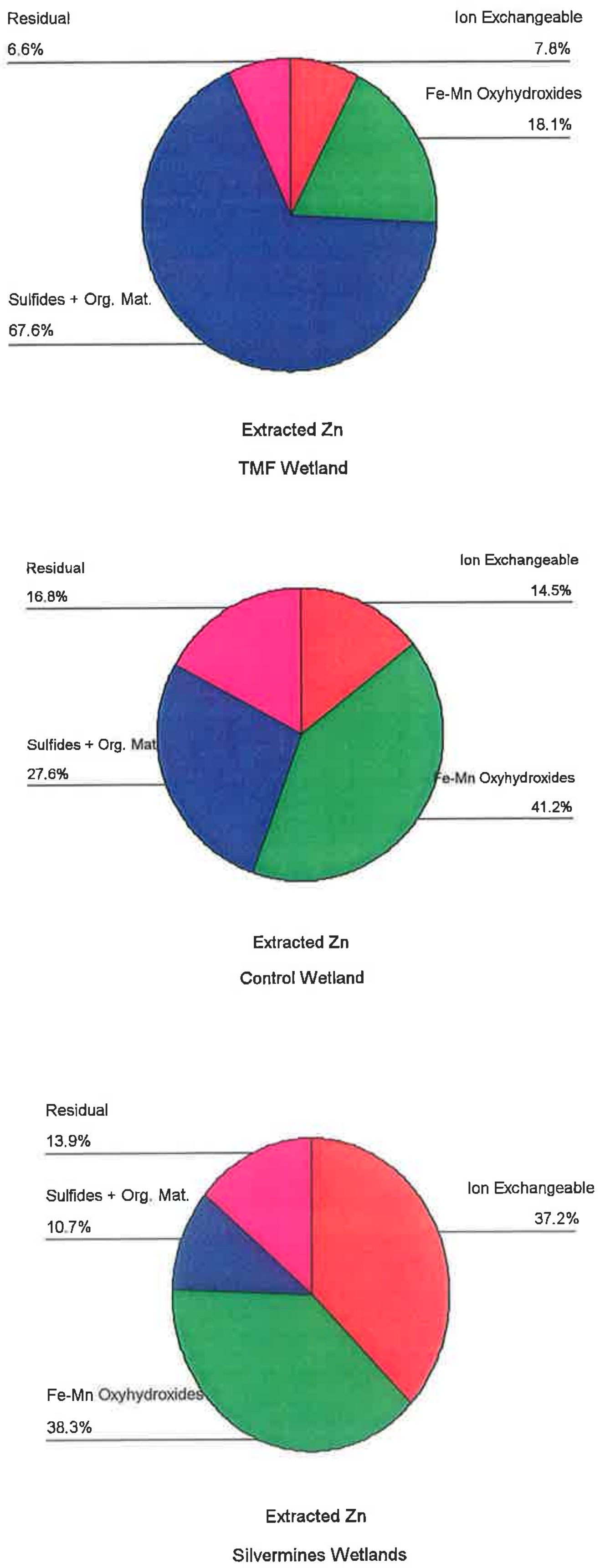


Fig. 6.23 (%) Zn ext. in different species in TMF, Control and Silvermines wetlands, 2000



Zn extracted from Silvermines sediments in all fractions are higher than in the TMF and Control wetlands. These values, particularly for ion-exchangeable and reducible Zn (3,021 mg/kg and 3,107 mg/kg) are closer to the range reported for soils contaminated with metals from mining.

Figure 6.22a and b illustrate the differences in Zn extracted from the TMF, Control and Silvermines wetlands. From Figure 6.22a it is obvious that mean total Zn concentration is higher in the TMF wetland than in the Control, but the mean potentially bioavailable fraction is much closer between both systems. Again, this is due to the high concentration of Zn extracted in the oxidisable fraction of the TMF wetland. Figure 6.22b shows mean total and potentially bioavailable Zn are substantially higher in Silvermines wetland.

Figure 6.23 illustrates the % of Zn extracted in each of the four fractions for the three wetlands and shows that Zn is substantially enriched in the oxidisable fraction of the TMF wetland (67.6%). The high organic content of the peat substrate in the TMF system is likely to have influenced this speciation. Additionally, an examination of Figure 6.15 shows a similar pattern of enrichment for Zn in the oxidisable fraction for FeS and PbS. The enrichment of Zn in the oxidisable fraction of the TMF wetland also could be due to the presence of sulphides in the sediments of these system.

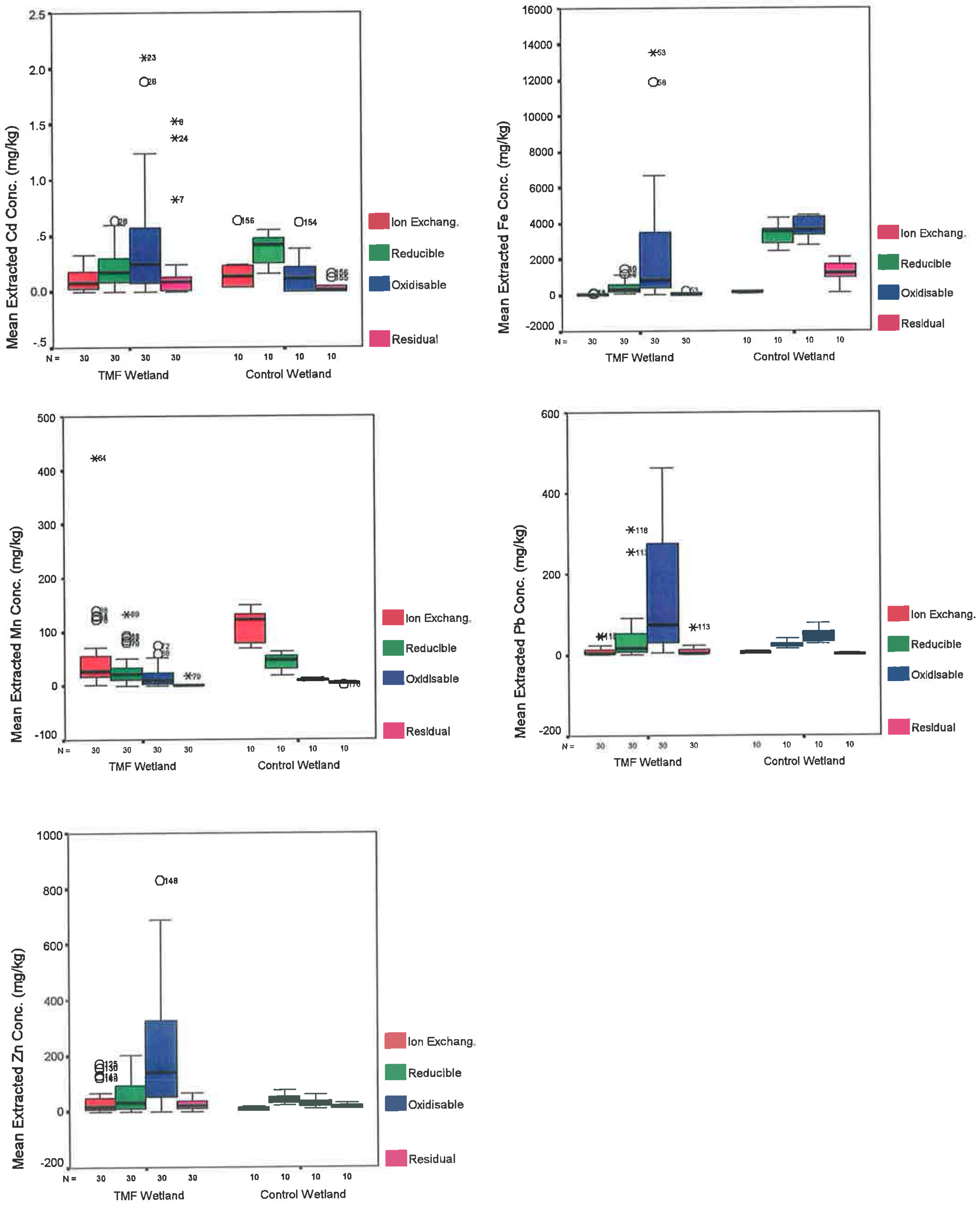
Figure 6.23 indicates that Zn is predominantly enriched in the reducible fraction of the Control (41.2%) and in the ion-exchangeable (37.2%) and reducible fractions (38.3%) of Silvermines wetlands.

6.1.5.6 ANOVA to Compare Metal Extractions in Wetland Sediments, 2000

A one-way ANOVA was conducted to compare mean metal concentrations in each of the four fractions extracted from the sediments of the TMF and Control wetlands in summer, 2000. Each variable was tested for normality and homogeneity of variance prior to ANOVA analysis and log transformed when they did not exhibit normality.

Boxplots comparing the median, interquartile range, outliers and extreme values for each metal extraction in both wetlands are presented in Figure 6.24. These boxplots

Fig. 6.24 Boxplots of Cd, Fe, Mn, Pb and Zn extractions in sediments of TMF and Control wetlands, 2000. (Outliers are desinated with O and extreme values with *. Numbers indicate position in data set.)



illustrate the overlap in confidence intervals between wetlands. F values and observed significance levels for each metal extraction are outlined below.

	Cd		Fe		Mn		Pb		Zn	
	F	p	F	p	F	p	F	p	F	p
Ion Exch.	0.007	0.936	28.176	0	11.82	0.001	0.108	0.745	1.452	0.236
Reducible	7.269	0.011	80.046	0	3.578	0.067	0.251	0.619	0.033	0.858
Oxidisable	0.499	0.485	8.872	0.005	0.127	0.723	2.066	0.159	23.208	0
Residual	1.252	0.273	85.341	0	41.387	0	6.101	0.018	0.108	0.744

The results of the ANOVA analysis indicate no significant difference in mean Cd extracted from TMF and Control sediments in the ion-exchangeable, oxidisable and residual fractions. There was a significant difference between wetlands in the reducible fraction ($p<0.05$) where mean Cd concentrations are higher in the Control.

There were significant differences in mean Fe extracted from all four fractions between both wetlands ($p<0.05$) due to higher Fe concentrations in the Control. Similarly, there are significant differences between wetlands in the reducible and residual fractions for Mn but concentrations are higher in the Control. Differences in the ion-exchangeable and oxidisable fraction are insignificant at the 0.05 level.

The analysis indicates no significant difference between wetlands in mean Pb extracted from the ion-exchangeable, reducible and oxidisable fractions. There is a significant difference ($p<0.05$) in the residual fraction with concentrations higher in the TMF wetland (8.704 mg/kg). However, this value is very low in comparison to residual Pb levels in uncontaminated sediments (see Table 6.9).

There was no significant difference in mean Zn extracted from both wetlands in the ion-exchangeable, reducible and residual fractions. There was a significant difference in the oxidisable fraction ($p<0.001$) where mean Zn concentrations are higher in the TMF wetland (316 mg/kg). This is within the range reported for contaminated soils but at the lower end of this range and is likely affected by outlier data (see boxplot for Zn extractions in Figure 6.24).

6.1.5.7 Metal Extractions from Silvermines Tailings, Peat and Sediment Standard

Table 6.14 outlines descriptive statistics for mean Cd concentrations in the four fractions extracted from Silvermines tailings, the peat substrate prior to its use in the TMF wetland, and the standard reference sediment (SRM 1944). The concentration of Cd extracted from Silvermines tailings are substantially elevated in all fractions with the highest value occurring in the ion-exchangeable fraction (16.28 mg/kg). These concentrations are similar to ranges reported for soils contaminated with metals from mining operations (Table 6.9). Concentrations of Cd in all of the extractions in the peat sample are low and well within values for uncontaminated sediments and soils. Cd extractions from the sediment standard elevated in the ion-exchangeable fraction (4.72 mg/kg) indicating contamination in this sediment.

Figure 6.25 illustrates the % of Cd extracted in each of the four fractions for the three samples. Cd is enriched in the ion-exchangeable fraction in the tailings (68.6%) and sediment standard (84.1%). The quantities of Cd extracted from the peat are very low with no obviously enriched fraction.

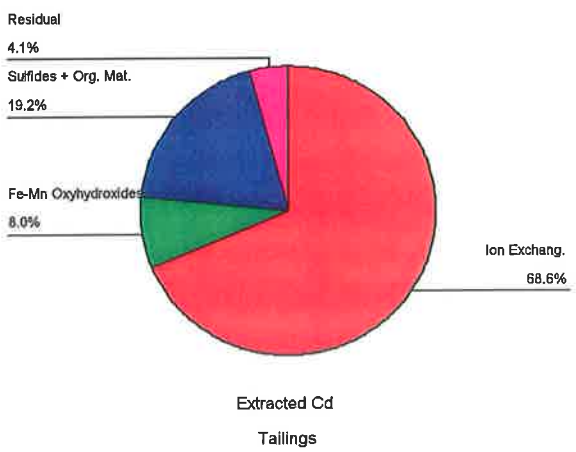
Table 6.15 outlines descriptive statistics for mean Fe concentrations in the four fractions extracted from the three samples. The concentration of Fe extracted from Silvermines tailings are substantially elevated with the highest value occurring in the oxidisable fraction (57,938 mg/kg). In comparison, concentrations of Fe in all of the extractions in the peat sample are low and well within values for uncontaminated sediments. Fe extractions from the sediment standard are also within reported ranges for uncontaminated sediment. Figure 6.26 illustrates the % of Fe extracted in each of the four fractions for the three samples. Fe is enriched in the oxidisable fraction of the tailings (76.2%), whereas the peat (though values are very low) and sediment standard are enriched in the residual fraction (40.9% and 64.4% respectively).

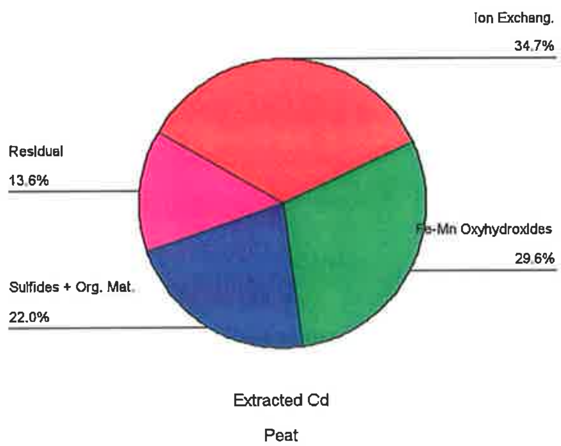
Table 6.16 outlines descriptive statistics for mean Mn concentrations in the four fractions extracted from the three samples. The concentration of Mn extracted from the tailings are again substantially elevated in comparison to the peat and sediment standard with the highest value occurring in the ion-exchangeable fraction (605.65

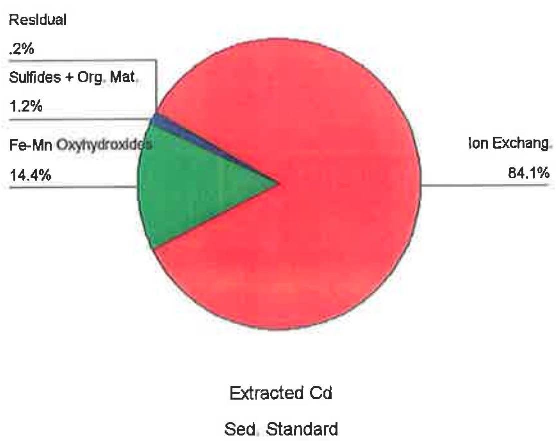
Tables 6.14 Descriptive statistics for Cd extractions from tailings, peat and sediment standard.

Cd (mg/kg)		Soil Sample		
		Tailings	Peat	Sed Standard
Ion Exchg.	**Mean**	**16.284**	**.160**	**4.720**
	Minimum	15.306	.123	4.459
	Maximum	17.261	.196	4.980
	Std Dev.	1.382	.052	.368
Reducible	**Mean**	**1.900**	**.136**	**.810**
	Minimum	1.707	.044	.664
	Maximum	2.092	.228	.956
	Std Dev.	.272	.130	.206
Oxidisable	**Mean**	**4.566**	**.101**	**.070**
	Minimum	4.093	.000	.014
	Maximum	5.038	.202	.126
	Std Dev.	.668	.143	.079
Residual	**Mean**	**.979**	**.063**	**.010**
	Minimum	.577	.035	.000
	Maximum	1.382	.090	.020
	Std Dev.	.569	.039	.014
Total Ext.	**Mean**	**24.755**	**.534**	**5.885**
	Minimum	24.686	.468	5.816
	Maximum	24.824	.599	5.953
	Std Dev.	.098	.093	.097

Fig. 6.25 (%) Cd ext. in different species in Silvermines tailings, peat, and sediment standard.



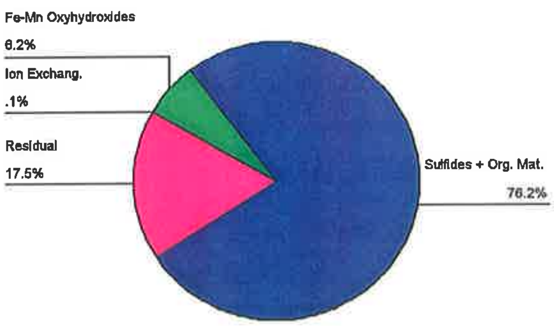




Tables 6.15 Descriptive statistics for Fe extractions from tailings, peat and sediment standard.

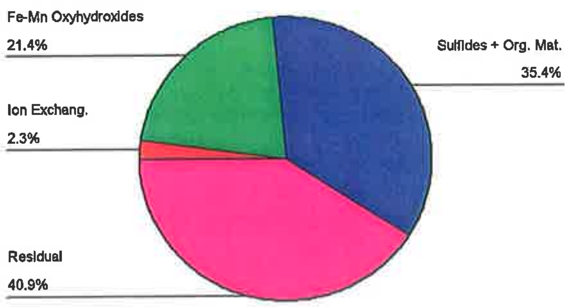
Fe (mg/kg)		**Soil Sample**		
		Tailings	Peat	Sed Standard
Ion Exchg.	**Mean**	**82.532**	**12.237**	**309.270**
	Minimum	71.816	10.389	97.270
	Maximum	93.247	14.085	521.271
	Std Dev.	15.154	2.613	299.814
Reducible	**Mean**	**4702.724**	**114.471**	**6038.876**
	Minimum	4348.086	94.496	5671.033
	Maximum	5057.362	134.447	6406.719
	Std Dev.	501.534	28.250	520.209
Oxidisable	**Mean**	**57938.001**	**189.722**	**5596.247**
	Minimum	44475.724	173.590	4362.524
	Maximum	71400.278	205.854	6829.969
	Std Dev.	19038.535	22.814	1744.747
Residual	**Mean**	**13267.397**	**219.135**	**21564.789**
	Minimum	12411.621	178.106	7571.834
	Maximum	14123.173	260.164	35557.744
	Std Dev.	1210.250	58.024	19789.027
Total Ext.	**Mean**	**76157.771**	**578.699**	**33701.336**
	Minimum	63207.741	565.617	20794.206
	Maximum	89107.800	591.780	46608.466
	Std Dev.	18314.107	18.500	18253.438

Fig. 6.26 (%) Fe ext. in different species in Silvermines tailings, peat, and sediment standard.



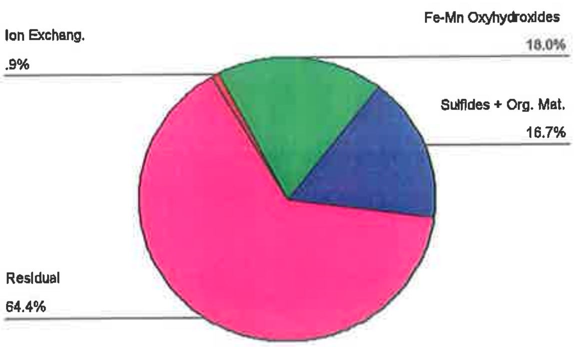
Extracted Fe

Tailings



Extracted Fe

Peat



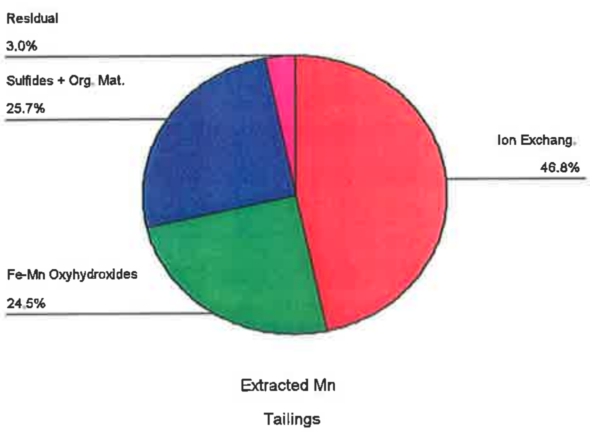
Extracted Fe

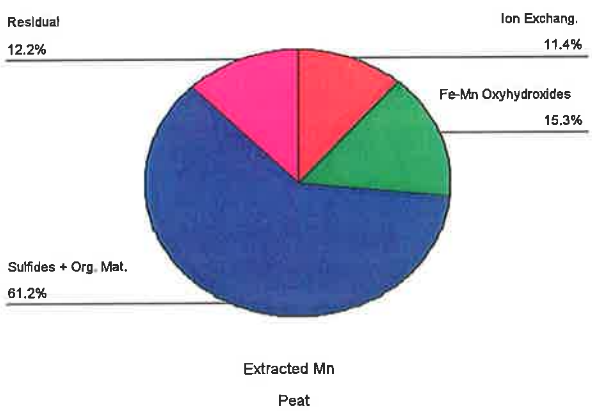
Sed. Standard

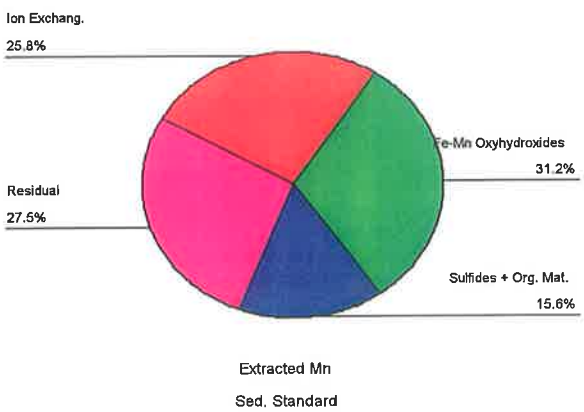
Tables 6.16 Descriptive statistics for Mn extractions from tailings, peat and sediment standard.

Mn (mg/kg)		Soil Sample		
		Tailings	Peat	Sed Standard
Ion Exchg.	**Mean**	**605.646**	**4.225**	**36.123**
	Minimum	594.331	3.636	31.477
	Maximum	616.960	4.814	40.769
	Std Dev.	16.001	.833	6.570
Reducible	**Mean**	**316.884**	**5.664**	**43.656**
	Minimum	264.386	4.775	37.196
	Maximum	369.381	6.553	50.115
	Std Dev.	74.243	1.257	9.135
Oxidisable	**Mean**	**332.930**	**22.705**	**21.796**
	Minimum	246.375	2.307	20.088
	Maximum	419.485	43.102	23.503
	Std Dev.	122.407	28.846	2.415
Residual	**Mean**	**39.100**	**4.513**	**38.446**
	Minimum	25.709	3.382	34.897
	Maximum	52.490	5.644	41.995
	Std Dev.	18.937	1.599	5.019
Total Ext.	**Mean**	**1332.195**	**38.733**	**150.561**
	Minimum	1167.777	20.602	141.989
	Maximum	1496.612	56.863	159.133
	Std Dev.	232.521	25.640	12.123

Fig. 6.27 (%) Mn ext. in different species in Silvermines tailings, peat, and sediment standard.







mg/kg). Concentrations of Mn in all of the extractions in the peat sample are very low. Figure 6.27 illustrates the % of Mn extracted in each of the four fractions for the three samples. Mn is enriched in the ion-exchangeable fraction of the tailings (46.8%) and the oxidisable fraction of the peat (61.2%, though concentrations are very low). The sediment standard has no obviously enriched fraction.

Table 6.17 outlines descriptive statistics for mean Pb concentrations in the four fractions extracted from each samples. The concentrations of Pb extracted from Silvermines tailings are substantially elevated in all fractions with the highest value occurring in the oxidisable fraction (1,770 mg/kg). These concentrations are similar to ranges reported for soils contaminated with metals from mining operations (see Table 6.9). Concentrations of Pb in all of the extractions in the peat sample are low and well within values for uncontaminated sediments and soils. Pb extractions from the sediment standard are elevated in the reducible fraction (174.24 mg/kg).

Figure 6.28 illustrates the % of Pb extracted in each of the four fractions for the three samples. High levels of Pb were extracted from all fractions of the tailings with enrichment occurring in the oxidisable fraction (34%). Although the quantities of Pb extracted from the peat are very low, there is an obvious enrichment in the oxidisable fraction (68.7%). Pb is substantially enriched in the reducible fraction of the sediment standard (80.7%).

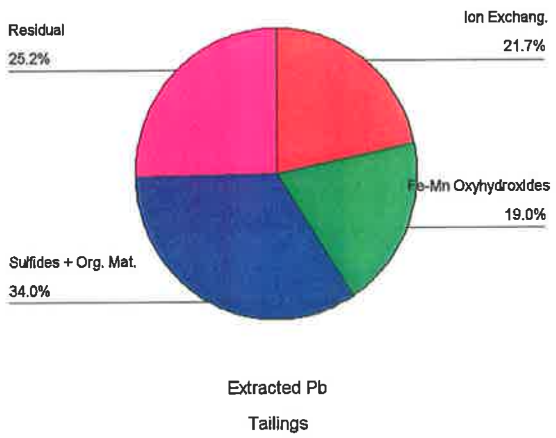
Table 6.18 outlines descriptive statistics for mean Zn concentrations in the four fractions extracted from each samples. Again, the concentrations of Zn extracted from Silvermines tailings are substantially elevated in all fractions with the highest value occurring in the ion-exchangeable fraction (11,044 mg/kg). These concentrations are similar to ranges reported for soils contaminated with metals from mining operations (see Table 6.9). Concentrations of Zn in all of the extractions in the peat sample are low and well within values for uncontaminated sediments and soils. Zn extractions from the sediment standard also are elevated in the ion-exchangeable fraction (388 mg/kg).

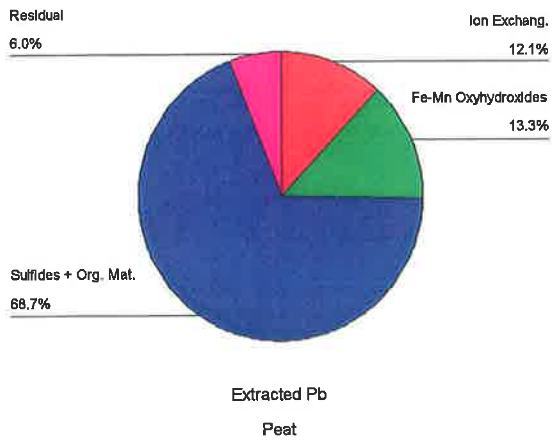
Figure 6.29 illustrates the % of Zn extracted in each of the four fractions for the three samples. High levels of Zn were extracted from all fractions of the tailings with

Tables 6.17 Descriptive statistics for Pb extractions from tailings, peat and sediment standard.

Pb (mg/kg)		Tailings	**Soil Sample** Peat	Sed Standard
Ion Exchg.	**Mean**	**1130.450**	**5.748**	**18.028**
	Minimum	996.758	2.745	16.977
	Maximum	1264.142	8.750	19.078
	Std Dev.	189.069	4.246	1.486
Reducible	**Mean**	**987.288**	**6.327**	**174.243**
	Minimum	912.019	2.984	171.263
	Maximum	1062.556	9.669	177.222
	Std Dev.	106.446	4.727	4.214
Oxidisable	**Mean**	**1769.756**	**32.668**	**17.906**
	Minimum	1712.372	5.244	9.449
	Maximum	1827.140	60.092	26.362
	Std Dev.	81.153	38.783	11.959
Residual	**Mean**	**1311.123**	**2.837**	**5.659**
	Minimum	1045.549	.799	2.750
	Maximum	1576.697	4.874	8.568
	Std Dev.	375.578	2.881	4.114
Total Ext.	**Mean**	**5668.580**	**51.321**	**218.638**
	Minimum	5316.353	30.220	205.708
	Maximum	6020.807	72.422	231.567
	Std Dev.	498.124	29.841	18.285

Fig. 6.28 (%) Pb ext. in different species in Silvermines tailings, peat, and sediment standard.





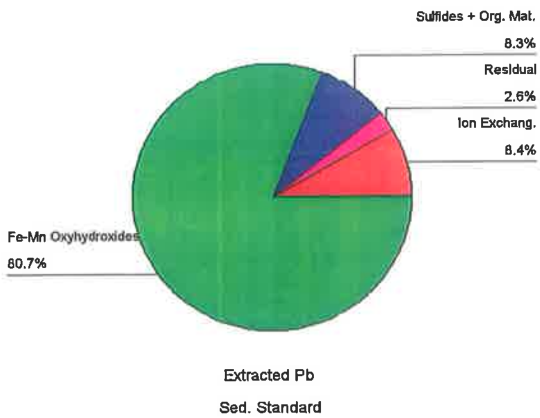
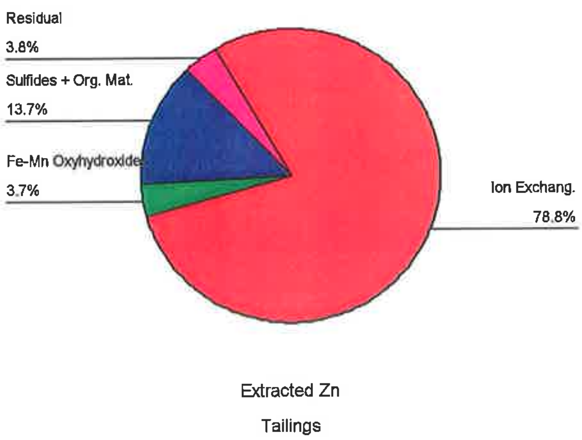
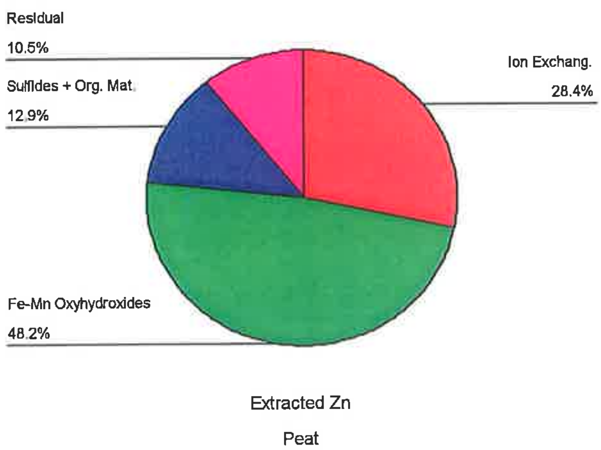


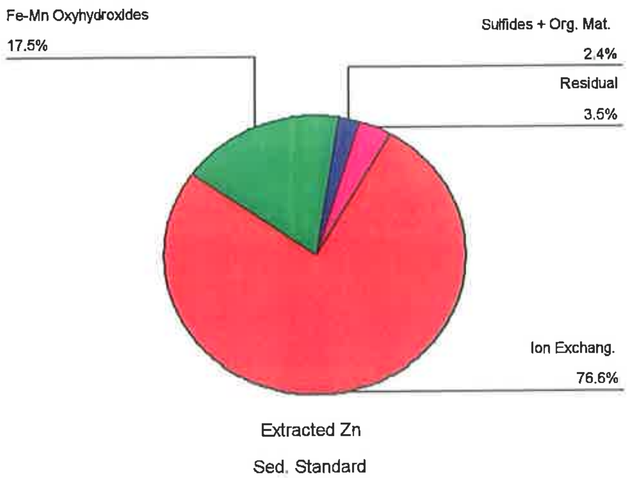
Table 6.18 Descriptive statistics for Zn extractions from tailings, peat and sediment standard.

Zn (mg/kg)		Soil Sample Tailings	Peat	Sed Stan.
Ion Exchg.	**Mean**	**11043.642**	**57.463**	**387.981**
	Minimum	3991.689	22.575	378.161
	Maximum	18095.594	92.351	397.800
	Std Dev.	9972.967	49.339	13.887
Reducible	**Mean**	**513.249**	**97.699**	**88.432**
	Minimum	482.427	26.890	73.953
	Maximum	544.070	168.507	102.910
	Std Dev.	43.588	100.138	20.476
Oxidisable	**Mean**	**1924.434**	**26.209**	**12.356**
	Minimum	1436.758	13.355	6.439
	Maximum	2412.109	39.063	18.272
	Std Dev.	689.677	18.178	8.367
Residual	**Mean**	**531.055**	**21.202**	**17.892**
	Minimum	439.682	6.493	17.635
	Maximum	622.428	35.910	18.148
	Std Dev.	129.221	20.801	.363
Total Ext.	**Mean**	**14365.314**	**257.102**	**530.396**
	Minimum	8094.259	97.882	522.276
	Maximum	20636.368	416.321	538.516
	Std Dev.	8868.610	225.170	11.483

Fig. 6.29 (%) Zn ext. in different species in Silvermines tailings, peat, and sediment standard.







substantial enrichment occurring in the ion-exchangeable fraction (78.8%). Although the quantities of Zn extracted from the peat are low, there is an enrichment in the reducible fraction (48.2%). Zn is substantially enriched in the ion-exchangeable fraction of the sediment standard (76.6%).

6.1.5.8 Kruskal-Wallis Test to Compare Metal Extractions from Silvermines Tailings and Wetland Sediments

The Kruskal-Wallis test, a nonparametric alternative to the one-way ANOVA, was conducted to compare mean metal concentrations in each of the four fractions extracted from Silvermines tailings and sediments from the TMF and Silvermines wetlands.

Chi-square values (H) and observed significance levels for comparisons in metal extractions between tailings and TMF wetland sediments are as follows:

	Cd		**Fe**		**Mn**		**Pb**		**Zn**	
	H	Sig.	H	Sig.	H	Sig.	H	Sig.	H	Sig.
Ion Exch.	5.514	0.019	2.188	0.139	5.455	0.020	5.455	0.020	5.456	0.020
Reduc.	5.494	0.019	5.455	0.020	5.456	0.020	5.455	0.020	4.100	0.043
Oxid.	5.466	0.019	5.455	0.020	5.455	0.020	5.455	0.020	4.752	0.029
Residual	4.148	0.042	5.455	0.020	5.457	0.019	5.455	0.020	5.455	0.020

The results of the Kruskal-Wallis test indicate a significant difference in mean Cd, Mn, Pb and Zn extracted from the tailings and TMF sediments in all four fractions. This is because the concentrations extracted from the tailings are substantially elevated in comparison to the TMF wetland. There also was a significant difference in Fe extracted in the reducible, oxidisable and residual fractions due to elevated concentrations in the tailings; however, there was no significant difference in Fe extracted in the ion-exchangeable fraction at the 0.05 level. This is because the Fe extracted from the tailings in this fraction was very low.

Chi-square values and observed significance levels for comparisons in metal extractions between the tailings and Silvermines wetland sediments are as follows:

	Cd		**Fe**		**Mn**		**Pb**		**Zn**	
	H	Sig.	H	Sig.	H	Sig.	H	Sig.	H	Sig.
Ion Exch.	4.941	0.026	4.941	0.026	0.260	0.610	3.630	0.057	2.042	0.153
Reduc.	0.908	0.341	4.941	0.026	0.721	0.396	0.630	0.427	1.235	0.266
Oxid.	3.050	0.081	0.227	0.634	0.115	0.734	4.941	0.026	3.630	0.057
Residua	0.101	0.751	4.941	0.026	1.846	0.174	4.941	0.026	1.613	0.204

Overall, the results of the Kruskal-Wallis test indicate a much higher degree of similarity between the tailings and the sediments from Silvermines wetland than between the tailings and the TMF wetland sediments. There was no significant difference in Cd extracted in the reducible, oxidisable and residual fractions at the 0.05 level; however, there was a significant difference in the ion-exchangeable fraction due to elevated concentrations in the tailings. With the exception of the oxidisable fraction, there was a significant difference in Fe extracted in all fractions due to higher levels in Silvermines wetland. Test results indicate no significant difference between tailings and Silvermines wetland in Mn extracted from all four fractions. There was no significant difference between the tailings and Silvermines wetland in Pb extracted from the ion-exchangeable and reducible fractions but significant differences exist for the oxidisable and residual fractions due to substantially elevated Pb levels in the tailings. Finally, there is no significant difference between tailings and Silvermines wetland in Zn extracted from all four fractions.

6.1.6 Estimated Free-Metal Ion Concentrations in Porewater of TMF, Control and Silvermines Wetland Sediments, 2000

As outlined in Section 2.5.3, a convincing body of evidence has been developed to support the proposition that the biological response elicited by a dissolved metal is usually a function of the free-metal ion concentration (Campbell, 1995). The free-metal ion concentration $[M^{z+}]$ is the concentration of metal in the solid sediment phases in equilibrium with the porewater and can be determined by the use of sediment extractions and geochemical models.

Tessier (1992) and Tessier *et al.* (1993) have developed geochemical regression models based on data obtained from Canadian lakes for determining free-metal ion concentrations to estimate dissolved $[Cd^{2+}]$, $[Pb^{2+}]$, and $[Zn^{2+}]$ at the root-sediment interface. These are as follows:

$$[Cd^{2+}](mol.L^{-1}) = \frac{\{Cd\}_T[H^+]^{1.79}}{10^{-1.30}\{Fe(F2)\}[H^+]^{0.97} + 10^{-2.45}\{OM\}[H^+]^{0.82}}$$

(Tessier *et al.*, 1993)

$$[Pb^{2+}](mol.L^{-1}) = \frac{\{Pb(S2)\}[H^+]^{0.81}}{10^{0.67}\{Fe(F2)\}}$$

(Tessier, 1992)

$$[Zn^{2+}](mol.L^{-1}) = \frac{\{Zn(S2)\}[H^+]^{1.21}}{10^{-2.83}\{Fe(F2)\}}$$

(Tessier, 1992)

Where $\{Cd\}_T$ is the sum of the Cd concentrations (mol/g) in the four fractions extracted from the sediment, $\{Fe(F2)\}$ is the Fe concentration (mol/g) in the reducible fraction extracted from the sediment, $[H^+]$ refers to sediment pH, $\{OM\}$ is the sediment organic C (mol/g), and $\{Pb(S2)\}$ or $\{Zn(S2)\}$ is the sum of the metal concentrations (mol/g) as found in the first two fractions extracted from the sediment (also termed the potentially bioavailable fraction).

While the equation used to estimate $[Cd^{2+}]$ has been refined and tested over a wide geographical area (Tessier et al., 1993), the geochemical models used to calculate $[Pb^{2+}]$ and $[Zn^{2+}]$ are less well tested (Tessier, 1992). Even though these models were developed for Canadian lakes, they were applied to specific metal and physico-chemical data from the pilot plant and from Silvermines wetland to obtain estimates of the bioavailable concentrations of free-metal ions in these systems.

In the absence of data for organic C, sediment organic content (mol/g) was used in the estimation of [Cd^{2+}] for the TMF and Control wetlands. Jackson *et al.* (1993) used sediment organic content in an investigation of the bioavailability of metals to rooted aquatic macrophytes. In the absence of data on sediment organic content for Silvermines, the readily extractable Cd concentrations in the sediments {Cd(S2)} were normalised with respect to the iron oxyhydroxide content {Fe(F2)} as a surrogate measure for the free-metal ion concentration.

In the case of Mn, the readily extractable Mn concentrations in the sediments were also normalised with respect to the iron oxyhydroxide content as a surrogate measure for the free-metal ion concentration.

Table 6.19 outlines mean values for potentially bioavailable metals, iron-oxyhydroxide concentrations and free-metal ion concentrations for each metal in the TMF, Control and Silvermines wetlands. The complete list of values for these metal species in addition to total metals and water concentrations in all three wetlands are outlined in Appendix E.

From Table 6.19 it is clear that mean potentially bioavailable metals are similar in the TMF and Control wetlands for all metals with Fe and Mn values slightly higher in the Control, and Pb and Zn values slightly higher in the TMF wetland. Interestingly, potentially available Cd and Zn in the TMF and Control wetlands are the same order of magnitude as concentrations reported by St-Cyr and Campbell (2000) for these species of metals in sediments from the St. Lawrence River in Canada (5.055 to 5.481E-09 mol/g for Cd and 1.16 to 1.62E-06 mol/g for Zn). Values for bioavailable Pb in both the TMF (3.36E-07 mol/g) and Control (1.72E-07 mol/g) wetland are higher than reported by St-Cyr and Campbell (6.59E-08 mol/g). Table 6.20 outlines this data and concentrations for Fe-oxyhydroxide and free-metal ions from the literature.

In comparison to the TMF and Control wetlands, potentially bioavailable metals are substantially elevated in silvermines wetlands. This is also the case for iron oxy-hydroxide concentrations in Silvermines sediments. The Control has higher iron oxy-

Table 6.19 Potentially Bioavailable Metals, Iron-oxyhydroxide, and Free-metal Ion Concentrations in sediments from TMF, Control and Silvermines wetlands, 2000.

Potentially Bioavailable Metal (mol/g) {M(S2)}					
Wetland	**Cd**	**Fe**	**Mn**	**Pb**	**Zn**
TMF	4.14E-09	1.16E-05	1.93E-06	3.36E-07	2.4E-06
Control	5.68E-09	6.51E-05	3.02E-06	1.72E-07	1.19E-06
Silvermines	1.61E-07	2.50E-03	4.08E-04	1.23E-05	1.04E-04
Iron Oxy-Hydroxide (mol/g) {Fe(E2)}					
		Fe			
TMF		8.62E-06			
Control		6.51E-05			
Silvermines		2.31E-03			
Free-Metal Ion Concentration (mol/L) $[M^{Z+}]$					
	$[Cd^{2+}]$		**$[Mn^{+}]$**	**$[Pb^{2+}]$**	**$[Zn^{2+}]$**
TMF	5.06E-12		2.24E-01	2.59E-08	1.21E-06
Control	1.21E-10		4.61E-02	7.28E-09	5.77E-07
Silvermines	1.13E-04		1.77E-01	1.93E-08	6.66E-07

Table 6.20 Potentially–bioavailable metals, Fe-oxyhydroxide concentrations, and free-metal ion concentrations of sediments from the literature.				
	Total	Potentially Bio-available Metals	Free-Metal Ion concentration	Fe-Oxyhydroxide
	µg/g	mol/g	mol/l	µg/g
St. Lawrence River, Canada (St. Cyr & Campbell, 2000)				
→ Cd				
1990	0.23 → 3.15	$5.055 \times 10^{-9} \rightarrow 5.481 \times 10^{-9}$	$3.22 \times 10^{-11} \rightarrow 3.96 \times 10^{-10}$	2,513 → 11,170
1991	0.22 → 1.38		$3.26 \times 10^{-11} \rightarrow 1.28 \times 10^{-9}$	1,731 → 14,521
→ Pb				
1990	17.6 → 56.2	6.59×10^{-8}	$6.86 \times 10^{-11} \rightarrow 6.91 \times 10^{-10}$	-
→ Zn				
1990	70.9 → 362	$1.16 \times 10^{-6} \rightarrow 1.62 \times 10^{-6}$	$8.69 \times 10^{-9} \rightarrow 8.43 \times 10^{-8}$	-
1991	59.2 → 552		$6.86 \times 10^{-9} \rightarrow 4.29 \times 10^{-7}$	-
49 littoral sites and 38 lakes in Quebec, Canada (Tessier et al., 1993)				
→ Cd				
Subject to AMD	0.150 → 12.14		$2.85 \times 10^{-10} \rightarrow 1.41 \times 10^{-8}$	4,915 → 38,146
Control	0.214 → 1.011		$4.1 \times 10^{-11} \rightarrow 1.10 \times 10^{-9}$	1,385 → 26,919 (179,390)*

** Single extreme value for control sediments* hydroxide concentrations (6.51E-05 mol/g) than the TMF wetland (8.62E-06 mol/g) but substantially less than Silvermines (2.31E-03 mol/g). Values of 2.48E-05 to 4.82E-04 mol/g (with an extreme value of 3.2E-03 mol/g) have been reported for uncontaminated sediments in Canada (see Table 6.20).

Calculated free-metal ion concentrations for Cd in the TMF and Control wetlands are lower or within ranges cited for $[Cd^{2+}]$ in uncontaminated sediments in Canada (3.26E-11 to 1.28E-09 mol/L) (see Table 6.20). Values for $[Cd^{2+}]$ in Silvermines wetland are much higher. Boxplots comparing free-metal ion concentrations for Cd, Mn, Pb and Zn and Fe-oxyhydroxide concentrations in the wetlands are illustrated in Figure 6.30 ($[Cd^{2+}]$ and Fe-oxyhydroxide concentrations for Silvermines are not included because they are too elevated). Figure 6.31 illustrates differences in free-metal ion and Fe-oxyhydroxide concentrations between the TMF and Control wetlands three-dimensionally. From these figures it is obvious that $[Cd^{2+}]$ and Fe-oxyhydroxide concentrations are higher in the Control.

Calculated free-metal ion concentrations for Mn in the TMF and Silvermines wetlands are similar with lower concentrations occurring in the Control.

Concentrations of $[Pb^{2+}]$ are relatively close but higher in the TMF than in the Control wetland and both are higher than values outlined in Table 6.20 for Canadian freshwater sediments (6.86E-11 to 6.91E-10 mol/L). The lower value for $[Pb^{2+}]$ in the Control is a result of the higher concentration of Fe-oxyhydroxide in this wetland than in the TMF wetland. Figure 6.30 also indicates the presence of higher values for $[Pb^{2+}]$ in the *Juncus* region of the TMF wetland that may have disproportionately affected the mean.

Concentrations of $[Zn^{2+}]$ are also relatively close but higher in the TMF than in the Control wetland. The concentration in the TMF wetland is higher than the range outlined for Canadian freshwater sediments (6.86E-09 to 4.29E-07 mol/L). The lower value for $[Zn^{2+}]$ in the Control also is a result of the higher concentration of Fe-oxyhydroxide in this wetland than in the TMF wetland. Figure 6.30 indicates the presence of higher values for $[Zn^{2+}]$ in the *Juncus* region of the TMF wetland that may have affected the mean.

Fig. 6.30 Boxplots of Cd, Free-Metal Ion and Iron-Oxyhydroxide concentrations in TMF, Control and Silvermines wetland sediments, 2000. (Note: Values for [Cd2+] and {Fe(E2)} for Silvermines are too high to for inclusion in these charts)

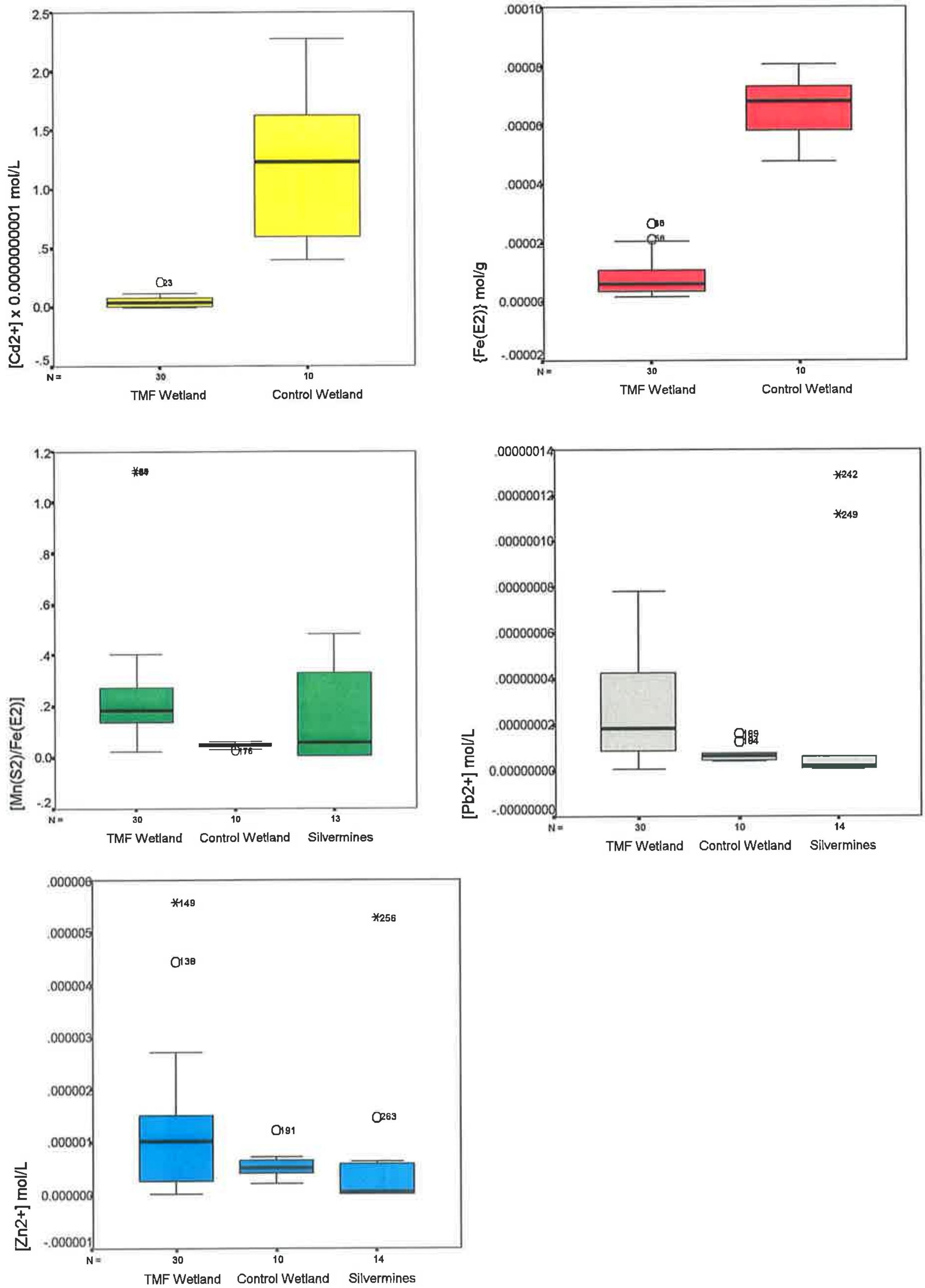
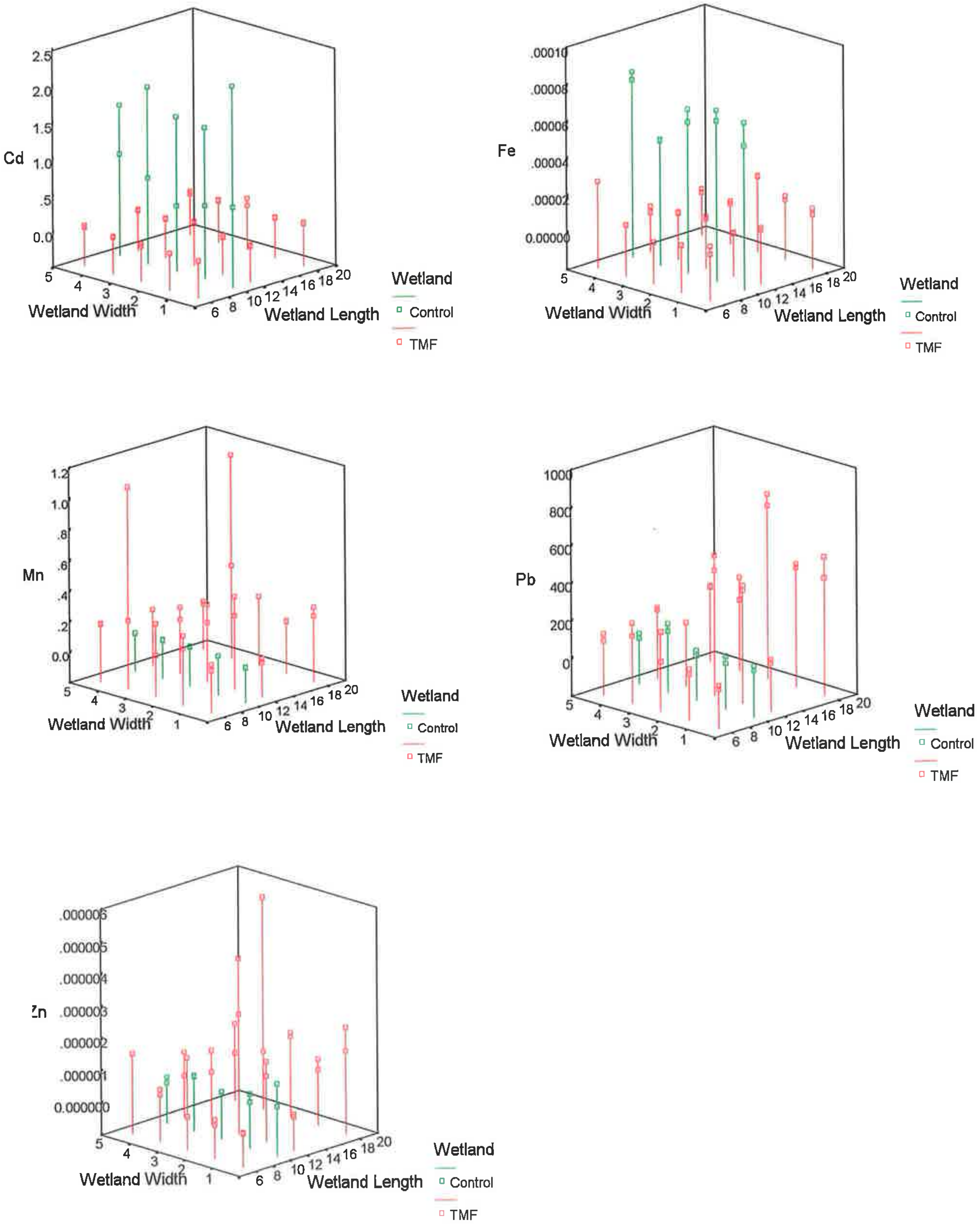


Fig. 6.31 Comparison in free-metal ion and iron oxyhydroxide concs. in TMF and Control wetrlands, 2000.



The influence of the high concentrations of Fe-oxyhydroxide in Silvermines wetland sediments becomes apparent when the calculated values for $[Pb^{2+}]$ and $[Zn^{2+}]$ concentrations are observed from Table 6.19. Even though potentially bioavailable Pb and Zn concentrations were substantially higher in Silvermines wetland, concentrations of $[Pb^{2+}]$ and $[Zn^{2+}]$ are similar to the TMF due to the potential for adsorption and coprecipitation of the metals with the higher concentrations of Fe-oxyhydroxides at Silvermines. It is important to note that typically adsorption of metals increases from near nil to near 100% as pH increases through a critical range 1-2 units wide (see Figure 6.32) and this means that a small shift in pH in surface water causes a sharp increase or decrease in dissolved metal levels (Forstner, 1985). Under normal conditions in surface water (and at the same concentration of adsorbates and adsorbents) Pb is more strongly bound to hydroxidic surfaces than Zn and Cd (Forstner, 1985).

Overall, these results indicate that potentially bioavailable metals are low within the TMF wetland and similar to values cited for natural wetlands. In addition, free-metal ion concentrations are low in this wetland.

6.1.6.1 ANOVA to Compare Free-metal Ion Concentrations in Wetlands

A one-way ANOVA was conducted to compare the means of free-metal ion concentrations in the TMF and Control wetlands. Each variable was tested for normality and homogeneity of variance prior to ANOVA analysis and log transformed when necessary.

F values and observed significance levels for each metal are as follows:

Metal	F	p
Cd	62.354	0
Fe	86.697	0
Mn	32.059	0
Pb	6.748	0.013
Zn	0.072	0.790

The results of the ANOVA analysis indicate a significant difference between the TMF and Control wetlands in the mean free-metal ion concentrations of Cd, Mn, and Pb and in Fe-oxyhydroxide concentrations at the 0.001 significance level. This is due to the higher concentrations of $[Cd^{2+}]$ and Fe-oxyhydroxide in the Control and the higher concentrations of $[Mn^{+}]$ and $[Pb^{2+}]$ in the TMF wetland. The analysis also indicates no significant difference in mean $[Zn^{2+}]$ concentrations between the TMF and Control wetlands.

6.2 SUMMARY

The main findings of the assessment of sediment indicators of ecosystem health and sustainability in the pilot wetlands are as follows:

- Total Cd, Fe, Mn, Pb and Zn concentrations were determined for the sediments in the TMF and Control wetlands during summer, 1999. ANOVA analysis indicates no significant difference in mean total Cd, Mn, Pb and Zn concentrations in the sediments of the TMF and Control wetlands. There was a significant difference in mean total Fe concentration due to higher concentrations in the Control. Overall, the results for mean total metal concentrations in the sediments of the TMF wetland in comparison to the Control in 1999, and in comparison to soils and wetland sediments contaminated by mining activities, indicate no significant adverse mobilisation of metals into the peat substrate from the tailings.

- The same general pattern of metal concentrations occurred between the TMF and Control wetlands in 2000 as in 1999, although mean concentrations were higher in both wetlands in 2000. ANOVA analysis indicated no significant difference in mean total Cd, Pb and Zn concentrations in the sediments of the TMF and Control wetlands. There was a significant difference in mean total Fe and Mn concentrations due to higher concentrations in the Control. Overall, the results for mean total metal concentrations in the sediments of the TMF wetland in comparison to the Control in 2000, indicate no significant adverse mobilisation of metals into the peat substrate from the tailings.

- A comparison between mean total sediment metals in 1999 and 2000 was conducted in order to investigate the potential for metal accumulations in the TMF wetland over time due to metal mobilisation from the tailings. Results show that metal concentrations in the majority of samples taken in 1999 and 2000 are similar for both years and do not indicate significant accumulation of metals in the peat substrate of the TMF wetland due to the presence of tailings.

- Mean total metal concentrations in Silvermines sediments in 2000 for Cd, Fe, Mn, Pb and Zn greatly exceed values for natural wetlands and more closely approximate soils and wetland sediments contaminated with metals from mining. Mean sediment concentrations for all five metals are substantially higher in Silvermines wetland than those measured in the TMF wetland. Sediment metal concentrations in Silvermines wetland were found to be similar to total metals values obtained for Silvermines tailings and for surface samples on the tailings dam at Silvermines.

- A series of four sequential extractions were also carried out on the wetland sediments in 2000 to evaluate metal speciation and potential bioavailability in these systems. The concentrations of Cd, Fe, Mn and Pb extracted in all fractions from the TMF wetland sediments are well within ranges reported for these fractions in uncontaminated sediments. The concentration of Zn extracted from TMF wetland sediments is below that outlined for contaminated soils, with the exception of the oxidisable fraction which is within the range reported for contaminated soils but at the lower end of this range.

- The concentrations of Cd, Fe, Mn, Pb and Zn extracted from Silvermines sediments are much higher than the TMF and Control wetlands, and closer to the range reported for soils and sediments contaminated with metals from mining.

- In the TMF wetland Cd, Fe, Pb and Zn are enriched in the oxidisable fraction which includes that bound to sulfides and organic matter. The majority of Mn was extracted in the ion-exchangeable fraction. The high organic content of the peat substrate is likely to have influenced the enrichment of these metals in the oxidisable fraction. A similar pattern of enrichment for these metals (predominantly associated with sulfides and organic matter) occurs for pyrite (FeS). Therefore, the enrichment of metals in the oxidisable fraction also could be due to the presence of sulphides in the sediments of the TMF wetland.

- In the Control Cd and Fe are predominantly enriched in the reducible fraction which includes that bound to Fe and Mn oxyhydroxides. Pb is enriched in the oxidisable fraction and Mn and Zn in the ion exchangeable and reducible fractions. In Silvermines Cd, Fe, Mn, Pb and Zn are enriched in the reducible fraction.

- ANOVA analysis indicated no significant difference in mean Cd extracted from the TMF and Control sediments in the ion-exchangeable, oxidisable and residual fractions. There were significant differences in mean Fe and Mn extracted from both wetlands due to higher Fe and Mn concentrations in the Control. The analysis indicates no significant difference between wetlands in mean Pb extracted from the ion-exchangeable, reducible and oxidisable fractions. There is a significant difference in the residual fraction with concentrations higher in the TMF wetland. However, this value is very low in comparison to residual Pb levels in contaminated sediments. There was no significant difference in mean Zn extracted from both wetlands in the ion-exchangeable, reducible and residual fractions.

There was a significant difference in the oxidisable fraction because mean Zn concentrations are higher in the TMF wetland. This concentration is within the range reported for contaminated soils but at the lower end of this range and is likely affected by outlier data.

- The results of a Kruskal-Wallis analysis indicate a significant difference for all fractions in mean Cd, Fe (except for ion-exchangeable metals) Mn, Pb and Zn extracted from the TMF sediments and Silvermines tailings because of the higher concentrations in the tailings extractions. Overall, the results of the Kruskal-Wallis test indicate much higher similarity between Silvermines tailings and sediments from Silvermines wetland than between the tailings and the TMF wetland sediments.

- Geochemical regression models were applied to specific metal and physico-chemical data from the pilot plant and from Silvermines wetland to obtain estimates of the bioavailable concentrations of free-metal. Mean potentially bioavailable metals were similar in the TMF and Control wetlands for all metals with Fe and Mn values slightly higher in the Control, and Pb and Zn values slightly higher in the TMF wetland. Potentially bioavailable Cd and Zn in both wetlands were the same order of magnitude as concentrations reported for uncontaminated sediments. Values for bioavailable Pb in both wetlands were slightly higher than reported for Canadian river sediments. In comparison to the TMF and Control wetlands, potentially bioavailable metals are substantially elevated in silvermines wetlands. This is also the case for iron oxy-hydroxide concentrations in Silvermines sediments.

- Calculated free-metal ion concentrations for Cd in the TMF and Control wetlands are lower or within ranges cited for [Cd^{2+}] in uncontaminated sediments in Canada. Concentrations of [Pb^{2+}] are higher in the TMF than in the Control wetland and both are higher than values for Canadian freshwater sediments. Concentrations of [Zn^{2+}] are also higher in the TMF than in the Control wetland. Even though potentially bioavailable Pb and Zn concentrations were substantially higher in Silvermines wetland, calculated values for [Pb^{2+}] and [Zn^{2+}] were similar to the TMF wetland due to the higher concentrations of Fe-oxyhydroxides at Silvermines.

This geochemical analysis of the wetlands sediments forms the basis for the regression analyses conducted in Chapter Eight to investigate whether correlations exist between sediment geochemistry and hydrology, water chemistry and ecological health that affect the potential sustainability of the TMF wetland.

CHAPTER SEVEN

RESULTS
BIOTIC INDICATORS

7.1 RESULTS – BIOTIC INDICATORS

In the pilot system three species of wetland rooted emergents, *Typha latifolia, Phragmites australis* and *Juncus effusus* were monitored for tissue accumulation of metals, to examine the potential phytotoxic impacts of contamination on wetland species. Emergents were selected for analysis because metal accumulation is more influenced by soil type for these plants and the wetland sediments were expected to have higher concentrations of potentially bioavailable metals then the water column.
The quantification of metal content in plants facilitates an investigation of eco-physiological indicators of sub-lethal stress in assessing wetland plant health (McNaughton *et al.*, 1992).

Aims of the biotic analysis were as follows:

- To compare mean metal concentrations of the roots, rhizomes and stems of *Typha latifolia*, *Phragmites australis*, and *Juncus effusus* in the TMF and Control wetlands with values from the literature.

- To compare mean metal concentrations of the roots, rhizomes and stems of *Typha latifolia*, *Phragmites australis*, and *Juncus effusus* in the TMF and Control wetlands using one-way ANOVA.

- To determine if plant tissue (roots, rhizome and stems) is an important factor influencing the extent of metal accumulation in *Typha latifolia*, *Phragmites australis*, and *Juncus effusus* in the TMF wetland.

- To determine if metal accumulations in the roots and stems of *Typha latifolia, Phragmites australis* and *Juncus effusus* in the TMF wetland are influenced by species.

7.2 BIOTIC SAMPLING IN TMF AND CONTROL WETLANDS, SUMMER 1999

During the summer 1999 sampling event, triplicate plant samples were taken in each quadrant of the *Typha*, *Phragmites* and *Juncus* regions of the TMF and Control wetlands. Figures 4.1 and 4.2 illustrate the locations of each quadrat. The species of plant harvested depended on the region being sampled. If three samples were not available (e.g. in the *Juncus* Region) a plant from either of the other two species was harvested. Total metals concentrations for Cd, Fe, Mn, Pb and Zn, were determined for the roots, rhizomes and stems of *Typha latifolia* and *Phragmites australis* and for the roots and stems of *Juncus effusus*.

7.2.1 Total Metal Concentrations in Wetland Species

7.2.1.1 Total Metal Concentrations in Typha latifolia

Descriptive statistics for mean total metals concentrations in the roots, rhizomes and stems of *Typha latifolia* for the TMF and Control wetlands are outlined in Table 7.1. Boxplots illustrating the median, interquartile range (25^{th}–75^{th} percentile), outliers and extreme values for each metal in each plant tissue are presented in Figure 7.1. Metal concentrations in *Typha latifolia, Phragmites australis* and *Juncus effusus* for each quadrat are outlined in Appendix D.

Mean total Cd concentrations are lower in the TMF wetland than in the Control for roots, rhizomes and stems of *Typha latifolia* (1.01 mg/kg, 0.49 mg/kg and 0.51 mg/kg versus 1.57 mg/kg, 0.68 mg/kg and 0.55 mg/kg respectively). As outlined in Table 7.2 these values are similar to Cd concentrations obtained for rhizomes and leaves of *Typha latifolia* (0.5 mg/kg to <2.0 mg/kg) in wetlands receiving drainage from Pb-Zn mining activities in Poland (Wojcik and Wojcik, 2000). However, they are lower than concentrations obtained for *Vallisneria american* a rooted aquatic plant (2.35 mg/kg to 4.3 mg/kg) in the St. Lawrence River in Canada (St. Cyr and Campbell, 2000). Table 7.2 outlines a range of metal concentrations in wetland plants growing in uncontaminated wetlands and wetlands impacted by mine drainage from the literature.

Table 7.1 Descriptive statistics for metal concentrations in root, rhizome and stems of *Typha Latifolia* in TMF and Control wetlands in summer 1999.

Typha Latifolia		TMF Wetland			Control Wetland		
		Root Conc. (mg/kg)	Rhizome Conc. (mg/kg)	Stem Conc. (mg/kg)	Root Conc. (mg/kg)	Rhizome Conc (mg/kg)	Stem Conc. (mg/kg)
Cd	**Mean**	**1.011**	**.491**	**.513**	**1.570**	**.684**	**.553**
	Minimum	.000	.000	.000	.274	.000	.000
	Maximum	4.601	1.573	1.942	10.972	5.316	4.326
	Median	.852	.408	.446	1.082	.363	.409
	Std Dev.	.837	.366	.411	1.943	.996	.744
Fe	**Mean**	**1140.720**	**288.253**	**43.514**	**7082.670**	**1635.367**	**216.705**
	Minimum	203.955	47.104	.000	2137.143	55.863	.000
	Maximum	3106.387	2521.444	122.540	17422.523	5408.652	1084.127
	Median	803.366	138.960	38.814	6221.588	1224.741	126.082
	Std Dev.	824.310	473.538	23.993	3261.497	1342.864	254.325
Mn	**Mean**	**67.062**	**51.372**	**183.390**	**185.067**	**208.816**	**514.393**
	Minimum	2.542	19.850	4.049	51.657	64.793	.000
	Maximum	203.992	163.280	491.878	645.025	1158.988	1397.853
	Median	57.509	42.007	156.140	154.978	164.388	429.264
	Std Dev.	39.451	29.766	94.029	116.799	175.263	287.982
Pb	**Mean**	**51.681**	**11.328**	**2.852**	**36.765**	**9.119**	**3.248**
	Minimum	.000	.000	.000	10.514	.000	.000
	Maximum	157.572	197.187	18.187	90.260	42.376	24.107
	Median	36.875	3.753	.000	31.933	7.871	1.597
	Std Dev.	45.244	33.931	4.448	19.779	7.905	5.427
Zn	**Mean**	**104.121**	**81.002**	**43.279**	**64.366**	**62.998**	**23.291**
	Minimum	14.243	5.149	.000	.517	13.260	.000
	Maximum	314.830	252.643	170.635	164.418	158.554	69.048
	Median	79.507	78.576	33.985	55.716	55.391	21.066
	Std Dev.	78.301	55.343	34.483	37.395	32.643	16.611

Fig. 7.1 Mean metal concentrations in tissues of *Typha L.* in TMF and Control wetlands summer, 1999. (Outliers are designated with O and extreme values with *. Numbers indicate position in data set.)

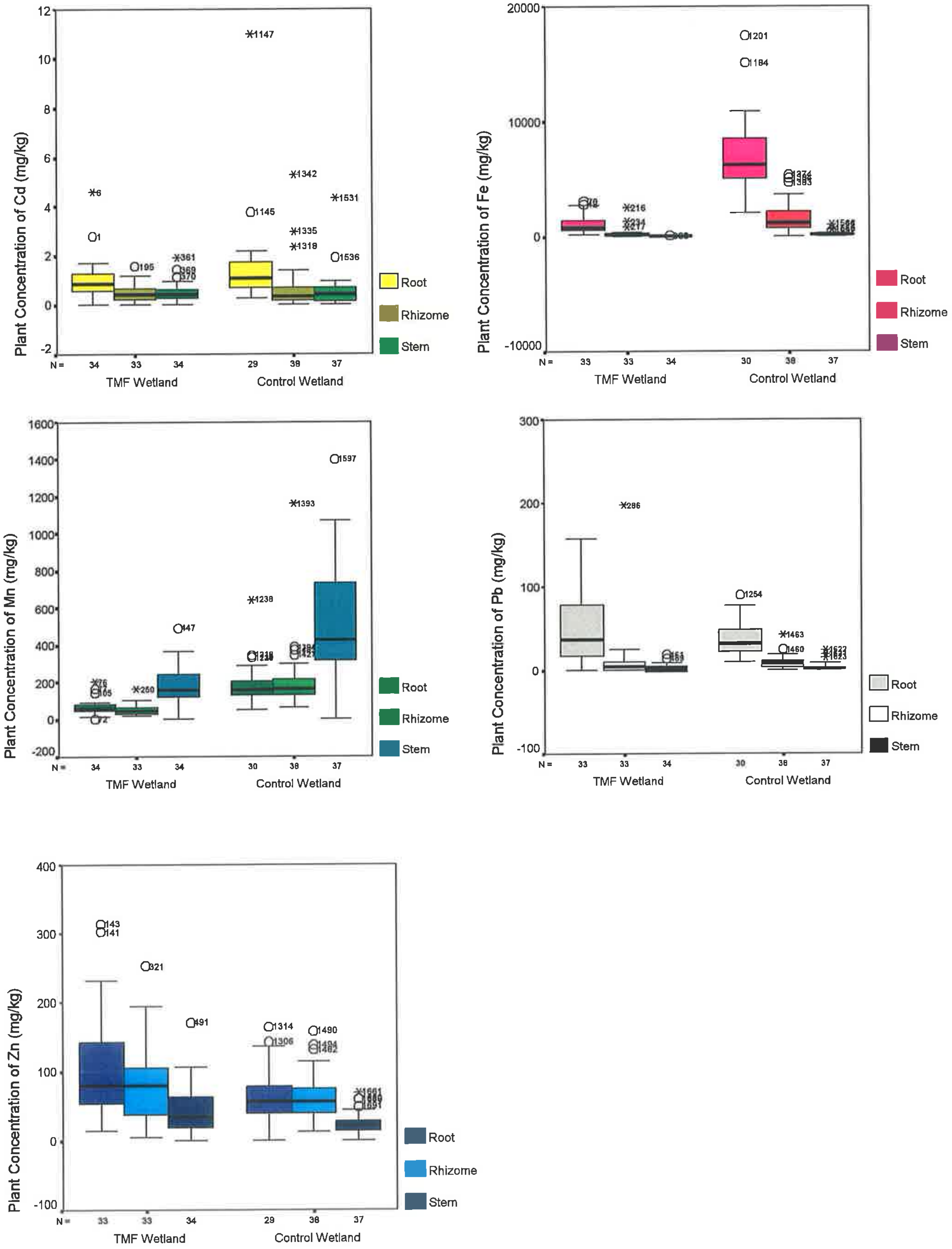


Table 7.2 Metal concentrations (mg/kg) in wetland plant species in natural wetlands and wetlands impacted by AMD.		Cd	Fe	Mn	Pb	Zn
(Sparling & Lowe, 1998)						
Aquatic Macrophytes						
Polygonum sagittatum	Control		340	3,020		
	Acidified soil		1,350	4,670		
Utricularia vulgaris	Control			5,920		
	Acidified soil			6,920		
(St. Cyr & Campbell, 2000)						
Rooted aquatic plant from St. Lawrence River, Canada						
Vallisneria Americana						
	Roots	4.3			20.2	246
	Leaves	2.35			10.9	351
(Gambrell, 1994)						
Greenhouse studies on plants under wetland conditions						
Smooth cordgrass		8.0			1.0	52.0
(Ton & Delfino, 2000)						
Studies on vegetation in Steele City Bay, Florida. Wetlands receiving Pb drainage from Superfund site.						
Juncus	Roots				1,241 → 2,068	
	Leaves				95.1 → 850	
Cypress *(Taxodium ascendens)*						
	Bark				5.0 → 112.5	
	Stem				5.0 → 175	
Water Lily						
(Nymphaea odorate)	Root				12.5 → 62.5	
(Eleocharis baldwinii)	Root				487.5	
Algae					150	
(Odum, 2000)						
Florida wetlands						
Duckweed					6 → 10	71 → 205
(Wójcik & Wójcik, 2000)						
Biala River Wetland, Poland						
Receiving Pb & Zn discharges from mining for 400 years						
Typha Latifolia						
	Rhizomes	0.5 → <2.0			50 → 250	160 → 265
	Leaves	0.5 → <2.0			5 → 30	5 → 68
Phragmites Australis						
	Rhizomes	2 → 8.5			123 → 218	153 → 280
	Stems	0.5 → <2.0			5 →40	45 → 268
	Leaves	2 → 40*			10 →160	25 → 245
Potamogeton natans						
	Whole Plant	48			797	2,037
** Outlier Value*						
(Lan et al., 1992)						
Wetlands draining Pb/Zn mine						
Typha latifolia					350	
(Pb in sediments – 4,942 and Pb in water – 1.6)						
Paspalum					850	
(Dunababin, 1988)						
Typha domingensis		54			228	15,078
(Kufel, 1989)						
Typha angustifolia						
	Roots				0.1 → 0.5	0.1 → 0.2
	Aerial shoots				0.04 → 0.5	0.04 → 0.2
Phragmites australis						
	Rhizomes				0.2 → 2.8	0.06 → 0.3
	Stems				1.7	
	Leaves				2.7	
(Lehtonen, 1990)						
Phragmites australis						
	Rhizomes	0.11 → 0.21				18 → 35
	Stems	<0.1				27→ 170
	Leaves	>0.11				12 → 33
(Levy et al., 1992)						
Contaminated soils from mining in Leadville, Colorado, U.S.A.						
Control	*Carex sp.*	0.55			0.92	27
	Juncus sp.	0.77			0.25	35
Contaminated Land						
	Carex sp.	0.98 → 3.04			1.27 → 1.76	74 → 263
	Juncus sp.	1.25[a] → 3.55[a]			0.52 → 12.7[b]	150 → 443[b]

[a] Exceeds level of 0.5mg/kg diet chronically tolerated by cattle and above normal foliage concentrations of 0.10 to 1.0 mg/kg dry weight
[b] Above normal foliage concentrations of 2 to 5 mg/kg Pb and 15 to 150 mg/kg Zn

Mean total Fe concentrations also are substantially lower in the TMF wetland than in the Control for roots, rhizomes and stems of *Typha latifolia* (1141 mg/kg, 288 mg/kg and 44 mg/kg versus 7083 mg/kg, 1635 mg/kg and 217 mg/kg respectively). The difference in Fe concentrations in the plants of the TMF and Control wetlands follows the same pattern detected in the Fe concentrations of the water column and sediments for both wetlands in 1999. These values are higher than those reported for the aquatic macrophyte *Polygonum saggittatum* (smartweed) outlined in Table 7.2 (340 mg/kg and 1,350 mg/kg).

Similarly, mean total Mn concentrations are lower in the TMF wetland than in the Control for roots, rhizomes and stems of *Typha latifolia* (67 mg/kg, 51 mg/kg and 183 mg/kg versus 185 mg/kg, 209 mg/kg and 514 mg/kg respectively). Again, the Mn concentrations in the plants of the Control reflect the higher Mn concentrations detected in the water column and sediments of the Control. Mn concentrations in *Typha* are lower than those reported for the aquatic macrophytes, *Polygonum saggittatum* (smartweed) and *Utricularia vulgaris* (bladderworth) outlined in Table 7.2 (3,020 mg/kg and 5,920 mg/kg).

Mean total Pb concentrations are higher in the TMF wetland than in the Control for roots and rhizomes of *Typha latifolia* (51.7 mg/kg and 11.3 mg/kg versus 36.8 mg/kg and 9.1 mg/kg respectively) but lower for stems (2.85 mg/kg versus 3.25 mg/kg respectively). These values are lower than Pb concentrations reported for rhizomes (50 mg/kg to 250 mg/kg) and leaves (5 mg/kg to 30 mg/kg) of *Typha latifolia* in wetlands receiving discharges from Pb-Zn mining activities in Poland (see Table 7.2). They are also substantially lower than Pb concentrations reported by Lan et al, (1992) for *Typha latifolia* (350 mg/kg) in a wetland draining a Pb-Zn mine (see Table 7.2). Increasing Pb values by 8 %[1] yields mean concentrations of 55.8 mg/kg, 12.20 mg/kg and 3.08 mg/kg for the roots, rhizomes and stems of *Typha latifolia* in the TMF wetland which remain below those reported for wetlands receiving mine drainage.

---

[1] To account for the discrepancy in Pb concentrations detected during analysis of the aquatic plant standard reference material and those specified in the standard certification as discussed in Chapter Three.

Mean total Zn concentrations are higher in the TMF wetland than in the Control for roots, rhizomes and stems of *Typha latifolia* (104 mg/kg, 81 mg/kg and 43 mg/kg versus 64 mg/kg, 63 mg/kg and 23 mg/kg respectively). These values are lower than Zn concentrations reported for rhizomes (160 mg/kg to 265 mg/kg) and leaves (5 mg/kg to 68 mg/kg) of *Typha latifolia* in wetlands receiving discharges from Pb-Zn mining activities in Poland (see Table 7.2). They are also lower than Zn concentrations reported for *Vallisneria american* (246 mg/kg and 351 mg/kg) in the St. Lawrence River in Canada (see Table 7.2).

7.2.1.2 Total Metal Concentrations in Phragmites australis

Descriptive statistics for mean total metals concentrations in the roots, rhizomes and stems of *Phragmites australis* for the TMF and Control wetlands are outlined in Table 7.3. Boxplots illustrating the median, interquartile range (25^{th}–75^{th} percentile), outliers and extreme values for each metal in each plant tissue are presented in Figure 7.2.

Mean total Cd concentrations are lower in the TMF wetland than in the Control for roots, rhizomes and stems of *Phragmites australis* (0.598 mg/kg, 0.210 mg/kg and 0.310 mg/kg versus 0.926 mg/kg, 0.310 mg/kg and 0.135 mg/kg respectively). As outlined in Table 7.2 these values are lower than Cd concentrations obtained for rhizomes (2 mg/kg to 8.5 mg/kg), stems (0.5 mg/kg to <2.0 mg/kg) and leaves (2 mg/kg to 40 mg/kg) of *Phragmites australis* in wetlands receiving drainage from Pb-Zn mining activities in Poland (Wojcik and Wojcik, 2000). They also are lower than Pb concentrations reported for rhizomes (0.2 mg/kg to 2.8 mg/kg), stems (1.78 mg/kg) and leaves (2.7 mg/kg) of *Phragmites australis* from the literature (see Table 7.2).

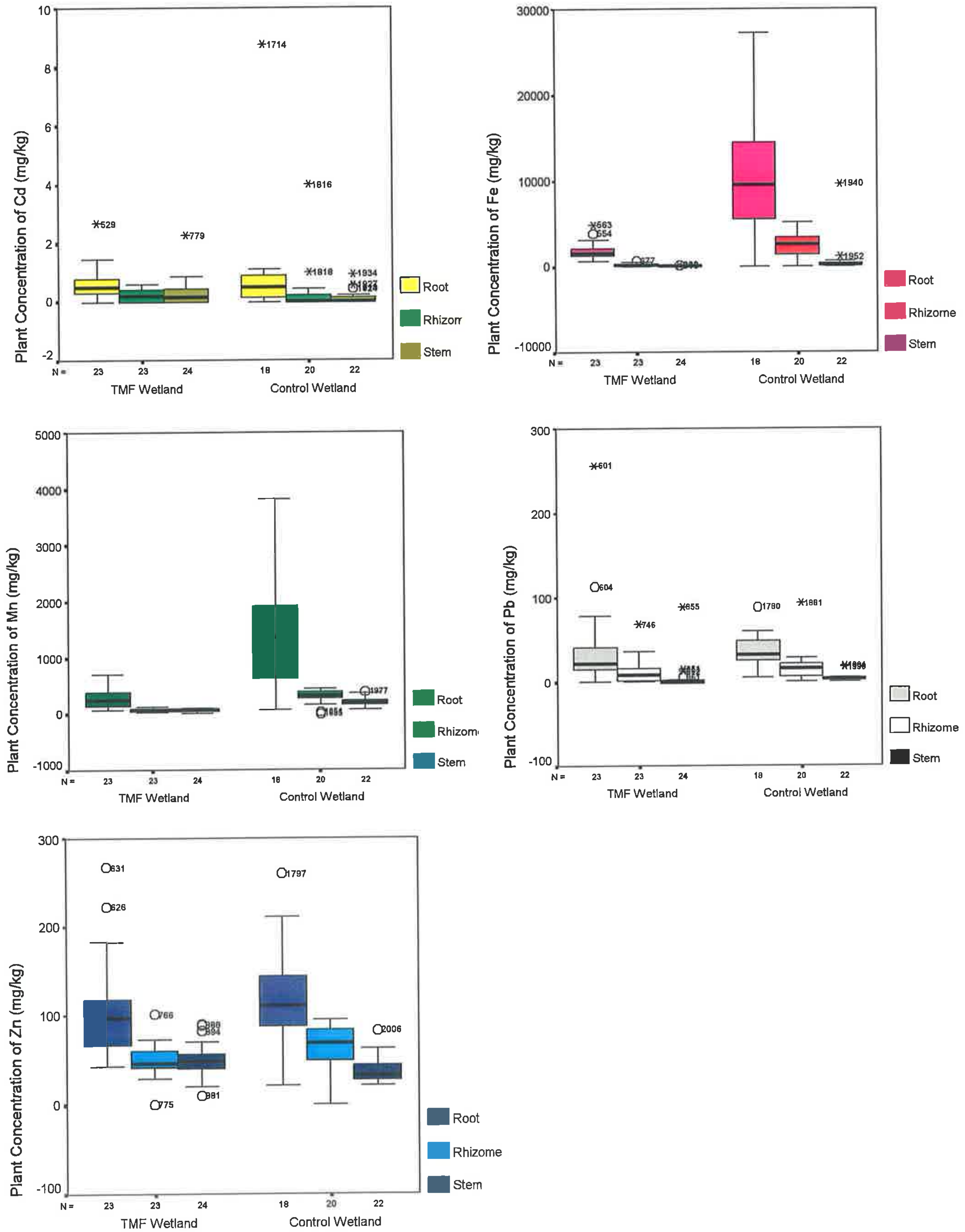
Mean total Fe concentrations also are substantially lower in the TMF wetland than in the Control for roots, rhizomes and stems of *Phragmites australis* (1843 mg/kg, 193 mg/kg and 54 mg/kg versus 10,367 mg/kg, 2,474 mg/kg and 688 mg/kg respectively). These values are higher than those reported for the aquatic macrophyte smartweed outlined in Table 7.2 (Sparling and Lowe, 1998).

Similarly, mean total Mn concentrations are lower in the TMF wetland than in the Control for roots, rhizomes and stems of *Phragmites australis* (289 mg/kg, 68 mg/kg

Table 7.3 Descriptive statistics for metal concentrations in root, rhizome and stems of *Phragmites australis* in TMF and Control wetlands in summer 1999.

Phragmites australis		TMF Wetland			Control Wetland		
		Root Conc. (mg/kg)	Rhizome Conc. (mg/kg)	Stem Conc. (mg/kg)	Root Conc. (mg/kg)	Rhizome Conc (mg/kg)	Stem Conc. (mg/kg)
Cd	**Mean**	**.598**	**.210**	**.310**	**.926**	**.310**	**.135**
	Minimum	.000	.000	.000	.000	.000	.000
	Maximum	2.669	.584	2.274	8.758	3.994	.926
	Median	.486	.189	.169	.512	.000	.000
	Std Dev.	.584	.207	.483	1.989	.899	.242
Fe	**Mean**	**1843.404**	**192.792**	**53.467**	**10366.922**	**2474.235**	**687.976**
	Minimum	589.728	25.578	22.947	58.744	.000	53.225
	Maximum	4923.433	682.043	181.818	27257.830	5124.529	9625.455
	Median	1584.836	132.894	44.110	9602.084	2516.612	200.174
	Std Dev.	1037.780	159.184	33.532	6380.281	1408.260	2009.729
Mn	**Mean**	**288.724**	**67.565**	**67.239**	**1448.940**	**305.563**	**200.981**
	Minimum	60.019	29.644	18.701	74.137	.000	66.425
	Maximum	710.997	122.733	106.693	3821.365	452.471	392.970
	Median	255.122	72.684	69.313	1356.180	322.414	197.652
	Std Dev.	194.410	23.035	21.346	1054.054	119.571	82.640
Pb	**Mean**	**40.214**	**12.047**	**5.921**	**36.373**	**17.909**	**3.815**
	Minimum	.000	.000	.000	4.555	.000	.000
	Maximum	256.638	68.363	89.247	89.178	93.595	18.891
	Median	21.581	7.701	.000	31.841	15.247	2.849
	Std Dev.	54.341	15.706	18.387	19.545	19.715	4.872
Zn	**Mean**	**104.951**	**49.756**	**49.484**	**121.399**	**63.797**	**37.613**
	Minimum	42.971	.000	10.556	21.139	.000	20.883
	Maximum	267.035	101.052	89.551	259.383	95.110	82.567
	Median	97.435	45.680	47.707	110.948	68.105	32.249
	Std Dev.	56.319	19.388	19.155	56.490	25.341	15.668

Fig. 7.2 Mean metal conc.s in tissues of *Phragmites* in TMF and Control wetlands in summer, 1999. (Outliers are designated with O and extreme values with *. Numbers indicate position in data set.)



and 67 mg/kg versus 1,449 mg/kg, 306 mg/kg and 201 mg/kg respectively). Mn concentrations in *Phragmites* are substantially lower than those reported for the aquatic macrophytes, smartweed and bladderworth outlined in Table 7.2 (3,020 mg/kg and 5,920 mg/kg).

Mean total Pb concentrations are higher in the TMF wetland than in the Control for roots, rhizomes and stems of *Phragmites australis* (40.2 mg/kg, 12.1 mg/kg and 5.92 mg/kg versus 36.3 mg/kg, 17.9 mg/kg and 3.81 mg/kg respectively). These values are substantially lower than Pb concentrations reported for rhizomes (123 mg/kg to 218 mg/kg), stems (5 mg/kg to 40 mg/kg) and leaves (10 mg/kg to 160 mg/kg) of *Phragmites australis* in wetlands receiving discharges from Pb-Zn mining activities in Poland (see Table 7.2). Increasing Pb values by 8 % yields mean concentrations of 43.4 mg/kg, 13.1 mg/kg and 6.39 mg/kg for the roots, rhizomes and stems of *Phragmites australis* in the TMF wetland which remain below those reported for wetlands receiving mine drainage. Pb concentrations in *Phragmites australis* in both the TMF and Control wetlands are higher than values reported by Kufel (1989) for the rhizomes (0.2 mg/kg to 2.8 mg/kg), stems (1.7 mg/kg) and leaves (2.7 mg/kg) of this plant (see Table 7.2).

Mean total Zn concentrations are similar but lower in the TMF wetland than in the Control for the roots and rhizomes of *Phragmites australis* (105 mg/kg and 49.8 mg/kg versus 121.4 mg/kg and 63.8 mg/kg respectively), but higher for stems (49.5 mg/kg versus 37.6 mg/kg). These values are lower, or at the lower end of the range, than Zn concentrations reported for rhizomes (153 mg/kg to 280 mg/kg), stems (45 mg/kg to 268 mg/kg) and leaves (25 mg/kg to 245 mg/kg) of *Phragmites australis* in wetlands receiving discharges from Pb-Zn mining activities in Poland (see Table 7.2). Zn concentrations in *Phragmites australis* in both the TMF and Control wetlands are higher than some values reported for the rhizomes (18 mg/kg to 35 mg/kg) of this plant in the literature, but within the range reported for stems (27 mg/kg to 170 g/kg) (see Table 7.2).

7.2.1.3 Total Metal Concentrations in Juncus effusus

Descriptive statistics for mean total metals concentrations in the roots, rhizomes and stems of *Juncus effusus* for the TMF and Control wetlands are outlined in Table 7.4. Boxplots illustrating the median, interquartile range (25^{th}–75^{th} percentile), outliers and extreme values for each metal in each plant tissue are presented in Figure 7.3.

Mean total Cd concentrations are lower in the TMF wetland than in the Control for roots and stems of *Juncus effusus* (0.41 mg/kg and 0.43 mg/kg versus 1.9 mg/kg and 0.78 mg/kg respectively). As outlined in Table 7.2 the values for the TMF wetland are lower than those reported for *Juncus* growing on uncontaminated soils (0.77 mg/kg) and soils contaminated from mining (1.25 mg/kg to 3.55 mg/kg) in Leadville, Colorado in the U.S. (Levy *et al.*, 1992).

Mean total Fe concentrations are substantially lower in the TMF wetland than in the Control for the roots of *Juncus effusus* (3,315 mg/kg versus 13,882 mg/kg respectively), whereas stem concentrations are similar for both wetlands (155 mg/kg and 152 mg/kg respectively). These values are higher than those reported for the aquatic macrophyte smartweed outlined in Table 7.2.

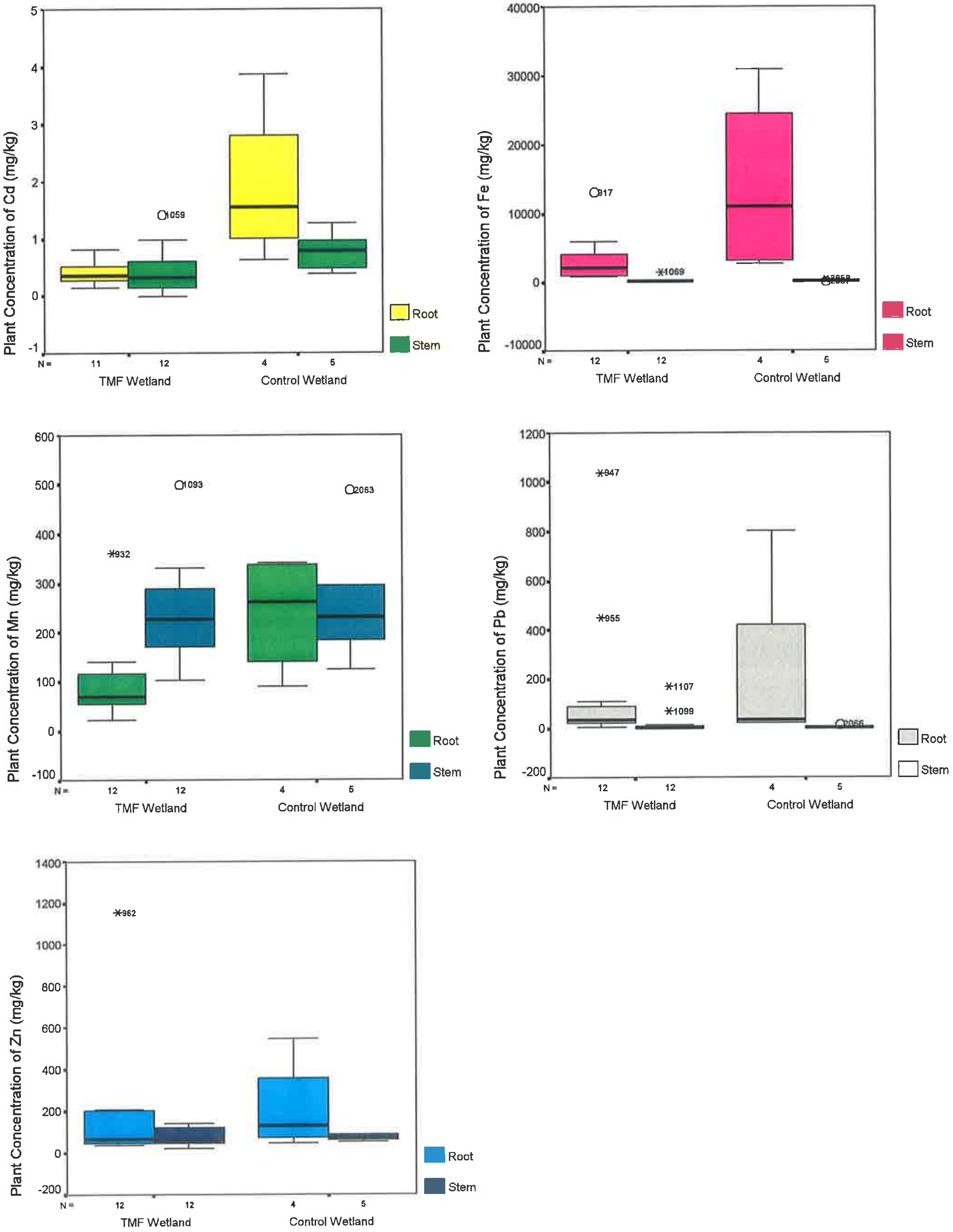
Similarly, mean total Mn values are lower in the TMF wetland than in the Control for the roots of *Juncus effusus* (100 mg/kg versus 239 mg/kg respectively) but similar for stem concentrations (238 and 265 mg/kg respectively). Mn concentrations in *Juncus* are substantially lower than those reported for the aquatic macrophytes *Polygonum saggittatum* (smartweed) and *Utricularia vulgaris* (bladderworth) outlined in Table 7.2.

Mean total Pb concentrations are lower in the TMF wetland than in the Control for the roots of *Juncus effusus* (157.6 mg/kg versus 222.4 mg/kg respectively) whereas stem concentrations are higher (23.7 mg/kg versus 5.7 mg/kg respectively). These values are substantially lower than Pb concentrations reported for roots (1,241 mg/kg to 2,068 mg/kg) and stems (95.1 mg/kg to 850 mg/kg) of *Juncus* in wetlands receiving Pb discharges from a Superfund site in Florida (see Table 7.2). Increasing Pb values

Table 7.4 Descriptive statistics for metal concentrations in roots and stems of *Juncus effusus* in TMF and Control wetlands in summer, 1999.

Juncus effusus		TMF Wetland		Control Wetland	
		Root Conc. (mg/kg)	Stem Conc. (mg/kg)	Root Conc. (mg/kg)	Stem Conc. (mg/kg)
Cd	**Mean**	**.405**	**.426**	**1.903**	**.780**
	Minimum	.148	.000	.634	.388
	Maximum	.825	1.426	3.867	1.271
	Median	.357	.317	1.555	.790
	Std Dev.	.210	.436	1.387	.359
Fe	**Mean**	**3314.958**	**155.194**	**13,881.837**	**152.148**
	Minimum	711.810	18.101	2712.460	67.600
	Maximum	13,049.970	1,410.945	30,921.492	335.878
	Median	2,097.355	35.027	10,946.698	122.542
	Std Dev.	3,511.508	395.921	13,409.469	105.271
Mn	**Mean**	**100.193**	**237.735**	**238.630**	**264.512**
	Minimum	22.456	104.279	90.234	125.308
	Maximum	361.338	499.802	341.609	487.399
	Median	70.542	226.253	261.340	230.487
	Std Dev.	89.822	109.717	120.470	139.312
Pb	**Mean**	**157.588**	**23.703**	**222.353**	**5.672**
	Minimum	6.335	.000	21.356	1.360
	Maximum	1,040.215	170.196	800.491	14.399
	Median	33.208	4.348	33.783	3.940
	Std Dev.	303.531	49.929	385.580	5.206
Zn	**Mean**	**180.955**	**75.441**	**212.522**	**68.998**
	Minimum	36.985	18.385	46.543	48.600
	Maximum	1154.688	140.697	543.867	85.005
	Median	63.726	58.775	129.838	67.600
	Std Dev.	313.947	42.516	226.367	15.238

Fig. 7.3 Mean metal concentrations in tissues of *Juncus* in TMF and Control wetlands summer, 1999. (Outliers are designated with O and extreme values with *. Numbers indicate position in data set.)



by 8 % yields mean concentrations of 170.2 mg/kg and 25.6 mg/kg for the roots and stems of *Juncus effusus* in the TMF wetland which remain below those reported for the Florida wetlands (Odum et al., 2000). Pb concentrations in *Juncus effusus* in both the TMF and Control wetlands are higher than values reported for this plant growing on uncontaminated soils (0.25 mg/kg) and soils contaminated from mining (0.52 mg/kg to 12.7 mg/kg) in Leadville, Colorado (Levy *et al.*, 1992).

Mean total Zn concentrations are lower in the TMF wetland than in the Control for the roots of *Juncus effusus* (180.9 mg/kg versus 212.5 mg/kg respectively) and similar but higher for stems (75.4 mg/kg versus 68.9 mg/kg). These values are lower, or at the lower end of the range, than Zn concentrations reported for *Juncus* (150 mg/kg to 443 mg/kg) growing on soils contaminated from mining in Leadville, Colorado (See Table 7.2).

7.2.1.4 ANOVA to Compare Metal Concentrations in Plant Species between Wetlands

A one-way analysis of variance (ANOVA) was conducted to compare metal concentrations in *Typha latifolia*, *Phragmites australis* and *Juncus effusus* in the TMF and Control wetlands. Each variable was tested for normality prior to ANOVA analysis using Shapiro-Wilk's and Kologorov-Smirov Lilliefors tests for normality. Each variable also was tested for homogeneity of variance using the Levene statistic. Variables were log transformed prior to ANOVA analysis when they did not exhibit normality.

The null hypothesis (H_o) in this analysis proposes that the population means for metal concentrations in similar plant tissues and plant species in both wetlands are the same.

F values and observed significance levels for Cd are as follows:

Cd	*Typha latifolia*		*Phragmites australis*		*Juncus effusus*	
	F	p	F	p	F	p
Roots	2.501	0.119	0.561	0.459	13.769	0.003
Rhizomes	0.328	0.569	0.271	0.605	-	-
Stems	0.420	0.519	2.023	0.168	2.389	0.146

The results of the ANOVA analysis indicate no significant difference in mean Cd concentrations of the roots, rhizomes and stems of *Typha latifolia* and *Phragmites australis* between the TMF and Control wetlands at a significance level of 0.05. There was a significant difference ($p<0.05$) between the wetlands in the mean Cd concentrations of the roots of *Juncus effusus* due to higher concentrations in the Control. However, there was no significant difference between the wetlands in the Cd concentrations of the stems of *Juncus effusus.* Comparisons of metal concentrations in the three wetland species between the TMF and the Control wetlands are illustrated three-dimensionally in Figure 7.4. From this figure it can be see that the majority of plant Cd concentrations are similar between the wetlands. The outlier values in Quadrats 39 and 51 are for *Typha* root tissues and *Phragmites* root tissues in the Control and do not create a significant difference between wetlands.

F values and observed significance levels for Fe are as follows:

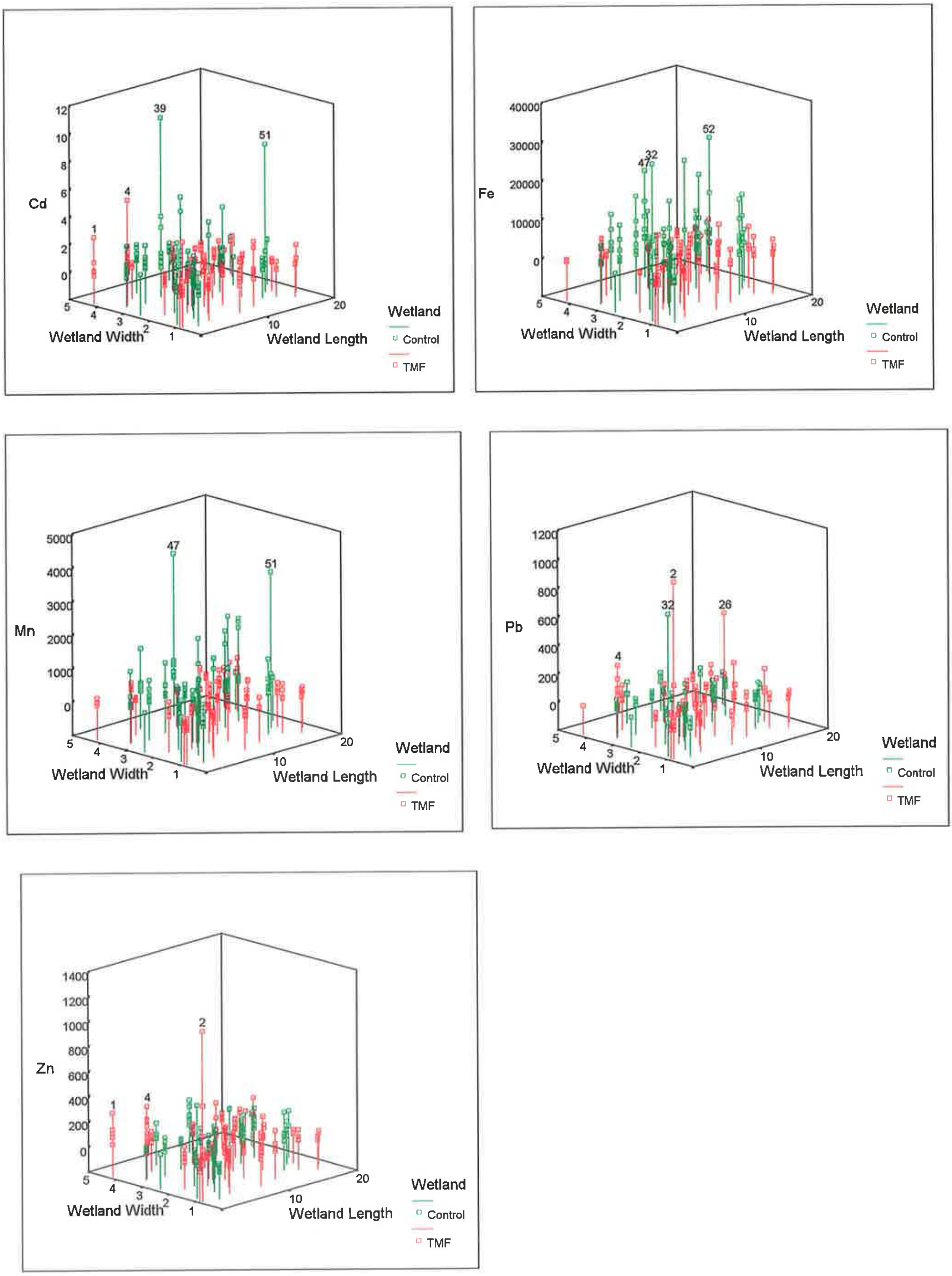
Fe	***Typha latifolia***		***Phragmites australis***		***Juncus effusus***	
	F	p	F	p	F	p
Roots	160.674	0	24.576	0	5.738	0.031
Rhizomes	75.127	0	143.881	0	-	-
Stems	70.042	0	39.901	0	3.087	0.099

The results of the ANOVA analysis indicate a significant difference ($p=0$) in mean Fe concentrations of the roots, rhizomes and stems of *Typha latifolia* and *Phragmites australis,* between the TMF and Control wetlands at a significance level of 0.05. This is due to higher Fe concentrations in the Control. Also, there was a significant difference ($p<0.05$) between the wetlands in the mean Fe concentrations of the roots of *Juncus effusus* due to higher concentrations in the Control. However, there was no significant difference in the mean Fe concentrations of the stems of *Juncus effuses,* but the significance value is marginal. Figure 7.4 illustrates overall higher concentrations of Fe in the plant species in the Control.

F values and observed significance levels for Mn are as follows:

Mn	***Typha latifolia***		***Phragmites australis***		***Juncus effuses***	
	F	p	F	p	F	P
Roots	40.814	0	34.033	0	6.212	0.026
Rhizomes	135.341	0	87.689	0	-	-
Stems	40.870	0	58.700	0	0.144	0.709

Fig. 7.4 Comparisons in metal concentrations in *Typha latifolia, Phragmites australis,* and *Juncus effusus* between the TMF and Control wetlands in summer, 1999.



The results of the ANOVA analysis for Mn reflect those for Fe, and indicate a significant difference ($p=0$) in mean Mn concentrations of the roots, rhizomes and stems of *Typha latifolia* and *Phragmites australis* between the TMF and Control wetlands, at a significance level of 0.05. This is due to higher Mn concentrations in the Control. Also, there was a significant difference ($p<0.05$) between the wetlands in the mean Mn concentrations of the roots of *Juncus effuses,* due to higher concentrations in the Control. However, there was no significant difference in mean Mn concentrations of the stems of *Juncus effuses,* but the similarity between wetlands is much higher than for Fe concentrations. Figure 7.4 illustrates overall higher concentrations of Mn in the plant species in the Control.

F values and observed significance levels for Pb are as follows:

Pb	*Typha latifolia*		*Phragmites australis*		*Juncus effusus*	
	F	p	F	p	F	p
Roots	0.116	0.734	0.587	0.448	0.088	0.770
Rhizomes	0.050	0.824	2.573	0.118	-	-
Stems	1.658	0.206	2.447	0.130	1.909	0.192

The results of the ANOVA analysis indicate no significant difference, at a significance level of 0.05, in the mean Pb concentrations of the roots, rhizomes and stems of *Typha latifolia* and *Phragmites australis* and the rhizomes and stems of *Juncus effuses,* between the TMF and Control wetlands. Figure 7.4 illustrates that the majority of plant Pb concentrations are similar between the wetlands. The outlier values in Quadrats 2 and 26, and in Quadrat 32, are for *Juncus* root tissues in the TMF and Control wetlands, but do not create a significant difference between wetlands.

F values and observed significance levels for Zn are as follows:

Zn	*Typha latifolia*		*Phragmites australis*		*Juncus effusus*	
	F	p	F	p	F	p
Roots	4.123	0.05	0.821	0.370	0.502	0.490
Rhizomes	0.371	0.544	5.403	0.025	-	-
Stems	3.963	0.051	5.235	0.027	0.030	0.865

The results of the ANOVA analysis indicate no significant difference between the wetlands in the mean Zn concentrations of the roots and stems of *Typha latifolia* at a significance level of 0.05, but the significance value is marginal. Also, there is no significant difference in the Zn concentrations of the rhizomes of *Typha latifolia*. There is no significant difference in the Zn concentration of the roots of *Phragmites australis,* but a significant difference exists for the rhizomes (due to higher Zn concentrations in the Control) and for the stems (due to a higher concentration in the TMF wetland). Mean Zn concentrations in the roots and stems of *Juncus effusus* do not differ significantly between wetlands. The outlier values in Quadrat 2 of Figure 7.4 is for *Juncus* root tissues in the TMF wetland, but does not create a significant difference between wetlands.

7.2.1.5 ANOVA to Compare Metal Concentrations in Tissues of Plant Species in TMF Wetland

A one-way ANOVA was conducted to compare metal concentrations in the tissues of *Typha latifolia*, *Phragmites australis* and *Juncus effusus* in the TMF wetland. This was followed by Tukey's Honestly Significant Difference (HSD) test for the calculation of Least Significant Difference at a significance level of 0.05 to denote significant differences between the plant tissues of *Typha* and *Phragmites*.

The null hypothesis (H_o) in this analysis proposes that the population means for metal concentrations in different plant tissues are the same. Results of one-way ANOVA followed by Tukey HSD analysis comparing metal concentrations between roots, rhizomes and stems of *Typha latifolia* in the TMF wetland are as follows:

Typha latifolia		**Cd**		**Fe**		**Mn**		**Pb**		**Zn**	
		F	p	F	p	F	p	F	p	F	p
		7.41	.001	144	0	30.1	0	22.4	0	9.46	0
Plant Segment	Plant Segment	Tukey HSD Sig.		Tukey HSD Sig.		Tukey HSD Sig.		Tukey HSD Sig.		Tukey HSD Sig.	
Root	Rhizome	.002		.000		.437		.000		.451	
	Stem	.010		.000		.000		.000		.000	
Rhizome	Root	.002		.000		.437		.000		.451	
	Stem	.837		.000		.000		.485		.009	
Stem	Root	.010		.000		.000		.000		.000	
	Rhizome	.837		.000		.000		.485		.009	

These results indicate plant tissue (roots, rhizome and stems) is an important factor influencing the extent of metal accumulation in *Typha latifolia*. There is a significant difference between root and rhizome accumulations of Cd, Fe and Pb in *Typha latifolia* but no significant difference occurs for Mn ($p=0.437$) and Zn ($p=0.451$).

There is a significant difference ($p<0.05$) in the accumulation of metals between roots and stems of *Typha latifolia* for all metals. Finally, there is no significant difference between rhizome and stem accumulations of Cd ($p=0.837$) and Pb ($p=0.485$) in this plant. These results are presented graphically in Figure 7.5. From this figure it is obvious that there is a differential pattern of metal accumulation between root, rhizome and stem tissue of *Typha latifolia*. For Cd, Fe, Pb and Zn, most metal accumulation occurs in the roots. The exception occurs for Mn where most metal accumulation occurs in the stems.

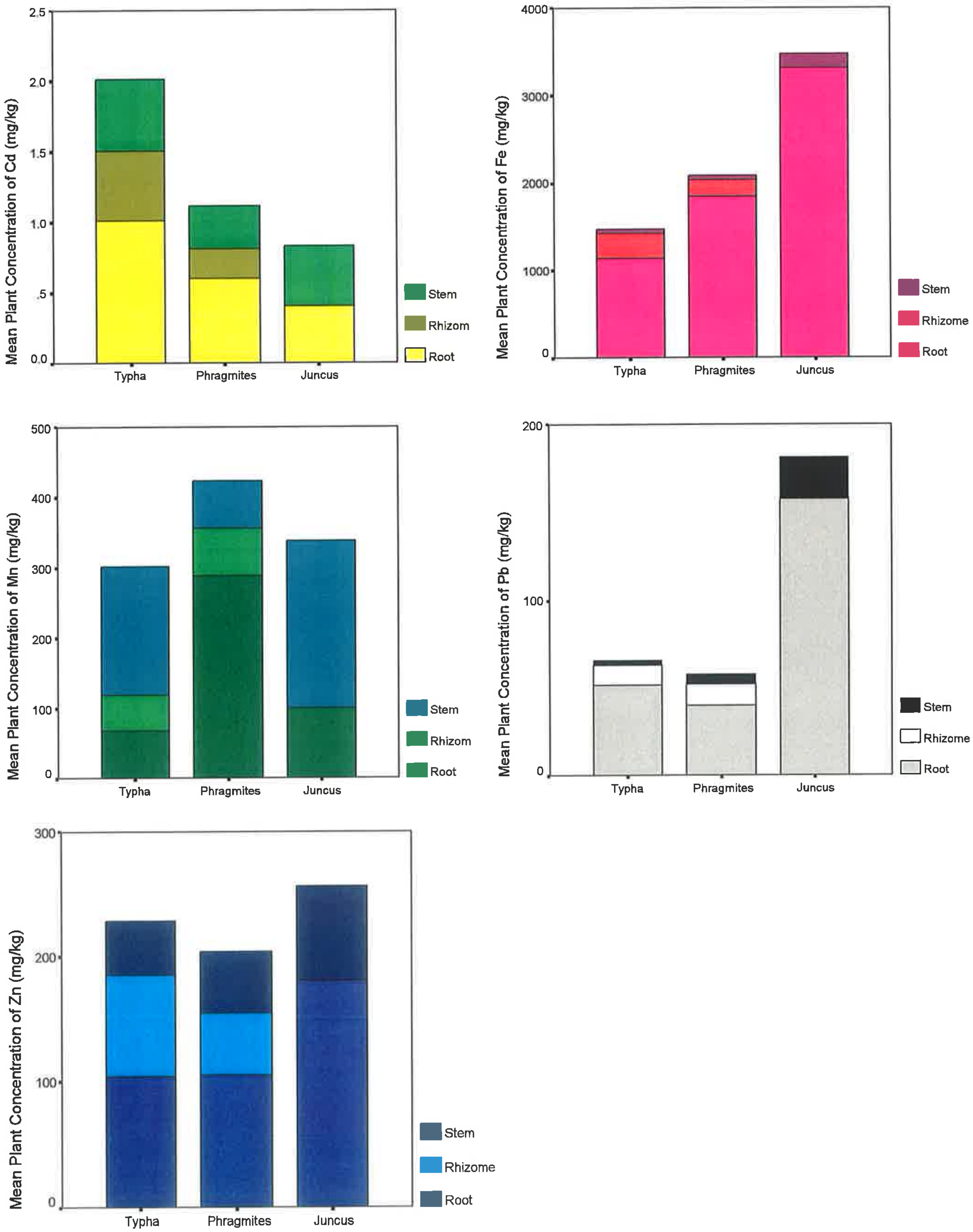
Results of one-way ANOVA followed by Tukey HSD analysis comparing metal concentrations between roots, rhizomes and stems of *Phragmites australis* in the TMF wetland are as follows:

Phragmites australis		**Cd**		**Fe**		**Mn**		**Pb**		**Zn**	
		F	p	F	p	F	p	F	p	F	p
		4.13	.022	204	0	45.9	0	4.72	.014	20	0
Plant Segment	Plant Segment	Tukey HSD Sig.		Tukey HSD Sig.		Tukey HSD Sig.		Tukey HSD Sig.		Tukey HSD Sig.	
Root	Rhizome	.016		.000		.000		.035		.000	
	Stem	.379		.000		.000		.046		.000	
Rhizome	Root	.016		.000		.000		.035		.000	
	Stem	.335		.000		.998		.892		.744	
Stem	Root	.379		.000		.000		.046		.000	
	Rhizome	.335		.000		.998		.892		.744	

These results indicate plant tissue (roots, rhizomes and stems) is an important factor influencing the extent of metal accumulation in *Phragmites australis*. There is a significant difference ($p<0.05$) in the accumulation of metals between roots and rhizomes of *Phragmites australis* for all metals. There is a significant difference between root and stem accumulations for all metals except Cd ($p=0.379$). Finally, there is no significant difference between rhizome and stem accumulations of Cd ($p=0.335$), Mn (0.998), Pb ($p=0.892$) and Zn (0.744) in this plant. The exception occurs for Fe which shows a significant difference at the 0.05 significance level. From Figure 7.5 it is obvious that there is a differential pattern of metal accumulation between root, rhizome and stem tissue of *Phragmites australis* with most metal accumulation occuring in the roots for all metals.

Results of one-way ANOVA analysis comparing metal concentrations between the roots and stems of *Junus effusus* in the TMF wetland are as follows:

Fig. 7.5 Mean metal concentrations in roots, rhizomes and stems of *Typha latifolia, Phragmites australis*, and *Juncus effusus* in TMF wetland in summer, 1999.



Juncus effusus		Cd		Fe		Mn		Pb		Zn	
Plant Segment	Plant Segment	F	p	F	p	F	p	F	p	F	p
Root	Stem	.283	.601	78.8	0	17.8	0	5.74	.027	1.10	.304

These results indicate plant tissue (root and stem) is an important factor influencing the extent of accumulation of some metals in *Juncus effusus*. There is a significant difference ($p<0.05$) in the accumulation of Fe, Mn and Pb between roots and stems of *Juncus effusus*. Fe and Pb differentially accumulate in the roots of this plant whereas Mn, in similar fashion to *Typha latifolia*, accumulates in the stems of *Juncus effusus*. There is no significant difference between root and stem accumulations for Cd ($p=0.601$) and Zn ($p=0.304$). Figure 7.5 illustrates this pattern of metal accumulation between the root and stem tissue of *Juncus effusus.*

7.2.1.6 ANOVA to Compare Metal Concentrations between Plant Species in TMF Wetland

A one-way ANOVA was conducted to compare metal concentrations in the tissues of *Typha latifolia*, *Phragmites australis* and *Juncus effusus* in the TMF wetland. This was followed by Tukey's Honestly Significant Difference (HSD) test for the calculation of Least Significant Difference at a significance level of 0.05 to denote significant differences between the three different wetland plant species.

The null hypothesis (H_o) in this analysis proposes that the population means for metal concentrations in similar plant tissues of the three wetland species are the same. Results of one-way ANOVA followed by Tukey HSD analysis comparing metal concentrations in the roots of *Typha, Phragmites* and *Juncus* in TMF wetland are as follows:

Roots		Cd		Fe		Mn		Pb		Zn	
		F	p	F	p	F	p	F	p	F	p
		3.09	.053	9.15	0	26.2	0	1.5	.232	.402	.670
Plant Species	Plant Species	Tukey HSD Sig.		Tukey HSD Sig.		Tukey HSD Sig.		Tukey HSD Sig.		Tukey HSD Sig.	
Typha	*Phragmites*	.094		.007		.000		.537		.693	
	Juncus	.143		.001		.364		.627		.811	
Phragmites	*Typha*	.094		.007		.000		.537		.693	
	Juncus	.992		.472		.000		.214		.999	
Juncus	*Typha*	.143		.001		.364		.627		.811	
	Phragmites	.992		.472		.000		.214		.999	

These results indicate Cd, Pb and Zn accumulation in the roots of *Typha, Phragmites* and *Juncus* is not significantly influenced by plant species. There also is no significant difference in the accumulation of Fe in the roots of *Phragmites* and *Juncus* but there is a signifiant difference ($p<0.05$) between these plants and *Typha*. There is no significant difference in the accumulation of Mn in the roots of *Typha* and *Juncus* but there is a significant difference ($p<0.05$) between these plants and *Phragmites*. Mean Cd, Pb and Zn concentrations in the three wetland species and their associated plant tissue concentrations are presented three-dimensionally in Figure 7.6. From this figure it is obvious that the majority of plant Cd, Pb and Zn concentrations are similar within the TMF wetland. The outlier values for *Typha* and *Phragmites* do not create a significant difference between plant species. Mean Fe and Mn concentrations in the three wetland species and their associated plant tissue concentrations are presented three-dimensionally in Figure 7.7. From this figure it can be seen that Mn concentrations vary more than other metals between plant species.

Results of one-way ANOVA followed by Tukey HSD analysis comparing metal concentrations in the stems of *Typha, Phragmites* and *Juncus* in the TMF wetland are as follows:

Stems		Cd		Fe		Mn		Pb		Zn	
		F	p	F	p	F	p	F	P	F	p
		2.78	.071	.794	.456	20.1	0	1.12	.340	4.00	.023
Plant Species	Plant Species	Tukey HSD Sig.		Tukey HSD Sig.		Tukey HSD Sig.		Tukey HSD Sig.		Tukey HSD Sig.	
Typha	*Phragmites*	.067		.583		.000		.909		.226	
	Juncus	.430		.541		.229		.310		.023	
Phragmites	*Typha*	.067		.583		.000		.909		.226	
	Juncus	.805		.964		.000		.634		.388	
Juncus	*Typha*	.430		.541		.229		.310		.023	
	Phragmites	.805		.964		.000		.634		.388	

Fig. 7.6 Mean Cd, Pb and Zn concentrations in roots, rhizomes, and stems of *Typha latifolia, Phragmites australis,* and *Juncus effusus* in the TMF wetland in summer, 1999.

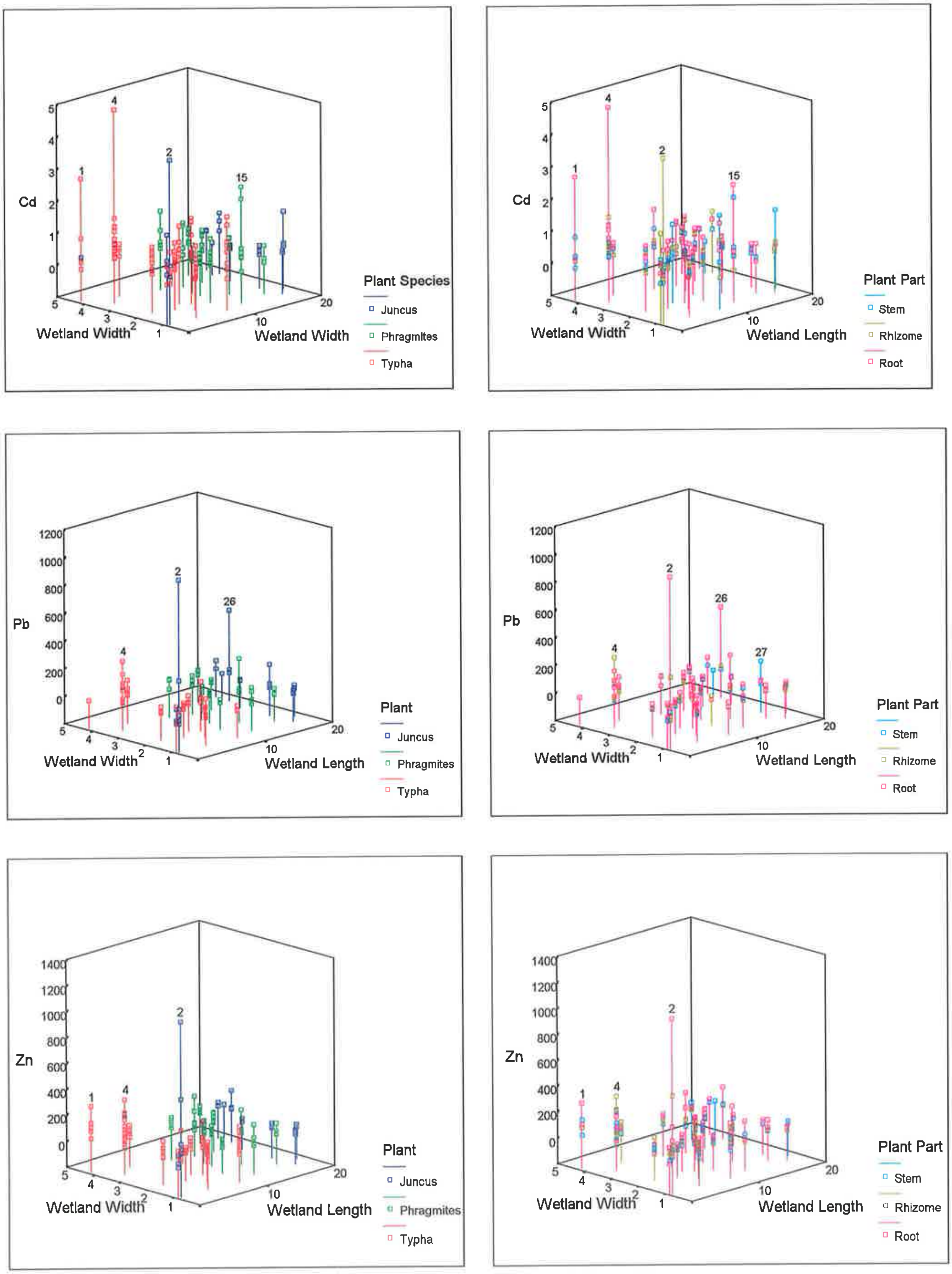
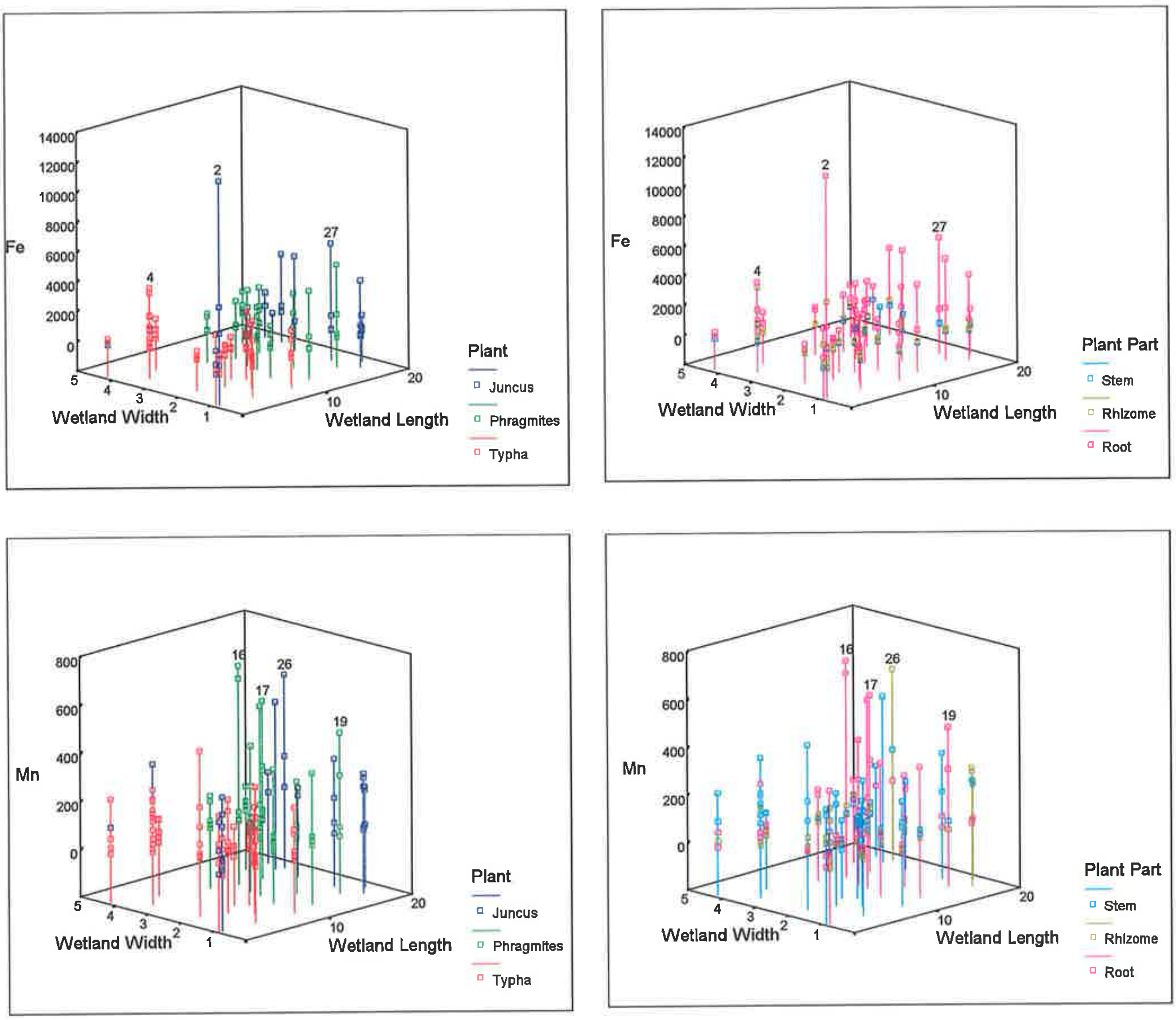


Fig. 7.7 Mean Fe and Mn concentrations in roots, rhizomes, and stems of *Typha latifolia, Phragmites australis,* and *Juncus effusus* in the TMF wetland in summer, 1999.



These results indicate plant species (*Typha, Phragmites* and *Juncus*) is not significant in influencing Cd, Fe, and Pb accumulation in the stems of these plants. There also is no significant difference in the accumulation of Mn in the stems of *Typha* and *Juncus* but there is a significant difference ($p<0.05$) between these plants and *Phragmites*. There is no significant difference in the accumulation of Zn in the stems of *Typha* and *Phragmites* but there is a significant difference ($p<0.05$) between *Typha* and *Juncus*. Figures 7.6 and 7.7 illustrate these results. It is obvious from Figure 7.7 that Mn concentrations are higher in the stems of these wetland plants whereas other metals are higher in the roots.

7.3 SUMMARY

The main findings of the assessment of biotic indicators of ecosystem health and sustainability in the pilot wetlands were as follows:

- Mean total Cd, Fe and Mn concentrations were lower in the TMF wetland than in the Control for roots, rhizomes and stems of *Typha latifolia*. The difference in Fe and Mn concentrations in plants from the TMF and Control wetlands follows the same pattern detected for Fe and Mn concentrations in the water column and sediments for both wetlands in 1999. Mean total Pb concentrations are higher in the TMF wetland than in the Control for roots and rhizomes of *Typha latifolia* but lower for stems. However, these values are lower than Pb concentrations reported for rhizomes and leaves of *Typha latifolia* in wetlands receiving discharges from Pb-Zn mining activities. Similarly, mean total Zn concentrations are higher in the TMF wetland than in the Control for roots, rhizomes and stems of *Typha latifolia* but again these values are lower than Zn concentrations reported for rhizomes and leaves of *Typha latifolia* in wetlands receiving discharges from Pb-Zn mining activities.

- Mean total Cd, Fe and Mn concentrations are lower in the TMF wetland than in the Control for roots, rhizomes and stems of *Phragmites australis*. Mean total Pb concentrations are higher in the TMF wetland than in the Control for roots, rhizomes and stems of *Phragmites australis*. However these values are substantially lower than Pb concentrations reported for rhizomes, stems and leaves of *Phragmites australis* in wetlands receiving discharges from Pb-Zn mining activities. Mean total Zn concentrations are lower in the TMF wetland than in the Control for the roots and rhizomes of *Phragmites australis* but higher for stems. These values are lower (or at the lower end of the range) then Zn concentrations reported for rhizomes, stems and leaves of *Phragmites australis* in wetlands receiving discharges from Pb-Zn mining activities.

- Mean total Cd concentrations are lower in the TMF wetland than in the Control for roots and stems of *Juncus effusus*. Mean total Fe and Mn concentrations are lower in the TMF wetland than in the Control for the roots of *Juncus effusus* whereas stem concentrations are similar for both wetlands. Mean total Pb concentrations are lower in the TMF wetland than in the Control for the roots of *Juncus effuses*, whereas stem concentrations are higher. These values are substantially lower than Pb concentrations reported for roots and stems of *Juncus* in wetlands receiving Pb discharges from a Superfund site in Florida. Mean total Zn concentrations are lower in the TMF wetland than in the Control for the roots of *Juncus effusus* and similar but higher for stems. These values are lower (or at the lower end of the range) than Zn concentrations reported for *Juncus* growing on soils contaminated from mining.

- ANOVA analyses indicates no significant difference between the TMF and Control wetlands in mean Cd concentrations of the roots, rhizomes and stems of *Typha latifolia* and *Phragmites australis*. There was a significant difference between the wetlands in the mean Cd concentrations of the roots of *Juncus effusus* due to higher concentrations in the Control. There is a significant difference in mean Fe and Mn concentrations of the roots, rhizomes and stems of *Typha latifolia* and *Phragmites australis* between the TMF and Control wetlands due to higher Fe and Mn concentrations in the Control. Also, there is a significant difference between the wetlands in the mean Fe and Mn concentrations of the roots of *Juncus effuses*, due to higher concentrations in the Control.

- ANOVA analyses indicates no significant difference in the mean Pb concentrations of the roots, rhizomes and stems of *Typha latifolia* and *Phragmites australis* and the rhizomes and stems of *Juncus effusus* between the TMF and Control wetlands. Also, there is no significant difference between the wetlands in the mean Zn concentrations of the roots, rhizomes and stems of *Typha latifolia*. There is no significant difference in the Zn concentration of the roots of *Phragmites australis* but a significant difference exists for the rhizomes (due to higher Zn concentrations in the Control) and for the stems (due to a higher concentration in the TMF wetland). Mean Zn concentrations in the roots and stems of *Juncus effusus* do not differ significantly between wetlands.

- Plant tissue (roots, rhizomes and stems) is an important factor influencing the extent of metal accumulation in *Typha latifolia* in the TMF wetland. For Cd, Fe, Pb and Zn, most metal accumulation occurs in the roots. The exception occurs for Mn where most metal accumulation occurs in the stems.

- Plant tissue is an important factor influencing the extent of metal accumulation in *Phragmites australis* in the TMF wetland. There is a differential pattern of metal accumulation between root, rhizome and stem tissue of *Phragmites australis*, with most metal accumulation occuring in the roots for all metals.

- Plant tissue (roots and stems) is an important factor influencing the extent of accumulation of some metals in *Juncus effusus*. There is a significant difference in the accumulation of Fe, Mn and Pb between roots and stems of *Juncus effusus*. Fe and Pb differentially accumulate in the roots of this plant whereas Mn, in similar fashion to *Typha latifolia*, accumulates in the stems of *Juncus effusus*. There is no significant difference between root and stem accumulations for Cd and Zn.

- Plant species is not significant in influencing Cd, Pb and Zn accumulation in the roots of *Typha, Phragmites* and *Juncus* in the TMF wetland. However, species significantly influences the accumulation of Fe and Mn in the roots of these plants. *Typha* accumulates less Fe in its roots than *Phragmites* and *Juncus*, and *Phragmites* accumulates more Mn in its roots than *Typha* or *Juncus*.

- Plant species is not significant in influencing Cd, Fe and Pb accumulation in the stems of *Typha, Phragmites* and *Juncus* in the TMF wetland. However, species significantly influences the accumulation of Mn and Zn in the stems of these plants. *Typha* and *Juncus* accumulate more Mn in their stems than *Phragmites*, and *Juncus* accumulates more Zn in its stems than *Typha*.

This biotic analyses forms the basis for the regression analyses conducted in Chapter Eight to investigate whether correlations exist between metal accumulations in wetland macrophytes and hydrology, water chemistry, sediment geochemistry and ecological health that affect the potential sustainability of the TMF wetland.

CHAPTER EIGHT

RESULTS
CORRELATION AND LINEAR REGRESSION ANALYSIS

8.1 RESULTS – CORRELATION AND LINEAR REGRESSION ANALYSIS

Following the analysis of ecological, hydrological, physio-chemical, sediment and biotic indicators in the pilot wetland system, a comprehensive correlation and regression analysis was conducted for the TMF wetland. The purpose of this analysis was to investigate relationships between these indicators to further assess the overall health of this ecosystem and to develop design parameters for ecologically engineering a sustainable wetland system over pyritic mine tailings.

Aims of the correlation and regression analysis were as follows:

- To conduct bivariate correlation analysis to measure the strength of the linear association between ecological variables and the physiochemical parameters of the water column of the TMF wetland, and between ecological variables and the metal concentrations in the water column, sediments and tissues of *Typha latifolia*, *Phragmites australis*, and *Juncus effusus* in 1999.

- To conduct bivariate correlation and regression analysis to measure the strength of the linear association between hydrological and physico-chemical variables in the water column of the TMF wetland in 1999 and 2000.

- To conduct bivariate correlation and regression analysis to measure the strength of the linear association between sediment variables (total, extracted and free-metal ion concentrations) and hydrological and physico-chemical variables in the water column of the TMF wetland in 1999 and 2000.

- To conduct bivariate correlation and regression analysis to measure the strength of the linear association between biotic variables (metal concentrations in the root, rhizome and stem tissues of of *Typha latifolia*, *Phragmites australis*, and *Juncus effusus*), and hydrological, physico-chemical and sediment variables in the TMF wetland in 1999.

- To conduct bivariate correlation and regression analysis to measure the strength of the linear association between hydrological, physico-chemical and sediment variables in Silvermines wetland in 2000 and to compare these with the TMF wetland.

8.2 CORRELATION ANALYSIS FOR ECOLOGICAL INDICATORS

Spearman rank correlation analysis was conducted in the TMF wetland to measure the strength of the linear association between ecological variables and the physiochemical parameters of the water column, and between ecological variables and the metal concentrations in the water column, sediments and tissues of *Typha latifolia*, *Phragmites australis*, and *Juncus effusus* in 1999. Scatterplots were used to show the relation between independent variables (depth, pH, metal concentration of sediments and plants) and vegetation (density, biomass).

8.2.1 Spearman Rank Correlation Analysis for Ecological and Physiochemical Parameters

Spearman rank correlation analysis was conducted for a range of ecological and physico-chemical parameters including: species richness; Margalef's Index of diversity; total cover; total density; *Typha* biomass, stem length and density; *Phragmites* biomass, stem length and density; *Juncus* biomass, stem length and density; pH of water and sediment; conductivity; depth; and, D.O. Correlations deemed significant (2-tailed) at the 0.05 (*) and 0.01 (**) levels were as follows:

	pH of Water	pH of Sed.	Conductivity	Depth	D.O.
Species Richness	** 0.260		* 0.188		*- 0.186
Margalef's Index	** 0.300		** 0.335	** 0.446	** - 0.390
Total Cover		** 0.337			**- 0.390
Total Density	* 0.180			*- 0.182	
			Typha latifolia		
T. Biomass		**- 0.5	**- 0.191	**- 0.467	**- 0.224
Stem Length				** 0.261	
T. Density	*- 0.183	**- 0.5	**- 0.191	** - 0.292	** - 0.243
			Phragmites australis		
P. Biomass	** 0.249		**- 0.350	**- 0.553	
Stem Length	** 0.409	** 0.400			** 0.244
P. Density	**- 0.437	** - 0.400	**- 0.454	**- 0.519	
			Juncus effusus		
J. Biomass	** 0.285	** 0.600	** 0.595	** 0.432	**- 0.436
Stem Length	* 0.188	** 0.500	** 0.230	** 0.336	**- 0.873
J. Density	** 0.580	** 0.410	** 0.353	** 0.217	

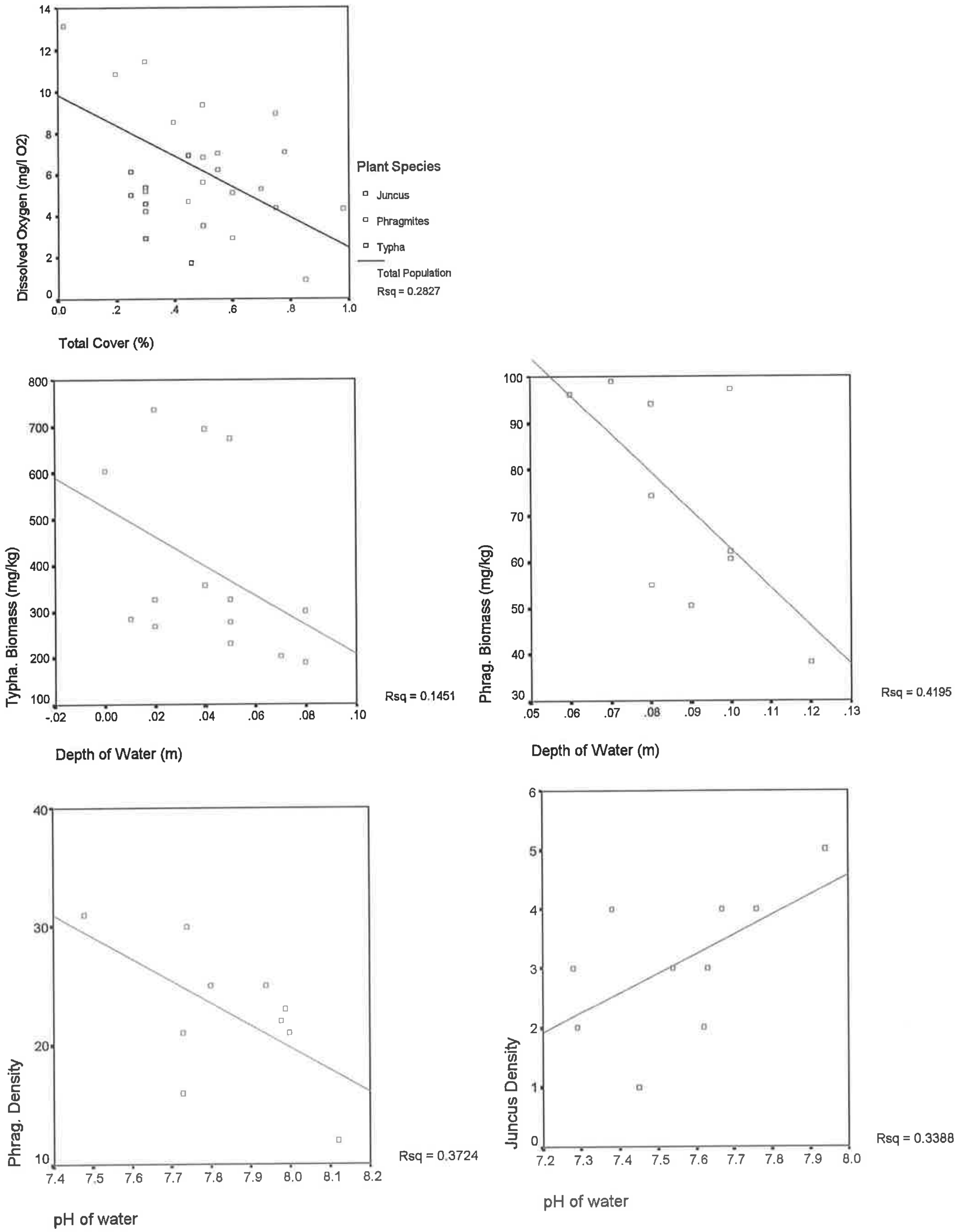
Species richness and Margalef's Index of diversity were positively correlated with pH of the water column, conductivity and depth. This indicates increasing plant richness and diversity with increasing water depth and corresponding increasing pH and conductivity. Species richness and diversity were negatively correlated with D.O. but this relates to decreasing D.O. concentrations with increasing depth. D.O. also is negatively correlated with total cover and increasing *Typha* and *Juncus* biomass indicating a fall in D.O. concentrations with increasing vegetative cover. Total density decreases with water depth as does *Typha* and *Phragmites* densities and associated biomass. Similarly, *Typha* and *Phragmites* densities decrease with increasing pH. Alternatively, *Juncus* density and biomass increase with increasing depth but this is due to planting patterns for this plant in the TMF wetland.

Figure 8.1 illustrates scatterplots of D.O. versus total cover, *Typha* and *Phragmites* biomass versus depth, and *Phragmites* and *Juncus* densities versus pH. These graphs outline the least-squares linear regression line and the square of the correlation coefficient (Rsq) which indicates the proportion of the variability of the dependant variable explained by the regression model.

8.2.2 Spearman Rank Correlation Analysis for Ecological Parameters and Metal Concentrations in the Water, Sediments and Plant Tissues

Spearman rank correlation analysis was conducted for a range of ecological parameters and total Cd, Fe, Mn, Pb and Zn concentrations in the water, sediments and plants of the TMF wetland including: species richness; Margalef's Index of diversity; total cover; total density; *Typha* biomass, stem length and density; *Phragmites* biomass, stem length and density; *Juncus* biomass, stem length and density; and metal concentrations of water, sediment, and plant tissues. Correlations deemed significant (2-tailed) at the 0.05 (*) and 0.01 (**) levels were as follows:

Fig. 8.1 Scatterplots of correlations between physiocochemical parameters of the water column and ecological parameters in the TMF wetland in 1999.



Typha latifolia Region

	Fe		Mn		Pb	
	Rhizomes	Stems	Sediment	Roots	Sediment	Rhizomes
Species Richness	* - 0.680			* - 0.603		
Margalef's Index			* - 0.248			
Total Density					* - 0.582	
T. Biomass	* 0.643	*0.657				
T. Stem Length			* - 0.664			* - 0.594

Phragmites australis Region

	Fe		Mn			Pb	Zn		
	Water	Roots	Wat.	Sed.	Roots	Wat.	Wat.	Sed.	Roots
Species Richness		*-0.665						-.70	
Total Cover	*-0.702								
P. Density	*0.689	**-.817	*.652	*-.74	**-.90	*.698	*.683	*-.67	*-.695

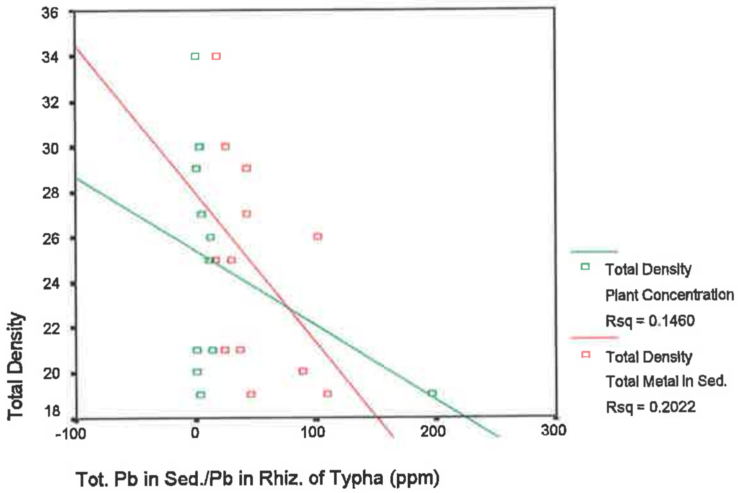
Juncus effusus Region

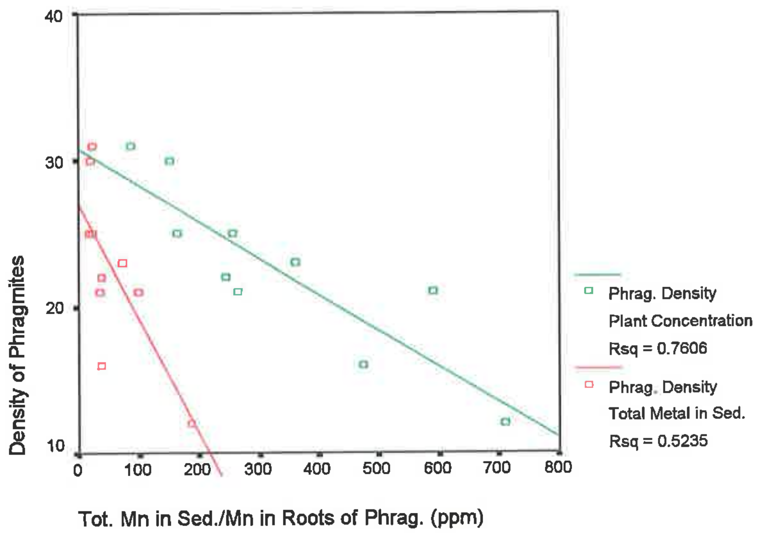
	Cd		Fe		Pb	Zn
	Sed.	Roots	Sed.	Stems	Sed.	Sed.
Species Richness	*- 0.613		*- 0.642			
Margalef's Index	* - 0.240					
Total Density	*- 0.667			** 0.815	*- 0.694	*- 0.639
J. Density		** 0.899				
J. Biomass				*- 0.667		

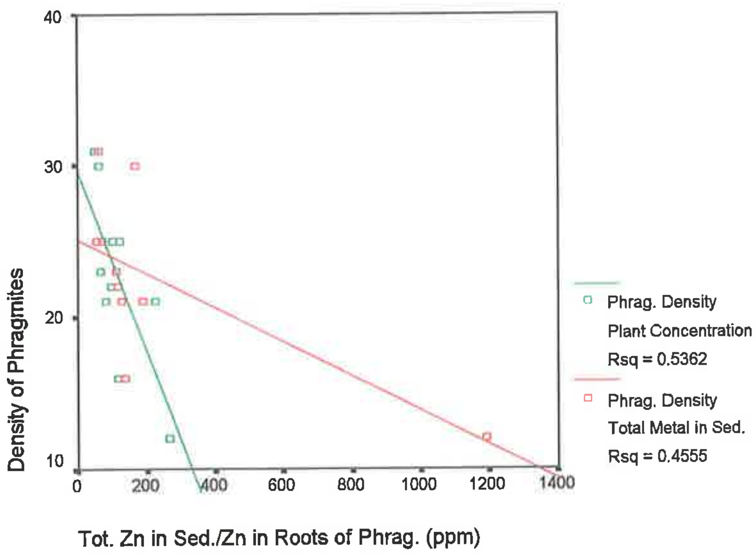
Species richness was negatively correlated with Fe and Mn concentrations in roots and rhizomes of *Typha latifolia* and negatively correlated with Fe concentrations in the roots of *Phragmites australis*. Species richness also was negatively correlated with Cd, Fe and Zn concentrations in the wetland sediments. Similarly Margalef's Index of diversity was negatively correlated with Cd and Mn concentrations in the wetland sediments.

Total density decreased with increasing Pb concentrations in the sediments and in the rhizomes of *Typha latifolia*. Figure 8.2 illustrates scatterplots of density versus total metals in sediments and metal concentrations in the tissues of *Typha* and *Phragmites*. *Phragmites* density decreased with increasing Fe, Mn and Zn concentrations in the roots of this plant, and with Mn and Zn concentrations in the sediments. Similarly total density decreased with increasing Cd, Pb and Zn in the sediments of the *Juncus*

Fig. 8.2 Scatterplots of correlations between metal concentrations of sediments and vegetation densities in the TMF wetland in 1999.







region of the TMF wetland. Figure 8.3 illustrates scatterplots of density versus total metals in sediments of the *Juncus* region.

8.3 CORRELATION ANALYSIS FOR HYDROLOGICAL AND PHYSICO-CHEMICAL INDICATORS

Bivariate correlation analysis was conducted to measure the strength of the linear association between hydrological and physico-chemical variables in the water column of the TMF wetland in 1999 and 2000. Pearson correlation coefficients were calculated for data with normal distributions having log transformed data prior to analysis if necessary. ANOVA analysis was used to test whether significant correlations exhibited linear relationships and then the least-squares linear regression line and the square of the correlation coefficient (to determine the proportion of the variability of the dependant variable explained by the regression model) were calculated.

Pearson correlation analysis was conducted for the following range of hydrological and physico-chemical variables for the 1999 and 2000 water chemistry data: pH of water column and sediments; conductivity, D.O.; temperature; depth; L.O.I.; and Cd, Fe, Mn, Pb and Zn concentrations of the water column. Correlations deemed significant (2-tailed) at the 0.05 (*) and 0.01 (**) levels were as follows:

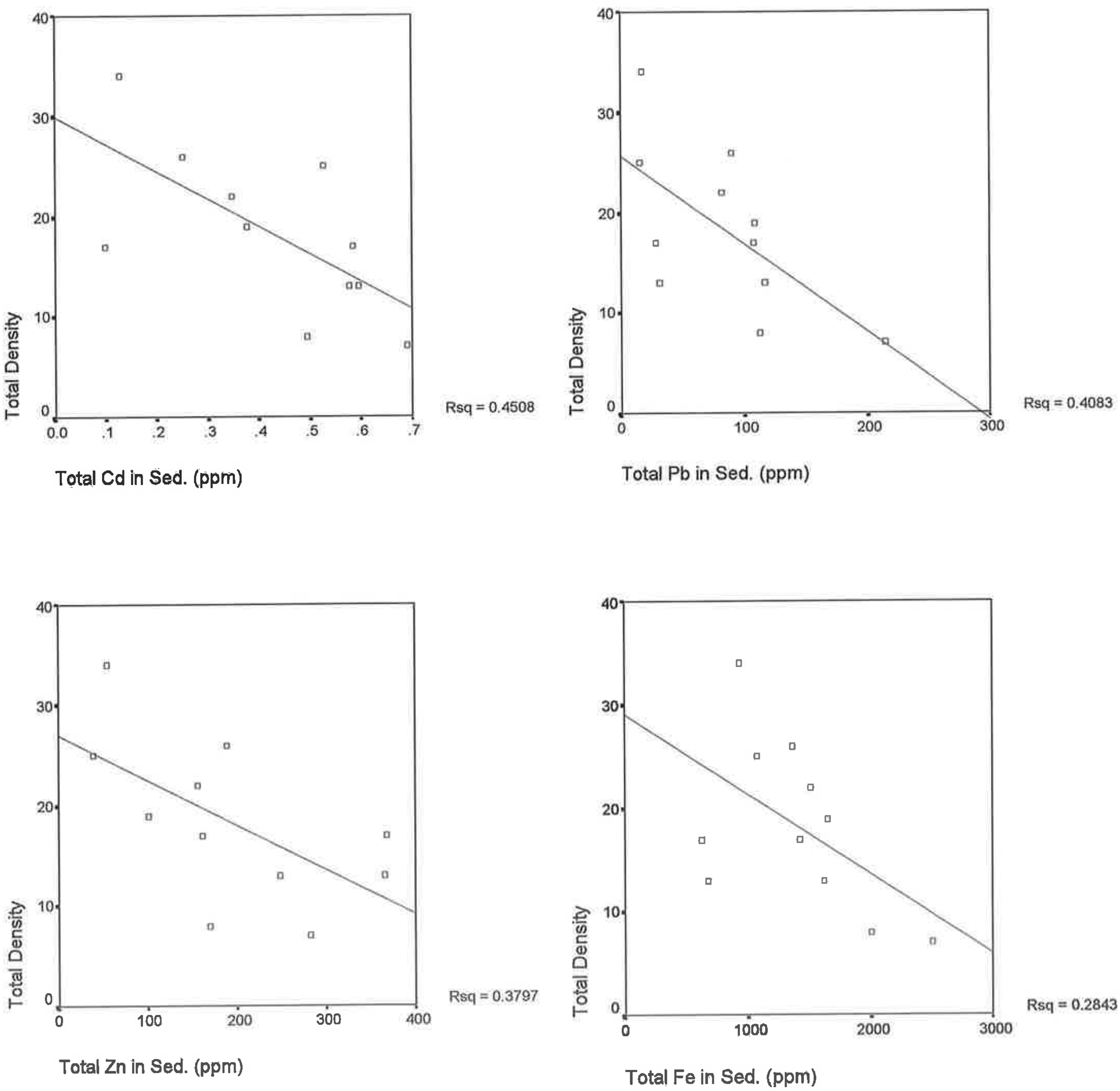
Water Chemistry in 1999

	pH Wat.	pH Sed.	Fe in Wat.	Mn in Wat.	Pb in Wat.	Zn in Wat.
pH of Water		*0.859	**- 0.468	** - 0.532		* - 0.396
Depth	*0.668	*0.636	*- 0.381	** - 0.553		* - 0.414
Temp.			*0.360	**0.346	*0.458	

Seasonal Water Chemistry in 1999-2000

	pH Water	D.O.	Fe in Water	Mn in Water
Conductivity	*0.369	**0.432		
Depth			* - 0.498	* - 0.478

Fig. 8.3 Scatterplots of correlations between metal concentrations of sediments and vegetation densities in the TMF wetland, in 1999.



Water Chemistry above Sediments subjected to Metal Extractions in 2000

	Depth	pH of Sed.	Fe in Wat.	Mn in Wat.	Pb in Wat.	Zn in Wat.
Cond.	**0.631		** - 0.826	** - 0.744	** - 0.700	** - 0.855
Depth			** - 0.958	** - 0.988	** - 0.996	
L.O.I.		- 0.329				

There is a positive correlation between the depth of water in the TMF wetland and the pH of the water column and of sediments. There also is a positive correlation between the pH of the water column and the pH of the sediments and conductivity. Therefore, as water depth increases, the pH of the water column and sediments increase as does conductivity. The results of the seasonal analysis also indicates a positive correlation between conductivity and D.O. which points to increasing D.O. levels with depth. Linear regression lines and the square of the correlation coefficient for depth and pH, pH and conductivity, and conductivity and D.O. are illustrated in Figure 8.4.

As pH and depth increase, the Fe, Mn, Pb and Zn concentrations of the water column decrease as indicated by the negative correlations between these metals and depth and pH throughout all the sampling events. Figure 8.5 illustrates linear regression lines and Rsq values for pH and Fe, Mn and Zn concentrations of the water column in 1999. Figure 8.6 illustrates linear regression lines and Rsq values for depth and Fe, Mn and Zn concentrations of the water column in 1999 and seasonally.

Alternatively, temperature is positively correlated with the concentrations of Fe, Mn and Pb in the water column in 1999. Linear regression lines and Rsq values for temperature and Fe, Mn and Pb concentrations of the water column are illustrated in Figure 8.7.

Finally, the organic matter of the sediment, which is measured by Loss on Ignition, was negatively correlated with sediment pH indicating a decrease in sediment pH with the rising content of organic matter in the sediments.

8.4 CORRELATION ANALYSIS FOR SEDIMENT INDICATORS

Bivariate correlation analysis was conducted to measure the strength of the linear association between sediment variables, and hydrological and physico-chemical

Fig. 8.4 Linear regression lines for physico-chemical parameters (pH and conductivity) in 1999 and seasonally in 1999 and 2000.

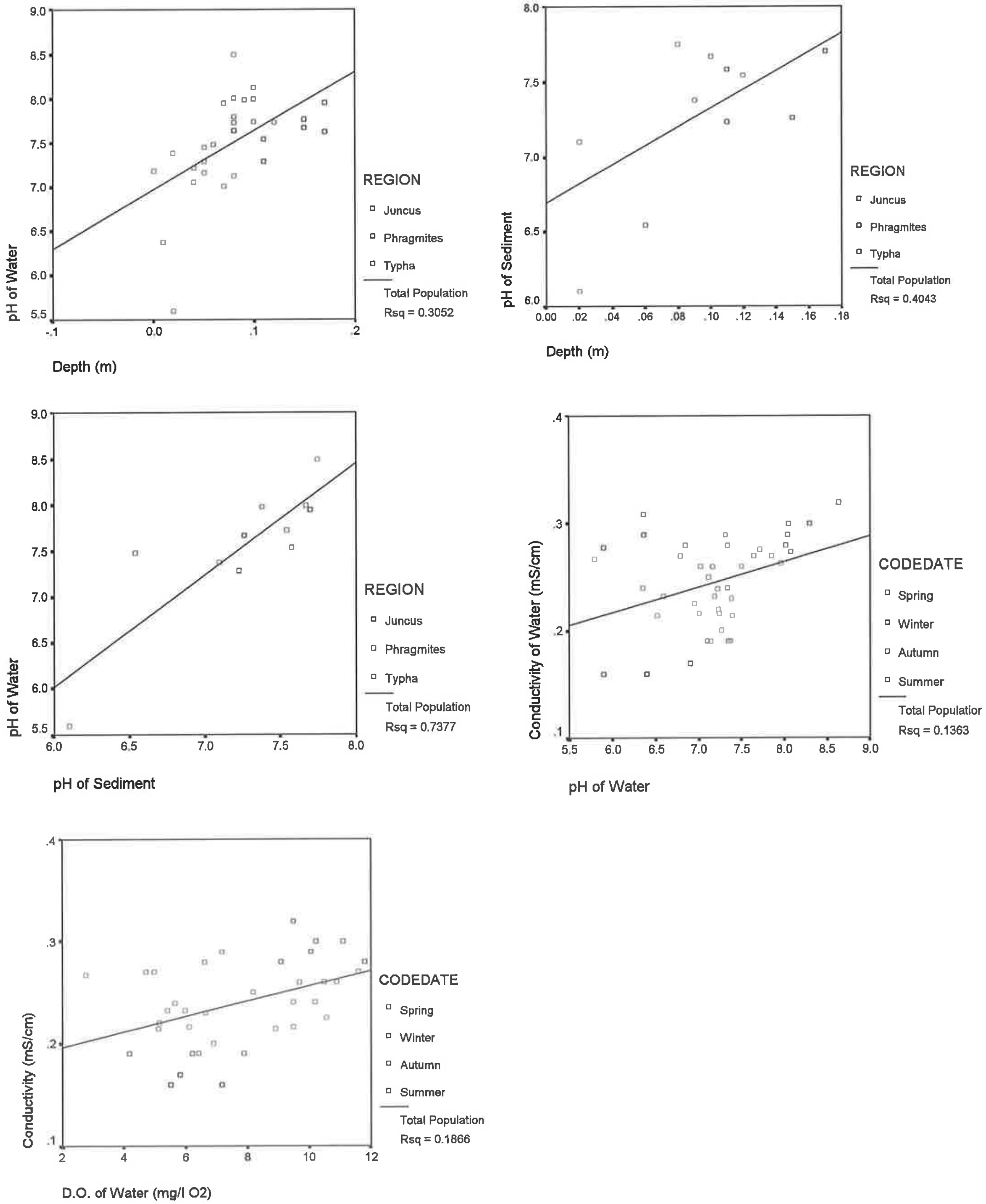


Fig. 8.5 Linear regression lines for Fe, Mn and Zn in the water column versus pH of water, 1999.

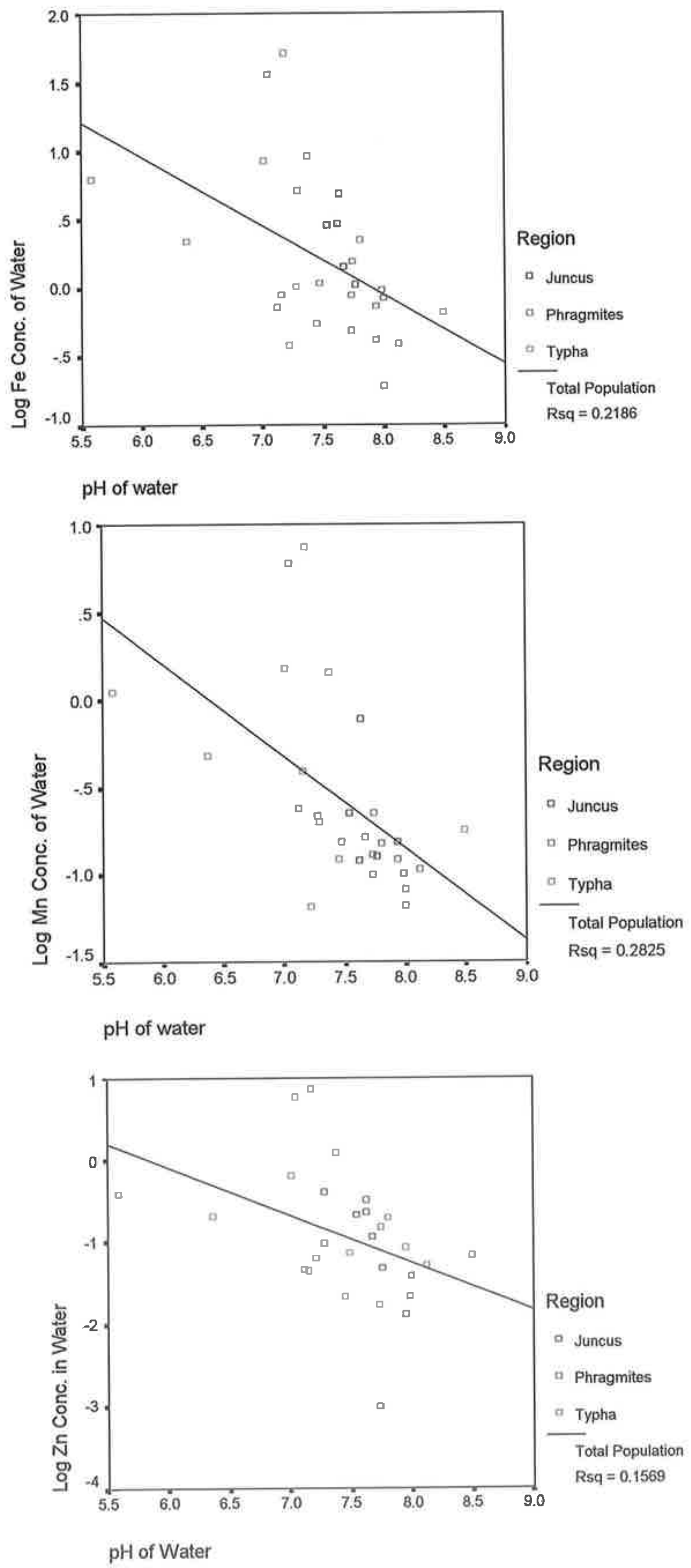


Fig. 8.6 Linear regression lines for Fe, Mn and Zn in the water column and water depth in 1999 and seasonally in 1999 and 2000.

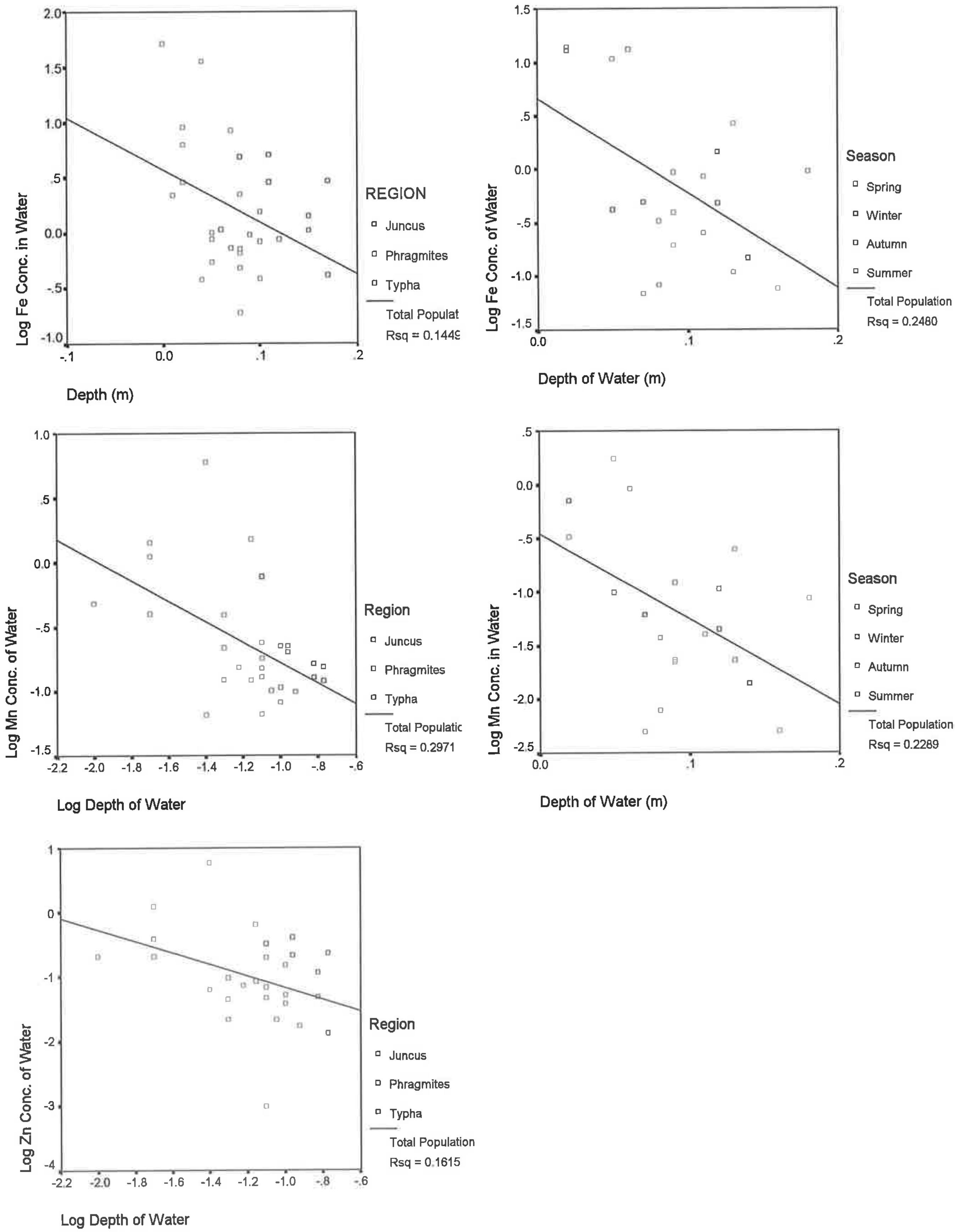
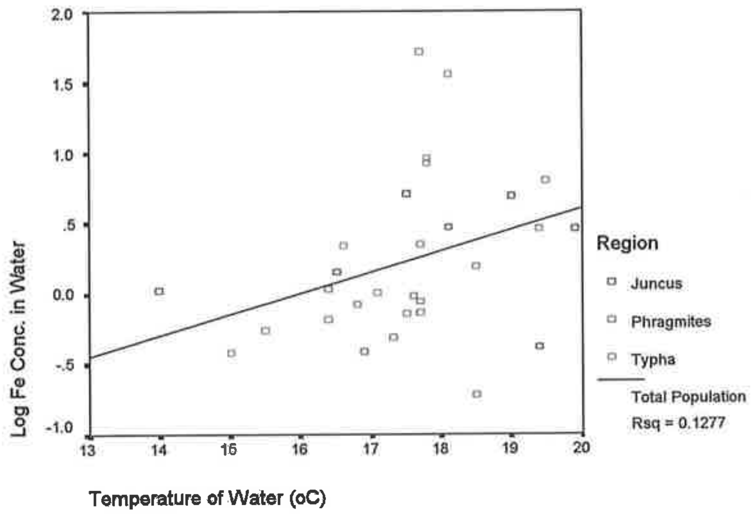
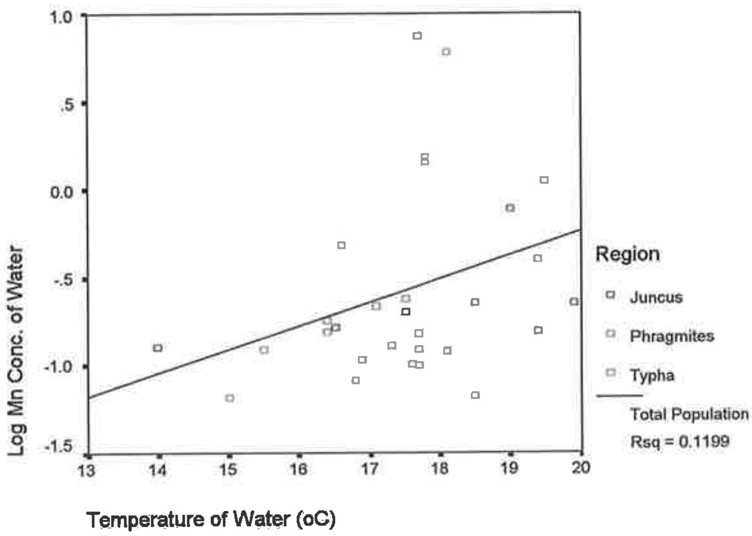
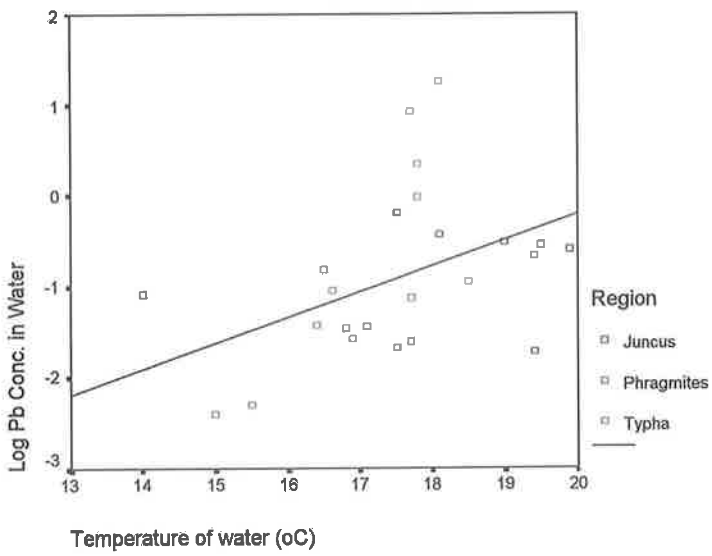


Fig. 8.7 Linear regression lines for Fe, Mn and Pb in the water column and water temperature in 1999.







variables in the water column of the TMF wetland in 1999 and 2000. Pearson correlation coefficients were calculated for data with normal distributions and ANOVA analysis was used to test whether significant correlations exhibited linear relationships and then regression lines and associated Rsq values were calculated.

Pearson correlation analysis was conducted for total Cd, Fe, Mn, Pb and Zn in the sediments in 1999 and metal extractions (ion exchangeable, reducible, oxidisable and residual fractions, total metals and free-metal ion concentrations) for all five metals in the sediments in 2000 with the following range of hydrological and physico-chemical variables: Cd, Fe, Mn, Pb and Zn concentrations in the water column; depth; pH of water and sediments; conductivity; D.O.; LOI; and, sulphate concentrations in the water column. Correlations deemed significant (2-tailed) at the 0.05 (*) and 0.01 (**) levels were as follows:

Sediment Total Metals in 1999

	Cd in Soils	**Fe in Soils**	**Mn in Soils**	**Pb in Soils**	**Zn in Soils**
Metal in Water Column	(Cd in Wat.) *0.654	(Fe in Wat.) * - 0.389		(Pb in Wat.) * - 0.385	
Depth				*0.426	*0.650
pH of Water					*0.431
D.O.			*0.378		*- 0.356

Metal Extractions in 2000

	Cd		**Fe**			**Mn**	**Pb**	**Zn**
	Ext 1	**Ext 2**	**Ext 1**	**Ext 2**	**Ext 4**	**Ext 4**	**Ext 2**	**Ext 3**
Metal in Wat.							(Pb in Wat.) * - .368	
Depth	**.683	*.431					.364	*.451
pH of Water			**.461	*.433	**.685	**.503		
Cond.	**.747							
Sulphate								(Tot Zn Sed) * - .341

Total Cd in sediments was positively correlated with Cd in the water column (although the data points are few) whereas total Fe and Pb in sediments were negatively correlated with Fe and Pb in the water column. Therefore, as concentrations of Fe and Pb in sediments increase, Fe and Pb concentrations in the water column decrease. Similarly, increasing Pb concentrations in the reducible fraction correlates with decreasing Pb in the water column. Increasing Pb and Zn in sediments are also positively correlated with water depth, therefore, Pb and Zn concentrations in sediments increase as water depth increases. Increasing Cd in the ion-exhangeable and reducible fractions and increasing Zn in the oxidisable fraction are also positively correlated with water depth. This may indicate a general increase in sediment metal concentration with water depth. Figure 8.8 illustrates linear regression lines and Rsq values for total Cd, Fe and Pb in sediments and the metal concentration in the water column, and for total Pb and Zn in sediments and water depth.

There were positive correlations between the pH of the water column and total Zn concentration in sediments, Fe concentrations in the ion-exchangeable, reducible and residual fractions, and Mn concentrations in the residual fraction. Therefore, as the pH of the water column increases, concentrations of Zn, Fe and Mn increase in the sediments. Figure 8.9 illustrates linear regression lines and Rsq values for metal concentrations in extractions and the pH of the water column.

Finally, sulphate concentration in the water column was negatively correlated with total Zn concentrations in the sediments indicating decreasing sulphate concentrations with increasing Zn in sediments.

8.5 CORRELATION ANALYSIS FOR BIOTIC INDICATORS

Bivariate correlation analysis was conducted to measure the strength of the linear association between biotic variables, and hydrological, physico-chemical and sediment variables in the TMF wetland in 1999. Pearson correlation coefficients were calculated for normal data having log transformed data prior to analysis if necessary. Spearman rank correlation coefficients were calculated for non-normal data. ANOVA analysis was used to test whether significant correlations exhibited linear relationships and then regression lines and associated Rsq values were calculated.

Pearson and Spearman correlation analyses were conducted for Cd, Fe, Mn, Pb and Zn concentrations in the roots, rhizomes and stems of the three wetland plants in 1999 and the following range of hydrological, physico-chemical and sediment variables: Cd, Fe, Mn, Pb and Zn concentrations in the water column and sediments; water

Fig. 8.8 Linear regression lines between Cd, Fe and Pb in the TMF sediments and the water water column, and between Pb and Zn in the sediments and the depth of water in 1999.

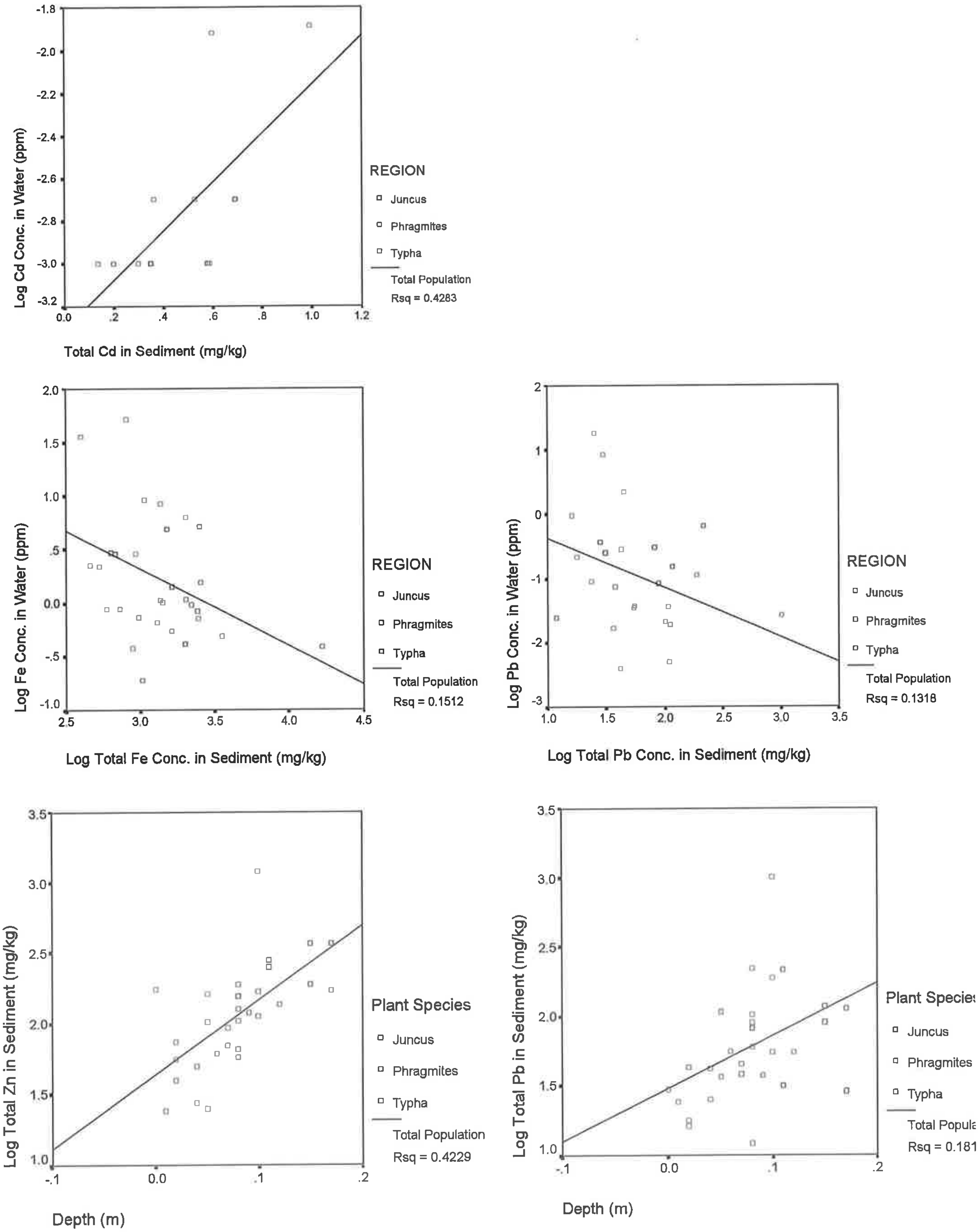
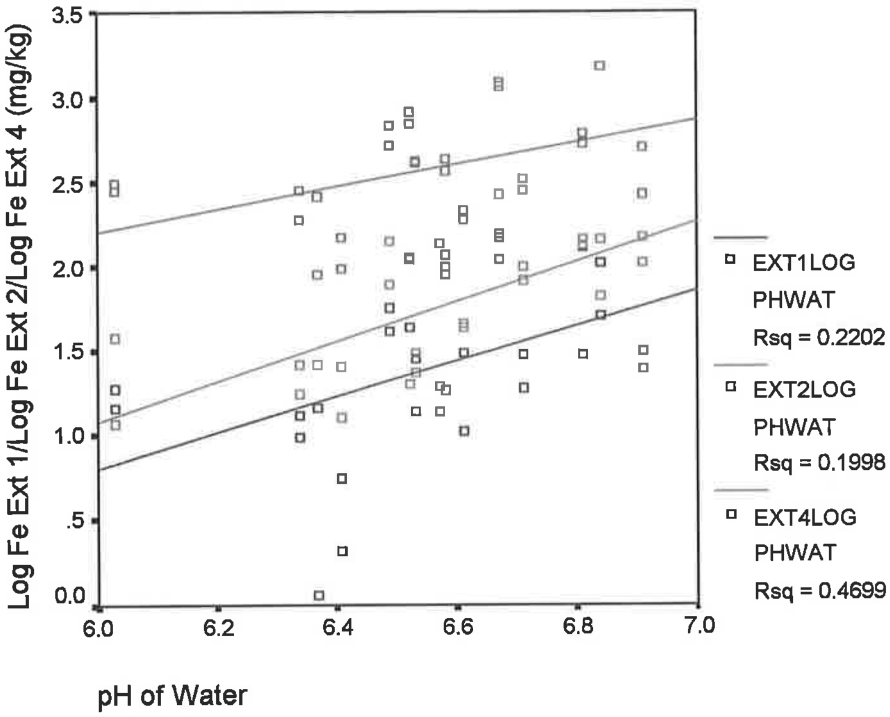
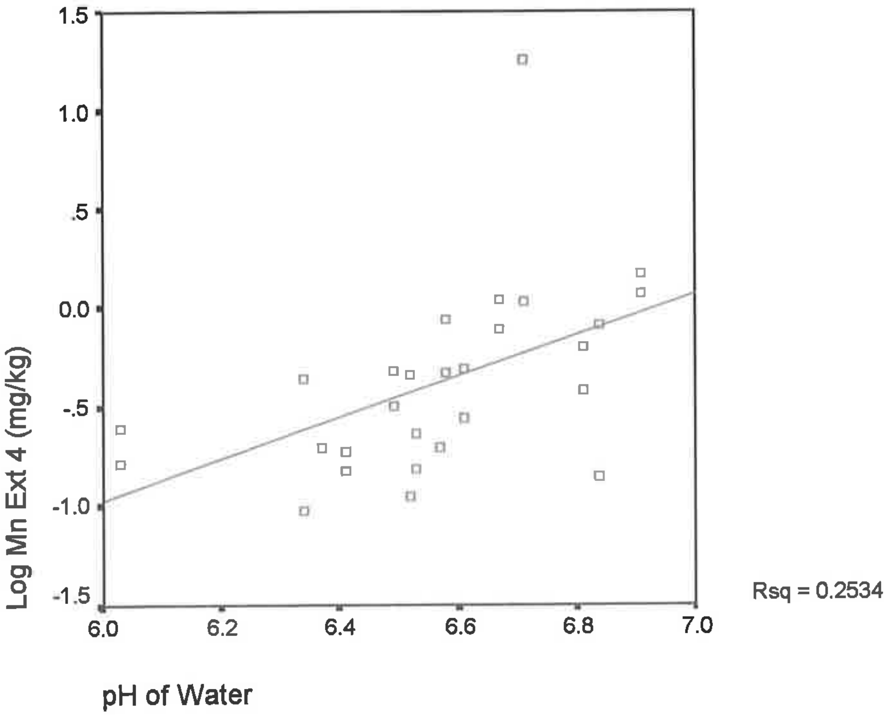


Fig. 8.9 Linear regression lines between Fe and Mn extractions and the pH of the water column in 2000.





depth; pH of water and sediments; conductivity; D.O.; temperature; and, LOI. Correlations deemed significant (2-tailed) for *Typha latifolia* at the 0.05 (*) and 0.01 (**) levels were as follows:

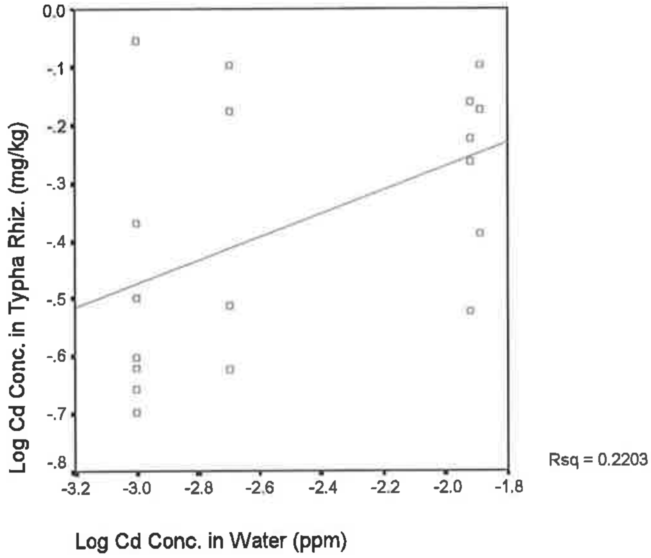
Typha latifolia	Cd in Plant Tissue	Fe in Plant Tissue	Mn in Plant Tissue	Pb in Plant Tissue	Zn in Plant Tissue
			Roots		
Cd in Sed.	* 0.347 *s*				
Mn in Sed.			* 0.433 *s*		
pH in Water				* 0.375	
Conductivity				** - 0.532	
			Rhizomes		
Cd in Water	* 0.469				
Cd in Sed.	* 0.382 *s*				
Mn in Sed.			** 0.474		
pH in Water				* 0.474	
pH in Sed.					
Depth					* -0.397 *s*
Conductivity					* -0.379
			Stems		
Mn in Water			** 0.449 *s*		
Mn in Sed.			* 0.412		
Pb in Sed.				** 0.646	
pH in Sed.		* - 0.772 *s*			** -0.949
Depth		* - 0.444			* - 0.378
D.O.				**- 0.679	
Temperature				**- 0.657	
Conductivity					*- 0.353 *s*

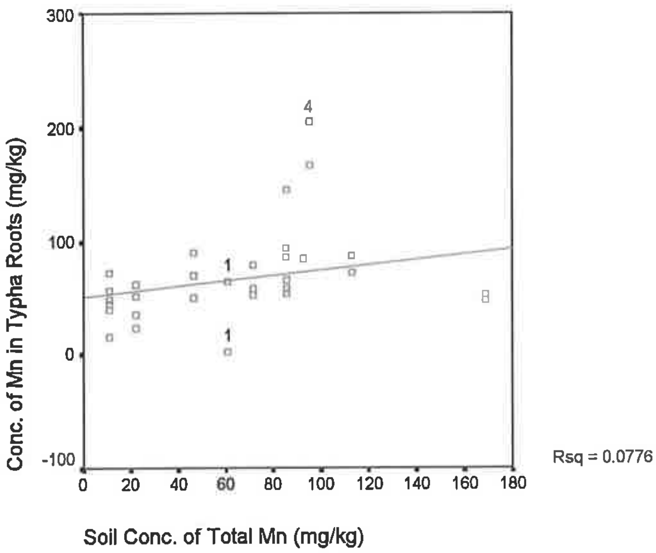
s = Spearman rank correlations, all others are pearson correlations.

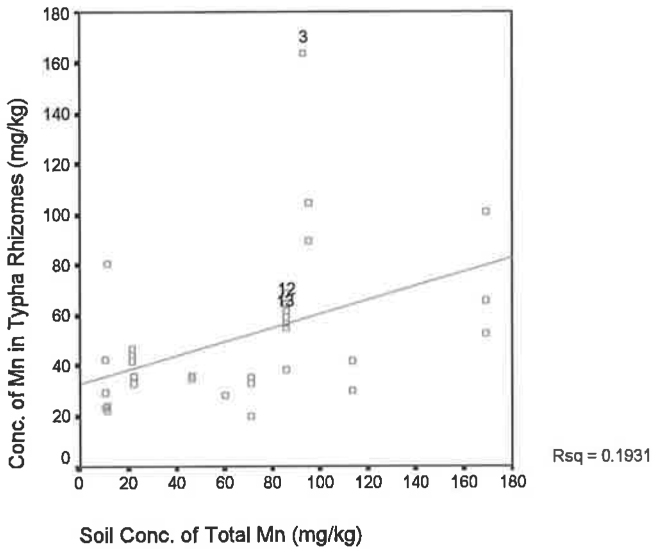
The concentrations of Cd and Mn in the rhizomes and stems of *Typha latifolia* are positively correlated with Cd (though few data) and Mn concentrations in the water column. Similarly, concentrations of Cd in *Typha* roots and rhizomes, and of Mn in *Typha* roots, rhizomes and stems, increase with increasing Cd and Mn concentrations in sediments. Pb concentrations in *Typha* stems also increase with increasing Pb concentrations in sediments. Figure 8.10 illustrates linear regression lines and Rsq values for metal concentrations in the sediments and the metal concentrations of *Typha* tissues.

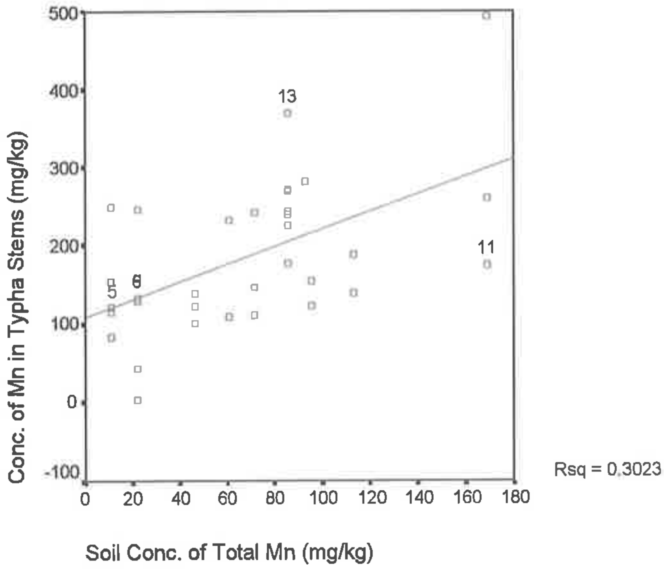
The concentrations of Pb in the roots and rhizomes of *Typha* are positively correlated with the pH of the water column, and Fe and Zn concentrations in *Typha* stems are negatively correlated with sediment pH (though few data). Zn concentrations in *Typha* rhizomes and stems are also negatively correlated with conductivity. Fe and Zn concentrations in *Typha* stems decrease with increasing water depth. Finally, Pb

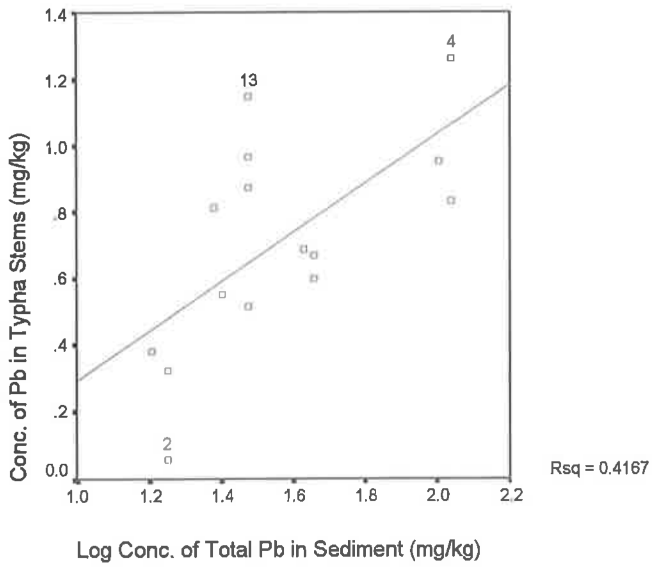
Fig. 8.10 Linear regression lines between metals in plant tissues of *Typha latifolia* and metals in sediments in 1999.











concentrations in *Typha* stems decrease with increasing temperature and D.O. Figure 8.11 illustrates linear regression lines and Rsq values for physico-chemical parameters in the water column and the metal concentrations of *Typha* tissues.

Correlations deemed significant (2-tailed) for *Phragmites australis* at the 0.05 (*) and 0.01 (**) levels were as follows:

Phragmites australis	**Cd in Plant Tissue**	**Fe in Plant Tissue**	**Mn in Plant Tissue**	**Pb in Plant Tissue**	**Zn in Plant Tissue**
			Roots		
Pb in Sed.				* 0.467	
D.O.	* 0.541			* 0.486 *s*	
Temperature	** - 0.563			* - 0.423 *s*	
			Rhizomes		
D.O.	* 0.523				
Temperature	*- 0.537				
			Stems		
Zn in Sed.					** - 0.524
D.O.	* 0.521	* 0.651		* 0.776	
Temperature	** - 0.684				
pH in Water	** - 0.686			** - 0.860	
Conductivity	** - 0.713	** - 0.873			

s = Spearman rank correlations, all others are pearson correlations.

The concentrations of Pb in the roots of *Phragmites australis* are positively correlated with Pb concentrations in the sediments. Alternatively, the concentrations of Zn in the stems of *Phragmites* are negatively correlated with Zn concentrations in the sediments. Figure 8.12 illustrates linear regression lines and Rsq values for metal concentrations in the sediments and the metal concentrations of *Phragmites* tissues.

D.O. concentrations are positively correlated with Cd concentrations in the roots, rhizomes and stems of *Phragmites,* with Fe concentrations in the roots, and with Pb concentrations in the roots and stems of *Phragmites.* Figure 8.13 illustrates linear regression lines and Rsq values for D.O. and the metal concentrations of *Phragmites* tissues.

Temperature is negatively correlated with Cd concentrations in the roots, rhizomes and stems of *Phragmites* and with Pb concentrations in the roots of *Phragmites.* The pH of the water column also is negatively correlated with Cd and Pb concentrations in the stems of *Phragmites.* In addition, conductivity is negatively correlated with Cd

Fig. 8.11 Linear regression lines between metals in plant tissues of *Typha latifolia* and physico-chemical parameters of the water column in 1999.

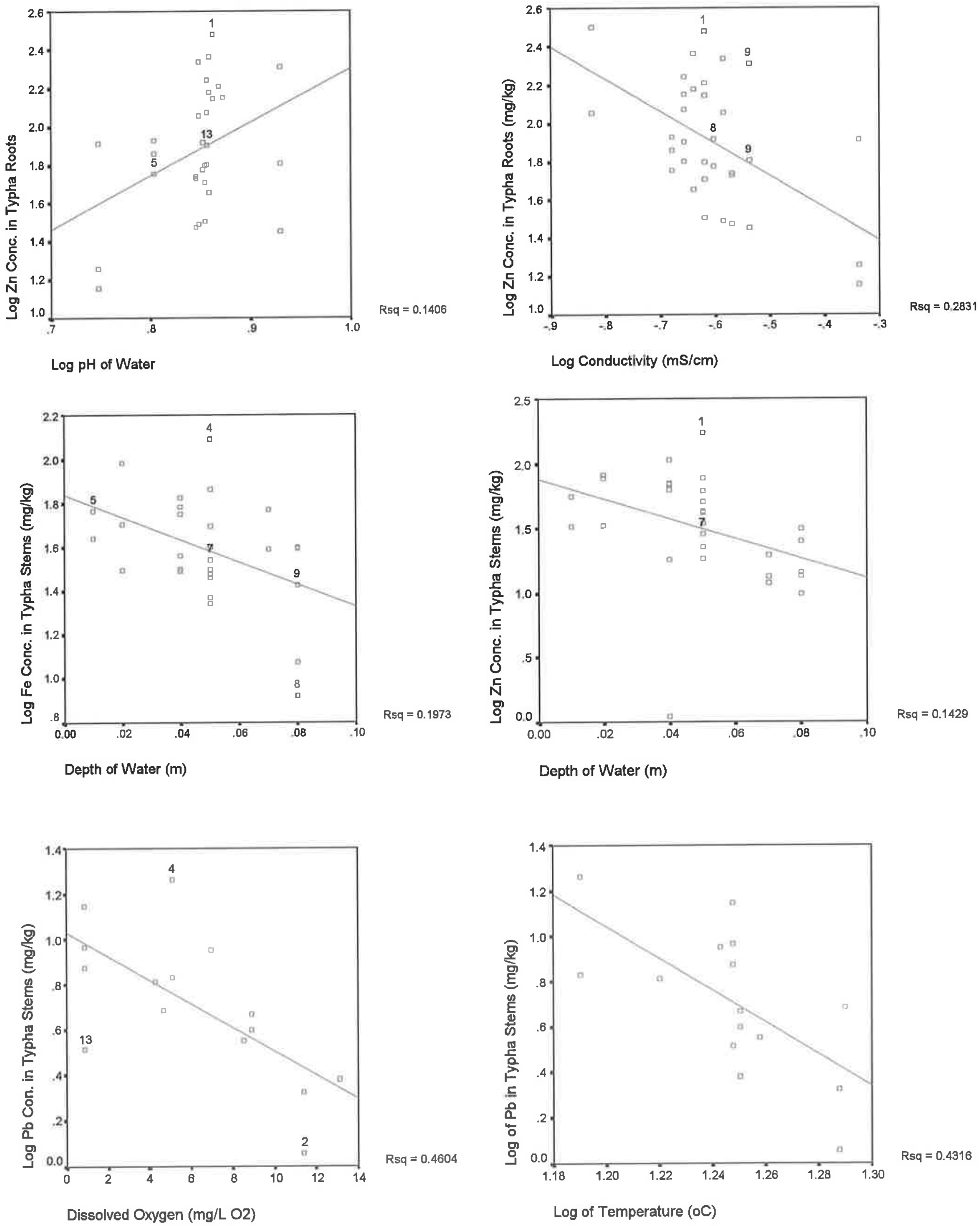
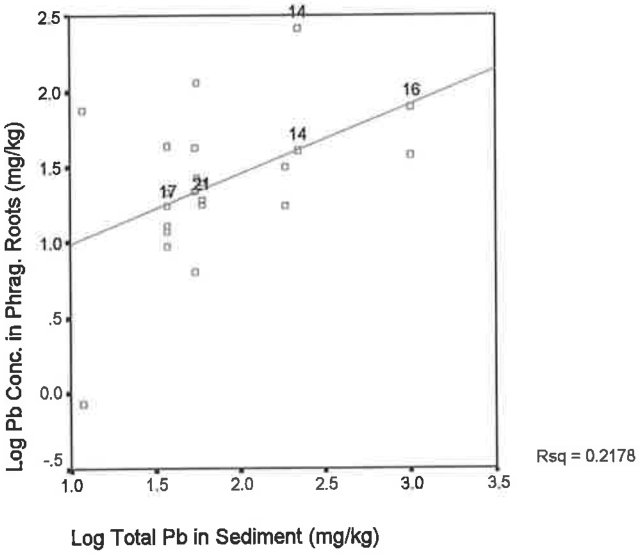


Fig. 8.12 Linear regression lines between metals in plant tissues and metals in sediments of *Phragmites australis* in 1999.



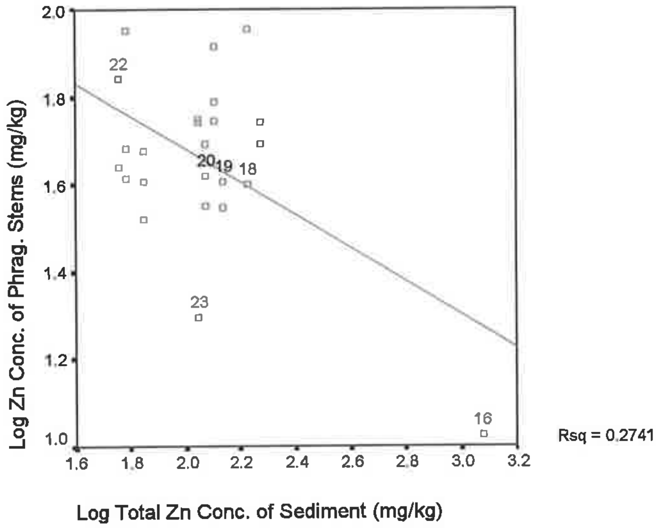
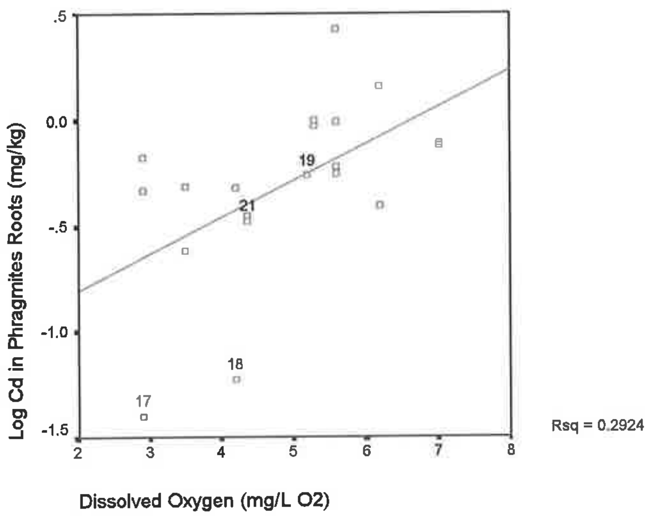
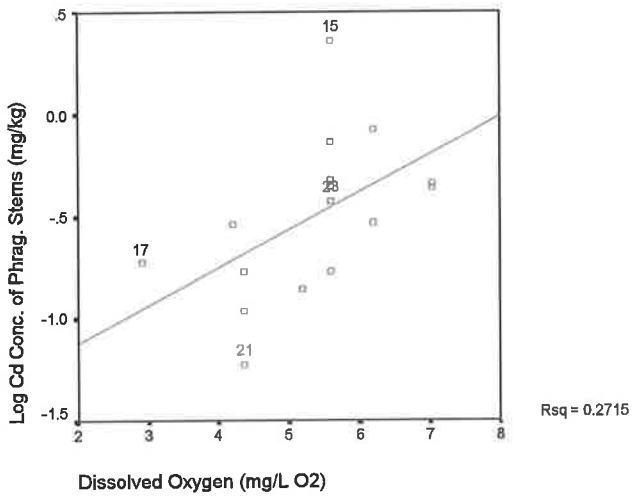
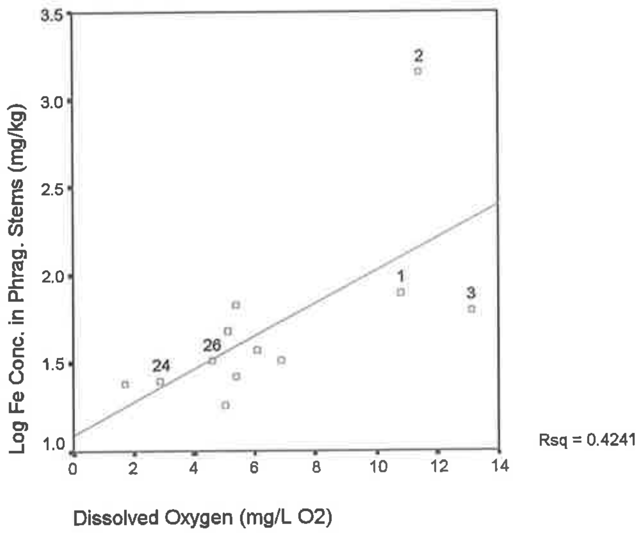


Fig. 8.13 Linear regression lines between metals in plant tissues of *Phragmites australis* and D.O.







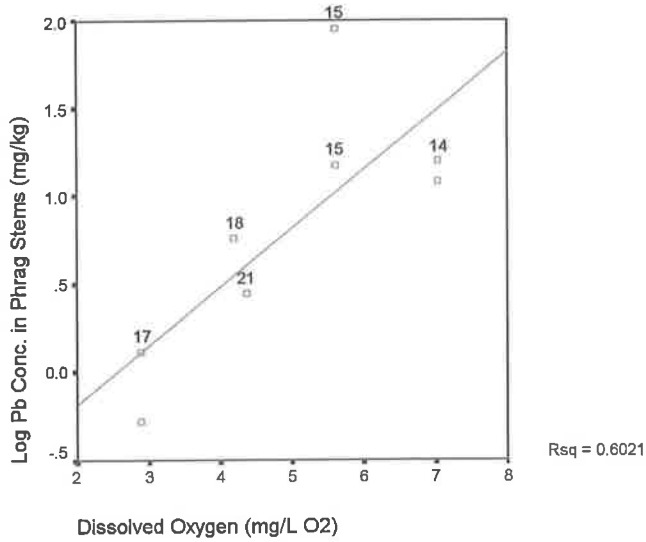
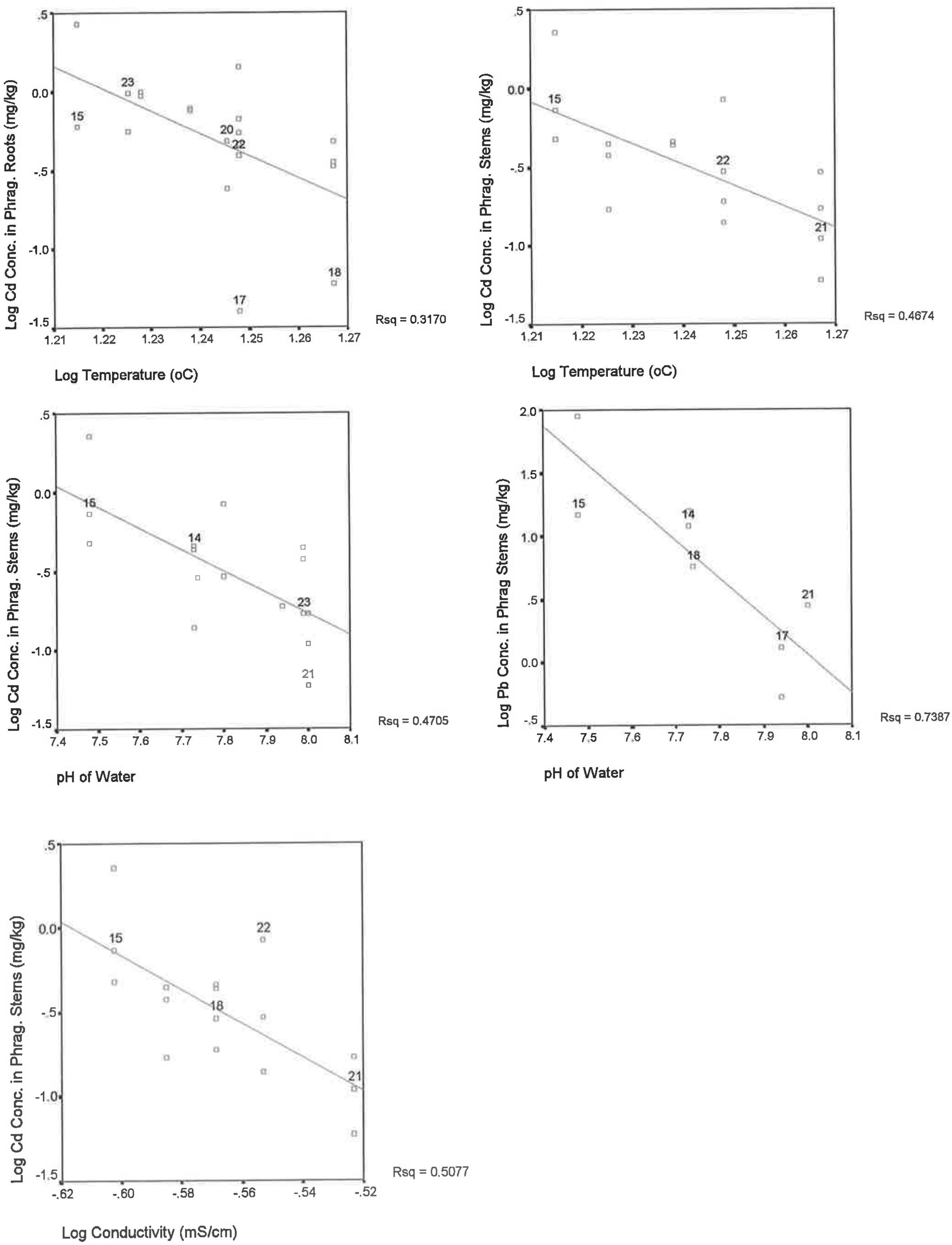


Fig. 8.14 Linear regression lines between metals in plant tissues of *Phragmites australis* and physiocochemical parameters of water column in 1999.



and Fe concentrations in the stems of *Phragmites*. Figure 8.14 illustrates linear regression lines and Rsq values for temperature, pH and conductivity and the metal concentrations of *Phragmites* tissues.

Correlations deemed significant (2-tailed) for *Juncus effusus* at the 0.05 (*) and 0.01 (**) levels were as follows:

Juncus effusus	**Cd in Plant Tissue**	**Fe in Plant Tissue**	**Mn in Plant Tissue**	**Zn in Plant Tissue**
		Roots		
Conductivity				- 0.747
L.O.I.	* - 0.647 *s*			
Temperature	* 0.622 *s*			
pH Water			** 0.997	
Depth			* 0.707	
		Stems		
Conductivity		** - 0.873		
Temperature	* 0.705			
D.O.		** 0.651 *s*		
L.O.I.	* - 0.702			

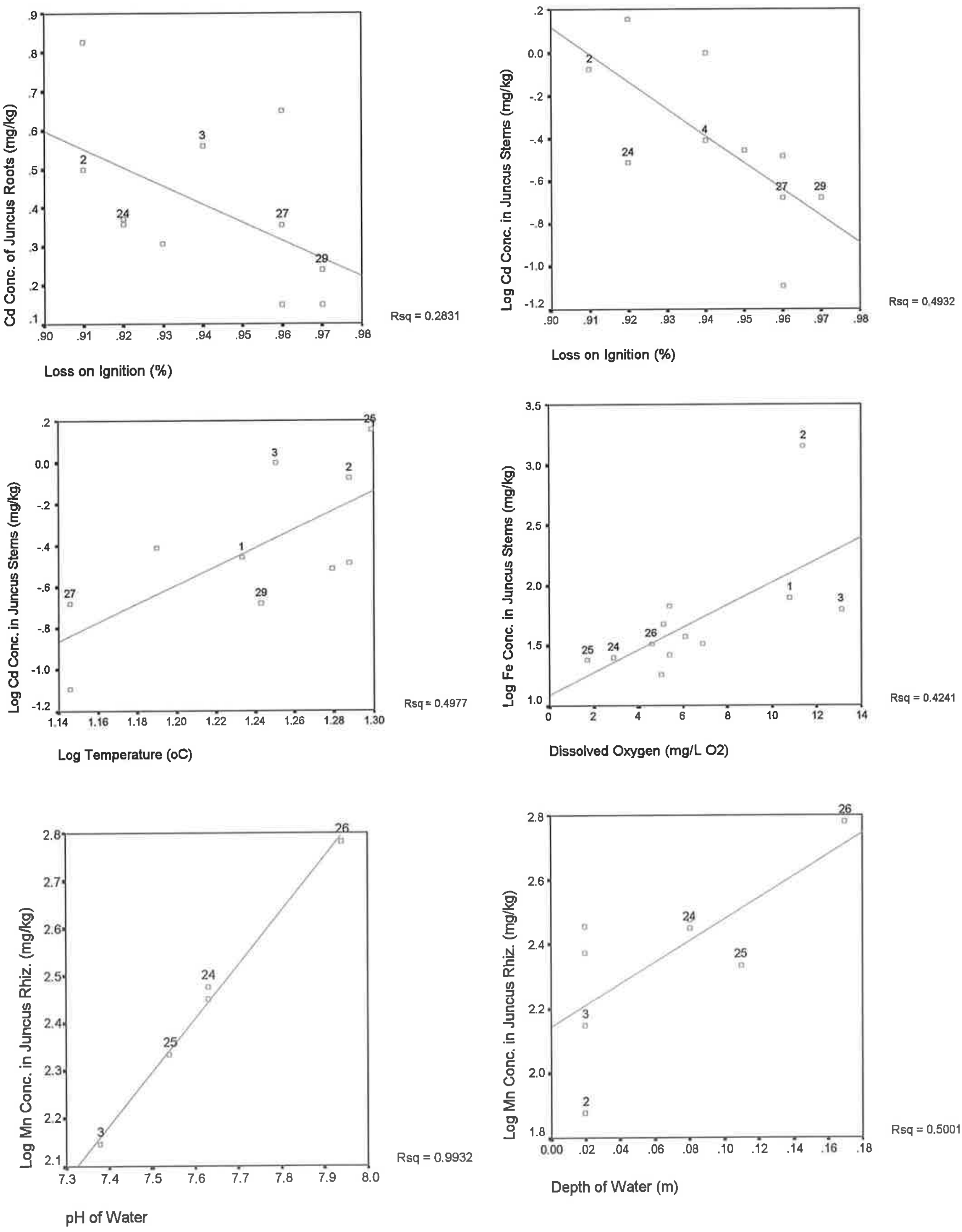
s = Spearman rank correlations, all others are pearson correlations.

Organic content is negatively correlated with Cd concentrations in the roots and stems of *Juncus effusus*. Therefore as organic matter rises in the sediments, Cd concentrations in the roots and stems of *Juncus* decrease. Alternatively, temperature is positively correlated with Cd concentrations in the roots and stems of *Juncus*. Similarly as depth and pH of the water column increase, Mn concentrations in the roots of *Juncus* increase. As conductivity increases, Zn and Fe concentrations in the roots and stems of *Juncus* decrease. Finally, as D.O. increases Fe in *Juncus* stems also increases. Figure 8.15 illustrates linear regression lines and Rsq values for physico-chemical parameters and the metal concentrations of *Juncus* tissues.

8.6 CORRELATION ANALYSIS FOR SILVERMINES WATER CHEMISTRY AND SEDIMENT INDICATORS

Multivariate correlation analysis was conducted to measure the strength of the linear association between hydrological, physico-chemical and sediment variables in Silvermines wetland in 2000. Pearson correlation coefficients were calculated for data with normal distributions having log transformed data prior to analysis if necessary.

Fig. 8.15 Linear regression lines between metals in plant tissues of *Juncus effusus* and physiocochemical parameters of water column in the 1999.



The least-squares linear regression lines and Rsq values were calculated for each significant bivariate correlation but do not show strong linear relationships due to limited physico-chemical data points. Pearson correlation coefficients were calculated for Silvermines wetland for comparison purposes with the TMF wetland.

8.6.1 Pearson Correlation Analysis for Physico-chemical Parameters in Silvermines Wetland

Pearson correlation analysis was conducted for the following range of hydrological and physico-chemical variables for the Silvermines water chemistry data in 2000: pH of water column; conductivity, D.O.; temperature; sulphate concentrations; and Cd, Fe, Mn, Pb and Zn concentrations of the water column. Correlations deemed significant (2-tailed) at the 0.05 (*) and 0.01 (**) levels were as follows:

	Sulphate	Cond	Cd in Wat.	Fe in Wat.	Pb in Wat.	Zn in Wat.
pH of Water	**0.851	**0.922	** - 0.811	** - 0.932	** - 0.896	** - 0.932
Sulphate		*0.582		** - 0.983		* - 0.603
Cond.			** - 0.974	** - 0.720	** - 0.998	** - 1.00

As for the TMF wetland, pH concentrations of the water column are positively correlated with conductivity and negatively correlated with Cd, Fe, Pb and Zn concentrations in the water column. Therefore as pH increases, conductivity increases and metal concentrations in the water column decrease. As expected, sulphate concentrations in the water column are positively correlated with conductivity and pH.

8.6.2 Pearson Correlation Analysis for Sediment Parameters in Silvermines Wetland

Pearson correlation analysis was conducted for total and extracted (ion exchangeable, reducible, oxidisable and residual fractions, and free-metal ion concentrations) for all five metals in the sediments in 2000 with the following range of physico-chemical variables: Cd, Fe, Mn, Pb and Zn concentrations in the water column; pH of water; conductivity; D.O.; and, sulphate concentrations. Correlations deemed significant (2-tailed) at the 0.05 (*) and 0.01 (**) levels were as follows:

	Cd					Fe				
	Ext 2	Ext 3	Ext 4	Total	FMI	Ext 1	Ext 2	Ext 3	Total	FMI
Metal in Wat.			*.58			**.73	**-.78	*-.60	**- .68	**-.87
pH of Wat.		**-.72	**-.70		*-56	*-.65	*.64	*.56	**.69	
Cond.			*-.35							
Sulphate	*-.55	**-91	*-.60	*-.55	*-.75	**-.73	**.81	*.59	*.64	**.92

	Pb					Zn
	Ext 2	Ext 3	Ext 4	Total	FMI	FMI
Metal in Wat.			*-.63		*.57	*.63
pH of Wat.	*-.63	*-.55	*.58		**-.85	
Cond.			*.64		*-.62	*-.62
Sulphate	**-.83	**-.68		**-.77	**-.95	**-.79

Cd concentration in the water column at Silvermines was positively correlated with Cd extracted in the residual fraction of the sediments. This is similar to the TMF wetland where Cd concentration in the water column increased with increasing total Cd in the sediments. Fe and Pb concentrations in the water column decrease with increasing concentrations of Fe and Pb in the sediment extractions. Again the same situation occurs for Fe and Pb in the TMF wetland. As expected Pb and Zn free-metal ion concentration is positively correlated with Pb and Zn in the water column.

The pH of the water column is positively correlated with Fe concentrations in extraction 2 and 3, and with total Fe in sediments, and with the Pb concentrations in the residual fraction. Likewise, Fe in extraction 2 and 4, and total Zn in the sediments of the TMF wetland are positively correlated with pH. In Silvermines Cd in extractions 3 and 4, Fe in extraction 1, and Pb in extractions 2 and 3 are negatively correlated with pH. Conductivity is negatively correlated with Cd in extraction 4, and positively correlated with Pb in extraction 4.

Sulphate concentration is negatively correlated with total, extracted and free-metal ion concentrations of Cd and Pb, Fe in the ion-exchangeable fraction, and free-metal ion concentrations of Zn. Fe concentrations in the reducible and oxidisable fractions and total Fe with increasing sulphate concentrations.

8.7 SUMMARY

The findings of the correlation and linear regression analysis were as follows:

- Regarding ecology, water depth is an important parameter influencing species richness and diversity with both rising with increasing depth in the TMF wetland. Alternatively, emergent plant densities (*Typha* and *Phragmites*) decrease with increasing water depth and corresponding increases in the pH of the water column. D.O. also decreases with increasing plant cover and plant biomass.

- Species richness decreased with increasing Fe and Mn concentrations in roots and rhizomes of *Typha latifolia* and *Phragmites australis* and decreased with increasing Cd, Fe and Zn concentrations in the wetland sediments. Plant density decreased with increasing Pb concentrations in the rhizomes of *Typha latifolia* and with increasing Fe, Mn and Zn concentrations in the roots of *Phragmites australis.* Total density also decreased with increasing Cd, Fe, Mn, Pb and Zn in the sediments.

- Regarding water chemistry, the pH of the water column and sediments increase with increasing water depth. Conductivity also increases with increasing pH and D.O. levels. As pH and depth increase, Fe, Mn, Pb and Zn concentrations of the water column decrease throughout all the sampling events. Alternatively, the concentrations of Fe, Mn and Pb in the water column in 1999 increased with increasing temperatures. Decreasing sediment pH also was correlated with the rising content of organic matter in the sediments.

- Regarding sediment geochemistry, increasing concentrations of total Fe and total and extracted Pb in sediments were correlated with decreasing concentrations of Fe and Pb in the water column. Pb and Zn concentrations in sediments increase as water depth increases. Extracted Cd and Zn concentrations also increase with water depth. In addition, concentrations of total and extracted Fe, Mn and Zn in sediments increase as the pH of the water column increases. These results indicate a general increase in sediment metal concentration with increasing water depth and pH and a corresponding decrease in the metal concentrations of the water column. Sulphate concentrations in the water column decreased with increasing Zn concentrations in sediments but sulphate concentrations in the TMF wetland overall were very low.

- Concentrations of Cd in *Typha* roots and rhizomes, and of Mn in *Typha* roots, rhizomes and stems, increase with increasing Cd and Mn concentrations in sediments. Pb concentrations in *Typha* stems also increase with increasing Pb concentrations in sediments, whereas Pb concentrations in *Typha* stems decrease with increasing temperature and D.O. In addition, Pb in the roots and rhizomes of *Typha* increase with increasing pH in the water column. Zn concentrations in *Typha* rhizomes and stems decrease with conductivity just as Fe and Zn concentrations in *Typha* stems decrease with increasing water depth.

- Concentrations of Pb in the roots of *Phragmites* increase with increased Pb concentrations in the sediments. Alternatively, Zn concentrations in the stems of *Phragmites* decrease with increasing Zn in the sediments. Cd, Fe, and Pb concentrations in the roots, rhizomes and stems of *Phragmites* increase with increasing D.O. levels. As temperature increases, Cd and Pb in the roots, rhizomes and stems of *Phragmites* decrease. Similarly, as pH and conductivity increase, Cd, Fe and Pb in the stems of *Phragmites* decrease.

- As organic matter rises in the sediments, Cd concentrations in the roots and stems of *Juncus* decrease. Alternatively, as temperature increases Cd concentrations in the roots and stems increase. Similarly as depth and pH of the water column increase, Mn concentrations in the roots of *Juncus* increase. As conductivity increases, Zn and Fe concentrations in the roots and stems of *Juncus* decrease. Finally, as D.O. increases Fe in *Juncus* stems also increases.

- As the pH of the water column increases in Silvermines wetland, conductivity increases and Cd, Fe, Pb and Zn concentrations in the water column decrease. These trends were also observed in the TMF wetland. As expected, as conductivity increases sulphate concentrations in the water column at Silvermines also increase. Again, as in the TMF wetland, Cd concentration in the water column increases as Cd extracted from the sediments increases, and Fe and Pb concentrations in the water column decrease with increasing concentrations of Fe and Pb in the sediment extractions. As expected Pb and Zn free-metal ion concentration in Silvermines is positively correlated with Pb and Zn in the water column.

- As for the TMF wetland, Fe concentrations in extractions increase as the pH of the water column increases. This also occurs for Pb at Silvermines. However, Cd, Fe and Pb in some extractions decrease with increasing pH. Conductivity is negatively correlated with Cd in the residual fraction, and positively correlated with Pb in the residual fraction .

- Sulphate concentration in the water column decrease with increasing total, extracted and free-metal ion concentrations of Cd and Pb, increasing Fe in the ion-exchangeable fraction, and increasing free-metal ion concentrations of Zn. Alternatively, Fe concentrations in the reducible and oxidisable fractions, total Fe, and Fe oxyhydroxide increase with increasing sulphate concentrations.

CHAPTER NINE

DISCUSSION

9.1 ECOLOGICAL INDICATORS OF ECOSYSTEM HEALTH

9.1.1 Species Composition, Density, Richness and Diversity

Species composition was used as an important indicator of ecological change over time to determine the rate at which the TMF wetland would develop the ecological characteristics of natural wetlands. Sixteen months after planting, as determined during the main field ecology event in summer 1999, a substantial cover of diverse wetland vegetation had been established over the TMF wetland. The species composition of this cover was extremely similar to the Reference/Control wetland. This was determined by plant identification, enumeration techniques, and importance values generated using % coverage, frequency and densities for each wetland species. Importance values for the three most dominant species *Gramineae* spp., *Typha latifolia* and *Phragmites australis* were calculated as 27 %, 22 % and 14 % in the TMF wetland and 23 %, 25 % and 15 % for the Control. The remaining species identified also had similar IV values for each wetland. An exception occurred for *Juncus effusus* which exerted a higher degree of dominance in the TMF wetland than in the Control. From quadrat data it appears *Typha l.* spread vigorously into the quadrats of the Control where *Juncus e.* was initially planted and possibly competed with the establishment of the latter.

Sistani *et al.* (1999) also used vegetative indicators to examine the biological and chemical changes that occurred in wetlands constructed on coal mine spoil. These authors determined that survival of *Typha l.* and *Scirpus validus* were lowest on an acidic coal mine spoil and these wetlands had a complete cover of emergent vegetation four years after planting. Burton (1986) cites several surveys of acidic, metal-polluted waters that indicated changes in community structure and species composition due to the combined effects of pollutants. For example, Yan (1979) found that although the total biomass of a Canadian lake approximately 12 km from a smelter was unaltered, the species composition had changed with *Peridinium inconspicuum* becoming dominant. This was attributed to the effect of low pH. In addition, the dominance of *Chlamydomonas* spp. in acid streams in British Columbia, Canada, in water with Zn concentrations of 40 mg/l was attributed to resistance to the acidic, largely anaerobic conditions which prevented growth of other normally encountered species (Wehr and Whitton, 1983). In an ecological assessment of a wetland system in Florida impacted by highly acidic Pb discharges from a battery plant, Pritchard (2000) determined the absence of tree species in areas where the most Pb had been absorbed. Wojcik and Wojcik (2000) also noted the absence of wetland species common to wetlands such as *Salix* spp. in the Biala River wetland in Poland which had received mine water discharges containing high concentrations of Zn and Pb for about 400 years.

In contrast, *Salix* spp. was observed growing in the TMF wetland during the course of this experiment. Overall, a range of similarity indices indicated between 77% and 98% similarity between the TMF and Reference wetland communities in the pilot system. The similarities in vegetative composition between the TMF and Reference wetlands does not indicate vegetative differences due to environmental stress from the impact of pH or metals on species composition in the TMF wetland

Vegetative and reproductive data from the pilot wetlands however do indicate greater densities and numbers of flowering plants of *Typha l.* in the Control than in the TMF wetland, similar mean densities of *Phragmites a.* between wetlands but higher numbers of flowering plants in the Control, and higher mean densities of *Juncus e.* in the TMF wetland. For these three wetland species, mean stem length is higher in the Control than in the TMF wetland. Similarly, mean total biomass values for *Typha l.* and *Phragmites a.* were higher in the Control than in the TMF wetland whereas mean values for *Juncus e.* were higher in the TMF wetland. Overall, data obtained in the field ecology study indicate that mean total vegetative density and cover is higher in the Control than in the TMF wetland.

However, it is important that individual species success not be the primary indicator of ecosystem health. For example, Mitsch (1992) argues that vegetative success, which has been the primary indicator of the success of constructed or restored wetlands, should be measured more by the success of the original objective of the wetland than by the success of individual species. Similarly, Odum (1987) reports that throughout the United States *Typha* spp. is championed by some and rejected by others as it is a rapid coloniser of limited wildlife value. Species composition in the TMF wetland is important but must be assessed in terms of the overall objective of the system which is to create a sustainable living wetland ecosystem. Often pollution causes the biodiversity of ecosystems to diminish (Pritchard, 2000). This view is reinforced by the United Nations Environment Programme which describe ecosystems as healthy when they have a high level of biodiversity (UNEP, 1990). Bagatto and Shorthouse (1999) recommended assessment of ecosystem sustainability include measures of biodiversity given they determined that the best reclamation strategy at a series of mine tailings sites occurs where diverse vegetation resulting from natural colonisation leads to more substantial litter and ground cover.

Consequently, in the case of the TMF wetland, species richness and diversity are considered more robust indicators of ecosystem health than individual plant densities. In this study vegetative data used to calculate species richness values indicate similar mean values for species richness for the TMF and Reference wetlands. Relative Abundance and Dominance-Density Curves prepared using density/abundance data, coverage, frequencies and importance values illustrate the similarity in floral diversity between both wetlands and also indicate that both wetlands have high species diversity and low species dominance. In addition, a variety of diversity indices were calculated (Margalef's Index, Simpson's Index, Shannon Diversity Index) that show both wetland communities exhibit a high degree of similarity in regard to floral diversity. Pritchard (2000) calculated lower diversity indices than calculated in this study (Margalef and Simpson) in wetlands stressed by acidic Pb discharges and similar values for reference wetland sites.

While ecotypic data indicates some morphological differences between the TMF and Control wetlands in terms of plant densities, stem lengths and numbers of flowering plants, the ecological data does not show evidence of structural impacts on the composition of the TMF wetland in terms of species richness, diversity and dominance which are considered more robust indicators of ecosystem health in this study.

9.1.2 Water Depth and Faunal Habitat

Water depth was an important parameter influencing species richness and diversity in the TMF wetland with both parameters rising with increasing depth. Alternatively, emergent plant densities (*Typha l.* and *Phragmites a.*) decrease with increasing water depth. D.O. decreases with increasing plant cover and plant biomass. This highlights the potential for low D.O. concentrations associated with dense wetland vegetation community types previously outlined by Nelson *et al.* (2000). These authors recommended that wetlands designed for habitat value should take into account the potential for low D.O. concentrations associated with vegetation community types. They suggested that the quality of habitat for waterfowl, as measured by invertebrate richness, improves from tall emergents with low D.O. but large amounts of detrital food, to short emergents that provide some detrital food but also allow for light penetration to water, and finally to open water with oxygen-producing submerged macrophytes. The relationship between D.O. and mesocosm plantings was also suggested by Canonical Correspondence Analysis conducted by Nelson *et al.* where plant height was almost directly opposed to D.O. The negative relationship of plant height to D.O. may be related to shading of oxygen-producing submerged plants and production of oxygen- consuming biomass.

Consequently, the variation in water depth in the TMF wetland appears to have enhanced its overall ecological health in terms of biodiversity and habitability. A variety of wetland cover types, including dense stands of emergent vegetation in addition to areas of open water, developed in the TMF wetland which are likely to produce more diversity and higher quality faunal habitat. Whereas the Control wetland developed into an area of continuous dense emergent vegetation. Evidence of the presence of aquatic fauna including frogspawn and a bird's nest was noted in the TMF wetland that was not observed in the Control.

9.1.3 Metal Concentrations, Acidity, and Density, Biomass and Diversity

A variety of researchers have shown that metals and acidity associated with tailings affect plant biomass, density, and diversity (Macnicol and Beckett 1985, Kabata-Pendias and Pendias 1992, Levy *et al.*, 1992) particularly for soil pH levels below 6.5

(Stoughton and Marcus, 2000). Stoughton and Marcus (2000) determined that metals in floodplain soils associated with dispersion of tailings exert a threshold relation over vegetation. Vegetation diversity, density and biomass all varied widely up to a certain trace metal level, at which point mean diversity, density, and biomass dropped significantly. There was a significant difference in the density and biomass of *Typha l.* between the TMF wetland and the Control. However, given the mean pH of the water column and sediments in the TMF wetland emulate normal wetlands and a comprehensive analysis of metal accumulation in plant tissues did not reveal significantly elevated metals levels as would be expected for plants under stressed conditions, this difference was not deemed evidence of ecological stress due to the presence of environmental pollutants. It was attributed to the seeding of the Control with natural wetland soils with higher nutrients than the TMF wetland

While metal concentrations and acidity within the TMF wetland did not appear to affect wetland ecology, a number of interesting correlations were determined between ecological, physico-chemical and sediment parameters. For example, species richness decreased with increasing Fe and Mn concentrations in the roots and rhizomes of *Typha latifolia* and *Phragmites australis* and also decreased with increasing Cd, Fe and Zn concentrations in the TMF wetland sediments. Plant density decreased with increasing Pb concentrations in the rhizomes of *Typha latifolia* and with increasing Fe, Mn and Zn concentrations in the roots of *Phragmites australis.*

Correlation analysis also determined as the pH of the water column rises, floral diversity rises. Concentrations of Cd and Pb in *Phragmites* stems also decreased with increasing pH, and Fe, Mn and Zn concentrations in *Typha* and *Phragmites* stems also decreased with increasing depth. Decreased metal concentrations in the water column were positively correlated with increasing depth. These data suggest that plants absorb metals into stems from the water column. St Cyr and Campbell (2000) noted that foliar uptake may occur particularly under running water conditions.

Given that water chemistry, sediment and biotic data in this study overwhelmingly indicate a lack of acidity and mobilisation of metals associated with tailings in the TMF wetland, these correlations do not prove adverse ecological impacts within the system from metals. Rather, they point towards the potential ecological impacts of toxic accumulations of metals in sediments. These empirical relationships between density and biomass and, trace metals and pH levels were also documented by Stoughton and Marcus (2000) in their examination of the impact of mine tailings and ecological mechanisms on the community structure in the riparian zone. These authors documented that the vegetation/metal (Cu and Ni) and vegetation/pH associations in grasses growing on floodplains contaminated by tailings are more of a threshold than a linear relationship. While data from the pilot study indicate no significant build-up of metals in the TMF wetland sediments between 1999 and 2000, the potential threshold effects of accumulating metals on wetland ecological health must be further examined in field-scale trials.

Overall, the results of this research indicate that the ecological health of the TMF wetland was not adversely impacted on from acidity or metals from tailings.

9.2 HYDROLOGICAL AND PHYSICO-CHEMICAL INDICATORS OF ECOSYSTEM HEALTH

9.2.1 Water Depth and Flooding

In agreement with Mitsch's (1992) observations for constructed wetlands, this research establishes the primacy of hydrology as the most important variable in the design of the TMF wetland. While mean surface hydraulic loadings for both the TMF and Control wetlands were approximately equal, the water depth in the TMF wetland increased significantly across its length facilitating a beneficial examination of the impact of varying water depths on the overall establishment of a sustainable ecosystem in this wetland.

In addition to the ecological implications of increasing depth outlined above, correlations relating hydrology to water chemistry parameters in the TMF wetland show that the pH of the water column and the sediments increases with increasing water depth. This is related to soil oxidation and reducing conditions. As oxidised soils are flooded and become anaerobic or reducing, the pH tends to converge toward 7 (neutrality) regardless of whether the soil was acid or alkaline initially (Gambrell, 1994; Patrick and Mikkelsen, 1971; and Ponnamperuma, 1972). Thus the range of pH in typical wetland soils is much smaller than found for upland soils and the pH of natural wetland soils generally ranges from around 6.5 to 7.5 with a few exceptions (some predominantly organic wetland soils may be moderately to strongly acidic) (Gambrell, 1994).

Therefore, soil oxidation condition influences pH which is a major factor influencing metal chemistry. Gambrell (1994) reported that flooded, predominantly mineral wetland soils and sediments are going to be near neutral in pH and favour metal immobilisation whereas under non-flooded, oxidized conditions, changes can occur in soil pH, redox potential and metal mobility. The near neutral pH conditions of wetland soils favours metal immobilisation whereas upon long term oxidation wetland soils may become sufficiently acid to increase metals release in more mobilre forms (Gambrell, 1994).

According to Salomons and Förstner (1984) direct precipitation of metal compounds may take place when external factors change. These precipitation barriers commonly arise because of changes in pH, oxidation potential, or in concentrations of precipitating substances. A rise in pH and oxygen content promotes the formation of metal hydroxides, carbonates and other metal precipitates. Hydrous Fe and Mn oxides constitute significant "sinks" for heavy metals through the effects of sorption/coprecipitation (Salomons and Förstner, 1984). In waters rich in organic matter, minerals may be solubilised by the combined processes of complexation and reduction (Theis and Singer, 1974), and reincorporation of metals into the sediment involves the mechanisms of adsorption, flocculation, polymerisation and precipitation (Jonasson, 1977).

The variation in metal concentrations in the water column of the TMF wetland also were related to variation in hydrological characteristics, specifically depth. As pH and depth increase, Fe, Mn, Pb and Zn concentrations in the water column decrease throughout all the sampling events. Therefore, flooding the sediments in the TMF wetland favours increased pH levels and metal immobilisation.

These results are in agreement with a broad range of research into the effects of flooding on metal mobilisation in sediments and its importance for controlling the bioavailability of metals in wetlands. For example, research conducted by Caldwell and Canavan (1998) and Snodgrass *et al.* (2000) suggest that intermittent or periodic drying and flooding associated with changes in water levels in reservoirs and wetlands can enhance metal bioavailability. In addition, Odum *et al.* (2000) suggests that ecological engineering practices for retaining Pb in wetlands should keep the sediment covered with water and prevent oxidation. Maintaining the water level for these goals may also ensure continuous accretion of organic matter (Nixon and Lee, 1986; Giblin, 1985) which will both continue to sorb lead from surface waters and eventually form a natural cap as lead contaminated sediments are progressively buried (Odum *et al.*, 2000).

Elevated metal concentrations in the TMF wetland, for all metals, occurred consistently only in two quadrats that had no standing water over a large percentage of the peat substrate (75% and 95%). Sediment cores indicate a thin covering of 0.04 m of peat over tailings in one of these quadrats whereas the other averaged 0.10 m thickness. In both of these quadrats roots of *Typha l.* were found growing directly into the tailings substrate. Plant roots were discovered growing into the tailings substrate in ten other quadrats where no elevated metal loading was determined in the water column. Two of these quadrats had very shallow water depths over the entire quadrat of 0.01 and 0.02 m. Consequently, the design depth of 0.05 m appeared adequate to prevent metal mobilisation in the TMF wetland system.

Using deeper water depth to prevent drying occurring must be balanced by the need to promote a diverse wetland habitat. Results of a study by Nelson *et. al* (2000) support conclusions by others about the importance to wetland macroinvertebrates of shallow (approx. 0.5 m depth) open water. These authors suggest that some combination of oxygen-producing open water and detritus-producing emergent plant zones maximises invertebrate biodiversity. The variation in water depth in the TMF wetland provided a combination of diverse zones of vegetation while providing flooded conditions that prevented metal mobilisation into the water column.

9.2.2 Water Chemistry

Several water column chemistry parameters (pH, conductivity and metal concentrations) were deemed good predictors of both sediment and water column toxicity in a study of an AMD impacted watershed by Soucek *et al.* (2000a; 2000b). Stations that had significantly altered water chemistry (low pH, high conductivity, and high water column Fe and Al) and significantly higher sediment Fe concentrations had significantly decreased benthic macroinvertebrate richness and abundance relative to unimpacted stations. An earlier study by McCann (1993) also suggested that waterborne metals have a greater influence on aquatic biota than sediment-bound metals in an area influenced by mining activities. Emerson *et al.* (1999) reported river pH values as low as 3.5 as a result of acidity generated by mining spoils from pyrite mines. In light of these facts, seasonal physio-chemical analysis of the water column was conducted to investigate temporal changes in the water chemistry of the TMF wetland.

However, statistical analysis of this water chemistry data indicated no significant difference between the TMF and Control wetlands for seasonal mean values of water and sediment pH, conductivity, D.O., and temperature which reflected those of natural wetland ecosystems. Mean sulphate concentrations also did not differ between the TMF and Control wetlands and fell well below the acceptable E.U. maximum standard for potable water abstractions (EC Surface Water Directive 75/440/EEC). Overall, data indicate that pH, conductivity and sulphate concentrations in the TMF wetland are not adversely impacted by the acid-generating potential or sulphate concentration of the tailings substrate and the tailings porewater.

Regarding the impacts of metals in the overlying water column of the TMF wetland, mean Cd concentrations did not differ significantly between wetlands and mean Fe and Mn concentrations were lower in the TMF wetland than in the Control. Fe and Mn concentrations in the Control wetland were impacted by the natural wetland soils used to seed this wetland which had higher Fe and Mn values than the predominantly peat soils of the TMF wetland. Mean Pb and Zn concentrations in the TMF wetland were higher than standards established under Irish water quality regulations but did not differ significantly between wetlands. The concentrations of Pb and Zn in the water column of the TMF wetland over the course of the experiment were much lower than concentrations of these metals in river water impacted by AMD in South Africa, Poland and the U.S.A (Salomons and Förstner, 1984; Wojcik and Wojcik, 2000; and Wildeman and Laudon, 1989). Ultimately, mean seasonal metal concentrations for outflows from the TMF wetland met the most recent E.U. water quality regulations for all metals (E.C. Directive 75/440/EEC). In addition, ANOVA analysis indicated no significant difference in mean seasonal inflows and outflows from the TMF wetland. From these results we can infer there was no enhanced seasonal metals burden with associated toxicity from the tailings on the water column of the TMF wetland and no adverse impact on the final water quality of the outflows from this wetland.

Lau and Chu (2000a), suggest that an increase in temperature (namely in summer) may elevate metal release from sediments to overlying water. This may be due to increased temperatures enhancing water evaporation processes and leading to shallow water depths which may lead to oxidised conditions and increased metal mobilisation. Alternatively, higher temperatures may enhance plant growth and oxygen transfer to the rhizosphere which can enhance the oxidation of sediments. Therefore, extensive metal analysis of the water column was conducted in summer 1999 and correlation analysis indicated that concentrations of Fe, Mn and Pb in the water column at this time increased with increasing temperatures. Impacts on temperature on the release of metals from sediments requires further analysis in future field-scale trials.

9.3 SEDIMENT INDICATORS OF ECOSYSTEM HEALTH

9.3.1 Total and Extracted Sediment Metal Concentrations

Statistical analysis indicates no significant difference in mean total Cd, Pb and Zn concentrations between the sediments of the TMF and Control wetlands in 1999 and again in 2000. There was a significant difference in mean total Fe and Mn concentrations between wetland sediments, but this is because the Control sediments had higher concentrations of these metals. Additionally, mean total Cd, Fe, Mn, Pb and Zn concentrations in the sediments of the TMF wetland from 1999 to 2000 do not differ significantly. Overall, these results indicate no significant mobilisation of metals into the peat substrate of the TMF wetland from the tailings and no significant accumulations of metals in the peat substrate over the two-year experimental period. It appears the peat and water layers covering the tailings have effectively inhibited the oxidation of pyrite in the tailings and consequently inhibited acid production and metal mobilisation. Metals are effectively retained in wetland sediments by a variety of mechanisms, including adsorptive bonding on fine-grained substances; precipitation of discrete metal compounds; co-precipitation of metals by hydrous Fe and Mn oxides; associations with organic molecules; and incorporation in crystalline minerals (Gibbs, 1973; Förstner, 1985).

In addition to comparisons in total metals, comparisons were made in extracted metals between the TMF and Control wetlands, including ion exchangeable, reducible, oxidisable and residual species. There is no significant difference between both wetlands in Cd concentrations in all four extractions from the sediments. Fe and Mn concentrations in all extractions are higher in the Control than in the TMF wetland. Pb is higher only in the residual fraction of the TMF sediments which includes those tightly bound in the lattice structure of sediments and levels are very low in comparison to residual Pb levels in contaminated sediments (Basta and Gradwohl, 2000; Levy *et al.* 1992). Zn is higher in the oxidisable fraction of the TMF sediments than in the Control. This concentration is within the range reported for contaminated soils, however, it is closer to the lower end of this range and is likely affected by outlier data. The concentrations of Cd, Pb and Zn extracted from the TMF and Control wetland sediments in all fractions are well within ranges reported for extractions of these metals in uncontaminated soils and sediments (St Cyr and Campbell, 2000; Salomons and Förstner, 1984; Gambrell, 1994; Tessier *et al.*, 1993; and, Carapeto and Purchase, 2000).

9.3.2 Metal Speciation and Bioavailability

As outlined by Gambrell (1994) and others (Mota and Correia Dos Santos, 1995; Campbell, 1995; and, St Cyr and Campbell, 2000), elevated total concentrations of metals in sediments do not necessarily result in problem releases to water or excessive plant uptake. Rather it is the chemical forms or species of metals present and the processes affecting transformations between these forms that are important to assessing ecotoxicological risk. As cited above the results of this research indicate little significant difference in the mean metal concentrations of metals in the various extractions from the sediments of the TMF and Control wetlands. Interestingly though, a comparative review of the metal speciation between the TMF and Control sediments indicate a distinct difference between wetlands in regard to the enrichment of metals in particular fractions.

Metals in the soluble and exchangeable forms are considered readily mobilised and available (Gambrell, 1994). In the TMF wetland only 11%, 3.5% and 7.5% of Cd, Pb and Zn respectively were in the ion-exchangeable fraction, whereas 48%, 73% and 68% of Cd, Pb and Zn were in the oxidisable fraction (metals bound to sulfides and organic matter). This suggests that the release of contaminants across the sediment-water interface to overlying water may be relatively low. Similarly, Lau and Chu (2000b) determined less than 10% of contaminants (nutrients and heavy metals) in marsh sediments (surface and bottom) were water soluble.

Cd, Fe, Pb and Zn are substantially enriched in the oxidisable fraction of the sediment extractions from the TMF wetland, and Mn was enriched in the ion-exchangeable fraction. In comparison Cd, and Fe are enriched in the reducible fraction (metals bound to Fe and Mn oxyhydroxides) of the sediments extracted from the Control, Pb in the oxidisable fraction, and Zn in both the ion exchangeable and reducible fractions. Similarly for Silvermines wetland sediments which receive run-off from the Gortmore tailings dam in Silvermines, metals are mostly enriched in the reducible fraction of the sediment extractions.

While ion-exchangeable metals are considered readily mobilised and available, the stability of those in reducible form is controlled primarily by system pH (Gambrell, 1994). At near-neutral to somewhat alkaline pH levels, metals tend to be effectively immobilized. If, however, pH becomes moderately to strongly acid, as can sometimes occur when reduced soils or sediments become oxidised, these metals may be released to more mobile forms (Gambrell, 1994). In systems rich in reactive organic matter the otherwise important role of Fe and Mn oxides as direct sorbants of metal ions is either overshadowed by competition from the more effective associations with humic acids or organic-clays (Jonasson, 1977), or is obscured by coating of organic matter (Salomons and Förstner, 1984).

The high organic content of the peat substrate in the TMF wetland is most likely to have influenced the enrichment of Cd, Fe, Pb and Zn in the oxidisable fraction of the extractions from these sediments. In aquatic systems with a high content of organic substances, humic matter plays a dominant role in the final distribution of metal (Mota and Correia Dos Santos, 1995). Organic soils are dominated by hydrogen ions and can remove some metals through ion exchange, although they can drive down pH which reduces the amount of metal that can partition to the organic carbon (Wood and Shelley, 1999). Most fine textured soils and sediments containing appreciable amounts of organic matter tend to become near neutral in pH upon the development of reducing conditions, however, these conditions have been shown to contribute to effective metal immobilisation (Gambrell, 1994). The high organic matter (95%) of the peat substrate in the TMF wetland provides a large capacity for binding metals and the mean pH is not below that for natural wetland soils therefore these conditions favour the binding of metals to organic material in this wetland.

Wood and Shelley (1999) determined that long term control of metal bioavailability is related to the build up of organic carbon binding sites in a developing wetland. Therefore, using organic rich soils in the TMF wetland appears to have been beneficial for controlling metals toxicity in this system. Additionally, Thompson-Roberts and Pick (2000) proposed that while containing more metal, organic-rich wetland sediments may not pose a greater risk to organisms given that organic-rich sediments also provide the anoxic conditions necessary for sulfide production and hence additional sequestering of metals.

There is evidence that at least some metals are more tightly bound by organics under anoxic or reducing conditions compared with upland soils (Gambrell, 1994). However, the organic matter in upland soils is also effective in immobilising metals; thus, temporary oxidation of wetland soils or sediments may not result in major release of metals from humic materials (Gambrell, 1994).

A similar pattern of enrichment for Cd, Pb and Zn (predominantly associated with sulfides and organic matter) as occured for the sediments from the TMF wetland also occurs for extractions from pyrite (FeS) and galena (PbS) as illustrated in Figure 6.15. Given Silvermines tailings comprise 30 % to 35 % pyrite and < 4 % galena and other sulphosalts, the enrichment of metals in the oxidisable fraction may also be due to the presence of sulphides in the sediments of the TMF wetland. Unlike metal-humic material associations where the change in metal immobilisation may be modest for a transition from strongly reduced to oxidising conditions, oxidising sulfide-containing soils and sediments for extended periods will result in loss of all sulfide and subsequent major release of metals (Gambrell, 1994). Consequently, it is necessary to distinguish the percentage enrichment of metals in the organic and sulfide fractions in future field-scale trials.

Species differentiations can be used for the estimation of the remobilization of metals under changing environmental conditions (Förstner, 1985). This research indicates patterns of increased metal mobilisation occurring in the TMF wetland with oxidising conditions and corresponding decreasing pH as would occur in natural wetlands.

Low pH conditions in surface water or sediments can significantly increase metal bioavailability (Wood and Shelley, 1999). Förstner (1985) noted that in the estuarine environment changes in pH and redox potential affects the exchangeable fraction in particular. This scenario also occured in the TMF wetland for Cd where the concentration of Cd in the exchangeable fraction was negatively correlated with sediment pH. Similarly, correlations between sediment and physico-chemical parameters of the water column in this wetland show increasing concentrations of total Fe and total and extracted Pb (reducible) in sediments occuring with decreasing concentrations of Fe and Pb in the water column. Total Pb and Zn concentrations in sediments, and extracted Cd (reducible), Pb and Zn (oxidisable) concentrations increase as water depth increases. In addition, concentrations of total and extracted Fe, and Mn in sediments increase as the pH of the water column increases. These results indicate a general increase in sediment metal concentration with increasing water depth and pH, and a corresponding decrease in some (Fe and Pb) metal concentrations of the water column. These data indicate increased metal immobilisation with increasing depth and pH and decreasing metal bioavailability as determined by metal concentrations in the water column.

The results concur with Campbell and Stokes (1985) who noted increased Pb availability with decreasing pH over the range 7 to 4. Mean seasonal sediment pH in the TMF wetland was 6.71 within the range of 5.89 to 7.44.

The rise of Pb concentrations in the sediments with increasing depth and pH and the decrease in Pb concentrations in the water column, may be due to adsorption and co-precipitation of Pb from the water column with organic material and sulphide at increasing depths under reducing conditions. These processes also explain the rise in Zn concentration in the oxidisable fraction of the sediment extractions with increasing depth. Gambrell (1994) attributed the release of metals under aerobic conditions to mineralisation of organic matter and sulfide oxidation.

Changes from reducing to oxidising sediment conditions does not usually result in a large release of metals from potentially available forms to the readily available forms, so long as pH does not change substantially (Gambrell, 1994).

9.3.3 Free-Metal Ion Concentrations and Bioavailability

Correlation analysis indicates as total Cd, Mn, and Pb increase in the sediments of the TMF wetland the concentrations of these metals in the roots and stems of *Typha latifolia* and *Phragmites australis* also increase. However, a convincing body of evidence has been developed to support the tenet that the biological response elicited by a dissolved metal is usually a function of the free-metal ion concentration (St. Cyr and Campbell, 2000; Tessier *et al.* 1993). Campbell (1995) cites several examples where the activity of the free-metal ion is a better indicator of metal bioavailability to aquatic plants and organisms than total metal concentration.

In this research, as a pre-requisite for calculating free-metal ion concentrations, potentially bioavailable metals were determined as the sum of the ion-exchangeable and reducible fractions of the sediment extractions. Mean potentially bioavailable metals were similar in the TMF and Control wetlands for Cd, while Fe and Mn values were slightly higher in the Control, and Pb and Zn values were slightly higher in the TMF wetland. Potentially bioavailable Cd and Zn in both wetlands were the same order of magnitude as concentrations reported for uncontaminated Canadian river sediments (St. Cyr and Campbell, 2000; Tessier *et al.*, 1993). Values for bioavailable Pb in both wetlands were slightly higher than reported for Canadian river sediments.

Approximate free-metal ion concentrations for Cd ([Cd^{2+}]) in the TMF and Control wetlands were lower or within ranges cited for [Cd^{2+}] in uncontaminated sediments in Canada (St. Cyr and Campbell, 2000; Tessier *et al.*, 1993). Concentrations of [Pb^{2+}] are close but higher in the TMF than in the Control wetland and both are higher than values for Canadian freshwater sediments. Concentrations of [Zn^{2+}] are also close but higher in the TMF than in the Control wetland. It is difficult to make definitive judgements regarding the potential toxicity from these free-metal ion concentrations given it was not possible to correlate these concentrations with plant uptake because plant metal concentrations were determined for the previous years growth. However, overall these results indicate that potentially bioavailable metals and free-metal ion concentrations in the TMF wetland sediments are similar to values cited for natural wetlands. Given [Pb^{2+}] and [Zn^{2+}] are somewhat higher in the TMF than in the Control wetland, it is important to conduct a more extensive investigation of free-metal ion activity in wetlands planted over pyritic tailings in future field-scale trials.

9.3.4 Optimum Thickness for Peat Substrate

In twelve quadrats, wetland plant roots were observed growing directly into the tailings beneath the peat substrate. The thickness of the peat substrate within these plots ranged from 0.04 m to 0.14 m (based on sediment cores with compressed soil measurements). Only one of these quadrats exhibited elevated levels of metals in plant tissues and this had a peat substrate thickness of 0.10 m. Only two of these quadrats exhibited elevated metals in the water column and these had peat thicknesses of 0.04 and 0.10 m. Peat thicknesses differed due to the movement of sediments with shifting water currents which occurred in the early stages of this research work before a wetland cover had been established. Overall, the selected design substrate thickness for peat of 0.20 m would appear to have been adequate to prevent oxidation of the tailings and subsequent mobilisation of metals in the TMF wetland.

9.3.5 Competing Metals and Precipitation of Metal Sulphides

Regarding competing metals, correlation analysis does not reveal potentially interfering metals in the TMF wetland, rather sediment metal concentrations are positively correlated for all metals.

Interestingly, sulphate concentrations in the water column decreased with increasing Zn concentrations in sediments, even though sulphate concentrations in the TMF wetland overall were very low. This negative correlation can be accounted for by considering individual metal competition for binding sites which are dependent on metal sulfide solubility products as outlined by Wood and Shelley (1999). The first metals released from the sulfide bond are, in the following order: Fe>Zn>Cd>Pb. Since Zn is both more soluble than Cd and Pb in sulfides and with organic complexes, it will probably produce the highest pore water concentrations in sediments with competing metals. A wetland receiving inflow with a mix of heavy metals, will likely exhibit toxicity in sediment from Zn or Cd first, before Pb becomes a problem (Wood and Shelley, 1999).

The increased concentrations of Zn in the TMF sediments with decreasing sulphate suggests the formation of highly insoluble sulphide following the reduction of sulphate. This leads to precipitation of sulphur and co-precipitation of metal sulphides such as Zn sulphide. Zn was significantly higher in the oxidisable fraction of the TMF than the Control, though importantly, neither sulphate concentration in the water column nor Zn concentration in the sediments was high enough to indicate adverse ecological health.

9.4 BIOTIC INDICATORS OF ECOSYSTEM HEALTH

9.4.1 Metal Concentrations in Wetland Plant Species

In the pilot system three species of wetland rooted emergents *Typha latifolia, Phragmites australis,* and *Juncus effusus* were monitored for tissue accumulations of metals to examine the potential phytotoxic impacts of contamination on wetland species.

Mean total Cd, Fe and Mn concentrations were lower in the TMF wetland than in the Control for roots, rhizomes and stems of *Typha latifolia* and *Phragmites australis*, and lower or similar for roots and stems of *Juncus effusus.* Mean Pb concentrations were higher in the TMF wetland than in the Control for roots and rhizomes of *Typha l.*, all tissues of *Phragmites a.*, and for stems of *Juncus e.*. However, these values were lower than Pb concentrations reported for similar plant tissues in wetlands receiving discharges from Pb-Zn mining activities (Ton and Delfino, 2000; Wojcik and Wojcik, 2000; Lan *et al.*, 1992; and Dunbabin *et al.*, 1988). Similarly, mean total Zn concentrations were higher in the TMF wetland than in the Control for roots, rhizomes and stems of *Typha l.* and stems of *Phragmites a.* and *Juncus e.* but again these values were lower than Zn concentrations reported for similar plant tissues in wetlands receiving discharges from Pb-Zn mining activities (Wojcik and Wojcik, 2000; Dunbabin *et al.*, 1988; and Levy *et al.*, 1992). Overall, total metals concentrations in the root and aerial tissues of *Typha l., Phragmites a.* and *Juncus e.* were either lower in the TMF wetland than in the Control or did not differ significantly as determined by statistical analysis.

Elevated concentrations of Pb were determined in the roots of *Juncus e.* in Quadrats 2 and 26. These quadrats occur at opposite ends of the TMF wetland and had approximately 0.10 m and 0.09 m thickness of peat substrate above tailings but roots were observed growing directly into the tailings in both quadrats. *Juncus e.* roots in Quadrat 2 also had elevated Zn and Fe concentrations. For the twelve quadrats where plants were observed rooting directly into tailings, only these two had elevated plant metal concentrations.

Plant and soil scientists generally agree that soil pH and redox potential exert the greatest influence on trace metal bioavailability in plants (Adriano 1986, Barbour *et al.* 1987, Kabata-Pendias and Pendias 1992, Alloway 1995). Jackson *et al.* (1993) demonstrated that low sediment pH coupled with elevated sediment metal concentrations and mildly oxic redox potential could increase macrophyte concentrations of several metals (Sparling and Lowe, 1998). Given approximately 50% of Quadrat 2 was dry, this points to the likelihood of lower sediment pH and increased metal mobility in this quadrat although elevated metals concentrations were not determined in the water column above this quadrat.

Pb is a toxic metal that has much less propensity for being translocated to the above-ground parts of plants than many other trace and toxic metals such as Cd and Zn (Gambrell, 1994; Broyer et al., 1972; Reddy and Patrick, 1977). Exceptions have been noted for marsh plants (Gambrell, 1994). Where contaminated dredged materials were used to construct wetlands at one experimental site, the plants did not accumulate more Pb than plants growing in nearby natural marshes (Simmers et al., 1989). However, the predictive plant bioassay test indicated greater Pb uptake by plants would have occurred if grown on highly contaminated sediments under upland conditions. Similarly for Zn, Simmers et al. (1989) reported that under simulated wetland conditions with contaminated sediments, marsh plants did not accumulate more Zn than plants in a nearby marsh. However, the bioassay tests indicated uptake would be much greater if the material were placed in an upland environment where plants would become established on oxidised material. Cd uptake from a sludge amended soil also was greater under dryer conditions (Kirkham, 1975) and Cd and Zn uptake by rice and corn decreased as sludge-amended soil became more reducing (Gambrell and Patrick, 1989).

Roots and rhizomes of *Typha l.* plants in Quadrats 1 and 4 had higher concentrations of Cd than *Juncus e.* in Quadrat 2 and higher concentrations of Pb and Zn than other plants, but still substantially lower Pb and Zn values than *Juncus* in Quadrats 2 and 26. Quadrats 1 and 4 had the same shallow water depth (0.045 m) and the same average thickness of peat above the tailings (0.07 m). The shallow water depth indicates the potential for low sediment pH and oxic redox potential which could increase the bioavailability of Pb and Zn in these quadrats. Even though a substantial number of *Typha* plants were found rooting directly into tailings in other quadrats, elevated metals were not found in these plant tissues. Also, elevated metal content in *Juncus e.* in Quadrat 2 was not an indicator of sub-lethal stress in plants given this quadrant had a relatively high density of *Typha*. In addition, the mean percentage of *Typha l.* stems infested per quadrat by *Lepidoptera* in both wetlands is 9 %, indicating that *Typha l.* stems in the TMF wetlands were neither more, nor less ,susceptible to infestation than in the Control. (This is indicative of the ecological similarity between wetlands rather than a statement on the positive or negative impact of *Lepidoptera* on wetland ecology.) *Typha* populations appear to be exhibiting metal-tolerant behaviour which is in agreement with other studies from the literature. Taylor and Crowder (1983) studied metal uptake by *Typha l.* acclimatised to soils with a high Cu and Ni content and found these metals were largely excluded from the above-ground parts of the plant, but accumulated in the root stock. Fe and Mn were accumulated by above and below-ground parts. Many plants have the ability to transport oxygen to the substrate and these plants tend to be emergents such as *Typha* species, *Phragmites communis* and *Juncus* species (Reed *et al.* 1995). An oxidised zone around the plant roots called the rhizosphere results. Oxidation of Fe^{2+} and Mn^{2+} ions in the rhizosphere has been reported for many wetland plants including *Typha l.* and *Phalaris* species (Good and Patrick, 1987) and plaques of Fe oxyhydroxides have been noted on *Typha* roots (Kleinmann, 1990). Rhizosphere oxygenation is thought to enable the plants to counteract the effects of soluble phytotoxins, including sulphides and metals. Michaud and Richardson (1989) compared the rate of oxygen release from the roots of wetland plants and found the descending order of oxygen release per unit mass to be *Typha latifolia, Juncus effusus, Sparganium americanum, Eleocharis quadranguta,* and *Scirpus cyperinus*. Consequently, *Typha* may have a tolerance to heavy metals as a result of the immobilisation of metal ions due to rhizosphere oxygenation.

Given, *Phragmites* did not exhibit elevated metal concentrations in any plant tissues, this suggests *Phragmites* may be a metal-tolerant ecotype. The potential for *Phragmites* to display metal tolerant mechanisms such as the prevention of uptake of heavy metals warrants further investigation.

9.4.2 Metal Accumulations and Potential Bioindicators

For Cd, Fe, Pb and Zn, most metal accumulation occurs in the roots of *Typha l.* The exception occurs for Mn where most metal accumulation occurs in the stems. Similarly, most metal accumulation occurs in the roots of *Phragmites a.* for all metals. In plants acclimatised to soil with heavy metals, metals may be excluded from parts of the plant but accumulate in the root stock. Fe and Pb differentially accumulate in the roots of *Juncus* whereas Mn, in similar fashion to *Typha l.*, accumulates in the stems of *Juncus e*. There is no significant difference between root and stem accumulations for Cd and Zn.

Concentrations of Cd, Mn and Pb in *Typha* plant tissues increase with increasing total Cd Mn and Pb concentrations in sediments. Similarly, concentrations of Pb in the roots of *Phragmites* increase with increased total Pb concentrations in the sediments. This indicates positive correlations between plant metal concentrations and sediment metals. Alternatively, Fe and Zn concentrations in *Typha* and *Phragmites* stems decrease with increasing water depth and increasing Fe and Zn in the sediments respectively. This points again to the adsorption of metals by stem tissues from the water column.

While Jackson et al. (1991) reported a significant positive relationship between metal concentrations in the above-ground tissues of aquatic plants and the total metal concentrations in the underlying sediments, St-Cyr and Campbell (2000) found metal concentrations in plant tissues correlated more closely with estimates of bioavailable sediment-bound metals ([Cd^{2+}], [Pb^{2+}], [Zn^{2+}]), than with total metal concentrations in sediments. Given concentrations of [Pb^{2+}] and [Zn^{2+}] concentrations in the TMF wetland are higher than in the Control as outlined in Section 9.3 above it is necessary to consider the role of the free-metal ion concentration in the sediment interstitial in relation to the potential bioavailability of metals to plants in future field-scale trials.

Fe, Mn, Pb and Zn concentrations in *Juncus* roots are negatively correlated with plant density. Stoughton and Marcus, (2000) determined that changes in the density of individual species associated with metals from tailings may provide a better estimate of plant health, while diversity measures illustrate broad vegetation patterns. Given

Juncus e. is neither an 'excluder' of metals nor an 'accumulator' of metals, it may be an appropriate bioindicator of sediment heavy metal contamination.

The ability to reflect gradients in contamination is of overriding importance in the selection of indicator organisms (Langston and Spence, 1995). There appears to be reasonable correlation between *Juncus* rooting in tailings and concentrations in the roots of the plant. Therefore, the concentration of metals within *Juncus* may be a good indicator of elevated levels in tailings substrates. In addition, as organic matter rises in the sediments, Cd concentrations in the roots and stems of *Juncus* decrease. This points to decreasing concentrations of bioavailable Cd with adsorption of metals by organic material. The use of *Juncus* as a possible bioindicator in assessing wetlands for rehabilitating tailings should be further investigated in future field-scale trials.

9.4.3 Rhizosphere Impacts on Metal Mobilisation

Wright and Otte (1999) investigated metal mobility regulating soil factors (Eh and pH) in waterlogged soils, through radial oxygen loss into adjacent sediments. These authors determined Fe and Zn mobility in stagnant Pb-Zn tailings was affected little by the presence of *Typha latifolia* beyond a narrow halo surrounding the roots and the overall influence of this plant on Eh and pH remained localised. In the TMF wetland penetration by roots into tailings may enhance water and oxygen penetration resulting in acidity and increased metal mobility to higher levels. *Typha* plants are rooting directly into tailings in twelve quadrats but no adverse increases in metal concentrations were determined in the sediments of any of these or in the water column of ten of these. This would seem to support Wright and Otte's findings that the overall influence of *Typha* plants on metal mobility remained localised. However, more extensive investigations into the rhizospheric impacts of plants in the field-scale trials is merited given the action of plants on metal mobility may be important particularly at the peat/tailings interface.

9.5 COMPARISONS WITH SILVERMINES WETLAND

The chemistry of the water column and sediments in Silvermines wetland were much more indicative of a wetland system impacted by heavy metal contamination than the TMF wetland. For example, mean Cd, Fe, Mn, Pb and Zn concentrations in the water column of Silvermines were substantially higher than those measured in the TMF wetland. Mean conductivity of the water column was 1.34 mS/cm, which also is substantially higher than seasonal mean conductivity measurements taken in the TMF wetland. Conductivity correlated well with mean sulphate concentrations in Silvermines which were substantially higher than those measured in the TMF wetland and closer to sulphate concentrations in waters associated with mining (Soucek *et al.*, 2000a).

Additionally, mean total Cd, Fe, Mn, Pb and Zn concentrations in Silvermines sediments greatly exceed values for natural wetlands and those determined for the TMF wetland, and more closely approximate soils and wetland sediments contaminated with metals from mining (Soucek *et al.*, 2000a; Levy *et al.,* 1992; Stoughton and Marcus, 2000; Basta and Gradwohl, 2000; Wojcik and Wojcik, 2000; Odum et al., 2000; and Emerson *et al.,* 1999). Similarly, the concentration of all metals extracted from the sediments at Silvermines were much higher than the TMF wetland and also closer to the range reported for soils contaminated with metals from mining. These metal concentrations were found to be similar to total metals values obtained for Silvermines tailings and for surface samples on the tailings dam at Silvermines.

As is similar for the Control wetland in the pilot plant, Cd, Fe, Mn and Pb are enriched in the reducible fraction of the sediment extractions from Silvermines and Zn is enriched in the ion exchangeable and reducible fractions.

Several correlations between physico-chemical and sediment parameters for Silvermines matched those determined for the TMF wetland and for natural wetlands in general. For example as pH increases in the water column of Silvermines wetland Cd, Fe, Pb and Zn concentrations decrease and as conductivity increases sulphate concentrations in the water column increase. As in the TMF wetland, Cd concentrations in the water column increase as Cd extracted from the sediments increase, and Fe and Pb concentrations in the water column decrease with increasing concentrations of Fe and Pb in the sediment extractions. As in the TMF wetland, these metal mobilisation dynamics for Fe and Pb suggest adsorption and coprecipitation of metals from the water column with organic material and ligands at increasing depths under reducing conditions.

Sulphate concentration in the water column also decreases with increasing total and extracted concentrations of Cd and Pb. This may point to the formation of insoluble Cd and Pb sulphides from soluble sulphate in waterlogged wetland soils. Once precipitated these metal sulphides are stable and insoluble providing the soil remains anaerobic.

Potentially bioavailable metals were substantially elevated in Silvermines wetland in comparison to the TMF and Control wetlands (100 times higher for Cd, Pb and Zn) and higher than those calculated for Canadian river sediments (St. Cyr and Campbell, 2000; Tessier, 1993). However, iron oxy-hydroxide concentrations in Silvermines sediments are also much higher than in the TMF and the Control wetlands. This is due to the higher concentrations of Fe in the sediments of Silvermines wetland and this significantly impacts the concentration of free-metal ions in the sediment porewater.

Approximate free-metal ion concentrations for Cd in Silvermines were higher than in the TMF and Control wetlands and higher than values cited for $[Cd^{2+}]$ in uncontaminated sediments in Canada (St. Cyr and Campbell, 2000; Tessier et al., 1993). Free-metal Cd concentrations for Silvermines sediments are surrogate measures only however, and not determined using the geochemical equations used for the TMF and Control wetlands because organic matter concentrations for Silvermines were unavailable. Lower Cd free-metal ion concentrations may be calculated for Silvermines once organic matter is taken into consideration.

Even though potentially bioavailable Pb and Zn concentrations were substantially higher in Silvermines wetland, calculated values for $[Pb^{2+}]$ and $[Zn^{2+}]$ were similar to the TMF wetland due to the higher concentrations of Fe-oxyhydroxides at Silvermines. In wetland transition zones and where seasonal changes occur in soil flooding, hydrous iron oxides may form and dissolve as a function of changing hydrology, consequently holding and releasing metals within the soil (Gambrell, 1994). For surface soils and sediment materials Fe oxyhydroxides may be effective in controlling metal retention during flooding and drainage cycles (Gambrell, 1994). Giblin *et al.* (1986) have shown Fe oxyhydroxides were important in retaining metals in the surface sediment of a salt marsh receiving trace and toxic metals in sewage sludge applications as a fertilizer. Similarly, Fe oxyhydroxides in Silvermines appear to be effective in controlling metal retention in this wetland.

As expected estimated values for Pb and Zn free-metal ion concentrations in the porewater of Silvermines sediments are positively correlated with Pb and Zn in the water column.

Overall, the results for Silvermines wetland indicate the importance of the location of this wetland adjacent to the Gortmore tailings dam. In particular free-metal ion concentrations for Pb and Zn, indicate this wetland is acting as a treatment wetland for drainage emanating from the tailings dam. In addition, based on comparisons with data from the TMF wetland, these results point dramatically to the potential for mitigating metal mobilisation from these pyritic tailings by placing a thin layer of peat over the tailings and flooding it as occurred in the TMF wetland.

CHAPTER TEN

CONCLUSIONS

"Today, the true measure of land reclamation success is conceived to be the degree to which the reclaimed land can look after itself. Self-sustaining geoecological systems are not created by human artiface. Consequently, practical land reclamation reduces to a variety of active or passive supplications to return the land to the biocybernetic, self-creating control of Nature. Self-sustainable reclaimed land develops from its own internal autopoietic, self-referenced processes. Since such a system is by definition natural and cannot be called artificial, it is an ethically apt objective."

Haigh, 2000

10.1 OVERVIEW

"In human economic self-organising, as with geobiological self-organising, available energy concentrates and transports materials, including metals, to concentrated centers". Thus determined Odum *et al.* (2000) in their review of lead in the geobiosphere which showed there are many similarities among heavy metals in energy hierarchical positioning and the way the self-organisation of the earth cycles and concentrates them in the geobiosphere. These elements are scarce in nature, with high transformity and physiological impact when concentrated. To use these elements well means developing patterns of human civilisation, industrial ecology and ecological engineering that keep their processes and uses in separate pathways from humans and natural ecosystems (Odum *et al.*, 2000). According to Odum *et al.*, the long-evolving geobiosphere does this by providing humic substances in all its ecosystems, especially in wetlands where peat deposits help regulate the earth's heavy metal cycles.

In the mining industry, tailings dams are designed to isolate tailings with high concentrations of metals from surrounding ecosystems. Upon cessation of mining activities, society expects the minerals industry to fully rehabilitate mining sites and tailings dams. Fundamental to pursuing a policy of sustainable development for this industry is achieving long-term rehabilitation strategies for tailings dams which include eventual walk-away solutions. The development of self-sustainable ecosystems are primary for the achievement of walk-away solutions which protect human health and the environment and do not necessitate continual maintenance and input from future generations. Consequently, self-sustainable mine tailings remediation strategies use ecological measures that try to work within natural processes. Their ambition is to help a self-sustaining system regenerate by itself into a dynamic, organic control-system that transcends the crude artifice of the reclamation process (Haigh, 2000).

The primary goal of this research was to investigate the potential for creating such a self-sustainable wetland ecosystem over pyritic mine tailings using the principles of ecological engineering. Such a cover must ensure the isolation of tailings from natural ecosystems and prevent the generation of acid mine drainage (AMD) with associated acidity and mobilised metals. This research involveded the design and construction of a wetland pilot plant and the development of a research methodology rigorous enough to accurately characterise the ecological health of the research wetlands. This characterisation was accomplished using environmental indicators to conduct an integrative assessment to evaluate the ecological, hydrological, physico-chemical, sediment geochemical and biotic interactions within the wetland system and to compare these with a reference wetland. The results of this assessment support the proposition that potential exists for a self-sustainable wetland ecosystem to be established over pyritic mine tailings.

10.2 RESULTS OF INTEGRATIVE ASSESSMENT TO EVALUATE ECOSYSTEM HEALTH

An integrative assessment was conducted over a two-year time period to integrate measures of environmental quality to make an overall assessment of the status of the ecological system. Data Quality Objectives based on statistical confidence and representative sampling (see Chapter Three) were used to establish the sampling protocol. Once enough data were obtained to support the development of scientifically sound inferences about the ecological status of the wetland, the data were analysed using appropriate statistical methods. This approach used a preponderance of evidence rather than relying on single measurements to determine if ecological degradation occurred.

Firstly, the ecology of the TMF wetland was examined to identify contaminant-induced ecologically degraded areas from control conditions. Sixteen months after planting, a diverse cover of wetland vegetation had been established over the tailings in the TMF wetland. The composition of wetland species therein exhibited between 77 % and 98 % similarity with the Control which acted as the reference wetland. Both wetlands had high species diversity and low species dominance. Ecological data indicate that in terms of species richness and diversity, (considered more robust indicators of ecosystem health than individual species survival), the TMF wetland was exhibiting the ecological characteristics of natural wetlands within two years.

Additionally, the variation in water depth in the TMF wetland appears to have enhanced its overall ecological health in terms of biodiversity and habitability. Species richness and Margalef's Index of diversity were positively correlated with the pH of the water column, conductivity and depth. This indicates increasing plant richness and diversity with increasing water depth and corresponding increasing pH. The variation in water depth in the TMF wetland provided a combination of diverse zones of vegetation including oxygen-producing open water and detritus-producing emergent plant zones while providing flooded conditions that prevented metal mobilisation into the water column. The presence of deep and shallow-water zones, and marsh segments produced more diversity and wildlife habitat as evidenced by the presence of aquatic and other wildlife and enhanced the TMF wetland's key functional requirements of toxicant retention and the creation of aquatic habitat.

In contrast, species richness and Margalef's Index of diversity were negatively correlated with Cd, Fe, Mn and Zn concentrations in the wetland sediments. However, the water chemistry and biotic data do not indicate potentially toxic accumulations of metals within this system resulting from metal mobilisation. Therefore, these correlations do not prove adverse ecological impacts within the system from metal mobilisation, instead they point towards the potential ecological impacts of toxic accumulations of metals in sediments. While data from the pilot study indicate no significant build-up of metals in the TMF wetland sediments between 1999 and 2000, the potential threshold effects of accumulating metals on wetland ecological health merits further examination.

It is important to investigate the long-term ecological changes that might occur over time in the establishment of the wetland community. For example, the occurrence of shifts in community diversity and composition leading to sucessional replacements of one community by another is likely in the TMF wetland. In the TMF wetland, bogland species such as *Bryophytes* spp. (sphagnum mosses) which provide substrate for other plants and animals and alter wetland hydrology were observed. Not only does the species composition of communities change as succession proceeds, but life forms and habitats change, there is an increased accumulation of biomass, increased productivity, and the development of a more complex community structure (Brower et al., 1990). These long-term changes must be further investigated in wetlands subjected to potential metal contamination.

Secondly, the integrative assessment examined whether contaminant concentrations in the TMF wetland were associated with hydrological effects. Correlations relating hydrology to water chemistry parameters in the TMF wetland show increases in the pH of the water column and the sediments occur with increasing water depth and corresponding decreasing metal concentrations in the water column. As pH and depth increase, Fe, Mn, Pb and Zn concentrations in the water column decrease throughout all the sampling events. This agrees with Gambrell (1994) who outlined that the near neutral pH conditions of wetland soils favour metal immobilisation whereas upon long-term oxidation, wetland soils may become sufficiently acidic to increase metal release in more mobile forms. Flooding the substrate in the TMF wetland prevented the oxidation of sediments and favoured increased pH levels and metal immobilisation. The free water design depth of 0.05 m appeared adequate to prevent sediment oxidation and metal mobilisation in the TMF wetland system.

Overall, the results indicate that hydrology is the most important variable in the design and establishment of the TMF wetland and indicate that a wetland cover is an ecologically viable alternative for pyritic tailings which are feasible to saturate. This strategy is also recommended by Odum *et al.* (2000) who suggest ecological engineering practices for retaining Pb should keep Pb-contaminated wetland sediments covered with water to prevent oxidation. This practice ensures a continuous accretion of organic matter which will eventually form a cap as the metal-contaminated sediments are progressively buried (Odum *et al.*, 2000).

Thirdly, a series of water chemistry indicators including pH, conductivity, D.O., Cd, Fe, Mn, Pb, Zn and sulphate concentrations were used to determine the water quality of the TMF wetland over the course of the experiment. Contaminant concentrations associated with water chemistry effects were examined using correlation and regression analysis. The results of this study indicate the water chemistry of the TMF wetland is statistically indistinguishable from that of the Control and reflects that of natural wetland ecosystems. Data indicate that pH and conductivity in the TMF wetland are not adversely impacted by the acid-generating potential nor sulphate concentration of the tailings substrate and its porewater. Similarly, no enhanced seasonal impacts from sulphate or metals in the water column, nor adverse impacts on the final water quality of the outflows, were detected in the TMF wetland. The metal concentrations of the water column of this wetland were substantially lower than those reported for rivers and wetlands impacted by AMD from the literature as referenced in Table 5.8. Consequently, a secondary treatment wetland was unnecessary in the pilot trials given that outflows from the TMF wetland did not require treatment in terms of pH, sulphate or metals content.

Fourthly, the integrative assessment provided empirical evidence of sediment quality and indicated the absence of contaminant-induced degradation of sediments. The 0.20 m depth of peat substrate in the TMF wetland adequately served as the substrate material for wetland vegetation. However, this research shows that during plant propagation, peat must be kept in place with careful water management and specific planting density. These conditions prevent patches of tailings being exposed prior to full cover being established. Overall, in the two-year experimental time-frame, the results for mean total metal concentrations in the sediments of the TMF wetland in comparison to the Control, indicate no significant adverse mobilisation of tailings metals into the peat substrate. Additionally, the results do not indicate significant accumulation of metals in the peat substrate of the TMF wetland from 1999 to 2000. However, the potential threshold effects of accumulating metals on wetland ecological health must be further examined in future work.

Correlation analyses indicate a general increase in sediment metal concentration in the TMF wetland with increasing water depth and pH, and a corresponding decrease in the metal concentrations of the water column. Sediment extractions also showed enrichment of Cd, Fe, Pb and Zn in the oxidisable fraction (including sulfides and organic matter) of the TMF wetland sediments. The high organic content of the peat substrate (95 %) is likely to have influenced this pattern of enrichment and also is likely to play an important role in controlling metal bioavailability. These data suggest that adsorption and coprecipitation of metals is occurring from the water column of the TMF wetland with organic material at increasing depths under reducing conditions. These results are in agreement with Snodgrass *et al.* (2000) who found that leaching of metals from sediments when dry, and binding of metal species by organic matter in the water column and the sediments, are primary factors controlling metal mobility in isolated depressional wetlands.

In aquatic systems with a high content of organic substances, humic matter, which represents 70 % to 90% of dissolved organic carbon in wetlands, plays a dominant role in the final distribution of metal (Mota and Correia Dos Santos, 1995). Organic soils can remove metal contaminants through ion exchange given their higher cation exchange capacity and also provide the anoxic conditions necessary for sulfide production and hence additional sequestering of metals. Wood and Shelley (1999) also determined that the organic carbon in the deep anaerobic sediment appears to have the largest influence on metal bioavailability even at moderately low pH. Thus, if control of metals toxicity is an important design criteria for wetlands, then seeding of the area with organic rich soils may prove beneficial even if otherwise unnecessary for quick successional development (Wood and Shelley, 1999). The long-term control of metal bioavailability in the TMF wetland will likely be related to the presence and continual build-up of organic carbon binding sites in the developing wetland above the tailings.

In addition to total and extracted metals concentrations, metal speciation including free-metal ion concentration and the impact of physico-chemical parameters particularly pH and organic matter, were investigated to assess ecotoxicological risk. This was an important element of the overall project given the body of research evidence which has been developed by aquatic toxicologists to support the position that the biological response elicited by a dissolved metal is a function of free-metal ion activity. Overall, results indicate that potentially bioavailable metals (the sum of the exchangeable and reducible fractions) within the TMF wetland are similar to values cited for natural wetlands. Estimated free-metal ion concentrations calculated from geochemical regression models developed by Tessier (1992) and Tessier et al. (1993) indicate lower concentrations of [Cd^{2+}] in the TMF wetland than natural wetlands and slightly higher concentrations of [Pb^{2+}] and [Zn^{2+}]. It was difficult to make definitive judgements regarding the potential toxicity from the free-metal ion concentrations of Pb and Zn calculated in the pilot wetland. This was because it was not possible to correlate these concentrations with plant uptake because plant metal concentrations were determined for the previous years growth. To conduct this work was beyond the scope of this project. Given calculated [Pb^{2+}] and [Zn^{2+}] were higher in the TMF than in the Control wetland, it is now clear that it is important to conduct a more extensive investigation of free-metal ion activity in wetlands planted over pyritic tailings, and particularly the role played by organic matter in determining concentrations of [Pb^{2+}] and [Zn^{2+}] in these systems.

Finally, the metal concentrations in the roots, rhizomes and stems of three emergent wetland macrophytes were examined to determine heavy metal availability to wetland biota from the tailings, sediments and water matrices. Overall, metals concentrations in the roots and aerial tissues of *Typha latifolia*, *Phragmites australis* and *Juncus effusus* were either lower in the TMF wetland than in the Control or did not differ significantly as determined by statistical analysis. These values were also lower than heavy metal concentrations reported for similar plant tissues in wetlands receiving discharges from Pb-Zn mining activities. Increased macrophyte concentrations of metals, therefore, did not occur in the TMF wetland as a result of low sediment pH, elevated sediment metal concentrations or oxic redox potential which are associated with increased bioavailability of metals to plants.

Elevated concentrations of metals were determined in the roots/rhizomes of *Typha latifolia* and *Juncus effusus* in four quadrats were plants were found rooting directly into tailings. The presence of shallow water depth where this occurred indicates the potential for low sediment pH and oxic redox potential which could increase the bioavailability of heavy metals in these quadrats. Additional work is necessary to investigate if plant roots will extend further into tailings and accumulate toxic levels of metals in the long term.

Even though a substantial number of *Typha latifolia* plants were found rooting directly into tailings in other quadrats, elevated metals were not found in these plant tissues. *Typha* populations appear to be exhibiting metal-tolerant behaviour. Given, *Phragmites* did not exhibit elevated metal concentrations in any plant tissues, this suggests *Phragmites* may also be a metal-tolerant ecotype. The potential for both of these macrophytes to display metal tolerant mechanisms in wetlands constructed over pyritic tailings warrants further investigation.

Typha spp. may have a tolerance to heavy metals as a result of the immobilisation of metal ions. This may be due to rhizosphere oxygenation and associated precipitation of metal oxyhydroxides. Alternatively, in the TMF wetland penetration by roots into tailings may enhance water and oxygen penetration resulting in acidity and subsequent increased metal mobility. The overall influence of *Typha* plants on metal mobility in the TMF wetland appeared to remain localised. However, more extensive investigations into the rhizospheric impacts of plants in further trials is merited given the action of plants on metal mobility may be important particularly at the peat/tailings interface.

Metal concentrations in some plant tissues increased with increasing metal concentrations in sediments. For many dissolved and transition metals most evidence supports the idea of passive entry into organisms (Langston and Spence, 1995). Under these circumstances uptake is usually envisaged as being proportional to the free ion concentration or activity, at least for divalent cations such as Cd^{2+} and Zn^{2+} (Campbell, 1995). It is necessary to consider the role of the free-metal ion concentration $[M^{z+}]$ in the TMF sediment interstitial water in relation to the potential bioavailability of metals to plants in future research. This is particularly important given recent research (St. Cyr and Campbell, 2000) determined metal concentrations in plant tissues correlated more closely with estimates of bioavailable sediment-bound metals ($[Cd^{2+}]$, $[Pb^{2+}]$, $[Zn^{2+}]$) than with total metal concentrations in sediments.

Metal concentrations in some plant aerial tissues also increased with increasing metal concentrations in the water column and with decreasing pH. These results point to the adsorption of metals by stem tissues from the water column and agree with Sparling and Lowe's 1998 study that showed acidification influenced plant concentrations of metals and was especially important in submerged species.

The differential accumulation of Mn in the aerial tissues of *Typha* and *Juncus* species may point to the importance of this metal as a nutrient in wetland systems. This dynamic merits further examination.

The pilot trials generated data that identified *Juncus effusus* as a potential bioindicator. The ability to reflect gradients in contamination is clearly of overriding importance in the selection of indicator organisms (Langston and Spence, 1995) and metal concentrations in the tissues of *Juncus effusus* appeared to indicate gradients in contamination. For example, elevated concentrations of Pb and Zn were observed in *Juncus* plants growing directly into the tailings. The suitability of *Juncus effusus* as a bioindicator requires further assessment in future trials.

An on-going goal of future studies should be the identification of appropriate bioindicator species including plant and invertebrate groups. Bagatto and Shorthouse (1999) suggest measures of biodiversity based on a variety of invertebrate taxa are more sensitive indicators of ecosystem function than biological accumulation of metals. Their work now focuses on evaluating function and sustainability of tailings ecosystems using arthropod groups. These bioindicators will contribute to the assessment of ecosystem health and identification of the best route to the development of sustainable ecosystems over mine tailings.

10.3 ASSESSMENT OF SILVERMINES WETLANDS CURRENTLY TREATING DRAINAGE FROM PYRITIC TAILINGS

The chemistry of the water column and sediments in Silvermines wetland were much more indicative of a wetland system impacted by heavy metal contamination than the TMF wetland. The results of the statistical analyses indicate much higher similarity between Silvermines tailings and sediments from Silvermines wetland, than between these tailings and the TMF wetland sediments. Mean Cd, Fe, Mn, Pb and Zn concentrations in the water column and sediments of Silvermines wetlands are substantially higher than in the TMF wetland and closely approximate concentrations in these matrices contaminated with metals from mining. In addition, the mean sulphate concentration in the Silvermines wetland is substantially higher than that found in the TMF wetland and is closer to sulphate concentrations in waters associated with mining.

Potentially bioavailable metals were substantially elevated in Silvermines wetland in comparison to the TMF and Control wetlands and higher than those calculated for natural river sediments. However, Fe oxy-hydroxide concentrations in Silvermines sediments are also much higher than in the TMF and the Control wetlands and this significantly impacts the concentration of free-metal ions in the sediment porewater.

In wetland transition zones and where seasonal changes occur in soil flooding, hydrous Fe oxides may form and dissolve as a function of changing hydrology, consequently holding and releasing metals within the soil (Gambrell, 1994). The role of sediment Fe oxyhydroxides in controlling metal availability to various aquatic species has also been reported by Campbell and Tessier (1996). This work is supported by earlier work reported by Förstner (1985) with respect to data on aquatic organisms from sediments in 20 estuaries in southern and western England. Förstner reported that the concentration of Pb in the deposit-feeding bivalve *Scrobicularia plans* is largely controlled by the concentration of Pb in the sediment as modified by the inhibitory effect of Fe. Fe-oxyhydroxides in Silvermines sediments also appear to be effective in controlling metal retention in this wetland.

The free-metal ion concentrations for Pb and Zn indicate that Silvermines wetland is retaining metals and acting as a treatment wetland for drainage emanating from Sivermines tailings dam. This is in agreement with Odum *et al.* (2000) whose studies indicate that point sources with concentrations of Pb and acidic mine drainages need to run through a series of constructed wetlands as an economical and efficient means of filtration and holding of Pb. Wherever a series of wetlands has functioned to absorb large concentrations of Pb in its sediments and peat, the Pb is not readily released as long as the wetlands receive their normal water regimes (Odum *et al.*, 2000). Wetland areas such as these have been of great value in protecting human health and the environment for many years.

10.4 SUMMARY

The impact of AMD on wetland systems is associated with increases in the concentration and availability of heavy metals such as Cd, Fe, Mn, Pb and Zn, decreased pH, and potentially high levels of sulphate. However, in the pilot trials the potential for the pyritic tailings in the TMF wetland to generate AMD and mobilise metals was not detected following extensive analyses of the water column, the wetland substrate and the biotic material within the system and extensive correlation and regression analyses to investigate the relationships between these matrices. In addition, an examination of ecological parameters did not indicate the system was stressed due to environmental pollutants. Based on a preponderance of evidence from a variety of environmental indicators, tailings-induced contamination was not determined to have an adverse impact on the ecological health of the wetland cover.

Thus, the empirical evidence generated from the pilot research plant, specifically when compared with data from Silvermines wetland, point clearly to the potential for mitigating metal mobilisation from pyritic tailings by placing a thin layer of peat over these tailings and flooding them. Many researchers (as cited in Odum *et al.*, 2000) have shown the ability of peat and humic substances to form binding complexes with heavy metals and many organic toxicants as well. Consequently, a wetland approach to preventing metal mobilisation in the environment has been advocated by engineers and scientists in Europe and the United States. These researchers suggest that where Pb has been concentrated in sedimentary depositions in estuaries and lakes, these levels should be allowed to be buried by normal sedimentation to become part of the geological cycle (Odum *et al.*, 2000).

The primary aim of this research was to investigate the potential for establishing a sustainable wetland ecosystem over pyritic tailings. Self-sustainable land reclamation strives to lend a helping hand to the re-establishment of natural processes. The overall aim is the replacement of technological management by natural control. The results of this research indicate there is potential for creating a sustainable wetland cover over pyritic tailings using the principles of ecological engineering.

However, further investigation is merited. The results of these trials were used to make specific recommendations for investigating the potential to foster a self-sustaining wetland system over pyritic tailings through Lisheen Mine's field-scale trials. They were also used to make generic recommendations for investigating metal mobilisation in wetland systems and the ecological status of these systems.

10.5 RECOMMENDATIONS

Upon closure Lisheen Mine will have concentrated 6.63 million tonnes of pyritic tailings in a Tailings Management Facility (TMF). This facility has been specifically engineered (with reservoir walls and impervious geomembranes) to concentrate these tailings in a limited area which provides appropriate conditions for flooding the tailings surface. The reclamation strategy selected for Lisheen's TMF proposes the development of a self-sustainable wetland ecosystem over pyritic tailings that prevents the generation of AMD and the mobilisation of toxic metals into surrounding ecosystems.

The following specific recommendations for field-scale trials, and overall generic recommendations, are based on the results from the pilot-scale trials:

Use of Environmental Indicators and a Functional Approach in Integrated Assessments to Assess Ecological Status

- An integrated assessment focusing on indicators of ecological health including ecological, hydrological, physico-chemical, sedimentary, biotic and invertebrate sampling and analyses should be conducted in the field-scale trials. This assessment should include water column and sediment toxicity testing. These trials provide an opportunity for enhancing the development of an overall functional approach for monitoring the key wetland functions of the final created wetland. Such an approach is necessary to evaluate the dynamics or changes in the wetland system over time. The key wetland functions of this wetland include toxicant retention and pollution prevention, sediment retention, creation of aquatic and wildlife habitat, uniqueness and educational potential.

  A key aim of the EU Water Framework Directive is achieving "good status" for all waters by 2015. This involves two elements "good ecological status" and "good chemical status". Good ecological status is defined in the Framework in terms of the quality of the biological community, the hydrological characteristics and the chemical characteristics of waters. The strategic document on the *Common Strategy on the Implementation of the Water Framework Directive* states that the development of methods for indication and assessment of the ecological status of waters is a key issue for the successful implementation of the Water Framework Directive. Further research into the use of environmental indicators and integrated assessments to assess the ecological status of Irish waters and to develop criteria for rehabilitation if necessary, is warranted given the need to implement the Water Framework Directive.

Given the problem of eutrophication in several Irish lakes (e.g. the main problem afflicting Lough Ree and Derg is over-enrichment caused mainly by phosphates) it is timely to thoroughly investigate the potential for nutrient removal in riparian wetlands. Given the requirements of the Water Framework Directive it is also timely to investigate the potential for enhancing existing riparian wetland systems in Ireland with a view to the surface water rehabilitation and pollution prevention.

Long-Term Water Depth and Permanency of Wetland Cover

- The wetland cells in the pilot system were fed by a continuous stream of mains water in addition to rainwater whereas Lisheen's final TMF will be fed by rainwater alone. The potential exists for an ombrotrophic bog rather than a wetland marsh to develop over Lisheen's TMF due to this difference in the major hydrologic forcing function. An extensive hydrological analysis will be required in the field-scale trials to examine the impact of hydrology on the development of the ecological system and on the TMF structure in the long term. Using deeper water to prevent sediment oxidation and mobilisation of metals must be balanced by the need to promote a diverse wetland habitat. The use of specific plant species more appropriate to highly exposed and bog-like conditions (e.g. *Juncus squarosus)* should be investigated in field-scale trials. A detailed evaluation of bogland species such as *Bryophytes* (sphagnum mosses) which alter wetland hydrology must be undertaken in these trials.

Impact of Wave Action

- Lisheen's closure plan for the TMF advocates the establishment of reedbeds and aquatic vegetation coupled with low mean maximum water depth, which with time, will eliminate the erosive power of waves on the beach protecting the impoundment walls. The spillway on the TMF is designed for a maximum water level of 0.5-0.7m on flat tailings surface. However, the pilot system shows much lower water levels are viable to prevent metal mobilisation and to create diverse vegetation patterns. Given that the reduction of water levels will directly mitigate the impact of wave action in the TMF, field-scale trials should be structured to investigate differences in water levels on metal mobilisation, plant growth and colonisation.

Rate of Sedimentation

- It is important to determine sedimentation rates based on organic production and primary productivity in the TMF. High sedimentation rates can indicate that a wetland is retaining metals by slowly burying them under sediments. High sedimentation rates can also indicate that a wetland may change rapidly as it fills with sediments and is possibly reduced in its ecological and hydrologic value.

Seasonal Investigations

- The impacts on community structure and function during a range of climatological conditions including stressful conditions of ice cover, severe anoxia, or drought should be examined in field-scale trials. The definition of normal condition should encompass not only a mean condition, but the naturally-occurring extremes in structure and function that may be expected over decades of time (i.e. temporal and spatial variability).

- Impacts of pH and temperature on the release of metals from sediments also requires further analysis in the field-scale trials. It is necessary to investigate the potential for enhanced enrichment of contaminants in sediments in winter and the potential for release of contaminants to the water column in summer with increases in temperature.

Water Column Characterisation

- It is necessary to fully characterise the water chemistry of the wetland in the field-scale trials. Ongoing seasonal physico-chemical analyses must be repeated to gain information on the degree of metal mobilisation into the overlying water. This is essential for the assessment of temporal variability in contamination upon the ecosystem as a whole.

- Sulphate concentrations in the water column should be investigated and associated correlations with total and extracted concentrations of metals determined. This will be particularly important during the initial drawdown and establishment of the wetland system. This will facilitate an investigation of the potential for the formation of insoluble metal sulphides from soluble sulphate in the initial peat substrate of the TMF wetland.

Total and Extracted Sediment Metal Analyses

- While data from this study indicate no significant build-up of metals in the TMF wetland sediments between 1999 and 2000, the potential threshold effects of accumulating metals on wetland ecological health must be further examined in the field-scale trials. Total and extracted concentrations of metals should be determined. The role that humic matter and sulfides will play in the final distribution of metals in the TMF wetland should also be evaluated during field-scale trials. Oxidising sulfide-containing sediments for extended periods will result in the loss of all sulfide and subsequent release of metals. Therefore, it is necessary to distinguish the percentage enrichment of metals in the organic and sulfide fractions in the field-scale trials.

Free Metal Ion Activity

- Given calculated [Pb^{2+}] and [Zn^{2+}] were higher in the TMF than in the Control wetland, it is important to conduct a more extensive investigation of free-metal ion activity in wetlands planted over pyritic tailings in the field-scale trials. It is necessary to continue to review the impact of changing environmental conditions on metal speciation, accumulation, transport and bioavailability in wetland sediments to fully assess the potential remobilisation of metals. These changing environmental conditions include varying pH and redox potential, organic carbon bonding sites and other ligands, and the presence of other metals that may act synergistically or competitively.

Further research is necessary to examine the use and development of specific geochemical regression equations to calculate free-metal ion concentrations in Irish rivers, lakes and wetland systems. This will facilitate more accurate evaluations of the bioavailability of sediment-bound metals under Irish environmental conditions.

- Using the available peat at Lisheen Mine for the TMF wetland cap makes sense due to its organic carbon binding potential. In the field-scale trials, it is necessary to investigate the long-term control of metal bioavailability through the use of peat and the implications of the continual build-up of organic carbon binding sites.

Labile Metals in Oxic and Anoxic Sediments

- In the field-scale trials it is necessary to evaluate metal speciation throughout the peat profile including within oxic and anoxic sediments and at the oxic/anoxic interface. Therefore, it is important to understand that differences exist in the geochemistry of oxic and anoxic sediments. An investigation of speciation in the field trials would involve evaluating the free-metal ion concentration in the oxic sediments and the concentration of acid volatile sulphide (AVS) in the anoxic sediments to assess the overall potential bioavailability of sediment heavy metal burdens.

Fe and Mn Oxy-hydroxides

- Given evidence of the role of Fe hydroxides and Fe oxy-hydroxides in retaining metals in marsh wetlands observed at Silvermines, it is necessary to assess the potential build-up of Fe hydroxides in the sediments of the TMF during the field-scale trials.

Plant Metal Accumulations and Plant Physiology

- In the field-scale trials further research is required on metal concentrations, and bioaccumulation and bioconcentration rates in wetland plants and invertebrates.

- Phytotoxic impacts of potential contamination in the TMF wetland require careful examination. Testing of eco-physiological indicators in combination with community and ecosystem level indicators could be investigated in the field-scale trials. A review of plant physiology, particularly in regard to marsh and bogland ecosystems should be conducted during field-sale trials. It is necessary to examine the phytotoxic impacts of contamination on indigenous floral species including bogland species.

- It is necessary to consider the role of the free-metal ion concentration $[M^{z+}]$ in the TMF sediment interstitial water in relation to the potential bioavailability of metals to plants in the field-scale trials.

Bioindicators

- The use of *Juncus* spp. as possible bioindicators in assessing wetlands for rehabilitating pyritic tailings should be further investigated in the field-scale trials at Lisheen. An on-going goal of field-scale studies should be to identify appropriate bioindicator species including plant and invertebrate groups.

Rhizosphere Impacts on Metal Mobilisation

- More extensive investigations into the rhizospheric impacts of plants in the field-scale trials is merited given the action of plants on metal mobility may be important particularly at the peat/tailings interface.

Model Development

- During the field-scale trials work could commence on the development of a model to investigate potential long-term changes in the wetland system. In this thesis linear regression analysis was used to examine the relationship between dependant variables and independent variables. This existing baseline data can be used to perform multiple linear regression analyses to formulate regression equations for the initial calibration of this model which takes multiple variables into consideration. The model is validated by comparing simulation results to observations made in the field and improved using an iterative process.

Reference Wetlands

- Measurements made in potentially stressed wetlands should be compared with measurements from structurally similar reference wetlands. In the field-scale trials appropriate reference wetlands in close proximity to the TMF, particularly bogland ecosystems, should be evaluated and selected.

REFERENCES

Adams, D.D. (1994). Sediment pore water sampling. In: Mudroch A. and S.D. MacKnight (eds.) *Handbook of Techniques for Aquatic Sediments Sampling, 2nd Ed.* Lewis Publishers, Boca Raton, Fla. pp. 171-202.

Adamus, P. (1992). Choices in monitoring wetlands. In: McKenzie, D.H., D.E. Hyatt, and V.J. McDonald (eds.) *Ecological Indicators, Volume 1.* Elsevier Applied Science, London, New York.

Adriano, D.C. (1986). *Trace Elements in the Terrestrial Environment.* Springer-Verlag, New York, 533 pp.

Agricola, G. (1556). De re metallica, H.C. Hoover and L.H. Hoover (trans.), Dover, 1950.

Albers, P.H. and M.B. Camardese (1993). *Environ. Toxicol. Chem.* 12, 959.

Alloway, B.J. (ed.). (1995). *Heavy Metals in Soils.* John Wiley and Sons, Somerset, New Jersey, 339 pp. As cited in Stoughton and Marcus 2000.

Anderson, M.A., F.M.M. Morel and R.R.L. Guillard. (1978). Growth limitation of a coastal diatori by low zinc ion activity. *Nature*, 276, 70.

Apte, S and G.E. Batley. (1995). Trace metal speciation of labile chemical species in natural waters and sediments: non-electrochemical approaches. In: Tessier, A. and D.R. Turner (ed.s). *Metal Speciation and Bioavailability in Aquatic Systems.* John Wiley and Sons Ltd., Chichester, UK.

Armstrong, W., M.E. Strange, S. Cringle, and P.M. Beckett. (1994). Microelectrode and modelling study of oxygen distribution in roots. *Ann. Bot.* 74: 287-299.

Arthurs, J.W. (1994). *Investigations into Acid Mine Drainage and Hydrology at the Silvermines Tailings Dam, County Tipperary.* Tailings Research Project, September 1994.

Bagatto, G. and J.A. Shorthouse. (1999). Biotic and abiotic characteristics of ecosystems on acid metalliferous mine tailings near Sudbury, Ontario. *Canadian Journal of Botany*, 77, 410-425.

Barbour, M.G., J.H. Burk, and W.D. Pitts. (1987). *Terrestrial Plant Ecology.* Benjamin/Cummings Publishing, Menlo Park, California, 604 pp.

Basta, N. and R. Gradwohl. (2000). Estimation of Cd, Pb, and Zn bioavailability in smelter-contaminated soils by a sequential extraction procedure. *Journal of Soil Contamination.* 9 (2): 149-164.

Bates, S.S., Tessier, A., P.G.C. Campbell and J. Buffle. (1982). Zinc adsorption and transport by *Chlancydomonas variablis* and *Scenedesmus subspicatus. (Chlorophyceae)* grown in semicontinuous culture, *J. Phycol.,* 18, 521.

Batzer, D.P. and V.H. Resh. (1992). Macroinvertebrates of a California seasonal wetland and responses to experimental habitat manipulation. *Wetlands* 12: 1-7.

Baudo, R. (1982). The role of the speciation in the transfer of heavy metals along the aquatic ford web. In: Ravaera, O. (ed.) *Ecological Effects on Heavy Metals Speciation in Aquatic Systems.* Ispra-Courses, Ispra/Italy. Unpublished manuscript, 31 pp.

Baudo, R. and G. Galanti. (1998). *Unio elongatulus* as an indicator of trace element Pollution. *Verh. Int. Ver. Limnol,* 23, 1652. As cited in Langston and Spence, 1995.

Benjamin, M.M., M.M. Hayes and J.O. Leckie (1982). Removal of toxic metals from Power-generation waste streams by adsorption and co-precipitation. *Journal of Water Pollution Control Fed.* 54, 1472-1481.

Block, M., and W.A. Glynn. (1992). Influence of xanthates on the uptake of Cd by Eurasian dace *(Phoxinus Phoximus)* and rainbow trout *(Oncorhynchus mykiss). Environ.Toxicol, Chem.,* 11, 873. As cited in Campbell 1995.

Bradshaw, A.D. and M.J. Chadwick. (1980). *The Restoration of Lan*d. Blackwell Scientific Publications. Oxford, England.

Brix, H. (1993). Macrophyte-mediated oxygen transfer in wetlands: transport mechanisms and rates, p. 391-398. In: Moshiri, G. (ed.), *Constructed Wetlands for Water Quality Improvement.* CRC press, Boca Raton, Fla.

Brodie, G.A. (1993). Staged, aerobic constructed wetlands to treat acid drainage: Case history of Fabius Impoundment 1 and overview of the Tennessee Valley Authority's program. In: Moshiri, G. (ed.), *Constructed Wetlands for Water Quality Improvement.* Lewis Publishers, CRC Press, Boca Raton, FL.

Brodie, G.A. (1991). Achieving compliance with staged, aerobic constructed wetlands. In: *Proc. 1991 Annul Meeting Am. Soc. Surface Mining Reclamationists.* Durango, CO, 151.

Brodie G.A., C.R. Britt, T.M. Tomaszewski and H.N. Taylor. (1993). Anoxic limestone drains to enhance performance of aerobic acid drainage treatment wetlands. In: Moshiri, G. (ed.), *Constructed Wetlands for Water Quality Improvement.* Lewis Publishers (CRC Press). Boca Raton, FL.

Brodie, G.A., D.A. Hammer and D.A. Tomljanovich. (1989). Treatment of acid drainage with a constructed wetland at the Tennessee Valley Authority 950 coal mine. In: Hammer, D.A. (ed.), *Constructed Wetlands for Wastewater Treatment, Municipal, Industrial and Agricultural.* Lewis Publishers, Inc.

Brower, J.E., J.H. Zar and C.N. von Ende. (1990). *Field and Laboratory Methods for General Ecology, Third Edition.* Wm. C.Brown Publishers.

Broyer, T.C., C.M. Johnson, and R.E. Paul. (1972). Some aspects of lead in plant nutrition. *Plant Soil* 36: 301-313. As cited in Gambrell, 1994.

Bryan, G.W., Langston W.J., Hummerstone L.G. and Burt, G.R. (1985). A guide to the assessment of heavy metal contamination in estuaries using biological indicators, *Mar. Biol Assoc. UK,* Occasional Publ. No. 4. As cited in Langston and Spence, 1995.

Burgess, R.M. and K.J. Scott (1992). The significance of in-place contaminated marine sediments on the water column: processes and effects. In: Burton, G.A. Jr. (ed.) *Sediment Toxicity Assessment.* Lewis Publishers, Inc. CRC Press.

Burton, G.A. Jr. (1992). Sediment collection and processing: factors affecting realism. In: Burton, G.A. Jr. (ed.) *Sediment Toxicity Assessment.* Lewis Publishers, Inc. CRC Press.

Burton, M.A.S. (1986). *Biological Monitoring of Environmental Contaminants (Plants).* Technical Report. Prepared by Monitoring and Assessment Research Centre, Kings College London, University of London. MARC Report No. 32.

Cairns, J.Jr., B.R. Neiderlehner and E.P. Smith. (1992). The emergence of functional attributes as end points in ecotoxicology. In: Burton, G.A. Jr. (ed.), *Sediment Toxicity Assessment.* Lewis Publishers, Inc. CRC Press.

Caldwell, C.A., and C.M. Canavan. (1998). *Spatial and Temporal Distribution of Mercury in Caballo and Elephant Butte Reservoirs, Sierra County, New Mexico.* WRRI Tech. Completion Rep. 306, New Mexico Water Resources Research Institute, Las Cruces, N.M.

Campbell, P.G.C. (1995) Interactions between trace metals and aquatic organisms: a critique of the free-ion activity model. In: Tessier, A. and D.R. Turner (eds.), *Metal Speciation and Bioavailability in Aquatic Systems*. John Wiley and Sons Ltd., Chichester, UK. pp. 45-102

Campbell, P.G.C. and A.G. Lewis (eds*.)*. (1988). Biologically available metals in sediments. *Assoc. Comm. Sci. Criteria Environ.* Qual. Publ. No. 27694. National Research Council of Canada. Ottawa. Ont.

Campbell, P.G.C., and P.M. Stokes. (1985). Acidification and toxicity of metals to aquatic Biota. *Canadian Journal of Fisheries and Aquatic Sciences,* 42, 2034.

Campbell, P.G.C., and A. Tessier. (1996). Ecotoxicology of metals in the aquatic environment: geochemical aspects. In: M.C. Newman and C.H. Jagoe (eds.), *Ecotoxicology, A Hierarchical Treatment*. pp. 11-58.

Campbell, P.G.C., A.G. Lewis, P.M. Chapman, A.A. Crowder, W.K. Fletcher, B. Imber, S.M. Luoma, P.M. Stokes and M. Winfrey. (1988). *Biologically Available Metals in Sediments*, Rep-No. 27694, National Research Council of Canada, Ottawa.

Carapeto, C. and D. Purchase. (2000). Use of sequential extraction procedures for the analysis of cadmium and lead in sediment samples from a constructed wetland. *Environmental Contamination and Toxicology.* 64: 51-58.

Chapman, M., E.A. Power, and G.A. Jr. Burton. (1992). Integrative assessment in aquatic ecosystems. In: Burton, G.A. Jr. (ed.) *Sediment Toxicity Assessment.* Lewis Publishers, Inc. CRC Press.

Cherry D.S., L.G. Rutherford, M.G. Dobbs, C.E. Zipper, J. Cairns Jr, and M.M. Yeager (1995). *Acidic pH and Heavy Metal Impact into Stream Watersheds and River Ecosystems by Abandoned Mined Lands, Powell River, Virgina.* Report to Powell River Project Reach and Education Program Reports, Virginia Polytechnic Institute and State University, Blacksburg, VA. As cited in Soucek *et al.*, 2000a.

Christy, E.J. and R.R. Sharitz. (1980). Characteristics of three populations of a swamp annual under different temperature regimes. *Ecology*, 6, 454-60.

Clesceri, Greenberg and Eaton. (1998). *Standard Methods for the Examination of Water and Wastewater, 20th Edition.* American Public Health Association.

Coughlan, H.H. and H.J. Case. (1957). Early Metallurgy of Copper in Britain and Ireland. *Proceedings of the Prehistoric Society*, 23, 9 1-123. As cited in O'Brien, 1995.

Commission of the European Communities, Community Bureau of Reference. (1986). Certified reference material BCR No. 61, Aquatic Moss (*Platihypnidium ripanoides).*

Cooney, J. (2000). Mining and sustainable development: the next steps. *Mining Environmental Management,* 8:1, 19-20.

Cowan, C.E., E.A. Jenne and R.R. Kinnison. (1986). Methodology for determining the relationship between toxitity and the aqueous speciation of a metal. In: Poston, T.M and K. Purdy (eds.), *Aquatic Toxicology and Environmental Fate,* Spec. Pubil. No. 921 American Society for Testing and Materials, Philadelphia. p. 463. As cited in Apte and Batley, 1995.

Cox, G.W. (1990). *Laboratory Manual of General Ecology, Sixth Edition,* Kane, K. (ed.), Wm. C. Brown Publishers, IA, USA.

Crowder, A. (1991). Acidification, metals and macrophytes. *Environ. Poll.* 71:171-203

Csuros, M. (1994). *Environmental Sampling and Analysis for Technicians.* CRC Press, Inc.

Cundy A.B., I.W Croudace, J. Thomson and J.T. Lewis. (1997). Reliability of salt marshes as "geochemical recorders" of pollution input: a case study from contrasting estuaries in Southern England. *Environmental Science and Technology,* 31(4), 1093-1101.

DaSilva, M. (1996). Personal communication between M. DaSilva from Montana Department of Environmental Quality and Paula Treacy of Institute of Technology, Sligo.

Davidson, C.A., A.L. Duncan, D. Littlejohn, A.M. Ure and , L.M. Garden. (1998). A critical examination of the three-stage BCR sequential extraction procedure to assess the potential mobility and toxicity of heavy metals in industrially-contaminated land. *Analytical Chimica Data,* 363: 45-55.

Davidson, J. (1993). Sucessful acid mine drainage and heavy metal site bioremediation. In: Moshiri, G. (ed.), *Constructed Wetlands for Water Quality Improvement.* Lewis Publishers, CRC Press, Boca Raton, FL.

Department of Agriculture, Food and Rural Development. (2000). *Report of the Investigation into the Presence and Influence of Lead in the Silvermines Area of County Tipperary.* Inter-Agency Group, Published by Department of Agriculture, Food & Rural Development, Dublin.

DiToro, D.M., J.D. Mahony, D.J. Hansen, K.J. Scott, M.B. Hicks, S.M. Mayr and M.S. Redmond. (1990). Toxicity of cadmium in sediments: the role of acid volatile sulfide, *Environ. Toxicol. Chem.,* 9, 1487. As cited in Apte and Batley 1995.

Dunbabin, J.S., J. Pokorny and K.H. Bowmer. (1988). Rhizosphere oxygenation by *Typha domingensis* Pers. in miniature wetland filters used for mental removal from Wastewaters. *Aquatic Botany*, 29.

Dvorak, D.H., R.S. Hedin, H.M. Edenborn and P.M. McIntire. (1992). Treatment of metal-contaminated water using bacterial sulfate reduction: results of pilot-scale reactors. *Biotechnology and Bioengineering*, 40, 609-16. As cited in O'Sullivan *et al* 1999.

Eger, P., G. Melchert, D. Antonson, and J. Wagner. (1993). The use of wetland treatment to remove trace metals from mine drainage. In: Moshiri, G. (ed.), *Constructed Wetlands for Water Quality Improvement*. Lewis Publishers, CRC Press, Boca Raton, FL.

Emerson, D., J.V. Weiss and J.P. McGonigal. (1999). Iron oxidising bacteria are associated with ferric hydroxide precipitates (Fe-plaque) on the roots of wetland plants. *Applied and Environmental Microbiology* 65: (6), 2758-2761.

Environmental Protection Agency. (1999). *Report on Investigations of Recent Developments at Silvermines Tailings Management Facility, Co. Tipperary.* EPA Ireland, January 1999.

Erickson, P.M., , R.L. Kleinmann and P.S.A. Campion. (1982). Reducing oxidation of pyrite through selective reclamation practices. *Symposium on Surface Mining Hydrology, Sedimentology and Reclamation.* University of Kentucky, Lexington, Kentucky, December 5-10, 1982.

Faulkner, S.P. and C.J. Richardson. (1990). Iron and manganese fractionation in constructed wetlands receiving acid mine drainage. In: Cooper, P.F. and B.C. Findlater (eds.), *Constructed Wetlands in Water Pollution Control*, 419-428. Oxford, Pergamon Press.

Faulkner, S.P. and C.J. Richardson. (1989). Physical and chemical characteristics of freshwater wetland soils. In: Hammer, D.A. (ed.), *Constructed Wetlands for Wastewater Treatment, Municipal, Industrial and Agricultural.* Lewis Publishers, Inc. Chelsea, MI, pp. 41-72.

Feasby, Grant. (1996). Personal Communication between Grant Feasby from the Canadian Mine Environment Neutral Drainage Programme (MEND) and Paula Treacy of Institute of Technology, Sligo.

Förstner, U. (1985). Chemical forms and reactivities of metals in sediments. In: Leschber R., R.D. Davis and P.L. Hermite (eds.), *Chemical Methods for Assessing Bio-available Metals in Sludges and Soils.* Elsevier Applied Science Publishers.

Gambrell, R.P. (1994) Trace and toxic metals in wetlands – a review. *Journal of Environmental Quality.* 23, 883-891.

Gambrell, R.P., and W.H. Patrick, Jr. (1989). Cu, Zn and Cd availability in a sludge-amended soil under controlled pH and redox potential conditions. P. 89-106. In: B. Bar-Yosef *et al.* (eds.). *Inorganic Contaminants in the Vadose Zone.* Springer-Verlag, Berlin.

Gardner, L.R., Chen, H. and Seillemyr, J.L. (1978). Comparison of trace metals in South Carolina floodplain and marsh sediments. In: D.C. Adriano and I.C. Brisben (eds.) *Environmental Chemistry and Cycling Process.* Division of Technical Information. 446-461.As cited in Odum, *et al.*, 2000.

Gavis, J.R., Guillard, R.L.L. and Woodward, B. (1981). Cupric ion activity and the growth of phytoplankton clones isolated from different marine environments, *J. Mar. Res.*, *39*, 315.

Gentile, J.H. (2000) Hormesis in ecology and ecological assessments. *Human and Ecological Risk Assessment* 6:(2), 223-226.

Gibbs, R.J. (1973). Mechanisms of trace metal transport in rivers. *Science* 180, 71-73. As cited in Förstner (1985).

Giblin, A.E. (1985). Comparisons of the processing elements by ecosystems. II. Metals. In: Godfrey *et al.*, (eds.) *Ecological Considerations in wetlands Treatment of Municipal Wastewaters* Van Nostrand Reinhold, New York, 158-179.

Giblin, A.E., G.W. Luther, and I. Valiela. (1986). Trace metal solubility in salt marsh Sediments contaminated with sewage sludge. *Estuar. Coast. Shelf Sci.* 23: 477-498

Ginn, T.C. and Pastorak, R.A. (1992). Assessment and management of contaminated sediments in Puget Sound. In Burton, G.A. Jr. (ed.), *Sediment Toxicity Assessment.* Lewis Publishers, Inc. CRC Press, Inc.

GlooschenKo, W.A. (1986). Monitoring the atmospheric deposition of metals by use of bog vegetation and peat profiles. In: J.O. Nriagu (ed.) *Toxic Metals in the Atmosphere.* As cited in Odum, *et al*, 2000.

Good, B.J. and W.H. Patrick, Jr. (1987). Root-water-sediment interface processes. In: Reddy K.R. and W.H. Smith (eds.), *Aquatic Plants for Water Treatment and Resource Recovery* (Orlando, FL. 1986), 359-371, Orlando, FL. Magnolia Publishing Inc.

Good, D.M., V.T. Ricca and K.S. Shumate. (1970). The relation of refuse pile hydrology to acid production, in preprints, pp.145-151. *Third Symposium on Coal Mine Drainage Research,* Pittsburgh, PA. As cited in Erickson *et al.,* 1982.

Gray, N.F. (1999). *Water Technology*, Trinity College, Dublin.

Greenan, E. (1973). Personal communication with Eamonn Grennan from Institute of Technology, Sligo, regarding geological investigations conducted in 1973.

Gross, M.A., S.J. Formica, L.C. Gandy and J. Hestir. (1993). A comparison of local waste materials for sulphate-reducing wetlands substrate. In: Moshiri, G. (ed.), *Constructed Wetlands for Water Quality Improvement*. Lewis Publishers, CRC Press, FL.

Haigh, M.J. (2000). The aims of land reclamation. *Land Reconstruction and Management* 1, 1-20.

Hammer, D.A. (ed.) (1989). *Constructed Wetlands for Wastewater Treatment, Municipal, Industrial and Agricultural.* Lewis Publishers.

Hammer, D.A. and R.K. Bastian. (1989). Wetland ecosystems: natural water purifiers? In: Hammer, D.A. (ed.), *Constructed Wetlands for Wastewater Treatment, Municipal, Industrial and Agricultural.* Lewis Publishers.

Haygarth, P.M. and K.C. Jones. (1992). Atmospheric deposition of metals to agricultural surfaces. In: D.C. Adriano (ed.), *Biogeochemistry of Trace Metals*. Lewis Publishers, Boca Raton, Florida, 513 pp.

Hedin, R., S. and R. W. Nairn. (1993). Contaminant removal capabilities of wetlands constructed to treat coal mine drainage. In: Moshiri, G. (ed.), *Constructed Wetlands for Water Quality Improvement*. Lewis Publishers, CRC Press, Boca Raton, FL.

Hedin, R., S., R. W. Nairn and R. Kleinmann. (1994). *The Passive Treatment of Coal Mine Drainage*. Ohio State University, Columbus, Ohio. Pittsburgh Research Centre, USBM, Pittsburgh, PA.

Herskowitz, J. (1986). *Town of Listowel Artificial Marsh Project Final Report, Project No. 128RR.* Ontario Ministry of the Environment, Toronto, Ont., Sept. 1986.

Hsieh, Y.P. and C.H. Yang. (1997). Pyrite accumulation and sulfate depletion as affected by Root distribution in a *Juncus* (needle rush) salt marsh. *Estuaries,* 20(3), 640-5.

ICOLD (2001). Tailings Dams, Risk of Dangerous Occurances – Lessons Learnt From Practical Experiences, Bull, 121, International Commission on Large Dams.

Irving, P.M. (ed.) (1991). *Acidic Deposition: State of Science and Technology,* National Acid Precipitation Assessment Program, Washington, D.C. As cited in Sparling and Lowe, 1998.

Jackson, L.J., J. Kalff and J.B. Rasmussen. (1993). Sediment pH and redox potential affect the bioavailability of Al, Cu, Fe, Mn, and Zn to rooted aquatic macrophytes. *Can.J. Fish. Aquat. Sci.*, 50: 143-148.

Jackson, L.J. Rasmussen, J.B., Peters, R.H., and Kalff, J. (1991). Empirical relationships between the element composition of aquatic macrophytes and their underlying sediments. *Biogeochemistry*, 12: 71-86

Jantsch, E. (1980). *The Self-Organising Universe*. Pergamon, Oxford. As cited in Haigh, 2000.

Jaynes, M.L., and Carpenter, S.R. (1986). Effects of vascular and non-vascular macrophytes on sediment redox, and solute dynamics. *Ecology* 67(4):875-882.

Jenne, E.A. (1977). Trace element sorption by sediments and soils – sites and processes. In: W. Chappell and K. Petersen (eds.). *Symposium on Molybdenum.* Marcel Dekker, New York, pp. 425-553.

Jonasson, I.R. (1977). Geochemistry of sediment /wate interactions of metals, including observations on availability. In: Shear H. and A.E.P. Watson (eds.) *The Fluvial Transport of Sediment-associated Nutrients and Contaminants.* IJC/PLUARG, Windsor/Ont: 255-271. As cited in Salomons and Förster, 1984.

Kabata-Pendias, A. and H. Pendias. (1992). *Trace Elements in Soils and Plants.* CRC Press, Boca Raton, Florida, 365 pp.

Kadlec, R.H. (1989). *Vegetation Resistance in Wetland Water Flow* in preparation, as cited in Hammer, 1989.

Kadlec, R.H. and R. L. Knight. (1996). *Treatment Wetlands.* Lewis Publishers, CRC Press.

Keith, L.H. (ed.) (1996). *Principles of Environmental Sampling.* American Chemical Society.

Kent, D., R.J. Reihold, J.M. Kelly and C.E. Tammi. (1992) Coupling wetlands structure and function: developing a condition index for wetlands monitoring. In: Burton, G.A. Jr. (ed.) *Sediment Toxicity Assessment.* Lewis Publishers, Inc. CRC Press, Inc.

Kingston and Haswell. (1998). *Microwave Enhanced Chemistry.* American Chemical Society.

Kirkham, M.B. (1975). Trace elements in corn grown on long-term sludge disposal site. *Environ. Sci. Technol.* 9, 765-768

Kleinmann, R. (1996). Personal communication between Dr. Robert Kleinmann of U.S. Bureau of Mines and Paula Treacy of Institute of Technology, Sligo.

Kleinmann, R. (1990). Acid mine water treatment using engineered wetlands. In: P.J. Norton (ed.), *Acid mine water in Pyritic Environments*. 269-276. Lisboa, Portugal.

Kleinmann, R. and M.A. Girts (1987). Acid mine water treatment in wetlands: an overview of an emergent technology. In: Reddy K.R. and W.H. Smith (eds.), *Aquatic Plants for Water Treatment and Resource Recovery* (Orlando, FL. 1986), 359-371, Orlando, FL. Magnolia Publishing.

Kruckeberg, A.L., and L. Wu. (1992). Copper tolerance and copper accumulation in herbaceous plants colonizing inactive California copper mines. *Ecotoxicology and Environmental Safety,* 23, 307-319.

Kufel, J. (1989). Akamulacja mikroelementow w trzcinie i palce waskolistnej i drogi ich powrotu do srodowiska. Polska Akademia Nauk Instytut Ekologii Stacja Hydrobiologiczna. Praca doktorska, Mikolajki, 71 pp. As cited in Odum, *et al.*, (2000).

Ladd, S.C., W.A. Marcus and S. Cherry. (1998). Differences in trace metal concentrations among fluvial morphologic units and implications for sampling. *Environmental Geology*, 36 (3-4): 259-269.

Lan, C., G. Chen, L. Li and M.H.Wong. (1992). Use of cattails in treating wastewater from a Pb/Zn mine. *Environmental Management* 16 (1): 75-80.

Lan, C., G. Chen, L. Li and M.H.Wong. (1990). Purification of wastewater from a Pb/Zn mine using hydrophytes. In: Cooper, P.F. and B.C. Findlater (eds.), *Constructed Wetlands in Water Pollution Control*, 419-428. Oxford, Pergamon Press.

Langston, W.J. and S.K. Spence (1995). Biological factors involved in metal concentrations observed in aquatic organisms. In: Tessier, A. and D.R. Turner (eds.) *Metal Speciation and Bioavailability in Aquatic Systems*. John Wiley and Sons Ltd., Chichester, UK.

Lau, S.S.S. and L.M. Chu (2000a) The significance of temporal variability in sediment quality for contamination in a coastal wetland. *Water Resources* 34: (8), 2412.

Lau, S.S.S. and L.M. Chu (2000b) The significance of sediment contamination in a coastal wetland, Hong Kong, China. *Water Resources* 34: (2), 379-386.

Lehtonen, J. (1989). *Ann. Bot. Fenn.* 26, 39. As cited in Sparling and Lowe, 1998.

Lehtonen, J. (1990). *Effects of Acdification on the Metal Levels in Aquatic Macroplytes in Espog, Finland.* No. 12. Department of Environmental Conservation, University of Helsinki, Helsinki, Finland.

Levy, D.B., K.A. Barbarick, E.G.Siemer, and L.E. Sommers. (1992). Distribution and partitioning of trace metals in contaminated soils near Leadville, CO. *Journal of Environmental Quality,* 21: 185-195.

Linacre, E.T. (1976). Swamps. In: Monteith, J.L. (ed.) *Vegetation and Atmosphere, Vol. 2: Case Studies.* London Academic Press, pp.329-347.

Macnicol, R.D., and P.H.T. Beckett. (1985). Critical tissue concentration of potentially toxic elements. *Plant and Soil,* 85: 107-129.

Marcus, W.A. (1991). Managing contaminated sediments in aquatic environments: identification, regulation, and remediation. *Environmental Law Reporter,* 21: 10020-10032. As cited in Stoughton and Marcus, 2000.

Marin, B., M. Valladon, M. Polve and A. Monaco. (1997). Reproducibility - testing of a sequential extraction scheme for the determination of trace metal speciation in a marine reference sediment by inductively coupled plasma-mass spectrometry. *Analytical Chimica Data,* 342: 91-112.

Martin, C.W. (2000). Heavy metal trends in floodplain sediments and valley fill, River Lahu, Germany. *Catena* 39, 53-68.

Mason, A.Z. and K.D. Jenkins. (1995). Metal detoxification in aquatic organisms. In: Tessier, A. and D.R. Turner (eds.) *Metal Speciation and Bioavailability in Aquatic Systems.* John Wiley and Sons Ltd., Chichester, UK.

McCabe, O.M. and M. L.Otte. (1997). Revegetation of metal mine tailings under wetland Conditions. P. 99-103. In: J.E. Brandt, J.R.Galevotic, L. Kost, and J. Trouart (eds.) *Proceedings of the 14th Annual National Meeting – Vision 2000: An environmental Commitment.* American Society for Surface Mining and Reclamation, Austin, TX, USA.

McCabe, O.M. and Otte, M.L. (2000). The wetland grass *Glyceria Flutans* for revegetation of metal mine tailings. *Wetlands,* 20:(3), 548-559.

McCann, M.T. (1993). *Toxicity of Zinc, Copper and Sediments to Early Life Stages of Freshwater Mussels in the Powell River, Virginia.* Masters Thesis. Virginia Polytechnic Institute and State University, Blacksburg, VA, USA

McGrath, D. and R.J. McCormack. (1999). *The Significance of Heavy Metal and Organic Micropollutants in Soils.* End of Project Report. Teagasc. 31 pp.

McIntire, P.E. and H.M. Edenborn. (1990). The use of bacterial sulfate reduction in the treatment of drainage from coal mines. *Proceedings of the Mining and Reclamation Conference and Exhibition, Charlestown, WV*, April 24-9, 1994, 1-8. As cited in O'Sullivan *et al.*, 1999.

McNaughton, S.J., T.C. Folsom, T. Lee, F. Park, C. Price, D. Roeder, J. Schmitz, L.A. Mendelssohn and K.L. McKee. (1992). Indicators of environmental stress in Wetland Plants. In: Burton, G.A. Jr. (ed.) *Sediment Toxicity Assessment.* Lewis Publishers, CRC Press.

MEND. (1993a). *Panel Wetlands: A Case History of Partially Submerged Pyritic Uranium Tailings Under Water.* Mine Neutral Drainage Programme, Project 3.12.2. Sponsored by the Canadian Centre for Mineral and Energy Technology (CANMET) ` and Ontario Ministry of Northern Development and Mines. February 1993.

MEND. (1993b). *Treatment of Acidic Seepages using Wetland Ecology and Microbiology – Overall Program Assessment.* MEND Project 3.11.1. Sponsored by CANMET, Centre de Recerche Minerales, Dennison Mines Limited Environment Canada and INCO Limited. July, 1993.

Michaud, S.C. and C.J. Richardson. (1989). Relative radial oxygen loss in five wetland plants. In: Hammer, D.A. (ed.), *Constructed Wetlands for Wastewater Treatment, Municipal, Industrial and Agricultural.* Lewis Publishers, Inc.

Minorco Lisheen. (1995a). *Environmental Baseline Report.* Planning Submission for the Lisheen Zinc/Lead Project. Minorco Lisheen Ltd., Grand Canal House, 1 Upper Grand Canal Street, Dublin 4. December 1995.

Minorco Lisheen. (1995b). *Lisheen Zinc/Lead Project, Environmental Impact Statement Supporting Technical Reports Closure Plan.* December 1995.

Minorco Lisheen. (1995c). *Planning Study, Tailings. Management Facility, Volume I Technical Report and Volume II- Appendices C, D, E and F.* Minorco Lisheen Ltd., Dublin.

Mitsch, W.J. (1992). Ecological indicators for ecological engineering in wetlands. In: McKenzie, D.H., D.E. Hyatt, and V.J. McDonald (eds.), *Ecological Indicators, Volume 1.* Elsevier Applied Science, London, New York.

Mitsch, W.J. and J.G. Grosselink. (1986). *Wetlands.* New York, Van Nostrand Reinhold.

Mota, A.M. and Correia dos M.M. Santos. (1995). Trace metal speciation of labile chemical species in natural waters: electrochemical methods. In: Tessier, A. and D.R. Turner (eds.) *Metal Speciation and Bioavailability in Aquatic Systems*. John Wiley and Sons Ltd., Chichester, UK.

National Institute of Standards and Technology. (1999). *Standard Reference Material 1944*. New York/New Jersey Waterway sediment.

Nawrot, J.R. (1995). Attachment TR11/D of *the Lisheen Zinc/Lead Project, Environmental Impact Statement, Supporting Technical Reports, Closure Plan*: Review of Rehabilitation Plan and Additional Recommendations. December, 1995.

Nawrot, J.R. and J.E. Sandusky. (1993). Concentrated alkaline recharge pools for acid seep abatement: principles, design, construction and performance. In: Chugh Y. P. and D. C. Davin (eds.) *Proceedings NMLRC Symposium, 1993*.

Nelson, S.M., R.A. Poline, J.S. Thullen, J.S., Sartoris, J.J. and Bontwell, J.E. (2000) Invertebrate assemblages and trace element bioaccumulation associated with constructed wetlands. *Wetlands* 20(2), 406-415.

Nicholson, R., R. Gillham, R. Cherry and E. Reardon. (1989). Reduction of acid generation through the use of moisture retaining covers as oxygen barriers. *Canadian Geotechnical Journal*, 26, 1. As cited in Vick, 2002.

Nixon, S.W. and V. Lee. (1986). Wetlands and Water Quality: A Regional review of Recent Research in the United States on the Role of freshwater and Saltwater Wetlands as Sources, Sinks and Transformers of Nitrogen, Phosphorus, and Various Heavy Metals. Technical report Y-86-2. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. As cited in Odum *et al.*, (2000).

Norušis, M.J. (1998). SPSS® 8.0, *Guide to Data Analysis*. Prentice-Hall, Inc.

NR Canada. (1995). *Sustainable Devlopment and Minerals and Metals: An Issues Paper*. Ottawa: Natural Resources Canada: Mineral Strategies Branch.

Obarska – Pempkowiak, H. and K. Klimkowska (1999). Distribution of nutrients and heavy metals in a constructed wetland system. *Chemosphere* 39: (2), 303-312.

Odum, H.T., W. Wojcik, L. Pritchard Jr., S. Ton, J.J. Delfino, M. Wojcik, S. Leszczynski, J.D. Patel, S.J. Doherty, and J. Stasik. (2000). *Heavy Metals in the Environment, Using Wetlands for their Removal.* Center for Environmental Policy and Centre for Wetlands Environmental Engineering Sciences, University of Florida, Gainsville, Florida. CRC Press LLC, Boca Raton, Florida.

Odum, W.E. (1987). Predicting ecosystem development following creation and restoration of wetlands. In: Zelazny, J. and J.S. Feierabend (eds.) *Wetlands: Increasing our Wetland Resources*, 67-70. Proceedings of the conference, Corporate Conservation Council, National Wildlife Federation, Washington, D.C.

Otte, M.L. (1991). Contamination of coastal wetlands with heavy metals: factors affecting uptake of heavy metals by salt marsh plants. In: Rozema J. and J.A.C. Verkleij (eds.), *Ecological Responses to Environmental Stresses,* 126-33. The Netherlands. Kluwer Academic Publishers.

O'Brien, W. (1995). Ross Island and the origins of Irish-British metallurgy. In: Waddell, J. and Shea Tuohig, E. (eds.), *Proceedings of the Dublin Conference on Ireland in the Bronze Age, 1995.*

O'Sullivan, A.D., O.M. McCabe, D.S. Murray and M.L. Otte. (1999). Wetlands for rehabilitation of metal mine wastes. *Biology and Environment: Proceedings of the Royal Irish Academy.* 99B: (1), 11-17.

O'Sullivan, M. (1995). *Impact of Acid Mine Drainage on the Avoca River in Co. Wicklow.* Thesis awarded degree of Doctor of Philosophy from Trinity College, Dublin.

Patrick, W.H., Jr. and D.S. Mikkelsen. (1971). Plant nutrient behavior in flooded soil. In: Olson *et al.*, (eds.) *Fertilizer Technology and Use*. 2nd ed. P. 187-215. SSSA, Madison, WI. As cited in Gambrell, 1994.

Perry, A. and R. Kleinmann. (1991). Use of constructed wetlands in the treatment of acid mine drainage. *Natural Resources Forum,* 15(3): 178-84, August 1991.

Peterson, H.G. and F.P. Healy. (1985). Comparative pH department metal inhibition of nutrient uptake by *Scenedesnuis quadvicauda* (chlorophyceal). *J. Phycol.*, 21, 217.

Petersen, R. (1982). Influence of copper and zinc in the growth of a freshwater alga *Scenddesmus quadricauda* – the significance of chemical speciation. *Environ. Sci. Technol.*, 16, 443.

Ponnamperuma, F.N. (1972). The chemistry of submerged soils. *Adv. Agron.* 24:29. As cited in Gambrell, 1994.

Pritchard, L. (2000). Ecological assessment of the Steele City Swamps. In: Odum *et al.*, (eds.), *Heavy Metals in the Environment, Using Wetlands for their Removal.* CRC Press LLC, Boca Raton, Florida.

Rapin, F. and Förstner, U. (1983). On the selectivity of various extractants used in sequential leaching techniques for particulate metal speciation. *Proc. Int. Conf. Heavy Metals in the Environment, Heidelberg,* pp. 1074-1077.

Reddy, C.N., and W.H. Patrick Jr. (1977). Effect of redox potential and pH on the uptake of Cd and Pb by rice plants. *J. Environ. Qual.* 6: 259-262.

Reed, S.C., R.W. Giles and E.J. Middlebrooks. (1995). *Natural Systems for Waste Management and Treatment, Second Edition.* McGaw-Hill, Inc.

Rutherford J.E. and R.J. Mellow. (1994). The effects of an abandoned roast yard on the fish and macroinvertebrate communities of surrounding beaver ponds. *Hydrobiologia* 294: 219-228. As cited in Soucek *et al.*, 2000a.

Salomons, W. and U. Förster. (1984). *Metals in the Hydrocycle.* Springer-Verlag, Berlin, Heidelberg, New York, Tokoyo.

Sartoris, J.J. and J.S. Thullen. (1998). Developing a habitat-driven approach to CWWT (constructed wetlands for wastewater treatment) design. In: D.F. Hayes (ed.) *Engineering Approaches to Ecosystem Restoration, Proceedings of the 1998 Wetlands Engineering and River Restoration Conference, Denver CO.* P. 716-721. American Society of Civil Engineers (ASCE), Reston, VA. USA.

Schindler, D.W. (1987) Detecting ecosystem responses to anthropogenic stress. *Canadian Journal of Fisheries and Aquatic Sciences.* 44 (1), 6-25.

Schwartz, L.N. and G.K. Gruendling. 1985. The effects of sewage on a Lake Champlain wetland. *Journal of Freshwater Ecology,* 3: 35-46. As cited in Nelson, *et al.,* 2000.

Sculthorpe, C.D. (1967). *The Biology of Aquatic Vascular Plants.* St. Martin's Press, New York, NY, USA. As cited in Nelson, *et al.*, 2000.

Sikora, F., L. Behrends and G. Brodie. (1995). *Manganese and Trace Metal Removal in Successive Anaerobic and Aerobic Wetland Environments.* TVA Environmental Research Centre, Muscle Shoals, Alabama.

Simkiss, K. and M.G. Taylor (1995). Transport of metals across membranes. In: Tessier, A. and D.R. Turner (eds.) *Metal Speciation and Bioavailability in Aquatic Systems.* John Wiley and Sons Ltd., Chichester, UK.

Simmers, J.W., R.G. Rhett, S.H. Kay, and B.L. Folsom, Jr. (1989). *Synthesis of the Results of the Field Verification Program Wetland Disposal Alternative.* Tech. Rep. D-89-2. U.S. Army Corps of Eng. Waterways Exp. Stn., Vicksburg, MS.

Singer, P.C. and W. Stumm. (1970). Acidic mine drainage: the rate-determining step. *Science* (New York), 167, 1121-3.

Sistani, K.R., D.A. Mays and R.W. Taylor. (1999). Development of natural conditions in constructed wetlands: biological and chemical changes. *Ecological Engineering* 12, 125-131.

Snodgrass, J.W., C.H. Jagoe, A.L. Bryan Jr. H.A. Brant and J. Burger (2000) Effects of trophic status and wetland morphology, hydroperiod and water chemistry on mercury concentrations in fish. *Canadian Journal of Fish and Aquatic Science* 57, 171-180.

Soucek, D.J., D.S. Cherry and G.C. Trent. (2000a). Relative acute toxicity of acid mine drainage water column and sediments to *Daphnia Magna* in the Puckett's Creek Watershed, Virginia, USA. *Arch. Environmental Contamination and Toxicology* 38, 305-310.

Soucek, D.J, D.S. Cherry, R.J. Currie, H.A. Latimer and G.C. Trent. (2000b). Laboratory to field validation in an integrative assessment of an acid mine drainage-impacted watershed. *Environmental Toxicology and Chemistry* 1994), 1036-1043.

Sparling, D.W. and T.P. Lowe. (1998). Metal concentrations in aquatic macrophytes as influenced by soil and acidification. *Water, Air and Soil Pollution* 108, 203-221.

Sprenger, M. and A. McIntosh. (1989). *Arch. Environ. Contam. Toxicol,* 18: 225 As cited in Sparling and Lowe, 1998.

Spry, D.J. and J.G. Wiener. (1991). Metal bioavailability and toxicity to fish in low–alkalinity lakes: a critical review. *Environ. Pollut.,* 71, 243.

Stace, C. (1995). *New Flora of the British Isles.* Cambridge University Press.

Stockwell, C. (1974). Heavy metal tolerance in *Typha Latifolia* without the evolution of tolerant races. *Ecology*, 55 (5): 1163-5.

Stoughton, J.A. and W.A. Marcus (2000) Persistent impacts of trace metals from mining on flood plain grass communities along Soda Butte Creek, Yellowstone National Park. *Environmental Management* 25: (3), 305-320.

St. Cyr, L. and Campbell, P.G.C. (2000) Bioailability of sediment-bound metals for *Vallisneria Americana Michx,* a submerged aquatic plant, in the St. Lawrence River. *Canadian Journal of Fish and Aquatic Science* 57, 1330-1341.

St. Cyr, L., and Campbell, P.G.C. (1996). Metals (Fe, Mn, Zn) in the root plaque of submerged aquatic plants collected in situ: relations with metal concentrations in the adjacent sediments and in the root tissue. *Biogeochemistry*, 33: 45-76.

Tarutis, W.J. and R. F. Unz. (1990). Chemical diagenesis of iron and manganese in constructed wetlands receiving acidic mine drainage. In: Cooper, P.F. and B.C. Findlater (eds.), *Constructed Wetlands in Water Pollution Control*, 419-428. Oxford, Pergamon Press.

Taylor, G.J. and A.A. Crowder. (1983). Uptake and accumulation of copper, nickel and iron by *Typha latifolia* grown in solution culture. *Canadian Journal of Botany.* 61 (7): 1825-1830.

Tessier, A. (1992). Sorption of trace elements on natural particles in oxic environments. In: J. Buffle J. and H.P. Van Leeuwen (eds.), *Environmental Particles.* 1: 425-453. *Environmental, Analytical and Physical Chemistry Series.* Lewis Publishers, Boca Raton, Fla.

Tessier, A., Y. Couillard, P.G.C. Campbell and J.C. Aquclair. (1993). Modelling Cd partitioning in oxic lake sediments and Cd concentrations in the freshwater bivalve *Anodonta grandis. Limnol. Oceanogr.* 38: 1-17.

Theis, T.L. and P.C. Singer. (1974). Complexation of iron (II) by organic matter and its effect on iron (II) oxygenation. *Environ Sci Technol,* 8: 569-572. As cited in Salomons and Förster, 1984.

Thompson-Roberts, E.S. and F.R. Pick. (2000). Total mercury in the water and sediments of St. Lawrence river wetlands compared with inland wetlands of Temagami – North Bay and Muskoka – Haliburton. *Canadian Journal of Fisheries and Aquatic Sciences* 57 (suppl.1), 148-154.

Thompson-Roberts, E.S., F.R. Pick and G.E.M. Hall. (1999). Total Hg in water, sediment, and four species of aquatic macrophytes in the St. Lawrence River, near Cornwall, Ontario. *Journal of Great Lakes Research* 25 (2): 294-304.

Ton, S. (1990). *Natural Wetland Retention of Lead from a Hazardous Waste Site.* M.S. Thesis. University of Florida, Gainsville.

Ton, S. and J.J. Delfino. (2000). Lead distribution in Steele City Swamps. In: Odum *et al.*, (eds.), *Heavy Metals in the Environment, Using Wetlands for their Removal.* CRC Press LLC, Boca Raton, Florida.

Turner, D.R. (1995). Problems in trace metal speciation modelling. In: Tessier, A. and D.R. Turner (eds.) *Metal Speciation and Bioavailability in Aquatic Systems.* John Wiley and Sons, Chichester, UK.

Turner, D.R. (1984). Relationships between biological availability and chemical measurements. In: Siegel, H. (ed.), *Circulation of Metals in the Environment, Metal Ions in Biological Systems,* Vol. 18. Marcel Dekker, New York.

Tyler, G., A. M. Balsberg Påhlsson, G. Bengtsson, E. Bååth, and L. Tranvik. (1989). Heavy metal ecology of terrestrial plants., microorganisms and invertebrates. *Water, Air, and Soil Pollution,* 47:189-215.

Ure, A.M., P.H. Quevauviller, H. Muntau, B. Griepink. (1993). *Int. J. Environ Anal. Chem.* 51, 135.

UNEP/IUNC/WWF. (1990). *Caring for the World: A Strategy for Sustainability*, United Nations Environment Programme, United Nations Conservation Union and World Wide Fund for Nature, 2nd Draft (June 1990). In: Burton, G.A. Jr. (ed.) *Sediment Toxicity Assessment.* Lewis Publishers, CRC Press.

U.S Bureau of Mines. (1996). Listing of USBM's Top Ten Accomplishments on their Internet Home Page [www.usbm.gov]. April 1996.

U.S. Bureau of Mines. (1994). *Mine Drainage Characterisation for the Successful Design and Evaluation of Passive Treatment System.* Paper presented by D..M. Hyman and G.R. Waltzlaf at the 17th Annual National Association of Abandoned Mine Lands Conference, 1994.

USCOLD. (1994). Tailings Dam Incidents, U.S. Committee on Large Dams (USSD). As cited in Vick, 2002.

U.S. Environmental Protection Agency. (1995a). *Managing Environmental Problems at Inactive and Abandoned Metals Mine Sites.* Paper Presented at Anaconda, Montana, Denver, Colorado and Sacramento, California in 1994 by Thomas Durkin of South Dakota Department of Environment and Natural Resources, Office of Minerals and Mining, and Jonathan Herrmann of U.S. EPA's National Risk Management Research Laboratory.

United States Environmental Protection Agency. (1995b). *Method 3052, Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices.* U.S. EPA.

United States Environmental Protection Agency. (1988). *Design Manual, Constructed Wetlands and Aquatic Plant Systems for Municipal Wastewater Treatment.* Office of Research and Development, Center for Environmental Research Information, Ohio, EPA/625/1-88/022.

United States Office of Surface Mining. (1995). *Appalachian Clean Streams Initiative.* Information Bulletin, 1995-618-289. Alton, IL., USA.

Vick, S.G. (2002). Stability aspects of long term closure for sulphide tailings. *Mining Environmental Management,* 9:6, 19-23.

Vile M.A. and R.K. Wieder. (1992). Alkalinity generation by Fe (III) reduction versus sulphate reduction in wetlands constructed for acid mine drainage treatment. *Water, Air and Soil Pollution,* 69: 425-441.

Vymazal, J. (1995). *Algae and Element Cycling in Wetlands*. Lewis Publishers, Boca Raton, FL, USA. As cited in Nelson, *et al.*, 2000.

Warren-Hicks, W., B.R. Parkhurst and S.S. Baker, Jr. (1989). *Ecological Assessments of Hazardous Waste Sites: A Field and Laboratory Reference Document*. U.S. Environmental Protection Agency, Corvallis, OR, Report No. 600/3-89/013.

Weber, J.H. (1973). Reviews of possible paths for abiotic methylation of Hg (II) in aquatic environments. *Chemosphere*, 26: 2063-2077.

Wehr, J.D. and B.A. Witton. (1983). Aquatic cryptogams of natural acid springs enriched with heavy metals: the Kootenay Paint Pots, British Columbia. *Hydrobiologia*, 98, 97-105. As cited in Burton, 1986.

Wenerick, W.P., Stevens, S.E. Jr., Webster, H.J., Stark, L.R., and DeVeau, E. (1989). Tolerance of three wetland plant species to acid mine drainage: a greenhouse study. As cited in Odum *et al.*, 2000.

Wieder, R.K. (1993). Ion input/output budgets for five wetlands constructed for acid coal mine drainage treatment. *Water, Air and Soil Pollution.* 71: 231-270.

Wildeman, T.R. and L.S. Laudon. (1989). Use of wetlands for treatment of environmental Problems in mining: non-coal-mining applications. In: Hammer, D.A. (ed), *Constructed Wetlands for Wastewater Treatment, Municipal, Industrial and Agricultural.* Lewis Publishers, Inc.

Witthar, S.R. (1993). Wetland water treatment systems. In: Moshiri, G. (ed.), *Constructed Wetlands for Water Quality Improvement*. Lewis Publishers, CRC Press, Boca Raton, FL.

Wójcik, W., and Wójcik, M. (2000). Lead and Zinc retention in the Biala River wetland of Poland. In: Odum, *et al*. *Heavy Metals in the Environment, Using Wetlands for their Removal.* CRC Press LLC, Boca Raton, Florida.

Wood, J.M. and Wang, H.K. (1983). Microbial resistance to heavy metals. *Environ. Sci. technol.*, 17, 582A. As cited in Mason and Jenkins, 1995.

Wood, T.S. and M.L. Shelley (1999). A dynamic model of bioavailability of metals in constructed wetland sediments. *Ecological Engineering* 12, 231-252.

Wright, D.J., and Otte, M.L., (1999). Wetland plant effects on the biogeochemistry of metals beyond the rhizosphere. *Biology and Environment: Proceedings of the Royal Irish Academy,* 99 B (1): 3-10.

Yan, N.D. (1979). Phytoplankton community of an acidified, heavy metal-contaminated lake near Sudbury, Ontario: 1973-1977. *Water, Air, Soil Polution*, 11, 43-55.