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**The fate of non-limiting solutes and the processes of solute  
retention in the uMkhuze Wetland System,  
KwaZulu-Natal, South Africa**

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**Submitted in fulfillment of the requirements for the degree  
Doctorate of Philosophy in the School of Environmental Sciences,  
University of KwaZulu-Natal, Durban**

**2008**

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## ABSTRACT

Wetlands have long been recognised as enhancing the quality of inflowing waters, particularly regarding the plant macronutrients nitrogen and phosphorus. Any research into non-limiting solutes has largely been of a 'black box' nature, with no insights into mechanism of retention presented. Research in the Okavango Delta, Botswana and preliminary work in the uMkhuze Wetland System, South Africa has identified retention of large amounts of non-limiting solutes within these wetland systems. Chemical sedimentation in the Okavango accounts for 360 000 tonnes per year, while a rough mass balance in the uMkhuze Wetland System suggested retention on a scale of 16 000 tonnes per year.

The Yengweni and Totweni Drainage Lines are north-south oriented systems that, together with the uMkhuze River floodplain, were selected to investigate chemical retention in the uMkhuze Wetland System. These drainage lines were once tributaries of the uMkhuze River that have been dammed at their southern ends by alluvial deposition on the uMkhuze River floodplain to form tributary valley lakes. Considering seasonal variations in groundwater levels in combination with conductivity, sites of solute concentration were revealed in the groundwater. The use of chloride as a concentration tracer has indicated that solutes are progressively depleted in the groundwater under the influence of a concentration mechanism, with silicate minerals and calcite attaining saturation. Groundwater chemistry and hydrological factors have highlighted the southern Yengweni and floodplain regions as active sites of solute concentration. In these areas, groundwater elevations are variable, which is mirrored by variation in groundwater chemistry. Although elevated solute concentrations do occur elsewhere, the seasonal variation is less marked.

The search for solute sinks in the uMkhuze Wetland System also considered the sediment of the wetland system as a possible sink. Elevated solute concentrations in the groundwater could be linked to the accumulation of minerals in the soil, suggesting precipitation of minerals by saturation under a concentration process. In the southern Yengweni and floodplain regions, concentrated groundwater bodies were linked to high concentrations of minerals in the soil, including neoformed montmorillonite, and calcite deposits. Other sites of chemical concentration in the

groundwater in the northern Yengweni and Totweni Drainage Lines have produced little modification of the reworked marine sands on which the wetland is founded. Processes in the southern Yengweni and floodplain regions are clearly more efficient in removing solutes from the wetland surface water and immobilising them in the soil of the drainage line than is happening in the Totweni and northern Yengweni regions.

Transpiration by vegetation seems to be the major factor driving chemical sedimentation in this subtropical system, and as such vegetation in this wetland system is not the passive factor it is often assumed to be. The vegetation of the wetland is itself initiating and perpetuating the retention of chemicals in the system.

Hierarchical patch dynamics in combination with the theory of thresholds, derived from geomorphology, is useful for placing chemical sedimentation in wetlands into a spatiotemporal framework that increases understanding of the process, and allows identification of sites where chemical sedimentation is likely to occur in wetlands. There are a number of thresholds that define chemical sedimentation driven by evapotranspiration in the uMkhuze Wetland System, which may be considered at increasing spatiotemporal scales from the microscale of seconds within a limited section of the groundwater, to the macroscale thousands of years at the landscape scale of the wetland system. With increasing scale, the effects of the transformations at each hierarchical level have corresponding increasing influence on the structure and function of the wetland system. The initial threshold is surpassed once concentration products of evapotranspiration are retained to some degree within the wetland system, due to increased residence times of groundwater on modification of the hydrological regime from discharge to recharge. Increased residence times allow the products of seasonal concentration to persist beyond the timescale of seasons. The second threshold is the saturation and precipitation of mineral phases that accumulate within the soil profile. With sufficient accumulation of chemical sediments, the physical properties of the sediment are modified, which reduces the velocity of water flow in the soil (Threshold 3). This has implications for hydrological flows between the surface water and groundwater systems. Threshold 4 is attained once the sediment is modified to such a degree that the chemical sediments act as an aquitard, such that surface water and groundwater may be effectively separated.

Extrinsic factors influencing the process of chemical sedimentation, such as the atmospheric water demand, chemical composition and volume of inflowing waters, as well as the nature and density of vegetation, may indicate the potential of a system to sequester chemical sediments but cannot predict their occurrence completely, except maybe at the extremes of semi-arid and arid systems. It is the local and intrinsic factors of hydrological flows, their chemical composition and nature of clastic sediments that will govern residence times of water in the system, and therefore the location, nature and extent of chemical sedimentation. Furthermore, chemical sedimentation driven by evapotranspiration is not limited by sediment type as are adsorption and complexation reactions, which are dependent on the availability of active sites, nor by chemical composition of inflowing waters as this factor simply dictates the suite of minerals produced. Therefore, chemical sedimentation in wetlands is expected in a wide range of settings from temperate to arid, with varied substrates and hydrological regimes.

The large-scale removal and retention of solutes within wetland soil has system-wide implications for wetland structure and functioning. The ramifications of chemical evolution of the groundwater and soil extend from influencing the distribution of plants and animals, to geomorphological implications of accumulating chemical sediments, as well as off-site effects including water quality enhancement of water available to downstream systems and users. An understanding of the process of chemical sedimentation in wetlands may inform good management to protect this vital function of wetlands, particularly with increasing development and industrialisation pressures in many areas.

Extensive chemical sedimentation has been discovered in both the Okavango Delta, Botswana by Ellery, McCarthy and colleagues and through this study in the uMkhuze Wetland System, with the proposed driving force being transpiration. Vegetation-induced chemical sedimentation is a hitherto unknown, although seemingly important component, of chemical processing in tropical and subtropical wetlands, and under certain conditions, even in temperate wetlands. This insight into chemical transformations in wetland systems adds a further dimension to the accepted model of chemical cycling.



## PREFACE

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The work in this thesis was conducted in the School of Environmental Sciences, University of KwaZulu-Natal, Howard College Campus, under the supervision of Professors Fred Ellery of the School of Environmental Sciences and Andrew Kindness of the School of Chemistry.

This study represents original work of the author, and has not been submitted in any other form to another university. Where use was made of the work of other authors, it has been duly acknowledged in the text.

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## ACKNOWLEDGEMENTS

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To my heavenly Father who guides me in the path I should go, and to Whom I owe my life. Thank You for taking ‘a foolish thing of the world’ and breathing Your Life, Love and Direction into me. Even when I was doing my best to ignore You completely, You gave me a study direction that has delighted me, inspired me and brought me into contact with amazing people who share my delight in Your creation. I could not have imagined anything better.

To my supervisors, Fred and Andy, thank you for your constant guidance and encouragement, and your long-suffering in reading numerous drafts with sustained good cheer and enthusiasm.

To the Wetland Research Group, long may your fingers be muddy and the ground be wet beneath your feet! Thank you for fruitful discussions, encouragement, friendship and assistance in many ways. Thanks Becky, Donovan, Erwin, Fred, John, Kerry, Lisa, Marian, Mike, Olive, Ryan, Si, Su and Warren, and honorary members Andy and Tish. To Tish who, although was never convinced to join us in the field (one day my friend!), selflessly and patiently analysed many water samples.

To the School of Environmental Sciences, Geography Division, thank you for your support and friendship, for being wonderful colleagues as well as mentors in my ‘first real job experience’. I have learnt much about teamwork, high standards in academics and work relationships from you.

To Prof. Jeff Hughes of Soil Science, thank you for helpful advice, comments and being so ready to give guidance even at the last minute.

To Frank Sokolic thank you for your help with all matters technical on which your talents were wasted, but which you completed cheerfully and very carefully. To Isaac Abboy for assistance in the field, preparations for field work and for patiently assisting with many other requests, and for never being too serious!

To my Glenridge family, who constantly urged me to ‘Love the Lord your God with all your heart, soul, mind and strength, and love your neighbour as yourself’, many times unwittingly as they live out lives loving our Father and glorifying Him. To my home group, thank you for keeping me sane by just being yourselves and offering friendship, support, wisdom and presenting by example the freedom from expectations, performance and religion that the children of God enjoy.

To my family, for mirroring the unconditional love and generosity of God, for limitless support and encouragement, and for being sounding boards when my thoughts refused to be ordered.



## CHAPTER 1

### INTRODUCTION

---

#### 1.1. Chemical transformations in wetlands: a focus on solute retention and chemical sedimentation

The intrinsic value of wetland ecosystems within the landscape has been widely recognised, as exemplified in the Millennium Ecosystem Assessment (Millennium Ecosystem Assessment, 2005). Attempts have been made to define this concept practically for use by managers and planners, by identifying ecosystem values or services (Millennium Ecosystem Assessment, 2005; Mitsch and Gosselink, 2000). These values have been grouped by Kotze and Breen (1994) into functional values, such as water quality enhancement and erosion control, which are indirectly useful in the services provided, and resource values, such as crop production and recreation, which are directly useful. The hydrological benefits of wetlands, which are typically recognised as functional values, include water quality enhancement and flood attenuation.

Water quality enhancement is the removal of suspended sediments, plant nutrients and pollutants from wetland waters through interactions between water, vegetation and soil of the system (Kotze and Breen, 1994). Many studies have investigated the water treatment capacity of wetlands in removing nutrients, sediment and pollutants from source waters, which has resulted in the increasing use of wetlands downstream of waste waters, for both sewage and industrial wastewater treatment (Haberl, 1999; Sakadevan and Bavor, 1999; Salati *et al.*, 1999; Thompson and Finlayson, 2001; Wood, 1999).

Most research into mechanisms and sites of retention of chemicals in wetlands has focussed on the plant macronutrients, nitrogen and phosphorus (Boyt *et al.*, 1977; Fetter *et al.*, 1978; MacKay, 2000; Schilling and Lockaby, 2006; Van der Valk *et al.*, 1979). The consensus informed by studies at many wetland sites over varying conditions of climate (temperate, tropical and sub-tropical) and hydrogeomorphic setting (riverine, palustrine, lacustrine and tidal wetlands), is that most wetlands retain and incorporate nitrogen and phosphorus very effectively into the biomass of the ecosystem, transforming inputs from inorganic to organic forms (Klopatek, 1978; Mitsch and Gosselink, 1993; Van der Valk *et al.*, 1979). The reducing potential in many wetland soils slows the rate of organic matter decomposition, thereby retaining nitrogen and phosphorus more effectively than more oxidising environments (Vepraskas and Faulkner, 2000). Seasonal variation in the capacity of

wetlands to retain nitrogen and phosphorus inputs has been identified (Klopatek, 1978; Kotze and Breen, 1994; Van der Valk *et al.*, 1979), with more efficient removal and cycling through the system in the growing season, while during dry periods falling water tables may allow oxidation of organic matter, causing the wetland to become a source of these macronutrients (Van der Valk *et al.*, 1979).

Non-limiting chemicals, which may be non-nutrient solutes (such as the heavy metals cadmium and mercury), micronutrients (such as iron and zinc) or macronutrients (including calcium, magnesium and potassium) have been given far less attention in the literature. These non-limiting solutes have potential to modify wetland ecosystems. This is due to the capacity of wetland systems to retain such solutes in combination with the reduced capacity of plants to remove these solutes in large quantities, as only small amounts are likely to be incorporated into the biomass of the ecosystem.

Therefore, considering the growing dependence on wetland systems, both natural and constructed, around the world for the treatment of water resources, further attention should be given to the mechanisms of chemical retention and cycling through a wetland system, as well as the potential for remobilisation of these chemicals (Likens and Bormann, 1995). Research into natural undisturbed wetlands could provide insight into these mechanisms and pathways of chemical transformations. By identifying sites and processes of chemical retention, including interactions between the components of a wetland ecosystem, namely water, soil and plants; wetland management could be enhanced, providing the tools to predict effects of increased disturbance and input of anthropogenic chemicals from the catchment.

Much research has been conducted on the temperate wetlands of Europe and North America with few studies addressing the tropical and subtropical regions of Africa and South America. Any work in these areas has been mostly descriptive with no attempt to gain a process-based understanding (McCarthy and Hancox, 2000; Rogers, 1995). The exception is an in-depth research programme in the Okavango Delta, Botswana which has produced research in a wide range of fields including vegetation ecology, geomorphology, sediment and water chemistry (Ellery *et al.*, 1998; Ellery *et al.*, 2000; McCarthy and Ellery, 1995; McCarthy *et al.*, 1993; Wilson and Dinçer, 1976).

## 1.2. Chemical sedimentation in the Okavango Delta

Research in the Okavango Delta, Botswana, has indicated that wetlands may indeed have a profound influence on the chemical composition of their waters, particularly regarding certain macro- (calcium and magnesium) and micronutrient chemicals (iron and sodium) on a landscape scale. The Delta is situated in the Kalahari Desert in a harsh semi-arid climate where evapotranspiration exceeds rainfall in every month of the year, and only 2 % of the surface inflow leaves the system as surface outflow, with a further estimated 2 % leaving the system as groundwater outflow (Wilson and Dinçer, 1976). The remaining 96 % of all surface water inputs is lost to the atmosphere through evapotranspiration (McCarthy and Ellery, 1995). In such a setting, a saline lake (playa) would be expected rather than this vast freshwater swamp.

Hydrological and geochemical studies on the islands of the swamp have revealed sinks and mechanisms of non-limiting solute immobilisation. Steep hydraulic gradients exist from the wetland towards the central regions of islands, indicating that groundwater recharge takes place in these settings (McCarthy *et al.*, 1993). The hydraulic slope from swamp to island centre is maintained by transpiration in the densely wooded fringe, which removes water at a greater rate than recharge from the surrounding swamp. The groundwater at these points has a high electrical conductivity as trees remove water through transpiration while selectively excluding many of the dissolved solutes (McCarthy *et al.*, 1993). Considering both water and soil chemistry, it was suggested that concentration in the groundwater caused calcium and magnesium compounds to attain their respective saturation points and precipitate out of solution. Consequently, maximum soil oxide concentrations are correlated with the groundwater conductivity maxima in a manner consistent with an evaporation sequence (McCarthy *et al.*, 1993). Minerals are concentrated in the groundwater beneath islands in the Okavango Delta through the process of transpiration, to the point where saturation is attained and precipitation from solution occurs. In this way, chemicals are sequestered beneath islands in the swamp, allowing the surface water to remain surprisingly fresh with surface water conductivities often less than 0.15 mS/cm, resulting in a concentration factor of only about 2 across the vast swamp system in spite of a high potential evaporation (McCarthy *et al.*, 1993; McCarthy and Metcalfe, 1990). Thus, it seems that evapotranspiration can be viewed as the driving force of chemical retention beneath islands in the Okavango Delta, Botswana.

The results of the above studies raised the following question. Is the Okavango Delta unique in its mechanisms of chemical retention; or is chemical retention driven by evapotranspiration occurring in other wetlands?

### **1.3. The fate of solutes in the uMkhuze Wetland System**

Situated in the moist subtropical climate of northern KwaZulu-Natal, where potential evapotranspiration makes a significant contribution to the water budget but is moderated by high rainfall, and being based on a similar substrate to the Okavango of reworked sandy marine sediments, the uMkhuze Wetland System was selected as an ideal site to investigate this question. A preliminary investigation into the uMkhuze Wetland System provided evidence that this wetland is indeed acting as a sink for certain solutes. A mass balance approach was employed to compare inflow and outflow solute concentrations, while accounting for evapotranspiration through the swamp system by assuming that chloride was fully conserved in the chemical processing (Barnes *et al.*, 2002). The results indicated that silicon is most effectively retained at roughly 80 % of the influent silicon remaining in the swamp, while about 50 % of the calcium is retained. If these figures are re-calculated over the period of a year, it can be seen that tonnes of solutes are accumulating every year in the uMkhuze Wetland System. Assuming that these solutes are evenly spread throughout the 440 km<sup>2</sup> system, the results indicate that around 36.5 kg in total are being retained per km<sup>2</sup> per year.

It is possible that this solute retention discovered in the uMkhuze Wetland System is mediated by plants in the same way as the Okavango Delta. Despite the fact that the subtropical climate of the uMkhuze Wetland System does not have the same high evaporative demand as the semi-arid climate of the Okavango Delta, the ability of plants to modify their environment, as demonstrated in the Okavango, is both powerful and far-reaching (McCarthy and Ellery, 1995). Furthermore, given the location of the uMkhuze Wetland System and its contribution of around 56 % of the mean annual runoff to Lake St Lucia, any water quality enhancement performed by the wetland will be of utmost importance due to repeated periods of very high salinities that threaten the structure and function of the Lake.

By investigating the hydrology as well as groundwater and soil chemistry of the uMkhuze Wetland System, it is anticipated that insight into chemical processing within the wetland will be gained. On a broader scale, by considering heterogeneity in hydrological characteristics and the chemical

composition of source waters and sediments; the feedback between chemical processing, wetland hydrology, geomorphology and ecology will be explored in a general way. Thereby, the implications and consequences of solute retention and chemical sedimentation on a landscape level in the uMkhuze Wetland System may be considered.

#### **1.4. Aim and objectives**

##### Aim

To investigate the fate of non-limiting solutes and processes of solute retention within the uMkhuze Wetland System and consider the implications of solute retention for wetland structure and function.

##### Objectives

- To gain an understanding of the spatial and temporal characteristics of the surface water – groundwater interactions at the floodplain margin over a seasonal cycle;
- To identify solute sinks by examining both spatial and temporal heterogeneity in surface and groundwater chemistry over a seasonal cycle;
- To consider the extent to which sinks in the groundwater are translated into retention within the wetland soil by investigating spatial heterogeneity in soil chemistry;
- To consider the relationship between hydrology, soil and groundwater chemistry in chemical transformations on the floodplain margin in the uMkhuze Wetland System;
- To consider the implications of solute retention for system structure and functioning in the uMkhuze Wetland System;
- To broaden our understanding of chemical sedimentation in wetlands



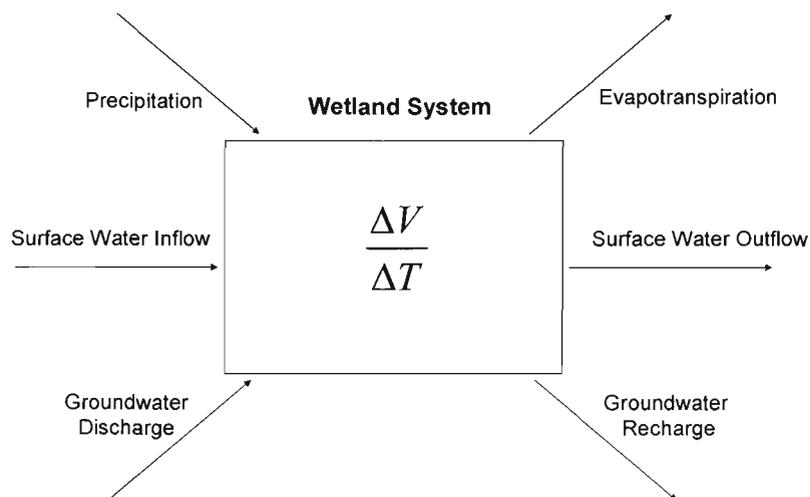
**CHAPTER 2**  
**LITERATURE REVIEW**  
**CHEMICAL TRANSFORMATIONS IN WETLAND SYSTEMS**

---

**2.1. Determinants of wetland structure and function**

Wetlands are defined as areas that are inundated for sufficient periods of time to produce anaerobic conditions in soils at some time during the seasonal cycle and that therefore support hydrophytic vegetation (Wang and Mitsch, 2000). It is widely recognised, as illustrated by the definition above, that the structure (the physical components and their arrangement) and functioning (the processes that link components) of wetland systems are primarily determined by the hydrological regime (Carter *et al.*, 1979; Gosselink and Turner, 1978; Kadlec and Kadlec, 1979; Wang and Mitsch, 2000).

Possible hydrological inputs to an inland wetland include: direct precipitation on the wetland, surface water inflow and groundwater discharge, while outputs can comprise evapotranspiration, surface water outflow and groundwater recharge (Figure 2.1.1). The combination of these factors constitutes the water balance.

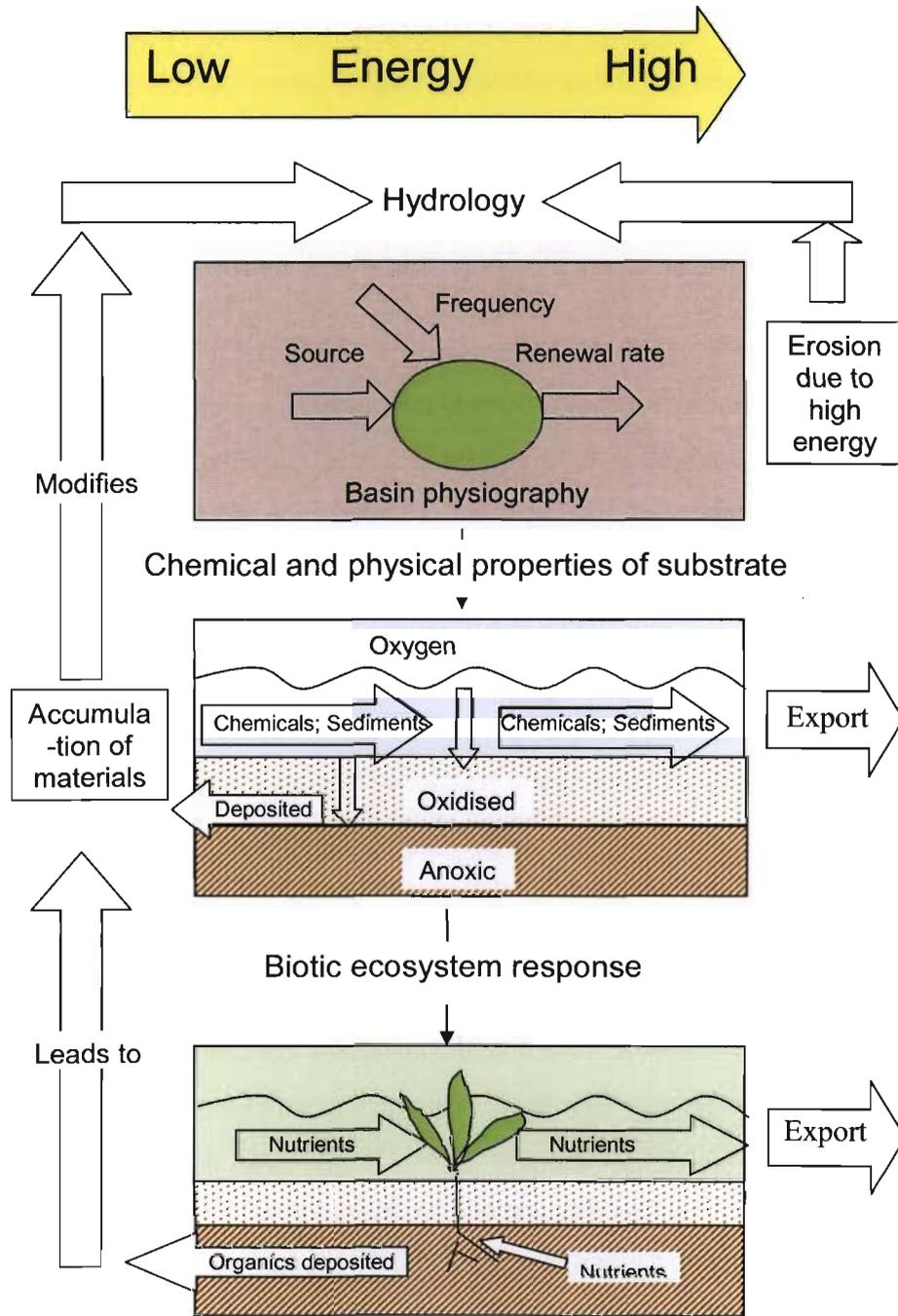


**Figure 2.1.1** The wetland water balance

Modified after: Mitsch and Gosselink (2000)

Water sources not only transport solutes and clastic sediments into a wetland, but also act as a reaction medium for chemical transformations within the wetland itself. The specific hydrological inputs and outputs of the water balance will differ in their contribution to the hydrological balance of each wetland. The inputs and proportions in which they combine provide the raw material, in both dissolved and suspended form, on which *in situ* processes such as evaporation and complexation reactions may act. In this way, the chemical composition of source waters to wetlands may be modified. For example, systems with predominantly rainwater inputs, such as ombrotrophic bogs, have very limited chemical inputs due to the low solute concentrations of rainfall. Furthermore, these systems are typically situated at altitudes or latitudes with cooler temperatures where there is little opportunity for solute enrichment through evapotranspiration. However, wetlands with high surface water inputs are more likely to have elevated solute concentrations, as surface water will add catchment-derived solutes to the wetland.

Water flowing within the wetland brings solutes into intimate contact with wetland sediments and biota. Amongst other factors, uptake by plants and micro-organisms, variations in redox potential and pH, as well as water loss through evapotranspiration, contribute to an increased potential for chemical transformations. Mitsch and Gosselink (2000) recognise this fundamental role played by hydrology and its implications for the other wetland components of soil and biota as illustrated in Figure 2.1.2. The hydrological regime of a wetland is determined by the volume and velocity of source waters entering the system, the frequency of inflows, the renewal rate and the basin physiography. The hydrological regime in turn influences and modifies the chemical and physical properties of the wetland substrate due to input of solutes (including plant nutrients) and sediments, as well as influencing environmental conditions such as the availability of oxygen. The availability of nutrients as well as conditions such as degree of anoxia, determine the biotic ecosystem response. At each point there is the potential for feedback processes modifying wetland structure and function, with the nature of modification related to the energy of the system, as governed by the velocity and volume of water flowing within the wetland. High velocities of inflowing waters initiate erosion and removal of wetland sediments, while low velocities promote retention of solutes and sediments within the wetland.



**Figure 2.1.2** A conceptual model of wetland structure and function  
Modified after: Mitsch and Gosselink (2000)

There are a number of factors that determine the extent to which a wetland will accommodate hydrological inputs. These factors include the physiography of the wetland basin, the velocity and volume of inflowing water, and the ability of the wetland to reduce the velocity of flow by promoting diffuse water flow and increasing roughness by the abundant growth of wetland plants (Figure 2.1.2). Interactions of these factors determine the residence time of water in the wetland and, therefore affect the fate of the dissolved and particulate load, as well as the extent to which organic sediments accumulate.

The timing, depth and duration of inflows influence the physical and chemical properties of the wetland substrate. Sediments are often an important source of nutrients, and may be deposited or removed depending on the energy of flowing water. The presence of water within the wetland, be it through surface accumulation or subsurface saturation of the soil profile, leads to reducing conditions within the wetland. The intensity and spatial distribution of these reducing conditions depends on the patterns of inundation and the residence time of water, the number of micro-organisms that deplete oxygen through respiration reactions, and the amount of organic substrate that consumes available oxygen and provides electrons to fuel reducing reactions (Vepraskas and Faulkner, 2000).

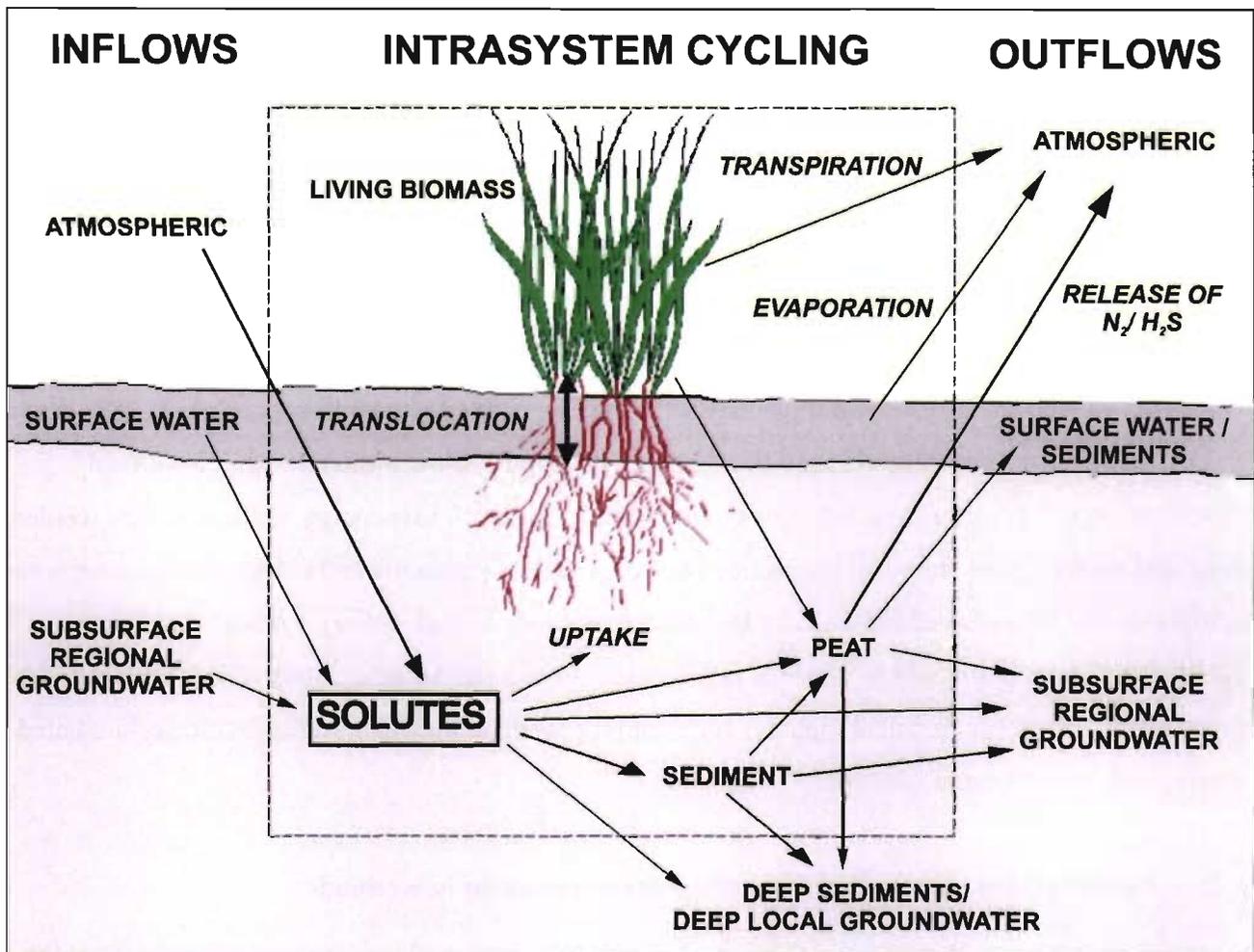
The distribution of wetland biota will be regulated by reducing conditions and nutrient availability as well as the velocity and depth of wetland waters (McCarthy and Ellery, 1995; Wang and Mitsch, 2000). The absence or depletion of oxygen in the root zone of plants is stressful for plant growth and reproduction, with many plants unable to survive the anaerobic conditions. Only plants specifically adapted to the lack of oxygen are able to tolerate prolonged anaerobic conditions in the root zone (Brix, 2004; Colmer and Garthwaite, 2004; Seago *et al.*, 2004; Visser *et al.*, 2004; Voesenek, 2004; Waldren *et al.*, 2004). However, biota do not simply respond to the hydrological and biogeochemical conditions, but influence wetland structure and functioning by modifying basin physiography through trapping of sediment, deposition of organic sediment or through animals such as hippopotami initiating erosion along trails through the wetland (Ellery *et al.*, 1990; Ellery *et al.*, 1993c; McCarthy *et al.*, 1998b; McCarthy *et al.*, 1986). These feedback processes, as illustrated by Mitsch and Gosselink (2000), are dependent on the energy of the hydrological regime (Bridge, 2003). In high energy environments, export of materials such as nutrients, clastic and organic sediments will be high, maintaining an open nutrient cycle and renewing wetland waters with high frequency (Breen *et al.*, 1988; Powell, 1989;

Sierszen *et al.*, 2006). In high energy systems the likelihood of sedimentation of any type is limited, and the wetland form and development will be dictated primarily by the hydrological regime (Wang and Mitsch, 2000).

In low energy environments, the biota will play a larger role in shaping the wetland landscape by reducing the velocity of influent water through dense macrophyte growth, as well as by modifying elevation in the wetland by promoting clastic sedimentation and/or the accumulation of organic matter (Ellery *et al.*, 1993c; Gosselink and Turner, 1978; McCarthy and Ellery, 1995; McCarthy *et al.*, 1986; Wang and Mitsch, 2000). Animal trails may have the opposite effect (McCarthy *et al.*, 1998b; Wang and Mitsch, 2000). Biotic factors may thus appreciably modify flow patterns within a wetland. Modification of hydrological conditions by plants and animals in low energy settings affects residence time, and therefore the chemical interactions between water, sediments and plants. Consequently, the nutrient cycles of such wetlands will be less open than those of high energy wetlands, and the likelihood that materials will be retained is increased (Wang and Mitsch, 2000). The potential for such a wetland to transform chemical inputs is high, and the wetland may experience biotically-mediated alteration in structure and function.

## **2.2. Potential sites and mechanisms of chemical retention in wetlands**

The basic components of any wetland comprise surface water, groundwater (including pore water), sediment (including organic and clastic material) and plants (Figure 2.2.1). Each component has a different capacity to immobilise or retain chemicals within it, depending on prevailing conditions, such as the hydrological regime, redox potential and pH, the chemical composition of hydrologic inputs, clastic sediment inputs and their properties, and the chemical composition of the component itself. The conditions and possible processes will be considered for each component, as well as their potential to immobilise solutes in the system.



**Figure 2.2.1** A conceptual model of potential solute inputs to, sites of chemical retention and solute outputs from a wetland system

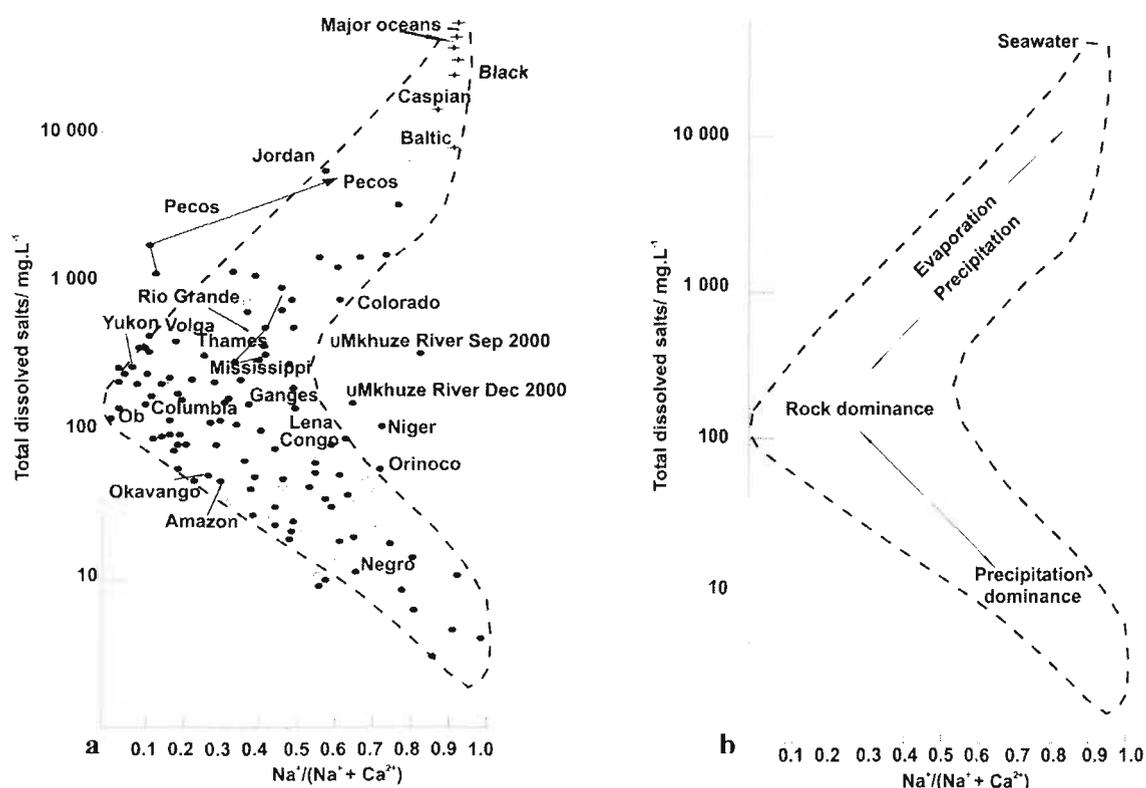
Modified after: Mitsch and Gosselink (2000)

## 2.2.1. Factors controlling surface water chemistry

### 2.2.1.1. Precipitation-weathering-evaporation processes

The chemical composition of surface water, in any surface water body including rivers, lakes and wetlands; is broadly dependent on three factors: precipitation chemistry, the addition of solutes derived from weathering processes, and the concentration of solutes through evaporation (Langmuir, 1997). Gibbs (1970) found that by plotting total dissolved salts (TDS) against the mass ratio of sodium to sodium plus calcium, three distinct regions of the plot could be attributed to the three main factors governing surface water chemistry namely precipitation, weathering inputs and evaporation (Figure

2.2.2 a and b). Waters plotting at low TDS, and high sodium to sodium plus calcium are dominated by precipitation inputs, with intermediate TDS and greater calcium contribution occur in waters dominated by weathering, and high TDS with high sodium to sodium plus calcium ratios associated with waters influenced by evaporation.



**Figure 2.2.2 a and b** The relationship between  $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$  and total dissolved salts describing processes controlling surface water chemistry

Modified after: Gibbs (1970)

Surface waters with predominantly precipitation inputs comprise relatively high sodium concentrations compared to calcium concentrations, and therefore they occur in the lower right section of the scatter plot at low TDS. The rivers populating this group are situated in the tropical regions of South America and Africa, where rainfall is consistently high throughout the year and highly leached catchments contribute few solutes (Gibbs, 1970). Furthermore, the influence of evaporation is not evident in surface waters dominated by precipitation inputs due to consistent dilution by precipitation (Figure

2.2.2b). If evaporation were to concentrate these surface waters, the expected evolutionary path would maintain the high sodium to sodium plus calcium ratio and there would be an increase in TDS towards the seawater samples.

The waters occurring at low sodium to sodium plus calcium ratios primarily reflects the weathering of rock, which has a high calcium to sodium ratio particularly for those of igneous origin. This enrichment in calcium, leads to lowering of the sodium to sodium plus calcium ratio. Further work into mechanisms controlling surface water chemistry by Kilham (1990) highlighted the different behaviour of African surface waters. Due to conditions favouring weathering with high average temperatures throughout Africa, water chemistry is primarily weathering-dominated. In regions of high rainfall, weathering is increased and precipitation adds terrigenous dust with low concentrations of cyclic salts, particularly in the vast expanse of the African interior. Thereby, the weathering signal in surface waters is intensified. In low rainfall areas, evaporation becomes ever more important with increasing sodium concentrations and decreasing calcium concentrations, primarily due to calcium carbonate precipitation.

Evaporation of surface waters that have moderate TDS concentrations due to weathering will lead to increased TDS loadings and is accompanied by the enrichment of sodium relative to calcium. This is due to calcium being removed from solution by chemical precipitation of its highly insoluble compounds. This evaporation sequence is represented by the series from waters dominated by rock weathering inputs at intermediate TDS towards the upper right end-member of Figure 2.2.2a at high TDS values, which is populated by the world's oceans. The surface waters represented in this evaporation series are situated in arid regions. Evolutionary paths for the Pecos and Rio Grande Rivers, which are situated in arid regions, are designated by arrows in Figure 2.2.2a (Gibbs, 1970). Water of the Pecos River in its headwaters initially plots at low sodium to sodium plus calcium ratios due to the addition of calcium from weathering of rock in its catchment, and intermediate TDS typical of waters with high weathering inputs. Water sampled along the length of the river, initially displays evidence of increased calcium concentrations from further weathering additions with a lower sodium to sodium plus calcium ratio, probably combined with evaporative concentration resulting in around  $1\ 000\ \text{mg.L}^{-1}$  increase in TDS. Waters of the Rio Grande display the same overall trend of increasing TDS and

sodium to sodium plus calcium ratios, although the initial values plotted show evidence of increased calcium additions from the catchment with some dilution by precipitation.

The Okavango Delta inflow waters plot near the Amazon River in Figure 2.2.2a, while the outflow waters are slightly more enriched in sodium just to the right of the Amazon River (McCarthy *et al.*, 1998a; McCarthy and Ellery, 1998; McCarthy and Metcalfe, 1990). The positioning of the Okavango Delta indicates that the predominant influences include weathering inputs from its vast catchment incorporating the Angolan highlands, as well as precipitation. It is interesting that evaporation isn't a major influence in spite of the Delta's semi-arid climatic setting, with loss of 96 % of inflowing waters to evaporation. The uMkhuze River occurs at higher TDS and higher sodium to sodium plus calcium ratios than the Okavango, indicating a greater influence of evaporation on the uMkhuze River water resulting in precipitation of calcium compounds from solution. The uMkhuze River plots near other African rivers (the Congo and Niger Rivers) and more closely fits the findings of Kilham (1990) than Gibbs (1970).

In regions where evaporation exceeds precipitation, the increased solute concentrations of waters are expected to play a major role in their chemical evolution. In arid or semi-arid settings, the progressive removal of water by evaporation will cause minerals to saturate, resulting in their precipitation from solution. The mineral precipitation sequence is predictable in a general way, ranging from the least soluble mineral to the most soluble finally deposited once most water has been removed. Initial evaporation studies were conducted on sea water samples, with extensive work by Van't Hoff and colleagues in the late 1800's and early 1900's (Harvie *et al.*, 1980). Further work incorporating more detailed calcium chemistry and equilibrium considerations, has defined an expected sequence of mineral precipitation with the most insoluble compound, calcium carbonate, precipitating out of solution first, to the highly soluble potassium-magnesium salts that require 98.7 % water loss before they saturate (Table 2.2.1; Harvie *et al.*, 1980; Matthes, 1982; Warren, 1989). However, seawaters display a remarkable degree of similarity both in solute concentrations and ratios and therefore produce relatively consistent evaporation sequences (Matthes, 1982; Sonnenfeld, 1984; Warren, 1989; Watson, 1983). Due to the more varied chemical compositions of surface waters, evaporation sequences tend to be more complex.

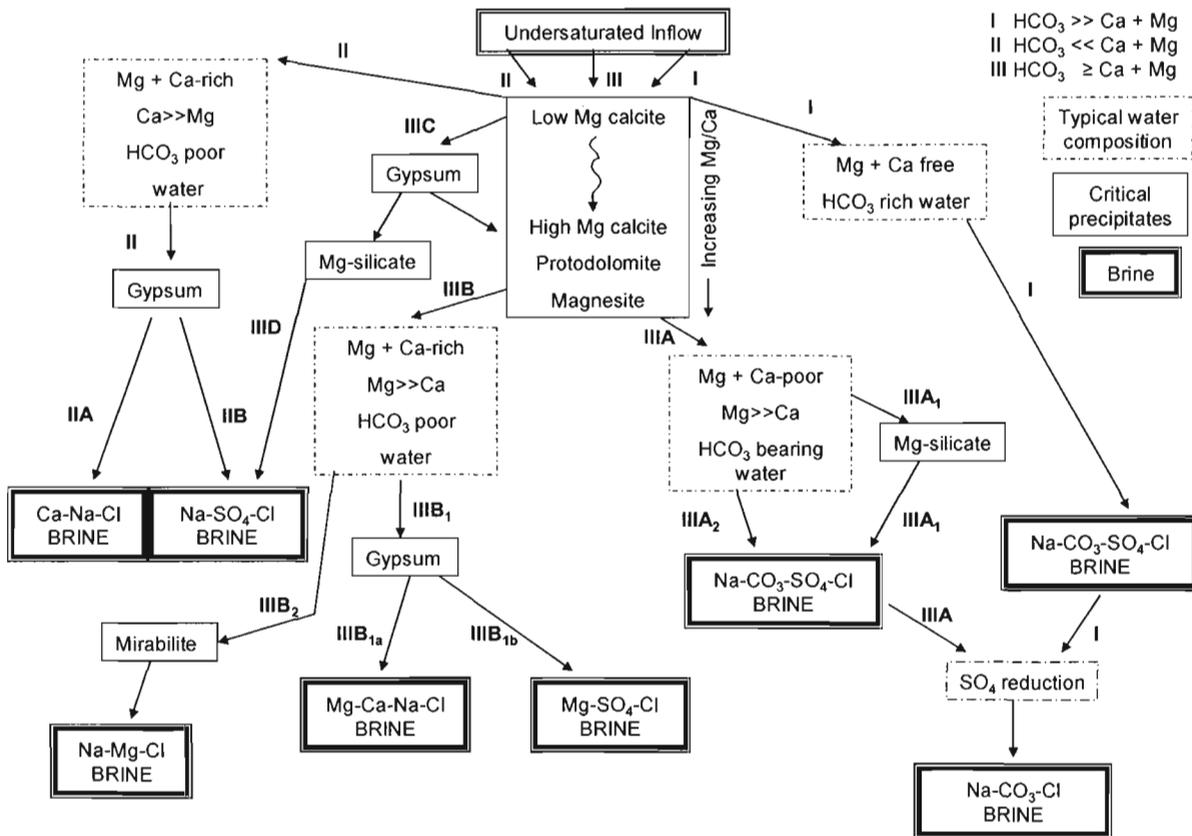
**Table 2.2.1** The expected mineral saturation sequence on evaporation of seawater

<b>Mineral</b>	<b>Concentration Factor</b>	<b>Percentage Water Loss</b>	<b>Brine Density/ g.cm<sup>-3</sup></b>
K-Mg salts	63	98.7	1.29
Halite	11	90	1.21
Gypsum/ anhydrite	5	80	1.13
CaCO <sub>3</sub>	2-3	50	1.10
Seawater	1	0	1.04

Modified after: Warren (1989)

Chemical transformations of surface waters by evaporation have been extensively studied by many researchers, particularly in arid settings where evaporation exceeds precipitation (Allen and Collinson, 1986; Boettinger and Richardson, 2001; Eugster and Jones, 1979; Eugster and Maglione, 1979; Salvany *et al.*, 1994; Schreiber, 1986). Eugster and Jones (1979) conducted studies on the evolution of surface water brines within closed basins, including Lake Magadi in Kenya as well as lakes in the USA and Canada. It was possible to identify general patterns of chemical evolution as hydrological inputs to the lakes were relatively homogeneous and dilute. In this way, the complication of lake water mixing with water of different composition could be disregarded.

The conceptual model of closed basin brine evolution developed by Eugster and Hardie (1978) as documented in Eugster and Jones (1979) is presented in Figure 2.2.3. This model still forms the basis for many studies of evaporative concentration of water bodies, and is widely referenced in fundamental texts (Arndt and Richardson, 1989; Domenico and Schwartz, 1990; Ortí *et al.*, 2003; Reading, 1986; Salvany *et al.*, 1994; Vepraskas and Faulkner, 2000; Yechieli and Wood, 2002).



**Figure 2.2.3** Geochemical evolution of closed-basin brines: a conceptual model of chemical divides  
Source: Eugster and Jones (1979)

The chemical evolution of surface water bodies through evaporation is largely determined by the nature and concentration of inputs. The redox potential is consistently oxidizing, therefore chemical transformations due to variations in redox potential will be insignificant in the shallow surface water basins being considered (Reddy and D'Angelo, 1994). In other surface water systems where shallow water bodies are transient or where inflows are limited leading to long residence times, oxidizing and reducing conditions may be present within the same system in close proximity and therefore play an important role in the chemical evolution of the water body. The importance of the nature and concentration of inputs in chemical evolution was recognised by Eugster and Hardie (1978) as reported in Eugster and Jones (1979), by identifying solute fractionation sequences for brines in closed basins. Variations in calcium, magnesium and bicarbonate and their relative concentrations are noted as being particularly important in affecting the chemical evolution of water during evaporative concentration.

Three distinct inflow categories are identified, the first being where carbonate species, particularly bicarbonate ( $\text{HCO}_3^-$ ) at neutral pH's are present in far higher concentrations than the sum of calcium and magnesium concentrations (Type I). The second type has calcium and magnesium present in far higher concentrations than bicarbonate ions (Type II). The third type has roughly equal concentrations of bicarbonate and the combined concentration of calcium and magnesium, tending towards a slight excess of bicarbonate (Type III). This initial division of inflows was based on the ratio of bicarbonate to calcium plus magnesium ions since in dilute continental waters the dominant anion is bicarbonate, with the contribution of carbonate being important at alkaline pH, and both calcium and magnesium are major constituents of most terrestrial waters. These two alkaline earth metals consistently play a major role in solute fractionation between water and mineral phases due to the low saturation thresholds of their carbonate compounds (Eugster and Jones, 1979; Stumm and Morgan, 1981).

The concentration process for all three starting solutions is initiated by calcite precipitation as it is typically the most insoluble mineral phase. The degree to which the sequence is retarded at this step depends on the relative concentrations of bicarbonate and the alkaline earth metals, with Type III requiring the almost complete removal of bicarbonate, calcium and magnesium, due to their presence in approximately equal concentrations. As calcite precipitation progresses, magnesium will be incorporated in increasing amounts until the bicarbonate or alkaline earth supplies are exhausted. The resulting precipitates range from low magnesium calcites through to protodolomite (poorly crystalline material approximating dolomite:  $\text{CaMg}(\text{CO}_3)_2$ ) and even magnesite ( $\text{MgCO}_3$ ) if sufficient bicarbonate is present.

For Type I waters, in which bicarbonate is present in greater concentrations than the sum of calcium and magnesium, evaporation leads to waters enriched in bicarbonate, with high concentrations of sodium, sulphate and chloride also expected in the brine ( $\text{Na-CO}_3\text{-SO}_4\text{-Cl}$ ). This brine may be further modified by sulphate reduction to form  $\text{Na-CO}_3\text{-Cl}$  brines. For the Type II waters that are depleted in bicarbonate, and where it is expected that calcium concentrations exceed magnesium concentrations, gypsum precipitation will occur. The possible brine compositions include  $\text{Ca-Na-Cl}$  and  $\text{Na-SO}_4\text{-Cl}$ . The studies indicated that Type III waters follow a range of possible paths depending on the concentrations and ratios of calcium and magnesium. Potential brine compositions of Type IIIA waters, which are low in calcium and magnesium with magnesium dominating, are identical to those of Type I,

and include Na-CO<sub>3</sub>-SO<sub>4</sub>-Cl and Na-CO<sub>3</sub>-Cl. Type IIIB waters are relatively more concentrated in calcium and magnesium, again with magnesium dominating, in spite of calcium depletion by calcite precipitation. Possible evaporation end members include Mg-Ca-Na-Cl, Mg-SO<sub>4</sub>-Cl and Na-SO<sub>4</sub>-Cl brines.

The general applicability of the above model has been confirmed by many studies, with lakes in mid-continental Australia, the western USA, south-western Canada and Africa displaying mineral precipitation sequences consistent with Eugster and Hardie's (1978) findings (Eugster and Jones, 1979; Langmuir, 1997). However, mass balances conducted for lakes can often not be reconciled, as solute inputs are not fully accounted for in evaporite mineral deposits and water column concentrations (Sanford and Wood, 1991; Wood and Sanford, 1990). This can be attributed to past chemical additions that are not consistent with current additions or variation in climatic conditions that affect paths of chemical evolution. However, it is most simply accounted for by groundwater recharge that has been documented in many lakes (Wood and Sanford, 1990). It thus seems that the mineral assemblages precipitated from solution and associated water chemistry are dependent on the ratio of groundwater discharge to recharge. Where this ratio is high, the full range of expected minerals is found in lake sediments. Conversely, with increasing recharge volumes, the range of minerals encountered in lake sediments decreases (Sanford and Wood, 1991; Wood and Sanford, 1990). In these systems with high recharge volumes, there is insufficient time for brines to develop to the full extent as described by Eugster and Jones (1979), mineral saturation is limited to the more insoluble compounds and limited mineral sequences are present (Sanford and Wood, 1991; Wood and Sanford, 1990).

However, Garrels and Mackenzie (1967) suggested that silicates such as sepiolite, or if base cations are limited, amorphous silica, are important transformation products in evaporation of closed-basin lakes, as did Hardie and Eugster (1970) reported in Von Damm and Edmond (1984). Subsequent work has indicated the presence of a magnesium sink in the concentration process, and therefore the model of chemical evolution in closed-basins is revised to include a magnesium-rich silicate, smectite or sepiolite depending on the chemical composition of evaporating waters (Borchardt, 1989; Ducloux *et al.*, 1995; Easterwood *et al.*, 1991; Gac *et al.*, 1977; Mees, 2001; Yuretich and Cerling, 1983). The position of this component within the model of chemical divides is debated (Gac *et al.*, 1977; Von Damm and Edmond, 1984; Yuretich and Cerling, 1983), but must be related to the relative

concentrations of calcium to magnesium and the other necessary elements for saturation of a magnesium-rich silicate.

Although wetlands differ from lakes in many respects, evapotranspiration is expected to play an important role in chemical processing of inflowing waters. The generally shallow surface water of wetlands together with long retention times and high primary productivity that is associated with high transpiration rates, predispose wetlands to chemical processing by evapotranspiration, particularly in tropical and subtropical settings. Furthermore, shallow water tables typical of wetland systems will also expose shallow groundwater to evapotranspirational modification of composition.

#### **2.2.1.2. Chemical transformations by other mechanisms**

Even in arid regions where evaporative concentration dominates chemical processing, other mechanisms may be responsible for chemical transformations. These mechanisms may include cation-exchange, adsorption to active surfaces, dissolution of minerals within the soil, degassing, and redox reactions, with redox potential and associated reactions considered of greater importance than the other mechanisms in chemical evolution of wetland groundwater (Eugster and Jones, 1979; Filella *et al.*, 1995; Matthes, 1982; Singer and Munns, 1996).

Cation-exchange reactions are non-specific, being purely driven by electrostatic factors, whereby ions such as potassium, ammonium, calcium, magnesium, hydrogen and sodium may be attracted to negatively charged particles including clays and other finely divided, colloidal material (Singer and Munns, 1996). Organic matter also has a high cation-exchange capacity, which is principally satisfied by hydrogen ions (Wang and Mitsch, 2000). Organic matter decomposition products can also form soluble complexes with metal ions such as ferric iron-humic acid complexes, which allow oxidised forms that are usually precipitated (in this case the ferric ion ( $\text{Fe}^{3+}$ )) to remain in solution (Cole, 1979; Filella *et al.*, 1995). Adsorption-desorption processes however, can be specific and cause metals to be tightly, possibly irreversibly bound, such as the adsorption of phosphorus onto colloidal iron and aluminium hydroxides (Matthes, 1982; Singer and Munns, 1996).

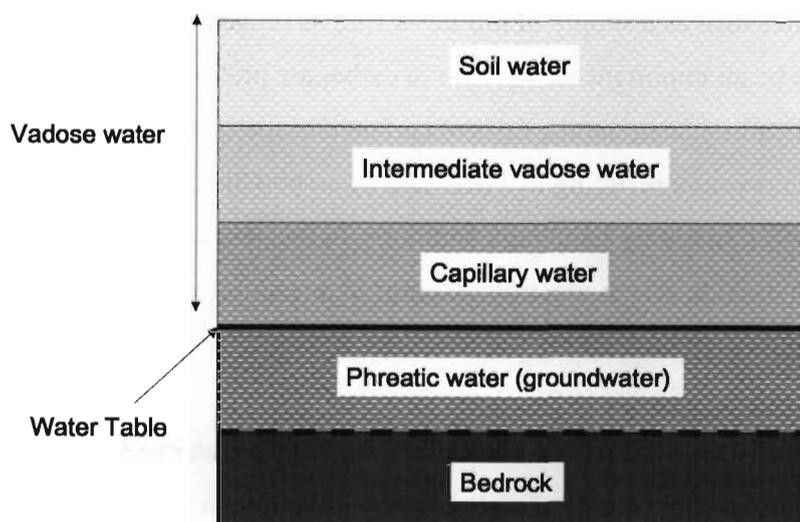
Degassing is of limited importance in large surface water bodies but may influence ion ratios to some degree in wetlands. Denitrification mediated by microbes reduces nitrates through a nitrite intermediate to dinitrogen ( $N_2$ ), which is released to the atmosphere. This reaction is likely to be more important in groundwater where sufficiently reducing conditions consistently prevail, and other requirements for denitrification are met such as a supply of nitrate as well as organic matter. Degassing of carbon dioxide is known to be an important mechanism in carbonate precipitation as the associated rise in pH causes saturation of carbonate minerals. Loss of carbon dioxide commonly occurs by plant uptake or an increase in water temperature resulting in a decrease of carbon dioxide solubility (Eugster and Jones, 1979; Langmuir, 1997). In highly reducing conditions, in the absence of other electron acceptors, at least locally, carbon dioxide acts as electron acceptor in a reaction mediated by microbes, and methane is formed (Mitsch and Gosselink, 2000).

Wetlands are commonly found at the interface between surface water and groundwater systems. Multidisciplinary research in hydrology, microbiology as well as water and soil chemistry has found that this interface is highly active and productive with respect to chemical transformations (Dahm *et al.*, 1998; Mulholland, 1992). This efficiency in chemical transformations in streams and rivers was reviewed by Dahm *et al.* (1998), and is attributed to the spatial and temporal variability of the interface in terms of biological, hydrological and chemical factors. Wetland systems comprise large areas that may be designated ecotonal with respect to surface water and groundwater. Solute retention within the shallow groundwater of wetland systems is dependent on the regional groundwater slope and the hydraulic conductivity of wetland soils, both of which in the case of shallow groundwater are conducive to long residence times. As a result, wetlands are likely to retain solutes more effectively than is documented by the above-mentioned studies for stream margins.

### **2.2.2. Factors controlling ground- and vadose water chemistry**

Soil water and groundwater exist as a fairly complex system in which several layers can be distinguished (Figure 2.2.4). The vadose zone, also known as the unsaturated zone, refers to water and air occurring in soil pores from the soil surface to the water table. The lower section of the vadose zone is referred to as capillary water, which ascends from the phreatic or groundwater zone as a

consequence of capillary rise. The phreatic or groundwater zone is fully saturated with its upper limit at the water table and its lower boundary at bedrock below.



**Figure 2.2.4** The water profile from the soil surface to bedrock

Modified after: Domenico and Schwartz (1990)

The controls on ground- and vadose water chemistry are more complex than those affecting surface water due to the varying conditions of redox and pH, as well as interactions with the gas phase. Atmospheric concentrations of most gases are relatively stable and therefore surface water relationships are easily predicted. However, groundwater gas concentrations may vary considerably depending on diffusion rate, degree of saturation, as well as organic matter decomposition (carbon dioxide and methane) and microbial activity (carbon dioxide and oxygen); (Langmuir, 1997). Gas dissolution and redistribution is particularly important with respect to carbon dioxide, as the carbonates produced may buffer the groundwater at neutral pH's and it may influence the chemical weathering ability of the water by dictating carbonic acid concentrations (Stumm and Morgan, 1981). Due to high microbial respiration at the water table surface, organic matter decomposition will be high, which in conjunction with plant root respiration in the soil zone, elevates carbon dioxide concentrations. In addition, restricted diffusion of gases within the vadose zone and groundwater will allow carbon

dioxide to accumulate, and therefore the dissolved forms of carbon dioxide, namely carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate and carbonate ( $\text{CO}_3^{2-}$ ), are expected to be higher in the vadose region and upper water table than elsewhere in the soil profile (Armstrong, 1975; Langmuir, 1997; Matthes, 1982). Therefore carbonate chemistry is likely to be the principal governing factor in groundwater and vadose water systems.

The chemical composition of recharging waters, filtering from the surface through the soil profile, is not only governed by rainfall and/or infiltrating surface water chemistry, but also by additional solutes and processes that may modify the chemical composition during infiltration. Solute additions may be derived from dissolution of salts precipitated under evapotranspiration from the soil profile, as well as weathering of soil minerals (Langmuir, 1997). Evapotranspiration may also act to concentrate inputs during infiltration (Matthes, 1982). Other processes that modify water chemistry during infiltration and within the soil water profile include microbially-mediated reactions - often related to redox conditions such as sulfide oxidation; acid-base reactions; ion-exchange; sorption of metals onto organic compounds and/or clay minerals; and oxidation of organic matter in the unsaturated zone (Domenico and Schwartz, 1990; Matthes, 1982).

Reactions in the saturated groundwater zone will mimic those in the unsaturated region (vadose zone), but will be distinguished by a wider diversity of reactions. Within the groundwater, dispersive mixing of reactants and products is possible, and there are widely differing geological, hydrogeological and geochemical conditions present (Domenico and Schwartz, 1990). This is particularly true of the upper section of the groundwater system, where oxidizing conditions may occur at or close to the water table, particularly in highly porous sediments with high connectivity between pore spaces that allow increased oxygen diffusion rates (Wang and Mitsch, 2000). Consequently, the surface of the water table and oxidising water of the vadose zone are most likely to be influenced by the release of solutes from the decomposition of organic matter, and from the chelating abilities of the organic compounds thus produced. Chemical weathering is also most active in the vadose zone and upper groundwater layers where water turnover and carbon dioxide levels are relatively high, particularly in shallow groundwater systems (Langmuir, 1997; Matthes, 1982).

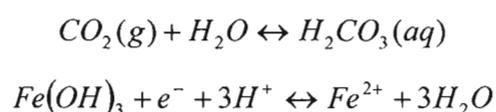
Deep groundwater is generally anoxic, unless recent recharge has taken place in the system. In general the chemical interactions of the groundwater compartment are dominated by reduced chemical forms, often being isolated from the atmosphere by overlying saturated sediment. As a result steep redox gradients generally exist between surface water and groundwater (Dahm *et al.*, 1998; Logan *et al.*, 1999). Furthermore, groundwater resources are generally protected from organic matter decomposition products by filtration in the sediment during percolation of surface water inputs to the water table (Singer and Munns, 1996). Nevertheless, the reducing conditions cause the rates of microbial activity to decline significantly and the range and extent of possible chemical transformations are thus reduced (Schlesinger, 1997). It is therefore the vadose zone and upper groundwater layer (which was the focus of sampling in this study) that are of primary importance in the chemical evolution of shallow groundwater, rather than the saturated zone beneath (Langmuir, 1997; Matthes, 1982).

### **2.2.3. Factors controlling soil chemistry in wetlands**

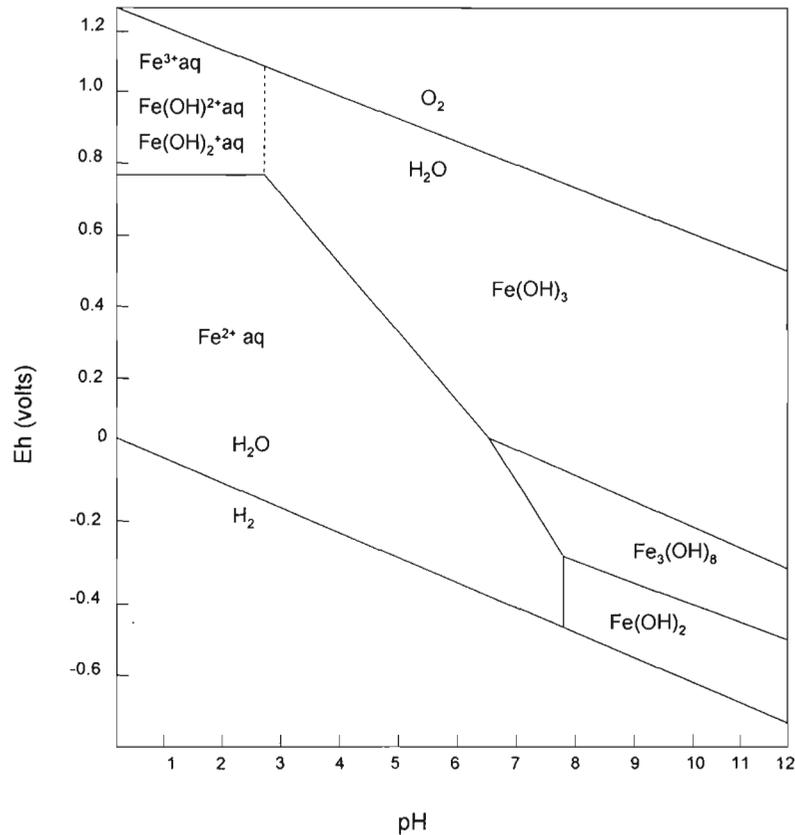
#### **2.2.3.1. Eh and pH: Main variables controlling chemical transformations in soils**

According to Chadwick and Chorover (2001) the main variables controlling chemical behaviour in soil are redox potential and pH. The redox potential governs the mobility of many chemicals. Redox-sensitive elements such as iron and manganese are insoluble under oxidising conditions, and soluble when reduced, while others such as nitrogen and sulphur remain mobile in their oxidised forms (Singer and Munns, 1996). The reduction of sulphur species to sulphides results in precipitation with elements such as iron, while on further reduction, sulphur is lost as hydrogen sulphide ( $\text{H}_2\text{S}$ ). Although some other chemicals, such as calcium, chloride, magnesium, phosphorus, potassium, silicon and sodium are insensitive to the redox potentials of natural systems, their mobility may be influenced due to their association with redox-sensitive elements, such as the adsorption of phosphate onto ferric ( $\text{Fe}^{3+}$ ) and manganic ( $\text{Mn}^{4+}$ ) oxyhydroxides (Cole, 1979; Wang and Mitsch, 2000). Other solutes that may be co-precipitated with or adsorbed to iron and manganese oxyhydroxides are copper, zinc, lead, nickel, cobalt and cadmium (Langmuir, 1997). The implications of redox reactions for nutrient transfer and release, as described above for phosphorus, are important biotic processes in wetlands (Reddy and D'Angelo, 1994).

Both the redox potential and pH govern the form in which iron exists, and therefore its availability for reactions and its mobility as illustrated in Figure 2.2.5. Upon submergence of wetland soils, the pH values of both acidic and alkaline soils tend to converge on neutral, with most soils in the pH range 6.7 – 7.2 (Ponnamperuma, 1972). The decrease of pH in alkaline soils is attributed to the accumulation of carbonic acid, resulting from increasing carbon dioxide concentrations, whereas an increase of pH values in acid soils is the result of ferric iron hydroxide reduction, described by the following equations (Mitsch and Gosselink, 1993):



With increasing pH, the stability region for each iron species is translated to lower redox potentials. Thereby, a range of chemical processes is influenced by pH and redox conditions due to their governing role on equilibrium positions. Thus chemical transformations involving hydroxides, carbonates, sulphides, phosphates and silicates are dependent on both pH and redox potential (Ponnamperuma, 1972).



**Figure 2.2.5** Iron stability diagram for iron hydroxides in flooded soils with an aqueous Fe<sup>3+</sup> activity of one millimole at 25 °C

Modified after: Armstrong (1975)

In terrestrial settings, systems subjected to high rainfall and with easily draining soils will tend to be oxidising in the upper soil layers, with low pH values since the acid neutralising capacity of the soil is decreased through loss of metal compounds to leaching (Chadwick and Chorover, 2001). The ability of the soil to retain chemicals is therefore low. On the other extreme, in arid terrestrial environments, solutes are retained at varying depths within the profile depending on the intensity of leaching, which is governed by the amount of rainfall and the solubility of the soil minerals present (Chadwick and Chorover, 2001). Due to the limited influence of rainfall in terms of solute inputs, there is very little solute addition to such systems. Therefore, the potential for rapid, large-scale pedogenic change of terrestrial humid or arid systems through the retention of solutes, is low.

It has long been recognised that chemical transformations in wetlands are largely influenced by the redox conditions prevailing in wetland water and soils. The flooding frequency and duration, as well as the rate of water movement, the number of micro-organisms, the availability of organic matter and the concentrations of redox-sensitive solutes govern the degree of anoxia of wetland substrates (Armstrong, 1975; Ponnampetuma, 1972; Vepraskas and Faulkner, 2000). The entire range of redox potentials found in natural systems are encountered in wetlands, including the two extremes of the highly oxidizing potentials of terrestrial settings, to the highly reducing potentials of deep water aquatic systems (Schlesinger, 1997). Not only do the redox conditions in wetlands vary widely across the geographical extent of the wetland, but they also vary temporally due to the uneven distribution and movement of floodwaters as dictated by local topography and climate. In addition, the vertical variation in redox potentials through the soil profile may be high, due to the dependence of redox potential on the position of the surface water – groundwater interface that may vary seasonally and over longer timescales. Consequently the vadose zone is generally rich in microbes, abundant in both number and metabolic group, such that the surface water – groundwater interface is an active site of microbial mediation in decomposition and mineralization reactions (Dahm *et al.*, 1998; Holden and Fierer, 2005; Kotze and Breen, 1994). Furthermore, the reducing conditions allow decomposition of organic matter by slow anaerobic pathways only, which results in a buildup of partially decayed organic matter in the system. This organic matter also has the potential to remove solutes from the water column (Damman, 1978; Dollar *et al.*, 2001; Fischer, 2000; Kotze and Breen, 1994; McCarthy *et al.*, 1989). Organic matter retained within a wetland system also acts as a substrate supplying electrons for microbially-mediated reactions such as the reduction of nitrate and sulfate (Mitsch and Gosselink, 2000). Humic substances, long considered to be resistant to microbial degradation, may also play an important role in the microbial reduction of iron oxides and possibly other metals (Lovley *et al.*, 1996). Humic acids are able to accept electrons as part of the anaerobic oxidation of organics and hydrogen, which then allows reduction of insoluble iron (III) oxides by the shuttling of electrons from the humic substances to the oxides as mediated by the humic-reducing micro-organisms (Lovley *et al.*, 1996; Nevin and Lovley, 2000). This variability of redox potentials in space and time across wetland systems, due to periodic saturation and drying, allows for a wide range of reactions to occur, partly accounting for the propensity of wetlands for chemical transformations (Vepraskas and Faulkner, 2000).

### 2.2.3.2. Possible sites of retention within wetland soils

González and Vargas (2004) consider pH, and the amount of organic matter and clays as “capacity-controlling parameters”. Organic matter and clays will not only contribute to cation exchange capacity of a wetland soil, but also participate in other reactions such as complexation of metals by organic ligands, and incorporation of cations within the lattice of clay minerals. These factors dictate the ability of sediments to retain metals (including contaminants) and plant nutrients. The cation exchange capacity describes a possible mechanism of solute retention in the soil, which may constitute a source of solutes through desorption if conditions allow (Singer and Munns, 1996). Clays have high cation-exchange capacities, with peat displaying particularly high capacities (Wang and Mitsch, 2000). Adsorption reactions of clay minerals involve the incorporation of chemicals into the lattice or the interlayer spaces of the clays (Sparks, 1995). Complexation reactions, where metal ions are tightly bound to organic compounds, account for many immobilised chemicals in peat deposits (Domenico and Schwartz, 1990; Wang and Mitsch, 2000). However, such retention depends on sufficient water flow to transport solutes to the adsorption sites, and also on sediment capacity or cation-exchange capacity, as adsorption, absorption or complexation sites are finite.

Chemical retention in wetlands has been primarily attributed to peat deposits, where long-term immobilization of metals has been well documented (Damman, 1978; Dollar *et al.*, 2001; Fischer, 2000; Kotze and Breen, 1994; McCarthy *et al.*, 1989). Organic material in wetland soils, as well as the large accumulations of organic matter known as peat, have very high cation exchange capacities, exceeding those of clays per unit dry mass (Miller and Donahue, 1990). Furthermore, peat may be accumulated in large volumes, which combined with a low bulk density, provides opportunity for solute immobilization from infiltrating water. The humic and fulvic acids provide adsorption sites for cation-exchange reactions, allowing metals to be loosely bound to organic material (Casagrande, 1984). Unless the peats are buried due to high litterfall and slow decomposition, the metals retained by cation-exchange will be readily available to plants (Nichols, 1983). Sequestration of metals by peat is attributed to organic chelation reactions; whereby organic ligands form ring structures known as chelates (Miller and Donahue, 1990).

Solutes may also simply be retained within pore or groundwater due to stagnant conditions of groundwater flow. The length of retention is dependent on the volumes such systems can accommodate, as well as current weather patterns and wetland type, with hydrologically closed systems likely to retain solutes for long time periods. The groundwater store is significant – in fact it is the ultimate sink for sodium in the Okavango, where sodium from island soils is leached to deep groundwater (McCarthy *et al.*, 1991; McCarthy and Metcalfe, 1990). Thereby, the surface waters, which are fresh, float on a brine of saline water of high density such that the two water bodies never mix.

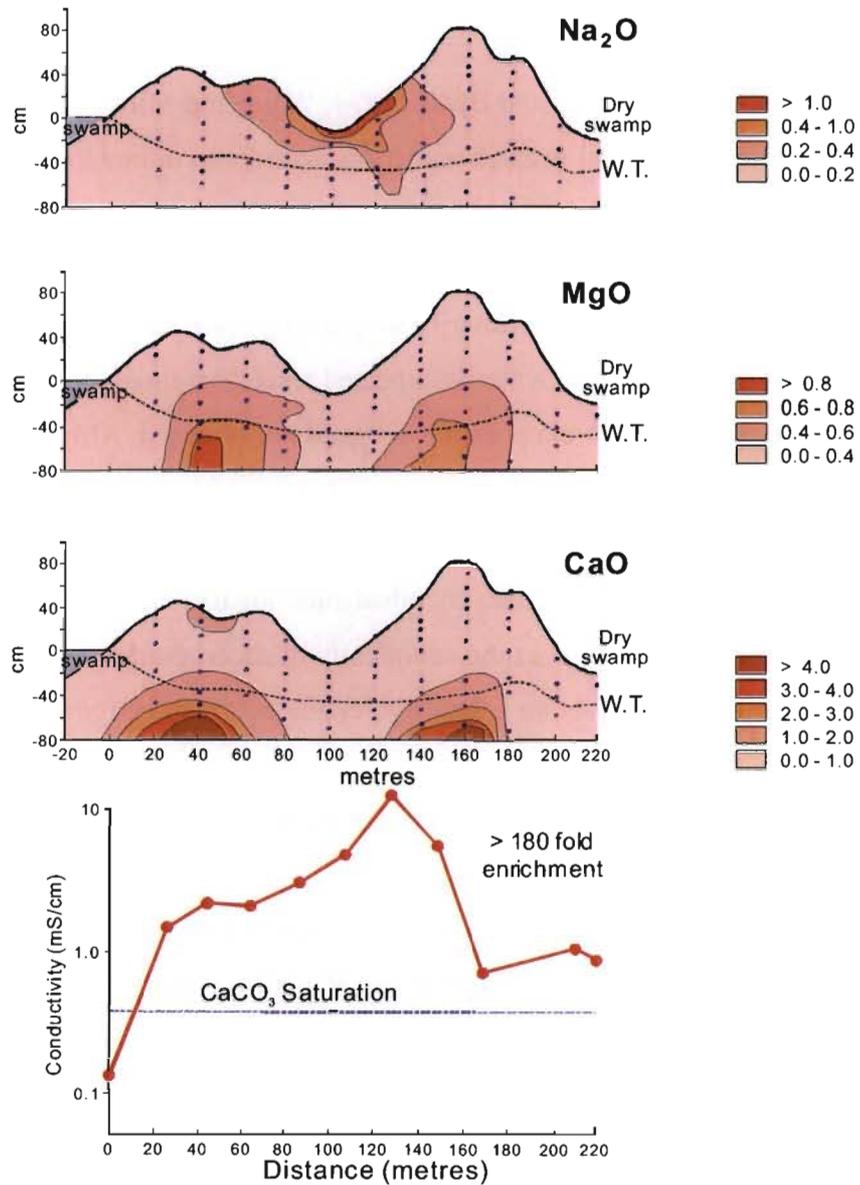
Evapotranspiration is a further process resulting in chemical transformations in soils through chemical precipitation induced by water loss. In contrast to cation exchange reactions, evapotranspiration is independent of reactive sites on sediment particles. Chemical precipitation and retention of solutes within soils as a result of the evaporation sequence presented by Eugster and Hardie (1978) has been widely documented, particularly in arid regions (Eugster and Jones, 1979; Goudie and Pye, 1983; Talbot and Allen, 1996; Warren, 1989). In these areas a high evapotranspiration potential may cause precipitation of evaporite minerals in the upper layers of the soil profile. During rainfall events the minerals may be transported to lower soil layers, where they accumulate due to insufficient infiltration of water to allow removal from the system. The formation of chemical sediments may be purely due to saturation of introduced solutes through a concentration process or may incorporate weathering residues derived from sediments *in situ*. The geochemical processes resulting in chemical sediments will be governed by the local sediment and water conditions, as well as their chemical compositions (Goudie and Pye, 1983).

Research in the Okavango Delta in Botswana has detected chemical sedimentation driven by evapotranspiration as an important mechanism of chemical retention. The Delta is a large alluvial fan that is flooded to a shallow depth with freshwater, due to extensive inundation of large areas by considerable volumes of water that originate in the highlands of eastern Angola about 1 000 km to the north-west. The Okavango Delta itself is situated in the semi-arid Kalahari with a mean annual rainfall of less than 500 mm *per annum*. Evapotranspiration exceeds precipitation in every month of the year and only 2 % of the total water input of surface inflow plus local rainfall, leaves the system as surface outflow, with a further estimated maximum of 2 % leaving the system as groundwater outflow

(McCarthy *et al.*, 1998a; Wilson and Dinçer, 1976). The remaining 96 % of all surface water inputs are lost to the atmosphere through evapotranspiration (McCarthy and Ellery, 1995). In spite of the substantial removal of water by evapotranspiration, which should concentrate the shallow waters of the swamp to a brine, the outflow waters only increase in concentration by a factor of two across 15 000 km<sup>2</sup> of swamp (McCarthy and Metcalfe, 1990).

Mass balances of clastic sediments and solutes conducted for the Delta, indicate that the predominant mass added to the system is of a chemical nature, at 360 000 tonnes *per annum*, rather than clastic with only 209 000 tonnes of clastic sediment retained per year (McCarthy and Ellery, 1998; McCarthy *et al.*, 1993). The distal floodplain reaches, and islands of the Delta, situated in both the permanently and seasonally flooded regions of the swamp, were identified as displaying unusual soil and water chemical compositions (McCarthy and Ellery, 1995). Amorphous silica and calcite were documented in distal floodplain regions associated with concentrated groundwater, indicating saturation of these compounds under a concentration process. Hydrological and geochemical studies on the islands have revealed sinks and mechanisms of solute immobilisation. Steep hydraulic gradients exist from the wetland towards the central regions of islands, indicating that groundwater recharge takes place in these settings (McCarthy *et al.*, 1993). The hydraulic slope from swamp to island centre is maintained by transpiration in the densely wooded fringe of the island, which removes water at a greater rate than recharge replenishes it. The groundwater at these points has a high electrical conductivity since trees remove groundwater through transpiration, while selectively excluding many of the dissolved solutes (Figure 2.2.6; McCarthy *et al.*, 1993). In considering both water and soil chemistry, it was suggested that concentration in the groundwater caused calcium and magnesium compounds to attain saturation and precipitate out of solution, producing soil chemistry maxima corresponding with the groundwater conductivity maxima in a manner consistent with an evaporation sequence (Figure 2.2.6; McCarthy *et al.*, 1993). Once evapotranspirative concentration of the groundwater has been initiated, Bauer-Gottwein *et al.* (2007) show that density-driven flow of concentrated solutes acts in opposition to the transpirative upward flow of solutes. The number of scenarios tested, including variations in the concentration of humic substances and salinity, all recorded the onset of density-driven flow over a range of timescales, with mineral precipitation and degassing of carbon dioxide delaying the onset. Density-driven flow removes solutes to the deep groundwater of the Okavango Delta, and causes stabilisation of solute concentrations in the shallow groundwater of the system (Bauer-Gottwein *et al.*,

2007). Numerical modeling of soil and water chemistry indicates that islands are ancient features of the swamp system. As such, the chemical sediments to which island growth are attributed, are the products of processes acting over long timescales of the order of tens to hundreds of thousands of years (McCarthy *et al.*, 1993).



**Figure 2.2.6** Profiles across an island in the Okavango Delta, Botswana showing soil Na<sub>2</sub>O, MgO, and CaO concentrations in mass % and conductivity of groundwater as well as the conductivity at which calcite saturates

Modified after: McCarthy *et al.* (1993)

## **2.2.4. The role of wetland biota in chemical cycling and retention**

### **2.2.4.1. Wetland biota as chemical sinks**

Certain biotic characteristics of wetlands also play a role in predisposing wetlands to chemical transformations. In general, wetlands have a high primary productivity that translates into high rates of nutrient uptake and cycling within the system, and a capacity to retain solutes within plant tissues over their lifetime and beyond (Kotze and Breen, 1994; Wang and Mitsch, 2000). The incorporation of some of this plant tissue into the soil organic matter pool results in immobilization of nutrients, provided that the organic matter is not mineralized (Garstang *et al.*, 1998).

The uMkhuze Wetland System is primarily supplied by river water draining a catchment of sedimentary and volcanic rocks, with the expected result that most macronutrients are supplied in fair quantities to the wetland, with the possible exception of nitrogen. Although, the system is situated on reworked marine sands that have a limited capacity to adsorb chemicals, high water tables and long residence times are expected to result in chemical retention. Due to the fact that vegetation does not satisfy the requirements of a persistent chemical sink due to senescence and the associated potential for remobilisation of solutes, as well as the complexity of ascertaining the magnitude of the chemicals within living plant material over an annual cycle, this pool will be ignored in the current study.

### **2.2.4.2. Wetland biota as ecosystem engineers**

The traditional view of plant ecology is that vegetation passively responds to environmental gradients and conditions. However, an increasing number of studies suggest that vegetation distribution is not simply affected by environmental conditions but that plants influence water and solute distribution within a system, often with far-reaching effects at a landscape level (Ellery *et al.*, 1993b; Kutzbach *et al.*, 1996; McCarthy *et al.*, 1986; Rodriguez-Iturbe and Porporato, 2004).

Vegetation interacts with the water component both physically and chemically. With respect to water chemistry, most processing takes place within the root zone of macrophytic plants where water and solutes are drawn into the plant tissues. Plants are, however, selective in their uptake of solutes such that limiting nutrients are selectively taken up, whereas non-limiting solutes are taken up in quantities

that are necessary for plant growth and metabolism but are otherwise excluded from uptake. Non-limiting solutes may be actively excluded from uptake at high concentrations and they therefore concentrate in the vadose zone and upper groundwater (Kramer and Boyer, 1995; Singer and Munns, 1996; Tinker and Nye, 2000; Trudgill, 1977). Thus, plants exert control over the distribution of nutrients in the surrounding soil. The extent of plants' influence on nutrient distribution has been demonstrated in a study on global soils, in which both horizontal concentration, particularly in arid systems, and vertical redistribution of plant nutrients has been documented such that nutrients are, to a large degree, maintained within the root zone (Jobbágy and Jackson, 2001).

The concentration of solutes in shallow groundwater as a consequence of water loss through transpiration by phreatophytes has also been recorded in the Amazon River floodplain (Furch and Junk, 1997), fen meadows in the Netherlands (Arndt and Richardson, 1989; De Mars and Garritsen, 1997), an Argentinian coastal plain (Logan *et al.*, 1999; Logan and Rudolph, 1997), a section of the Pantanal wetland in Brazil (Barbiéro *et al.*, 2002), wetlands in North Dakota (Wang and Mitsch, 2000), on an island in Denmark (Jørgensen, 2002), wetlands in West Africa from Ivory Coast, Burkina Faso and Nigeria (Roose and Lelong, 1981), as well as the Okavango Delta, Botswana (McCarthy *et al.*, 1993) among others. The wide distribution of groundwaters influenced by evapotranspiration from temperate conditions in Denmark and Argentina, to the harsh semi-arid climate of Botswana, indicates the importance of the process in the chemical evolution of shallow groundwater. The long-term effects of such concentration is dependent on the magnitude of diluting precipitation inputs, as well as the extent of solute additions from other sources such as catchment and *in situ* products of mineral weathering.

### **2.3. Chemical retention of non-limiting solutes in wetland systems**

Due to the differing chemical nature of solutes, and the potential interactions with their environments, including the modification of their concentrations by plant requirements, solutes will be retained by varying mechanisms. The plant macronutrients nitrogen and phosphorus, and to some extent potassium, are often limiting of plant growth and reproduction, and have consequently been the focus of research into chemical retention and processing in wetlands (Bashkin, 2002; Olde Venterink *et al.*, 2003; Reddy and D'Angelo, 1994; Wang and Mitsch, 2000). Due to their limited availability these macronutrients are cycled relatively quickly through an ecosystem, as highlighted by Jobbágy and

Jackson (2001) who document shallow distribution depths for both phosphorus and potassium in global soils due to the rapid uptake of these often limiting macronutrients by plants. Thereby, the macronutrients may be maintained within the wetland, but are also vulnerable to loss from the system, and the wetland may become a source of these solutes seasonally or due to disturbances to the nutrient storage sites (Wang and Mitsch, 2000; Yavitt *et al.*, 2006). Therefore, non-limiting and non-nutrient chemicals are potentially available in greater quantities than the limiting macronutrients in wetland systems. Depending on chemical sources, the nature of the element that dictates possible chemical interactions, and the specific wetland factors, non-limiting and non-nutrient chemicals may have greater potential to participate in and influence wetland chemical transformations, as documented in the Okavango Delta where non-limiting solutes account for around 300 000 tonnes of the 360 000 tonnes of solutes retained in the Delta (McCarthy and Ellery, 1998).

### **2.3.1. Documented retention of non-limiting solutes in wetlands**

Research in the Okavango Delta, Botswana, has indicated that wetlands may indeed have a profound influence on the chemical composition of their waters, particularly with respect to non-limiting chemicals including macro- (calcium and magnesium) and micronutrient solutes (iron and sodium) (Bauer-Gottwein *et al.*, 2007; McCarthy and Ellery, 1995). Plant-mediated solute precipitation of non-limiting solutes in island and floodplain soils is viewed as the sites of accumulation of non-limiting solutes. The mechanism is transpirational water loss as described previously.

A preliminary investigation into the uMkhuze Wetland System, KwaZulu-Natal provided evidence that this wetland is also acting as a sink for certain solutes. A mass balance approach was employed to compare inflow and outflow solute concentrations, while accounting for evapotranspiration through the swamp system by assuming that chloride was fully conserved in the chemical processing (Barnes *et al.*, 2002). The results indicated that silicon was most effectively retained such that roughly 80 % of the influent silicon was retained in the swamp, while about 50% of the calcium was retained (Table 2.3.1). If these figures are re-calculated over the period of a year, it seems likely that tonnes of solutes are accumulating every year in the uMkhuze Wetland System. Assuming that these solutes are evenly spread throughout the 440 km<sup>2</sup> of wetland area, the results indicate that around 36.5 kg of non-limiting solutes are being retained per km<sup>2</sup> per year.

**Table 2.3.1** Results of the mass balance model applied to the waters of the uMkhuze Wetland System, indicating solute retention

Solute Ions	~Percentage of Inflow Mass Retained	Mass retained/ kg/yr	Mass retained/ kg/km <sup>2</sup> /yr
Silicon	80	3400	18.9
Potassium	70	1100	6.1
Calcium	50	4500	25.0
Magnesium	20	1300	7.2
Sodium	20	5800	32.2

Silicon concentrations in water increase under reducing conditions probably due to the release of silica from ferrisilica complexes (Armstrong, 1975). This might suggest poor retention of silicon by wetlands. However, the Okavango Delta in Botswana and the uMkhuze Wetland System retain silicon in large quantities, probably through concentration-induced chemical sedimentation in the case of the Okavango (Barnes *et al.*, 2002; McCarthy *et al.*, 1993).

Calcium compounds, particularly carbonate, are insoluble and reach saturation in natural waters when photosynthesis removes carbon dioxide as in the Florida Everglades, USA, or due to concentration of calcium-bearing waters in the Okavango Delta (Browder *et al.*, 1994; McCarthy *et al.*, 1993). Calcium may also be bound to organic matter in peat deposits as documented in Scandinavian ombrotrophic peat bogs (Damman, 1978). Calcium retention is also reported in the Okefenokee Swamp and the uMkhuze Wetland System (Barnes *et al.*, 2002; Hyatt and Brook, 1984; Rykiel, 1984).

Magnesium should mimic the behaviour of calcium, as displayed in the Okavango Delta, because both are alkaline earth metals. However, in the presence of high chloride concentrations typical of coastal systems like the uMkhuze Wetland System, magnesium exists largely as the highly soluble compound, magnesium chloride (MgCl<sub>2</sub>); (Barnes *et al.*, 2002; Eugster and Jones, 1979; McCarthy *et al.*, 1993). In spite of the increased mobility of magnesium in the presence of chloride, net magnesium retention is documented in the uMkhuze Wetland System (Barnes *et al.*, 2002). The Okefenokee Swamp also retains magnesium (Hyatt and Brook, 1984; Rykiel, 1984).

The solubility of iron is particularly sensitive to variations in redox potential such that it is well retained in seasonally flooded systems, where periodic wetting and drying result in iron mottling within

wetland soils. In the presence of high organic concentrations, iron is effectively retained in wetlands (Damman, 1978; Dollar *et al.*, 2001; Kotze and Breen, 1994).

Both sodium and chloride are highly mobile solutes, although chloride is required in micro-quantities by plants and sodium may be adsorbed to clay particles. In spite of these retarding factors, chloride and sodium are the least likely solutes to accumulate in wetland systems (Damman, 1978; Rykiel, 1984). Despite being highly soluble, sodium is retained in wetlands through a number of mechanisms, including precipitation in island soils that are poisoned by sodium carbonate and dissolution before being leached to deep groundwater (McCarthy *et al.*, 1993). It is possible that sodium is retained in wetlands as indicated by a study in the Okefenokee Swamp, as well as in the uMkhuze Wetland System (Barnes *et al.*, 2002; Hyatt and Brook, 1984).

### **2.3.2. Chemical transformations of pollutant chemicals**

Although pollutants are largely unexpected in the uMkhuze Wetland System, the potential of the system to sequester pollutants is of interest as with increasing pressure from tourism developments and industries to support them, there is potential for pollutant additions from the catchment in the future.

Redox and pH conditions are very important in their effect on the fate of metals in wetland environments, with the mobility of redox-sensitive metals such as manganese and chromium (being in soluble or colloidal form, or precipitated as solid phase) largely determined in this way (Bartlett and James, 1993). Lead is likely to be immobilised in the short-term with potential for release and further contamination due to its association with iron-manganese sediments, which are released under anoxic conditions (Dollar *et al.*, 2001). Zinc may also be immobilised in wetlands as documented in a Chinese wetland by Wang *et al.* (2004).

In general, pollutant metals such as copper, chromium, iron and manganese are more strongly bound to particulate organic matter, while adsorption to clastic sediments is reversible (Coale *et al.*, 2004; Dollar *et al.*, 2001; Kotze and Breen, 1994). Metals bound to particulate organic matter are likely to be immobilised for long periods in wetlands where reducing conditions prevail due to consistent flooding. However, it must be noted that in certain cases, especially in the presence of dissolved organic matter

(although possibly even with particulate organic matter,) pollutant metals may be re-mobilised due to the action of microbes. An example of this microbe-mediated release of pollutants is the reductive dissolution of iron oxides allowing arsenic to be remobilised (Wang and Mulligan, 2006). Desiccation of the organic sediments allows oxidative decomposition that will release metals into the environment (Dollar *et al.*, 2001).

Precipitation of oxides, hydroxides, carbonates, phosphates and sulphides may also be an important mechanism of immobilisation, particularly among the transition metals (Kotze and Breen, 1994). Oxides and hydroxides will be vulnerable to extended reducing conditions due to flooding, which might result in dissolution, thereby releasing their adsorbed metals (Dollar *et al.*, 2001).

Mercury is increasingly added to the natural environment through anthropogenic sources, and mercury detection in wetland systems is therefore on the rise (Schlesinger, 1997). Under reducing conditions,  $\text{Hg}^{2+}$  is transformed to  $\text{Hg}^0$  and may be removed from wetlands. However, some metabolic pathways in wetlands produce methylmercury ( $\text{CH}_3\text{Hg}$ ), a highly toxic substance able to cross biological membranes and accumulate within biota (St Louis *et al.*, 1994). Studies in Sweden, as well as in New York State in the USA and in Ontario, Canada, report consistent methylmercury yields in wetlands, suggesting that they may be the primary source of methylmercury in the environment (Branfireun and Roulet, 2002; Schlesinger, 1997; St Louis *et al.*, 1994).

#### **2.4. Chemical sedimentation in wetlands: an important mechanism of solute retention?**

Wetland systems are predisposed to chemical sedimentation of their inflowing waters by a range of factors relating to wetland structure and function from the macroscale factor of large, shallow areas of inundation to the microscale of variations in redox potential across the surface water – groundwater interface. The ability of wetlands to retain the products of transformation is dictated by the nature of the hydrological regime within the wetland, being either of high or low energy, which in turn influences the residence times of water in the wetland. The influence of evapotranspiration has not been much addressed in wetland systems, in contrast to its effect on closed-basin lakes often in arid and semi-arid settings. Research in the Okavango Delta, Botswana has documented chemical sedimentation, on a scale normally attributed to brines in arid and semi-arid regions (McCarthy and

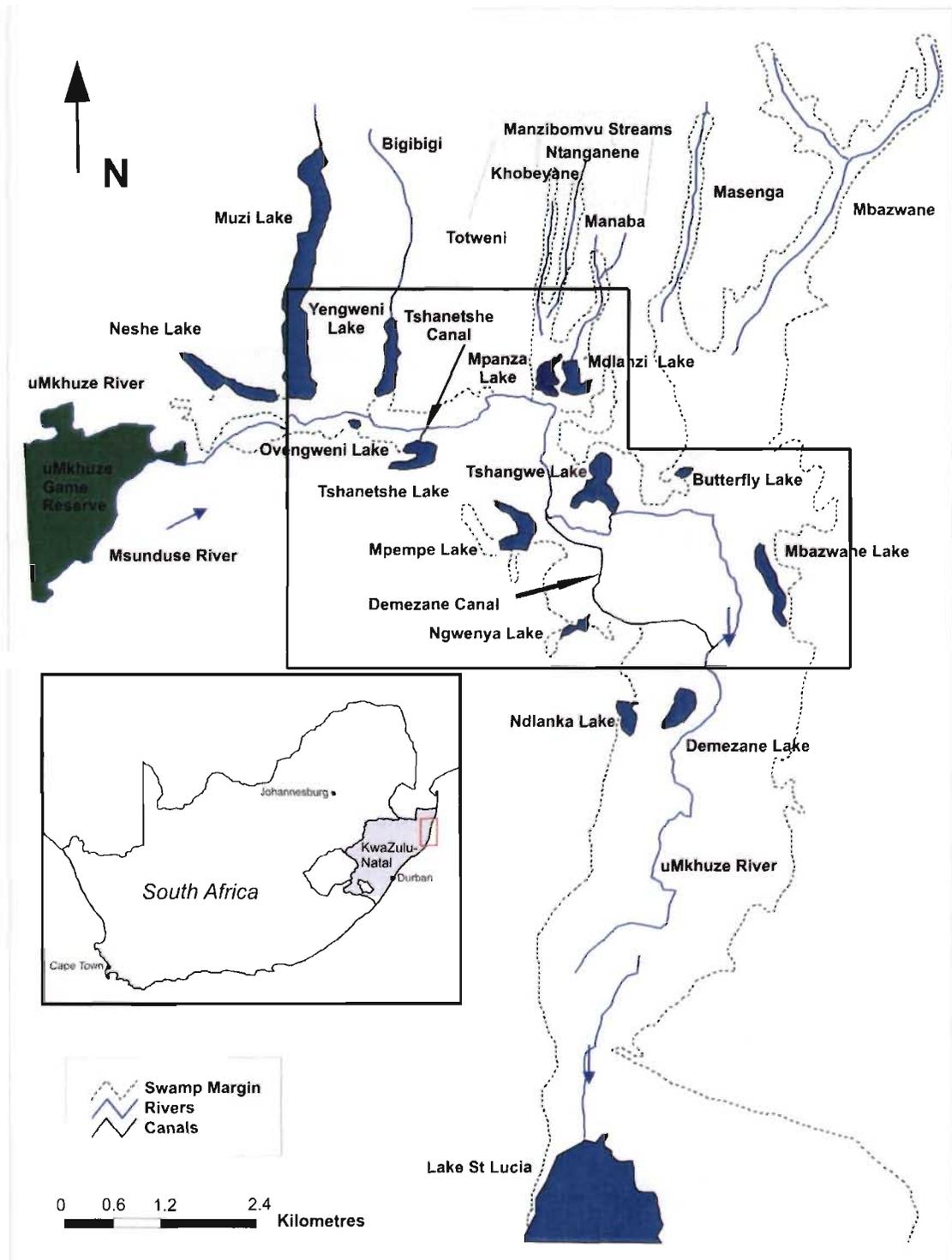
Ellery, 1998; McCarthy *et al.*, 1993). It seems that the driving force behind the accumulation of tonnes of solutes per year is evapotranspiration, thereby plants of the Delta actively modify their environment with far-reaching effects on wetland structure and function on a landscape scale. The chemical sediments accumulating are predominantly derived from non-limiting solutes, challenging the narrow focus on wetlands as sinks for mainly the plant macronutrients nitrogen and phosphorus. Further research on non-limiting solutes as well as the nature, extent and consequences of chemical sedimentation in wetlands is required.

## CHAPTER 3 STUDY AREA

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### 3.1. Introduction

The uMkhuze Wetland System in northern KwaZulu-Natal is situated on an extensive coastal plain that stretches from Somalia in the north through Kenya, Tanzania and Mozambique into South Africa, where the southernmost extension of the plain is the St Lucia Estuary mouth (Watkeys *et al.*, 1993). The Plain in the region of the uMkhuze Wetland System is called the Maputaland Coastal Plain. The uMkhuze Wetland System is the largest remaining swamp of its type in southern Africa, and is rich in biodiversity, comprising a range of wetland types from swamp forest to reed swamp to hygrophilous grasslands, incorporating seasonal to permanent wetland areas as well as open water bodies (McCarthy and Hancox, 2000; Stormanns and Breen, 1987). This system has been recognised as being regionally as well as internationally significant through its inclusion in the Greater St Lucia Wetland Park, together with the coastal strip including Lakes St Lucia, Sibayi and Kosi as well as Sodwana Bay; which was proclaimed a World Heritage Site by the International Union for Conservation of Nature (IUCN) in December 1999. In addition, the uMkhuze-Lake St Lucia system was designated a Wetland of International Importance in 1986 under the Ramsar Convention. Currently the Greater St Lucia Wetland Park is one of the foci of the Lubombo Spatial Development Initiative and forms a hub of ecotourism to promote development in the region.



**Figure 3.1.1** The uMkhuze Wetland System situated in the province of KwaZulu-Natal, South Africa (Blue arrows indicate the direction of flow along the uMkhuze River; the extent of Figure 3.6.1 is indicated by the box)

### 3.2 Climate

The Maputaland Coastal Plain is situated in a transition zone between tropical and subtropical conditions on its north-south axis, and also experiences a marked east-west gradation in climate factors. The coastal regions can be described as moist subtropical, while western regions approaching the Lebombo Mountains are dry subtropical (Watkeys *et al.*, 1993). The region experiences summer rainfall and associated dry winters. A strong latitudinal (east-west) gradient in rainfall produces a maximum of 1000 mm per annum at the coast to 600 mm per annum at the western margin of the coastal plain, while orographic uplift over the Lebombo Mountains results in 800 mm per annum in this region (Preston-Whyte and Tyson, 1997; Watkeys *et al.*, 1993).

Summer cyclones in the Indian Ocean result in periodic very high rainfall events such as that experienced in 1976 when 700 mm fell over three days and as a result of Cyclone Domoina in 1984, while winter flooding events are attributed to cut-off low pressure systems (Maud, 1980). Table 3.2.1 illustrates the frequency of tropical cyclones in the south Indian Ocean tropical cyclone belt, showing a peak from December to February. Although Cyclone Domoina in 1984 produce the greatest flood event, most flooding is accounted for by cut-off low pressure systems from the southwest (Watkeys *et al.*, 1993).

**Table 3.2.1** Frequency of tropical cyclones since 1948 (n=934)

Month	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May
% of Total	1	2	3	13	30	26	17	6	2

Source: Watkeys (1993)

Rainfall is also influenced by El Niño – Southern Oscillation events with drought cycles of a three to seven year cyclicality (Ramsay, 2005). The last event, initiated in 2001 subsequent to the extensive flooding of 2000, led to complete evaporation of Yengweni Lake and drastically reduced levels in Lake St Lucia.

Summers are hot, while winters are mild and dry. Mean annual temperatures also show an east-west variation with 21 °C at the Lebombo Mountains in the west, 23 °C in the central regions and 22 °C at the coast (Watkeys *et al.*, 1993). Humidity reaches levels of 97.9 % in summer, with a winter high of 50.8 % (McCarthy and Hancox, 2000).

In the coastal lowlands of KwaZulu-Natal, the mean total evaporation range is estimated at 1143 – 1295 mm per annum using the Symons pan method (Alcock, 1999). Evaporation rates measured at the uMkhuze Game Reserve vary from a high of 189.4 mm per month in January to a minimum of 82.3 mm per month in June, which gives an estimate of 1600 mm/annum (Watkeys *et al.*, 1993). Therefore, there is a precipitation deficit of 300 to 800 mm per annum in the uMkhuze Wetland System. Buol (1965) categorises climate regions by the annual precipitation deficit, which places the uMkhuze Wetland System in a semi-arid zone.

### 3.3 Geomorphology

The Maputaland Coastal Plain shows evidence of successive sea level fluctuations from the late Tertiary to the late Pleistocene or Holocene (Wright, 1999). Five dominant palaeodune cordons that represent major sea level stillstands are oriented north-south and range from the easternmost barrier dune formed during the late Pleistocene – early Holocene to the oldest stabilised dune cordon of Pliocene to Miocene age at the base of the Lebombo Mountains (McCarthy and Hancox, 2000; Wright, 1999). Segments of these dune cordons have been remobilised due to differing climatic conditions from those during which they formed, and obscure original patterning to some degree (Wright, 1999).

These dune cordons confine groundwater discharge from the elevated water tables to the interdune valleys (Maud, 1980; Watkeys *et al.*, 1993). The inter-dune valleys accommodate linear north-south tributaries of the uMkhuze River and are predominantly fed by groundwater and include from west to east: Muzi, Yengweni, Manzibomvu and the Mbazwane Streams. The uMkhuze River interrupts the dune cordon symmetry by flowing from west to east through the Lebombo Mountains to the vicinity of the Manzibomvu Streams, from where the river flows southwards between the stabilised dune systems.

During the last Glacial Maximum around 18 000 to 8 000 years ago, sea levels were 120 – 180m below the current level. This dramatic decrease in base level initiated large-scale erosion of coastal river

profiles (McCarthy and Hancox, 2000; Partridge and Maud, 1987). The uMkhuze River and the associated interdune tributaries mentioned above, responded to this base level alteration by eroding depths of up to 35 m below current channels, in the case of the uMkhuze River (Drennan *et al.*, 1997; Maud, 1980). Post-glacial transgression during the Holocene (Flandrian transgression) resulted in current sea level being attained at around 6 500 years before present, with minor fluctuations in the intervening period (Ramsay, 1995; Watkeys *et al.*, 1993). Lagoonal barriers formed at the combined outflow of the uMkhuze and Umfolozi Rivers to form Lake St Lucia. Due to the elevation of the base level, backflooding of the deeply eroded river channels and interdune valleys caused sedimentation to become dominant on the coastal plain.

Progressive aggradation of alluvial sediment on the uMkhuze River floodplain has allowed the accumulation of up to 35 m of sediment over the last 6 500 years. This estimate of the age of the uMkhuze Wetland System is reasonable, because the last major sea level fluctuation occurred prior to 6 500 years ago and radiocarbon dating of basal sediments in Lake St Lucia gives values of around 4 000 years (McCarthy and Hancox, 2000). The average rate of aggradation on the floodplain is therefore around 0.6 cm/ year. Furthermore, fluvial sedimentation has dammed the previous uMkhuze River tributaries Muzi, Yengweni and Totweni forming lakes at their southern end. Continued aggradation of the floodplain exceeded alluvial additions to the lake barriers due to greater volumes of sediment deposited in the vicinity of the river (Maud, 1980). As a result, the lakes have experienced increasing uMkhuze River input over time.

### **3.4 Geology**

The uMkhuze River drains a catchment of 4 820 km<sup>2</sup>, having its source east of Vryheid before meandering through the Lebombo Mountains and onto the Maputaland Coastal Plain (McCarthy and Hancox, 2000; Watkeys *et al.*, 1993). This large catchment area ensures an abundant supply of sediment to the coastal plain (Wright, 1999). To the west of the Lebombo Mountains, strata of the Dwyka, Ecca and lower Beaufort Groups of the Karoo Supergroup comprise the catchment geology, with Pongola granites and Jozini Formation rhyolites deposited in the Mesozoic to form the Lebombo Mountains themselves (Table 3.4.1; McCarthy and Hancox, 2000; Wright, 1999). The strata comprising the Karoo Supergroup of the Jurassic Period are overlain by the Msunduze Formation

conglomerate, basalts of the Mpilo and Movene Formations, followed by pyroclastics, rhyolites and trachytes of the Bumbeni Complex (Watkeys *et al.*, 1993).

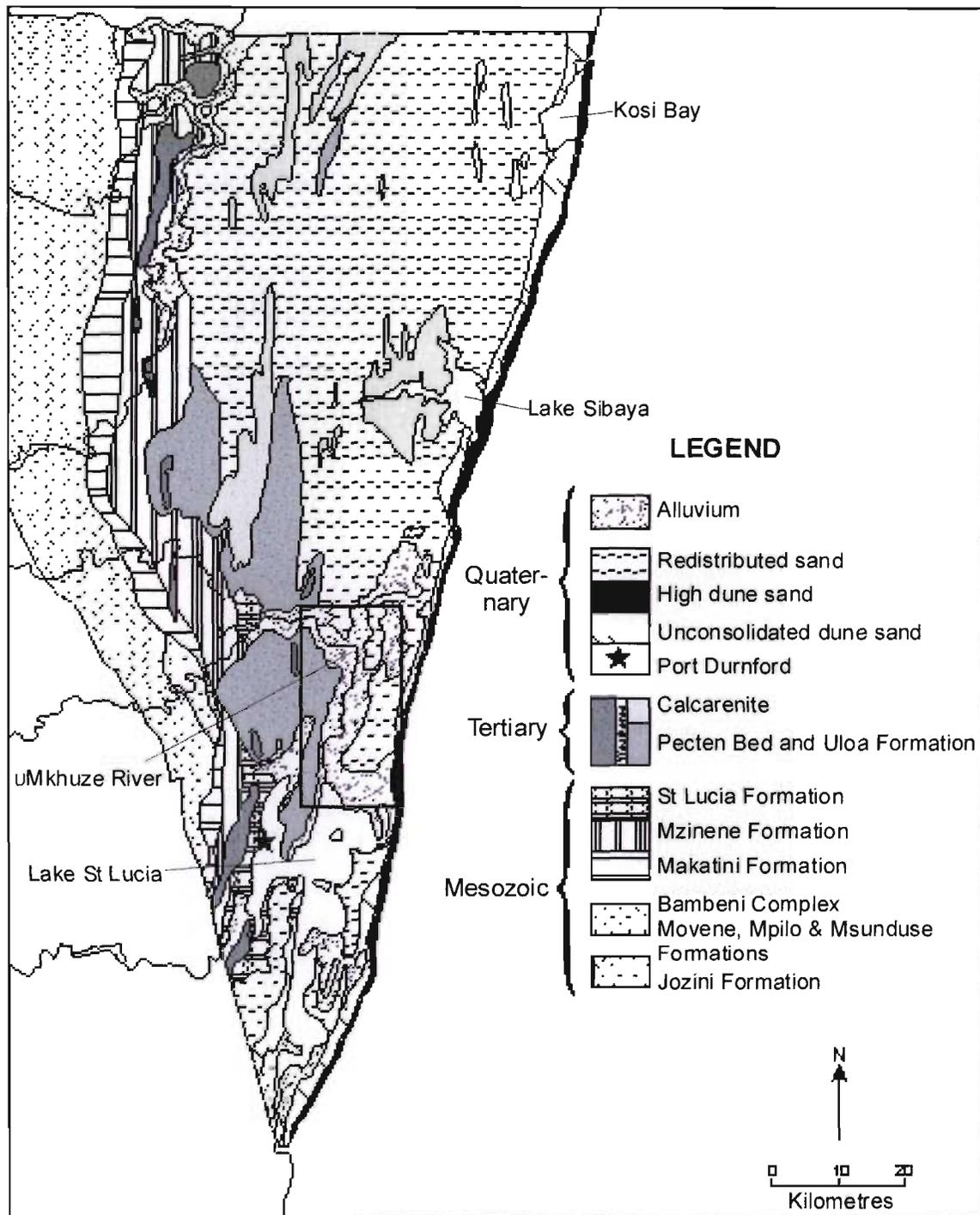
**Table 3.4.1** Maputaland stratigraphy – showing the sequence of strata outcropping from the Lebombo Mountains in the west to the unconsolidated dunes of the east

Era	Sub-Era	Period	Epoch	Group	Formation
Cenozoic	Quaternary	Pleistogene	Holocene	Maputaland	Redistributed sand
			Pleistocene		High dune sand of the Sibayi Formation (Botha, 2000)
					Unconsolidated dune sand (Kosi Bay Formation of Botha: orange to grey weathered dune sands)
	Tertiary	Pliocene to Miocene	Early		Port Durnford Formation
			Late		Aeolian calcarenite deposits of Umkwelane Formation (Botha)
					<i>Pecten</i> beds and Uloa Formation
Mesozoic		Cretaceous	Late	Zululand	St Lucia Formation
			Early		Mzinene Formation
					Makatini Formation
				Lebombo	Bumbeni Complex
			Mpilo and Movene Formations		
			Msunduze Formation		
	Jurassic	Middle		Jozini Formation	

Source: Watkeys *et al.* (1993)

This foundation of igneous strata is faulted and tilted eastward, over which further Cretaceous sediments were deposited (Maud, 1980; Watkeys *et al.*, 1993; Wright, 1999). Although these deposits are mostly buried they do outcrop in north-south oriented strips, allowing secondary weathered minerals to contribute significantly to the soils of the coastal plain (Watkeys *et al.*, 1993). The

Makatini Formation consists of alluvial and fluvial deposits of shallow estuarine and marine environments and consists of coarse sandstone and conglomerate with interspersed layers of sandy silt and sandy limestone with shell fragments, as well as concretions in the lower segments of the formation, to marine clays and sands in the upper segments (Figure 3.4.1; Watkeys *et al.*, 1993). Accumulation of glauconitic marine silts and clays with local pebble deposits, and sandy shelly concretions constitute the Mzinene Formation, which overlies the Makatini Formation (Watkeys *et al.*, 1993). The St Lucia Formation is poorly exposed on the coastal plain and comprises a range of sediment types. A conglomerate forms the base of the deposits on which interfingering silts and fine sands are found, above which are progressively finer deposits of buff and greenish-grey glauconitic silts and sands with interspersed calcareous concretions (Watkeys *et al.*, 1993). This Formation contains abundant invertebrate fossils (Watkeys *et al.*, 1993).



**Figure 3.4.1** Geology of the uMkhuze Wetland System  
 Modified after: Watkeys *et al.*, (1993)  
 (The box indicates the area represented in Figure 3.1.1)

Tertiary sediments on the coastal plain comprise the shallow marine deposits of the fossiliferous Uloa Formation, over which coquina limestone and biogenic calcareous deposits of the Pecten Bed are found, themselves overlain by calcarenite beach sediments (Maud, 1980; Watkeys *et al.*, 1993).

The early Quaternary (Pleistocene) Port Durnford Formation is poorly exposed and contains abundant fossils in a matrix of mudstone, aeolian calcarenite, lignite clay (indicating a coastal lake setting) and sand, interspersed with fossil coral deposited in shallow marine and terrestrial fresh water settings (Maud, 1980; Watkeys *et al.*, 1993). The exposed sections of the Port Durnford Formation extend from Mlalazi in the south to Cape St Lucia in the north and therefore are not visible in the uMkhuze River catchment, although it has been reported beneath dune cordons (Wright, 1999). The overlying sediments are predominantly unconsolidated dune sand (Watkeys *et al.*, 1993).

The coastal plain features sedimentary deposits of Cretaceous to Quaternary Age including the dune cordons consisting of red clay-sand of the Berea Formation, consisting of hard iron-rich sands at the base, probably cemented with iron and amorphous silica, overlain by unconsolidated sands (Botha, 2000; McCarthy and Hancox, 2000). These have been categorised as Pleistocene sediments formed from weathering of calcarenite cores. Similar red clay-sands are found just east of the Lebombo Mountains, but seem to be weathering products of the Uloa Formation calcarenites dated to the late Mio- Pliocene (Partridge and Maud, 1987).

### **3.5 Soils**

The uMkhuze Wetland System is situated on redistributed sand, interrupted by the silty clay alluvium of the uMkhuze River (Watkeys *et al.*, 1993). The range of dune sands display the effects of weathering with deep red profiles of the oldest dunes being mesotrophic in nature, while the younger dunes to the east are nutrient-poor and those on the coast are dystrophic pale sands (Watkeys *et al.*, 1993). Soil profile depth and clay content increase from west to east, with poorly weathered soils in the west to soils characterised by iron mottling in the eastern sections. Depressions or low-lying areas contain soils derived from parent material with high calcium contents (calcimorphic), grading from brown to dark brown calcimorphic soils in the west and vertisols in the east (Watkeys *et al.*, 1993). McCarthy and Hancox (2000) also note the presence of abundant smectitic clays at the base of the Lebombo Mountains.

### 3.6 Hydrology

The major hydrological input to the swamp, the uMkhuze River, arises in the Drakensberg and after running its course through the Lebombo Mountains enters the coastal plain. The river has eroded an eastward channel through the dune cordons. The channel then turns south in the regions of the confluence with the Mbazwane Stream flowing from the north, which constitutes the other major hydrological input to the wetland. The channel becomes ill-defined through the combined uMkhuze-Mbazwane swamps after which it is again consolidated in the south into a channel, which empties into Lake St Lucia. In this way, the uMkhuze Wetland System forms the most important contribution of mean annual runoff of around 56 % to Lake St Lucia (Stormanns and Breen, 1987).

A number of north-south oriented drainage lines occur north of the uMkhuze River in the west of the system. These are (from west to east) the Muzi and Yengweni Drainage Lines as well as the Manzibomvu Streams, all of which have been dammed at their southern ends. The Totweni Stream in the Manzibomvu System was the focus of sampling. Therefore to simplify references to the system, the drainage line will be referred to as the Totweni Drainage Line. The Mbazwane Stream is a similar linear drainage system, but this stream flows unchecked down the eastern flank of the wetland to a confluence with the uMkhuze River. These linear drainage lines have formed in the valleys between adjacent dune ridges. The water table beneath the constraining dunes is elevated relative to the surrounding floodplain resulting in groundwater discharge into the interdune valleys (Stormanns and Breen, 1987). As such these drainage systems are predominantly groundwater-fed.

The uMkhuze River typically transports predominantly fines (silts and clays) produced by the weathering of the volcanic strata found in the catchment. During the frequent flood events, larger particle sizes are transported into the wetland. This sediment is deposited along its floodplain with the extent of deposition at the delta south of the Mpanza and Mdlanzi Lakes (Neal, 2001). This section of the floodplain is an old delta formed when the uMkhuze River flowed directly into the sea at this point in the landscape. No or negligibly little sediment input occurs in the north-eastern section of the swamp as the low flows of the linear dune-constrained drainage systems and the coarse nature of the reworked marine sands they drain, results in a low capacity to transport sediment (McCarthy and Hancox, 2000).

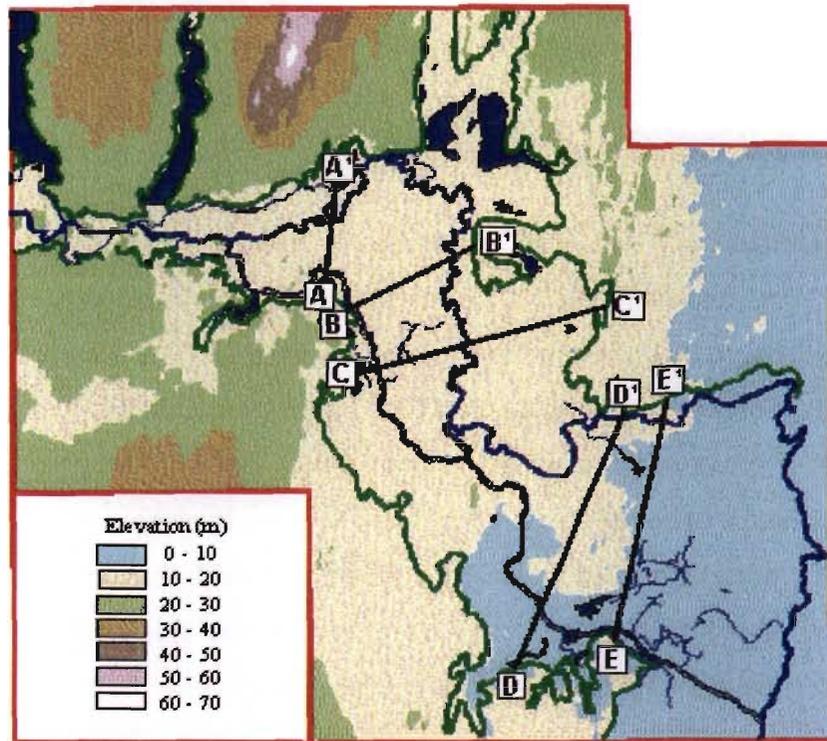
Consequently, the uMkhuze River constitutes the most important source of solutes and sediment to the wetland.

### **3.6.1. Anthropogenic disturbances of hydrology**

The hydrology of the system was substantially modified by a series of events spanning the 1970's. In the early 1970's the Natal Reclamation Unit, a parastatal body, excavated a canal from the uMkhuze River channel north to Mpempe Lake (the Mpempe canal), and a 13.5 km section from Mpempe Lake into the uMkhuze River north of Demezane Lake (Demezane Canal). Earth-moving machinery was used to create the canal with a width of about 5 m and 1.5 m in depth (Ellery *et al.*, 2003). This was done to increase the volume of freshwater entering Lake St Lucia bypassing the north-eastern section of the uMkhuze River, due to fears that the elevated salinities of the Lake were threatening the ecosystem. However, the uMkhuze River at the junction with the canal is a small poorly defined channel, and thus provided very little freshwater to the lake. As a result, the canal has maintained its original dimensions.

This operation of great expense and effort did not significantly alter water flow in the wetland. By contrast, in 1986 a commercial farmer created a canal about 100m from the uMkhuze River to the Tshanetshe Lake by enlarging an existing hippo trail. This canal, the Tshanetshe Canal, captured most of the flow from the uMkhuze River, which flowed through Tshanetshe Lake into the flood pathway created during the 1984 Domoina floods to Mpempe Lake. This section of the canal eroded rapidly and the series of canals have now become the main watercourse in the swamps.

A digital elevation model (DEM) was constructed that extends from Muzi Lake in the northwest, includes the Totweni system in the east and covers the channel of the uMkhuze River to Demezane Lake (Figure 3.6.1; Ellery *et al.*, 2003). In order to investigate the relationship of the uMkhuze River to its floodplain, a number of cross-sectional profiles were drawn across the floodplain, comprising elevation versus valley distance down the uMkhuze River (Figure 3.6.2; Ellery *et al.*, 2003).

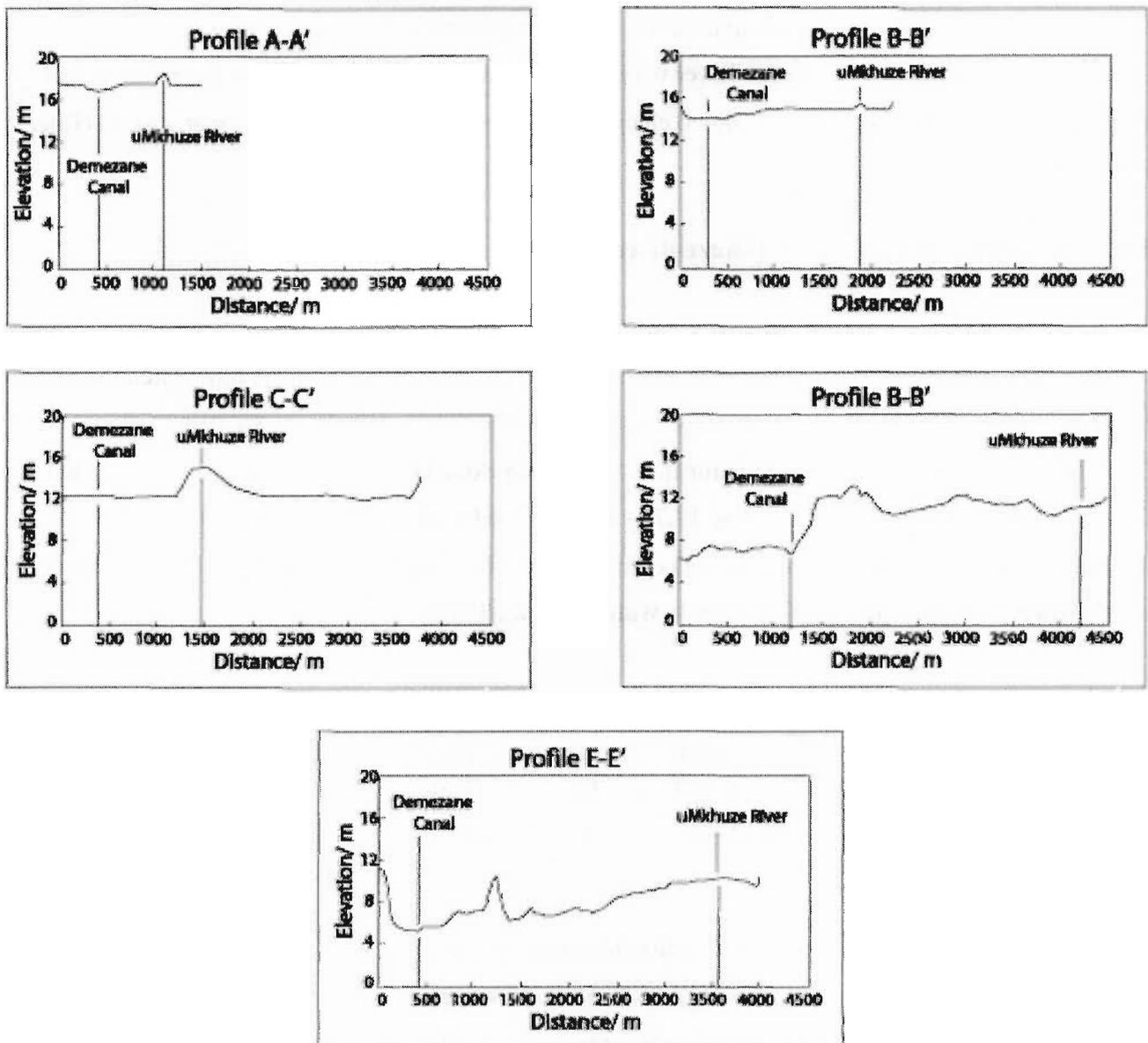


**Figure 3.6.1** Digital elevation model (DEM) of the uMkhuze River floodplain

Source: Ellery *et al.* (2003)

(The extent of Figure 3.6.1 is indicated on Figure 3.1.1)

These floodplain profiles reveal that alluvial deposition adjacent to the uMkhuze River has resulted in the formation of an alluvial ridge such that the river and its bed are elevated relative to the surrounding floodplain. This is particularly noticeable in transect C, the region where a flood path eroded between Tshanetshe and Mpempe Lakes, after construction of the Tshanetshe Canal as described above.



**Figure 3.6.2 a – e** Cross-sectional profiles across the uMkhuze River channel and surrounding floodplain, plotted from a DEM

Source: Ellery *et al.* (2003)

Therefore, any action that punctured the levee of the River (such as creating a small canal) would allow the river water to flow down a more hydraulically favourable gradient. Consequently, it is probable that the channel avulsion of the uMkhuze River would have occurred without human intervention, possibly due to continued erosion of the same hippo channel that provided the start of the farmer's canal (Ellery *et al.*, 2003).

### 3.6.2. Flooding regime of the uMkhuze River

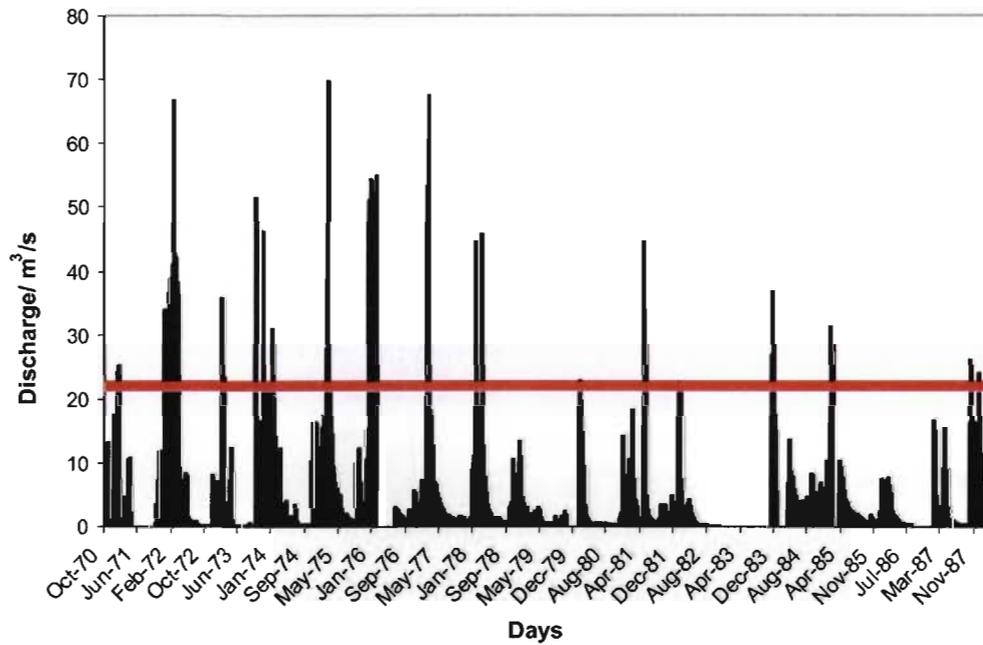
The uMkhuze River may be described as a 'flashy' river with high summer flows often accompanied by extensive flooding and very low to non-existent winter discharges. Flooding is most often the result of cut-off low pressure systems as mentioned above, although tropical cyclones, such as Cyclone Domoina of 1984, are also responsible for flood events. Cyclone Domoina produced the largest flood on record when the uMkhuze River rose 12.7 m above its bed with a discharge of 5 500 m<sup>3</sup>/s, although this figure is an estimate as the monitoring equipment was destroyed during the flood along with part of the Lower uMkhuze Bridge (Table 3.6.1; Watkeys *et al.*, 1993).

**Table 3.6.1** Large discharges in the uMkhuze River since 1925

Year	1925	1963	1974	1977	1984	1987	1989
Discharge (m <sup>3</sup> /s)	1 500	1 950	1 100	805	5 500	1 000	2 800

Source: Watkeys *et al.* (1993)

Flows in the uMkhuze River vary dramatically from very low to no flow in June to September to high flows in December to March (Figure 3.6.3). 95 % of the flows are less than 20 m<sup>3</sup>/s (highlighted by a red line in Figure 3.6.3). This discharge roughly translates into the channel capacity of the uMkhuze River. Any discharge larger than this can be described as flood conditions. Although the river typically has low flows, the system is subject to frequent flood events as can be seen from the graph, at least annually, during which extensive flooding of the wetland occurs. The result is a large area of inundation.



**Figure 3.6.3** Daily flows of the uMkhuze River, October 1970 to February 1988

Data source: Department of Water Affairs and Forestry

In contrast the uMkhuze River tributaries are sustained by groundwater and precipitation inputs. The Mbazwane Stream maintains a relatively low flow throughout the year as it is sustained by groundwater (Stormanns and Breen, 1987).

### 3.7 Biota of the uMkhuze Wetland System

The high biodiversity on the Maputaland Coastal Plain can be attributed to its position within a tropical-subtropical convergence zone, with many tropical faunal and floral species having colonised the area from the north and those preferring subtropical conditions having access from the south and west (Watkeys *et al.*, 1993).

#### 3.7.1. Vegetation

The uMkhuze Wetland System is situated in a vegetation type known as Coastal Bushveld-Grassland (Granger *et al.*, 1996). The vegetation comprises a mosaic of forest patches set in a matrix of grassland

and open savanna. In northern KwaZulu-Natal, the vegetation type is also known as sandveld and is characterised by grassland with scattered clumps of palms (*Hyphaene natalensis*), while in many areas it consists of grassland with scattered dwarf shrubs.

The wetland supports a wide range of plant communities including hygrophilous grassland, sedge marsh, sedge and reed swamp, floodplain forest, riparian forest, swamp forest and palmveld (Stormanns and Breen, 1987). Approximately 275 plant species are found in the wetland system, which supports at least 32 rare and endangered species (Stormanns and Breen, 1987).

### 3.8 Choice of study area

The choice of the Totweni and Yengweni Drainage Lines in the west of the uMkhuze Wetland System, including the floodplain of the uMkhuze River to the south of these systems was made for a number of reasons. It was impractical to sample the 440 km<sup>2</sup> wetland system in order to conduct the envisioned intensive research into chemical transformations. However it was also important to identify a section of the swamp that provided the most variation within a small geographical area so that a range of conditions could be sampled, within which chemical transformations may occur. Although the Totweni and Yengweni are adjacent drainage lines, situated on the reworked marine sands of the system, and influenced by the same general conditions such as rainfall and evaporation, as well as both being predominantly groundwater-fed from the north, they differ markedly in many ways. The Totweni Drainage Line is characterised by extensive peat deposits of more than 8 m in depth, supporting beds of emergent macrophytes, while the Yengweni occupies shallow, open water, clay-lined depression. The associated uMkhuze River floodplain areas have higher inputs of uMkhuze River water and sediment, and occur on the alluvial silts and clays of the lake barriers. Regarding vegetation, the Totweni and northern Yengweni are colonized by sandveld communities on the drainage line banks, while the southern Yengweni and floodplain margin are distinctly different being dominated by *Acacia xanthophloea* (fever trees). Therefore, something of the heterogeneity of the uMkhuze Wetland System has been sampled, which will allow a broad understanding of the potential of the wetland to transform and retain its chemical inputs.

Furthermore, the Totweni and Yengweni Drainage Lines and the adjacent floodplain margin of the uMkhuze Wetland System, represent the range of habitats on the floodplain margin of the uMkhuze River. These habitats include large lakes formed by backflooding of past tributaries of the uMkhuze River, such that tributary valleys have been filled with clastic sediment (Yengweni and Muzi Lakes). Other tributary valleys also having been dammed by alluvial deposition on the floodplain of the uMkhuze River, have only been partly filled by clastic sediment and have organic sediments along their length (Mpanza and Mdlanzi Lakes of the Totweni Drainage Line, similar to the Mbazwane system further east). Also included in the study area is the floodplain margin adjacent to and between the two drainage lines, the Yengweni and Totweni systems. Therefore, insights gained on this limited spatial scale can be extrapolated to the uMkhuze Wetland System (MWS) as a whole.



## CHAPTER 4

### SURFACE WATER – GROUNDWATER INTERACTIONS: HYDROLOGY

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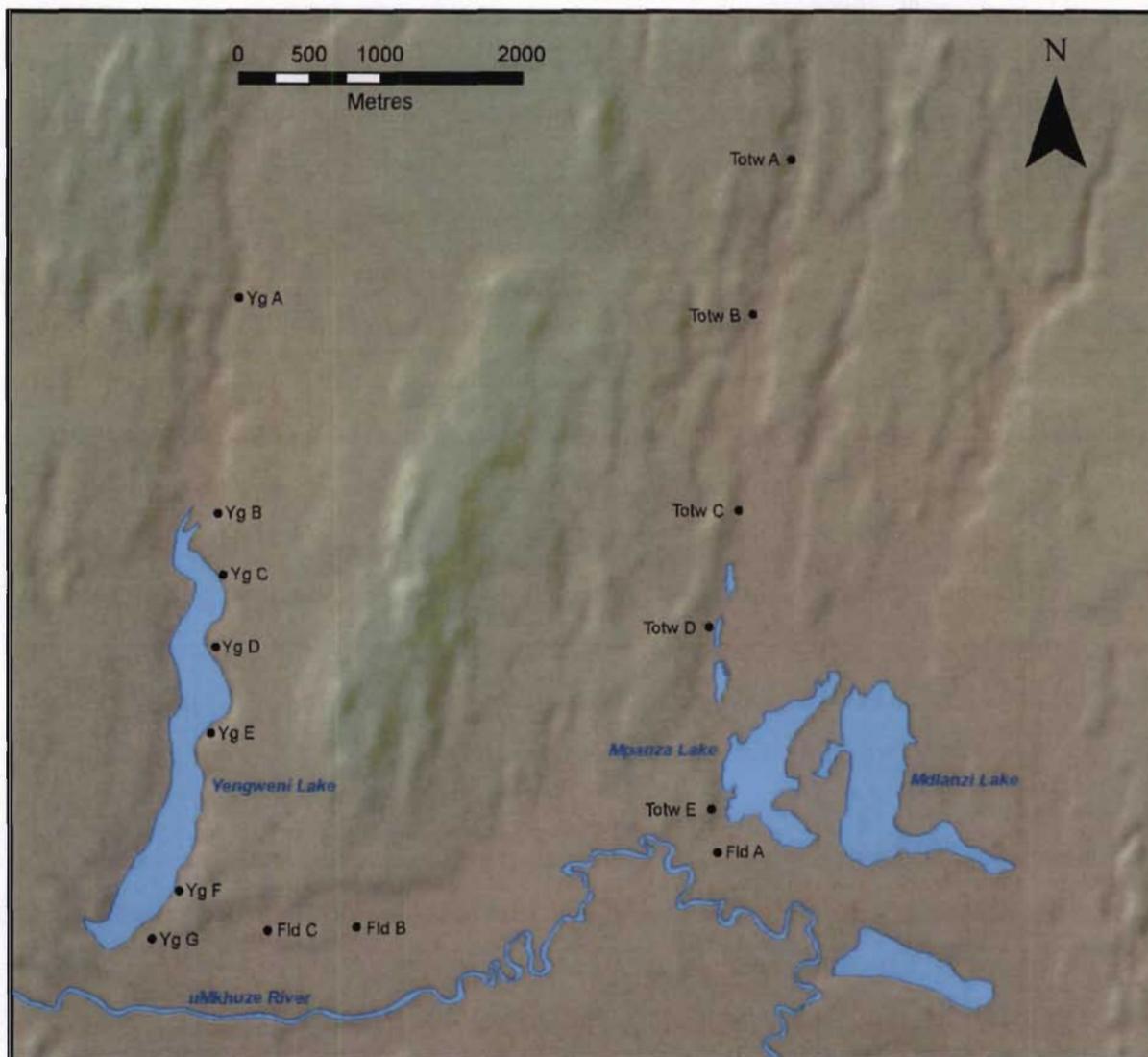
#### 4.1. Introduction

The uMkhuze Wetland System has been identified as a sink for solutes that are typically non-limiting for vegetation in wetland systems, due to the accumulation of approximately 16 tonnes of non-limiting solutes per annum across the wetland system (Barnes *et al.*, 2002). Retention of this magnitude is likely to have far-reaching consequences for the structure and functioning of the wetland. The initial study of Barnes *et al.* (2002) raised questions such as where are solutes accumulating and what are the mechanisms of solute retention?

The uMkhuze Wetland System is a heterogeneous system considering its origins on a regularly patterned sandy coastal plain. Palaeo-dune cordons are present as pronounced north-south oriented linear features, although the fluvial influences of the uMkhuze River during and after the last Ice Age have disrupted this patterning. As presented in Chapter 3, the incision of river channels into the coastal plain during low sea levels was reversed when sea level rose at the end of the last Ice Age, causing the system to change from an erosional to a depositional system. Alluvial sedimentation on the uMkhuze River floodplain has had a damming effect on a number of interdune streams that were once tributaries of the uMkhuze River, including the Muzi, Yengweni and Totweni Drainage Lines (Figure 3.1.1; McCarthy and Hancox, 2000). These macroscale geomorphological processes of channel incision and sediment deposition have produced heterogeneity with respect to topography, substratum characteristics, flooding regime, surface-water – groundwater interactions and vegetation distribution. This heterogeneity is also likely to be associated with spatial variation in solute inputs and transformations that take place on the floodplain.

Water within a wetland system is both the means of transport for dissolved and suspended sediment, and the reaction medium for chemical transformations. The distribution of water in space and time fundamentally affects physical and chemical conditions of the soil within the wetland, with the result that factors influencing wetland hydrology will have a bearing on biogeochemical processes in the system. Consequently, chemical transformations in wetland systems cannot be adequately addressed independently of investigations into the prevailing hydrological regime (Dahm *et al.*, 1998).

In an attempt to develop an understanding of the fate of non-limiting solutes, the study focused on two contrasting adjacent drainage lines, the Totweni and Yengweni, including the floodplain of the uMkhuze River between these two tributary systems (Figure 4.1.1). Although both drainage lines are situated on the reworked marine sands of the coastal plain, and are influenced by the same general environmental conditions such as rainfall and potential evaporation, they differ markedly in many ways. The Totweni Drainage Line is characterised by extensive peat deposits with beds of emergent macrophytes, while the Yengweni is an open water body in a depression with a bed of clay. Adjacent to the drainage lines, sandveld vegetation dominates the Totweni and the northern Yengweni, while the southern Yengweni is characterised by microphyllous *Acacia xanthophloea* (fever tree) woodland.



**Figure 4.1.1** A shadow relief map of the Totweni and Yengweni Drainage Lines and the associated uMkhuze River floodplain, indicating the location of transects sampled

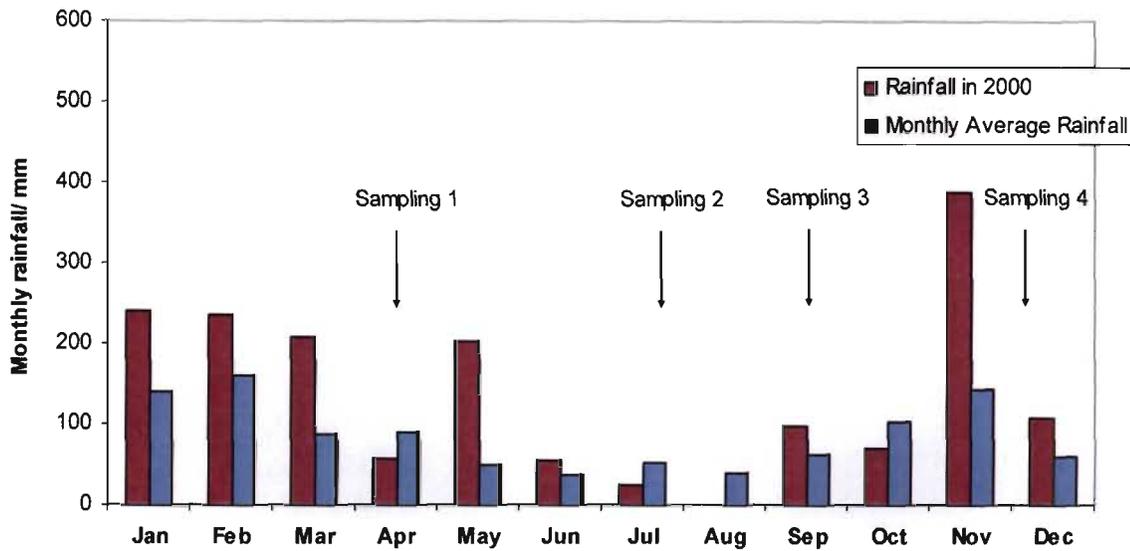
## **4.2. Description of hydrological inputs**

Hydrological inputs to the uMkhuze Wetland System provide solutes and sediments that constitute the raw material for chemical processing in the system. Possible inputs include local rainfall, surface water inflow from the uMkhuze River and regional groundwater inputs from the coastal plain.

### **4.2.1. Rainfall**

Local rainfall is an important source of water for surface water and groundwater in the system. Wherever rainfall falls onto surface water in the wetland it contributes directly to the surface water in the system. Wherever it falls onto the land surface it may flow by overland flow into surface water if rainfall intensity exceeds the local saturated infiltration rate. Where rainfall intensity is lower than saturated infiltration rate it will enter soil water and some of it will enter groundwater.

Prior to sampling at the end of April 2000, around 207 mm rain was recorded in March, exceeding the average monthly rainfall for the month of April by 119 mm (Figure 4.2.1). This local rainfall input was associated with heavy rainfall in the catchment that produced considerable runoff, which jointly resulted in widespread flooding of the system. July and August were the driest months during 2000, with only 24 and <1 mm measured respectively. During June 56 mm of rain fell in the area. The second sampling trip took place in the last two weeks of July. Approximately 97 mm of rain fell during September, which is 35 mm greater than the average for this month. Samples were collected in the last week of September. In November 386 mm of rain fell, exceeding the November monthly average value by 244 mm, such that extensive flooding was evident during the December sampling period.



**Figure 4.2.1** Monthly rainfall at Charters Creek for the year 2000, compared to the average rainfall for April 1994 to May 2003  
(South African Weather Bureau)

#### 4.2.2. uMkhuze River

As presented in Chapter 3, the uMkhuze River is typified by annual to biennial floods, which add vast amounts of water to the floodplain system. Although the records only extend to 1988 when cyclone Domoina destroyed the gauging station at the Lower uMkhuze River Bridge, the record from 1970 to 1988 is consistent, with each flood event flanked by periods of low to no flow during the winter months. A similar regime was noted during sampling, with high rainfall and flooding prior to the April 2000 sampling trip, followed by very low flows during the winter months of July and September 2000, during which period the section of the uMkhuze River south of Yengweni, Mdlanzi and Mpanza Lakes was almost dry. In late November 2000, extensive flooding inundated the region, which limited sampling in December as the lower portions of each transect were under water.

#### 4.2.3. Groundwater

No data exists on surface-water – groundwater relationships in the uMkhuze, and the perception is that this is a region of general groundwater discharge from the sandy dune features into drainage

lines and onto the floodplain . Hutchison and Pitman (1973) estimate that groundwater contributes 8-10 % of the hydrological input to the surface waters of the uMkhuze Wetland System.

### 4.3. Methods

Sampling was planned to cover spatial and temporal variation across two adjacent but contrasting drainage lines draining southwards onto the west-east oriented uMkhuze River floodplain. Five transects were sampled along the western margin of the Totweni Drainage Line (Totw A to E from north to south; Figure 4.1.1). Most transects were sampled in April, July, September and December, 2000. Seven transects were established along the eastern margin of the Yengweni Drainage Line (Yg A to G from north to south; Figure 4.1.1). Yg C to G were bounded to the west by the Yengweni Lake, while the valley at Yg A and B was generally dry. Most Yengweni transects were sampled in July, September and December, 2000.

Three transects were sampled on the floodplain of the uMkhuze River perpendicular to the river. Fld A extended from the Mpanza Lake in the north to an old oxbow lake forming the southern boundary of the transect (Figure 4.1.1). A further transect was sampled between the Totweni and Yengweni Drainage Lines (Fld B), while Fld C was located south of Yengweni Lake. The floodplain transects B and C were submerged during the December sampling period.

The topography of each transect was surveyed relative to a permanent stake using a dumpy level and staff. GPS readings of each stake position were recorded and are presented in Appendix A. Three to six boreholes were augered along the length of each transect at each sampling period, from which groundwater was sampled and the depth to water table measured after allowing the water level to come to rest. Fresh boreholes were augered at each sampling period. Water was sampled using a bottle attached to the end of auger poles. The bottle was rinsed a few times before collecting a sample from each borehole. Water samples were stored in acid-rinsed polyethylene bottles. Conductivity readings were taken in the field using a Corning 311 conductivity meter and subsequently a Corning Checkmate Deluxe meter for conductivity on later field trips.

Bathymetric data were collected for the Totweni and Yengweni Drainage Lines. In the case of the Totweni Drainage Line, peat thickness was measured by pushing a steel pole attached to a peat corer through the peat until the substratum sands of the coastal plain were encountered. This was verified by the presence of sandy material at the base of the peat corer. A GPS was used to locate

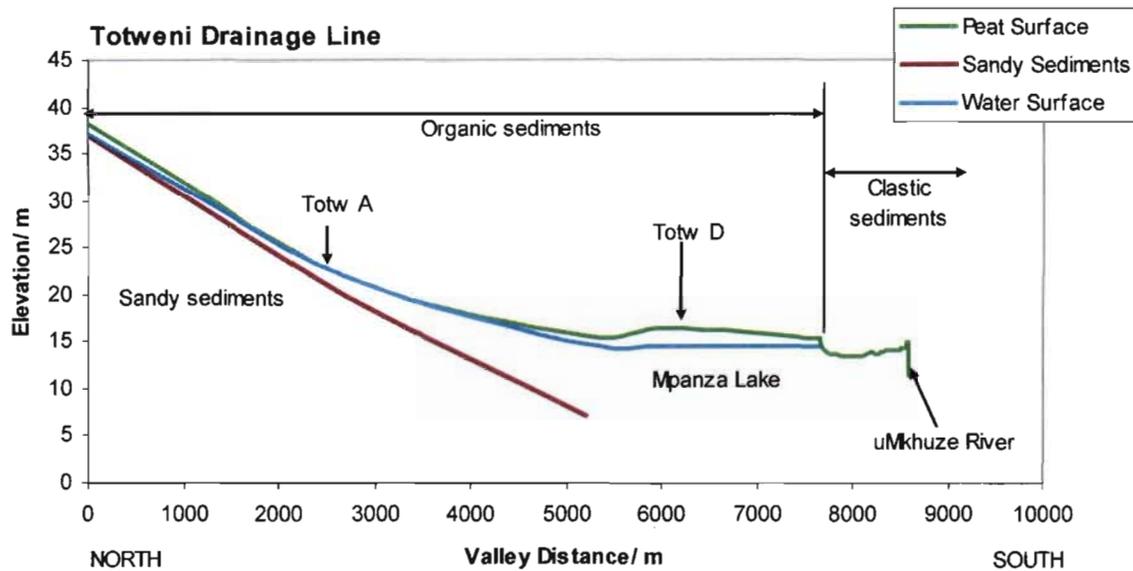
the points at which depth measurements were made along each transect across the drainage line (Totw A to C indicated in Figure 4.1.1). Depths of the Yengweni Lake were measured from a boat using a steel pole and a GPS. The depth measurements were linked to the survey data and elevations plotted from 1:10 000 orthophotographs to produce longitudinal profiles that are accurate to within approximately 1m.

A Digital Elevation Model (DEM) was produced from 1:10 000 orthophotographs issued with 5m contours by the Surveyor General. This was used to compare the elevation of the Yengweni Lake and the lakes of the Totweni Drainage Line (Mpanza and Mdanzi Lakes) to the elevation of the uMkhuze River, relative to their distance along the uMkhuze River.

#### **4.4. Results**

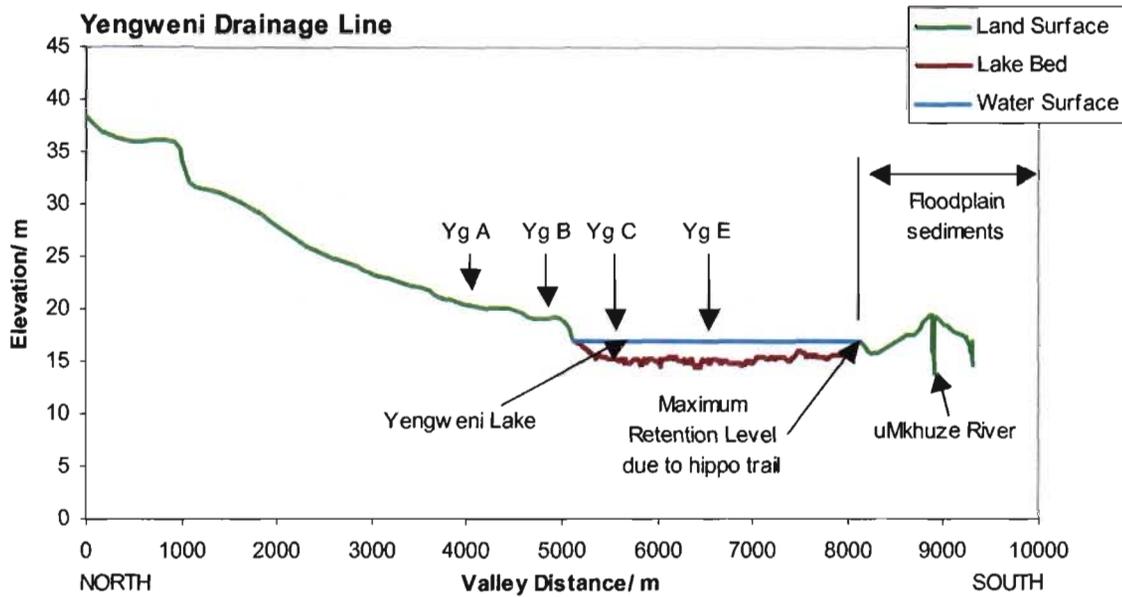
##### **4.4.1. Topographic relationships between the uMkhuze River Floodplain and former tributary streams**

Elevation of the Totweni Drainage Line varies from approximately 38 m to 15 m above mean sea level (amsl) over a distance of nearly 9 km (Figure 4.4.1). The valley has a logarithmic longitudinal profile that is steepest in its headwaters and gets progressively shallower towards the floodplain. Mpanza Lake is situated in a slightly elevated area relative to both the Floodplain and the Totweni Valley immediately upstream of the Lake. The distribution of surface sediments shows that peat occurs in the Totweni Drainage Line as far downstream as the southern end of Mpanza Lake. The elevation of the levee of the uMkhuze River at approximately 15 amsl is slightly lower than the elevation of the mound of peat that surrounds Mpanza Lake. Although peat both surrounds and underlies Mpanza Lake, the elevation of the mound of peat is of interest in this context.



**Figure 4.4.1** Longitudinal profile of the Totweni Drainage Line showing substratum depth, extent of peat deposits and the position of Mpanza Lake relative to the uMkhuze River

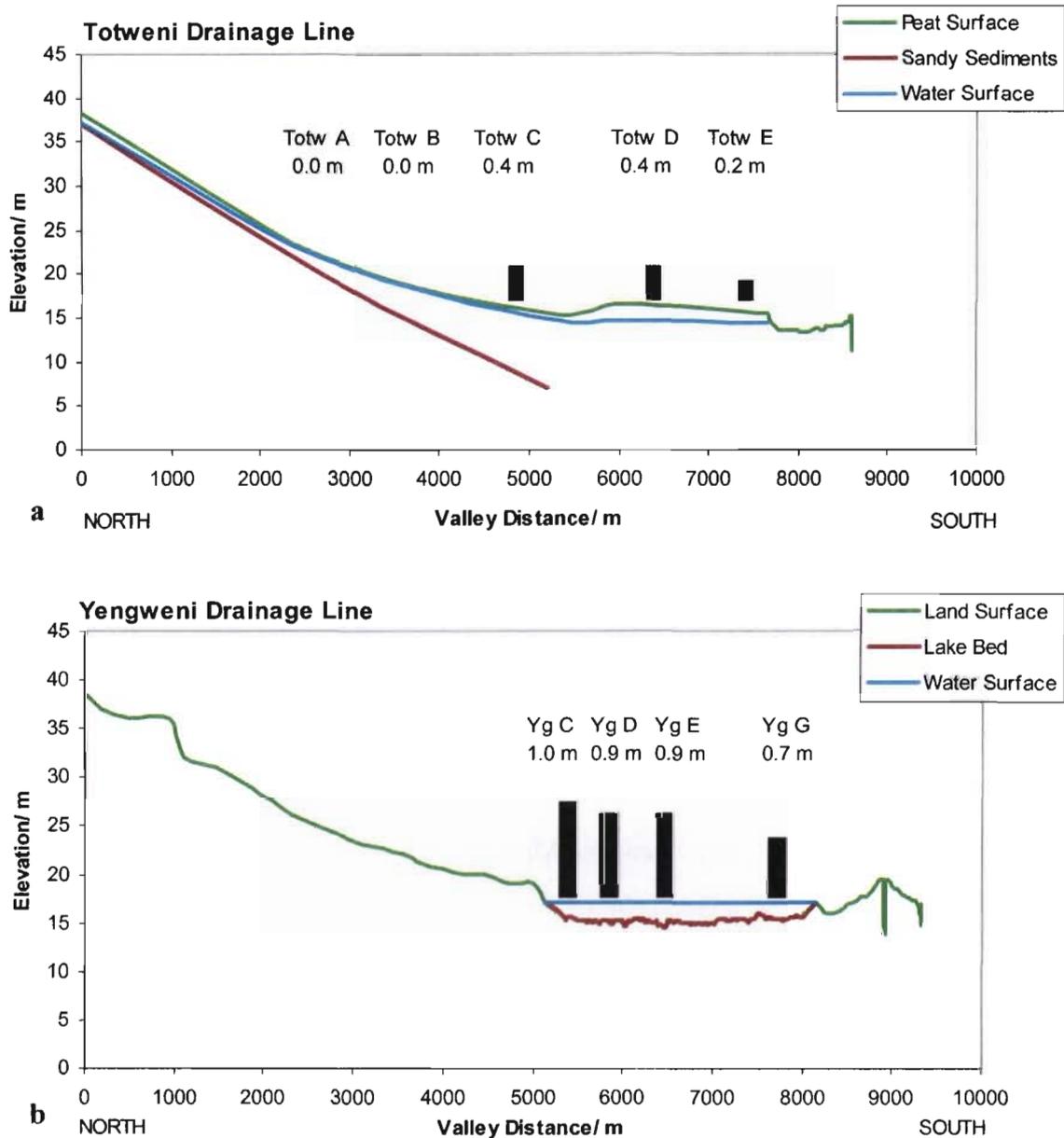
The elevation of the Yengweni Drainage line varies from approximately 38 m to 15 m, with the elevation of the water surface in the lake at approximately 16.3 m amsl (Figure 4.4.2). The slope along the valley floor is more irregular than the Totweni Drainage line, particularly in the upper reaches. As in the case of the Totweni drainage line the longitudinal gradient of the valley gets progressively shallower downstream, but it steepens as the valley approaches the lake. The bed of the lake is relatively flat at an elevation of approximately 15.0 m amsl. This mound of sediment at the southern end of the lake is intersected by a number of hippo trails leading from the lake onto the floodplain, and it is the bed of these trails that determines the maximum retention level of the lake. There is a zone of low-lying ground on the floodplain just south of the Lake that has a similar elevation to the bed of Yengweni Lake. The floodplain surface then slopes gradually up to the top of the levee of the uMkhuze River, which is situated at a height of almost 20 m amsl.



**Figure 4.4.2** Longitudinal profile of the Yengweni Drainage Line showing land surface, lake bed and the position of Yengweni Lake relative to the uMkhuze River

#### 4.4.2. Variation in water levels in the Totweni and Yengweni Drainage Lines

Variation in the elevation of surface water in the Totweni and Yengweni Drainage differed longitudinally within each drainage line from April to December 2000, and also varied between the drainage lines in relatively systematic ways as illustrated in Figure 4.4.3. Variation in water elevation in the Totweni Drainage Line was greatest (0.4 m) in the middle of the valley. It was not measurable in the upper part of the drainage line, and was 0.2 m in Mpanza Lake. In contrast, the elevation of the water surface varied by approximately a metre in the Yengweni, with all elevations being relatively uniform along the length of the lake.

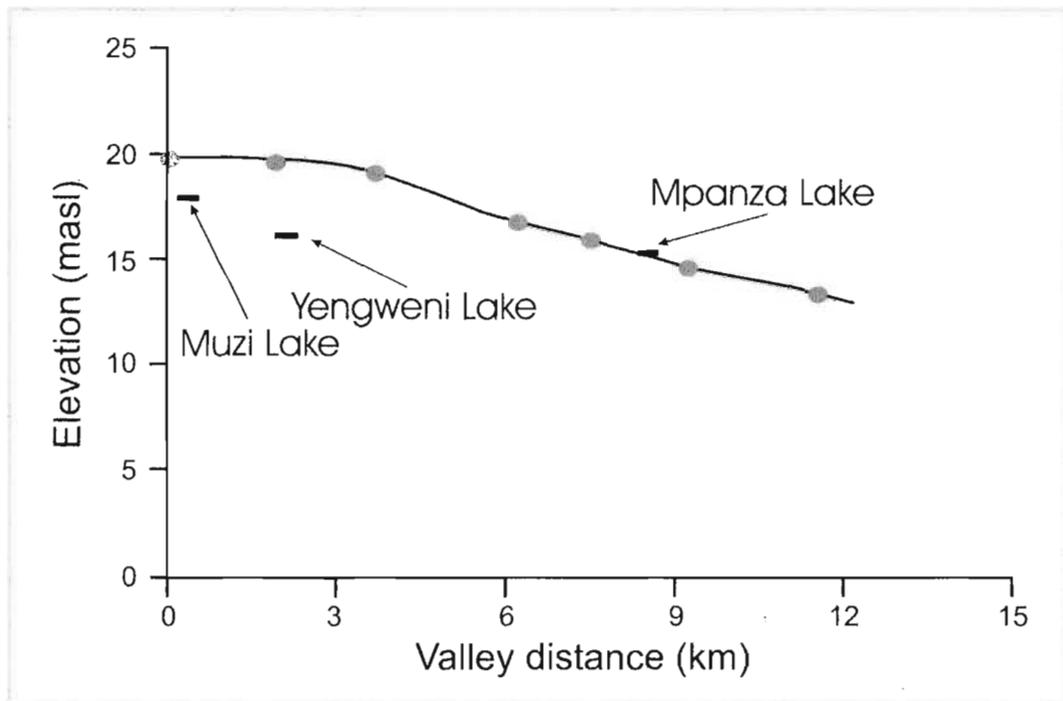


**Figure 4.4.3** The effect of the November floods on surface water elevation, as illustrated by an increase in surface water level from July to December as indicated by shaded columns in (a) Totweni Drainage Line (b) Yengweni Drainage Line.

Note: Yg A, B and F were not sampled in December 2000 after the November 2000 flooding, and transects Fld B and C were submerged during December sampling.

A longitudinal profile of the mean elevation of the banks of the uMkhuze River (solid line) as determined using differential GPS (Ellery *et al.*, 2003) showing the elevations of Muzi, Yengweni and Mpanza Lakes at the distance along the course of the uMkhuze River at which they occur (Figure 4.4.4). Both the Muzi and Yengweni Lakes are situated at lower elevations than the

uMkhuze River. In contrast, the more distal Mpanza Lake is at a similar elevation to the uMkhuze River.



**Figure 4.4.4** Elevation of the Muzi, Yengweni and Mpanza Lakes relative to the uMkhuze River as plotted in relation to valley distance from upstream of the Muzi Lake

#### 4.4.3. Surface water-groundwater interactions in the Totweni Drainage Line

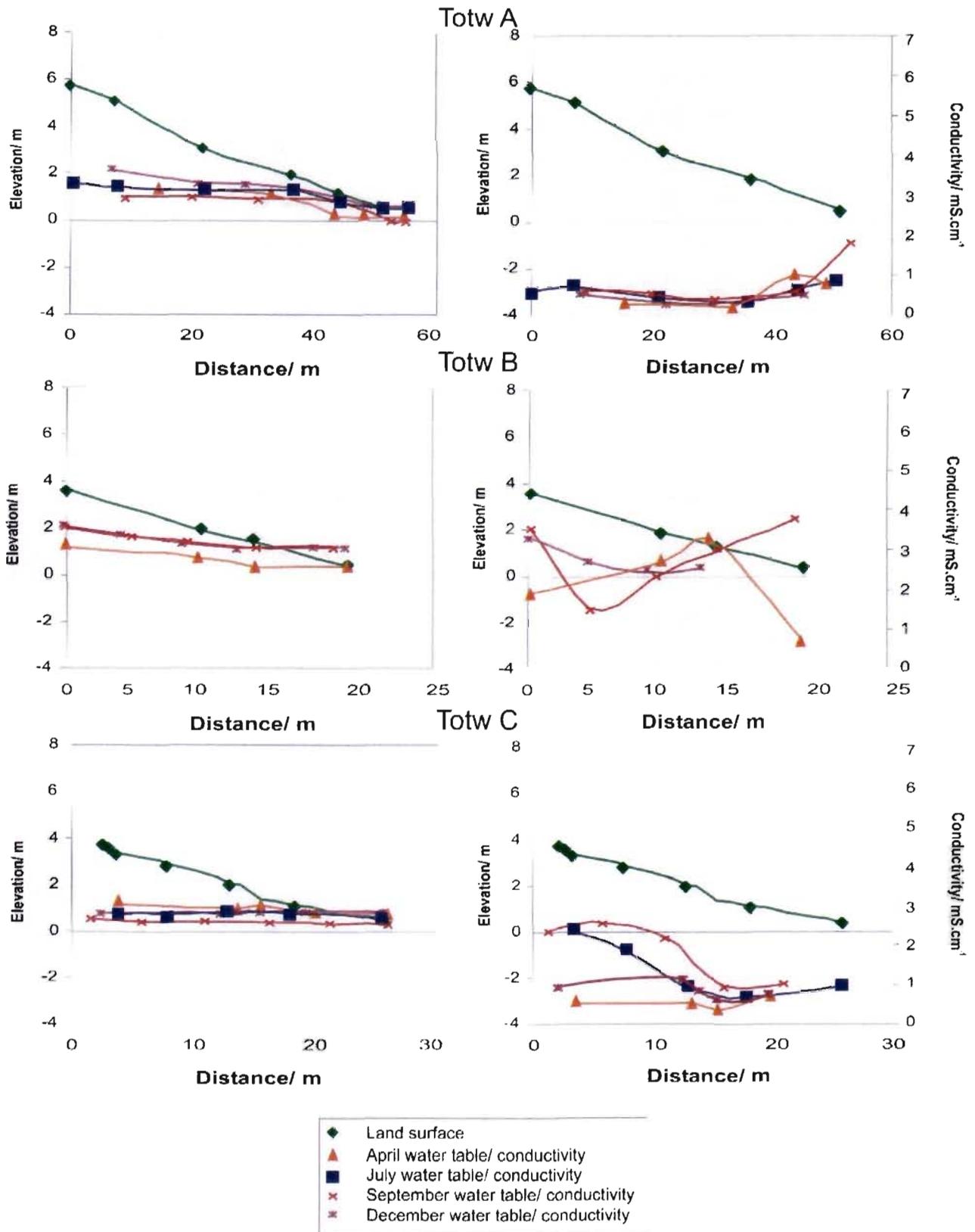
The groundwater slopes gently towards the wetland throughout the sampling period for the northern part of the Totweni Drainage Line (Totw A – C; Figure 4.4.5). This implies that groundwater discharged into the drainage line over the sampling period. For the purposes of the presentation of results, the term ‘groundwater discharge’ will be used where the water table is elevated above and slopes towards the wetland, while the term ‘groundwater recharge’ will be used where the water table is situated at a lower elevation than the surface water, and therefore, slopes away from the wetland. However, in the southern part of the drainage line, at Totw D and E, the water table was relatively flat with some degree of seasonal variation producing very slight recharge or discharge slopes.

Water table fluctuations in the Totweni Drainage Line were relatively limited, maintaining a fairly constant elevation throughout the year. In general, the water tables measured in July and September

during the dry season occurred at the lowest elevation, while the December water table measured in the wet season was at the highest elevation. The flooding in November raised the water table by over one metre at one site, although other sites varied by less than half a metre.

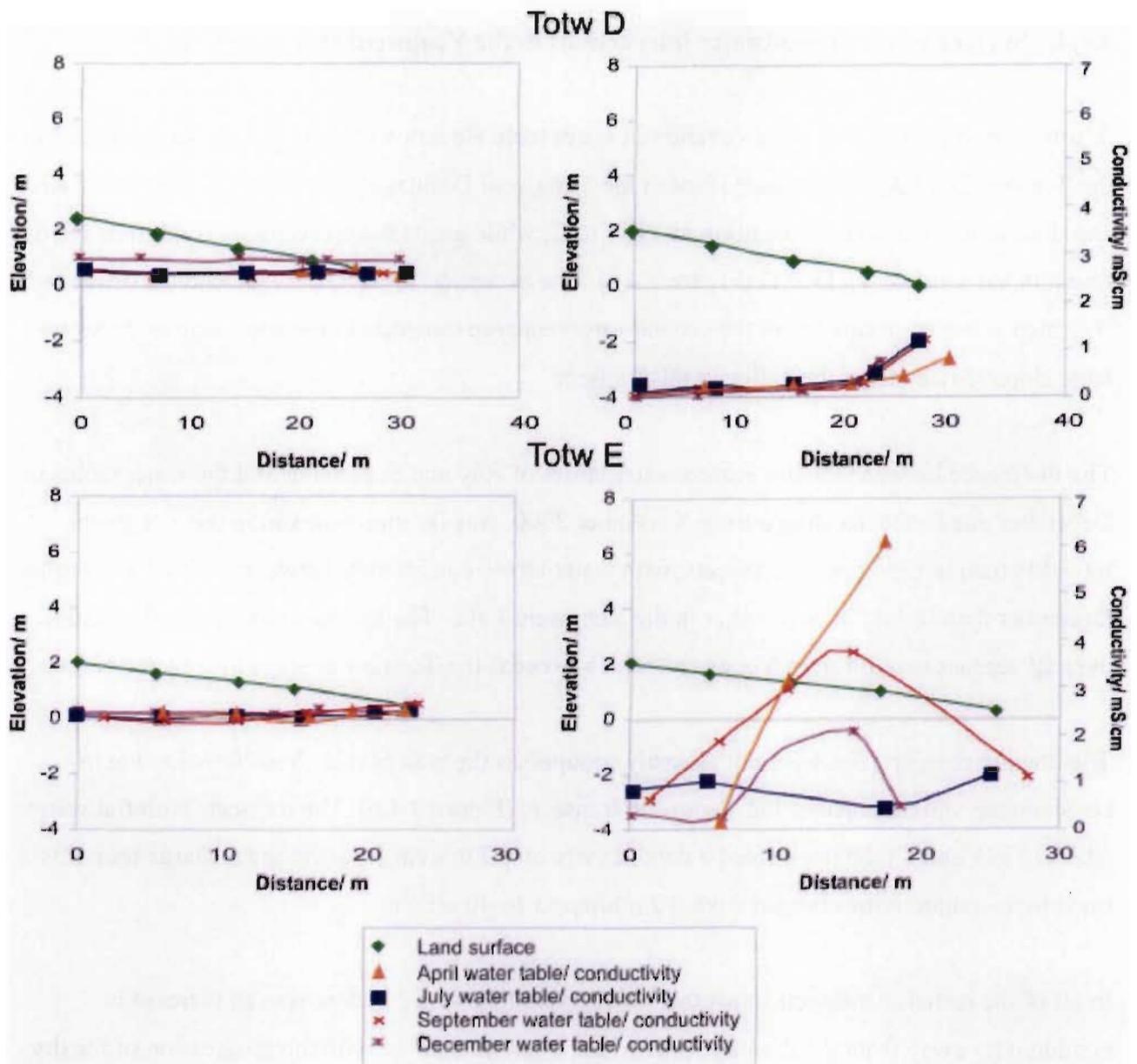
The electrical conductivity values of the groundwater in the Totweni Drainage Line ranged from 0.116 to 6.02 mS/cm, although most samples had conductivities less than 3 mS/cm. Totw A, the northernmost Totweni transect, and Totw D in the south had particularly low conductivity ranges. The variation in conductivity between seasons was greater in all the remaining Totweni transects, usually with the highest conductivities in July and September, and lowest conductivities in December. There was no systematic trend of an increase or decrease in conductivity with distance along the Totweni transects. Surface water conductivities exceeded those of the groundwater in three out of the five transects, with the middle transect, Totw C, and the southernmost transect, Totw E, having higher conductivities in the groundwater than the adjacent surface water features.

In general, depressions in the water table could be related to increased conductivity readings, such as in the April profile of Totw B at about 14.5 m on the transect where a conductivity maximum was associated with a decline in water table elevation. The reverse condition was encountered at Totw C in April, where a pronounced water table mound was associated with a conductivity minimum at 15 m on the transect. The overall effect of groundwater dilution by high rainfall in late November was evident in most conductivity profiles for December.



**Figure 4.4.5** Variation in water table elevation (left panels) and conductivity (right panels) of the Totweni transects A to C

Note: Water tables have been extended past land surface to highlight differences in surface water level.



**Figure 4.4.5 (cont.):** Variation in water table elevation (left panels) and conductivity (right panels) of the Totweni transects D and E.

Note: Water tables have been extended past land surface to highlight differences in surface water level

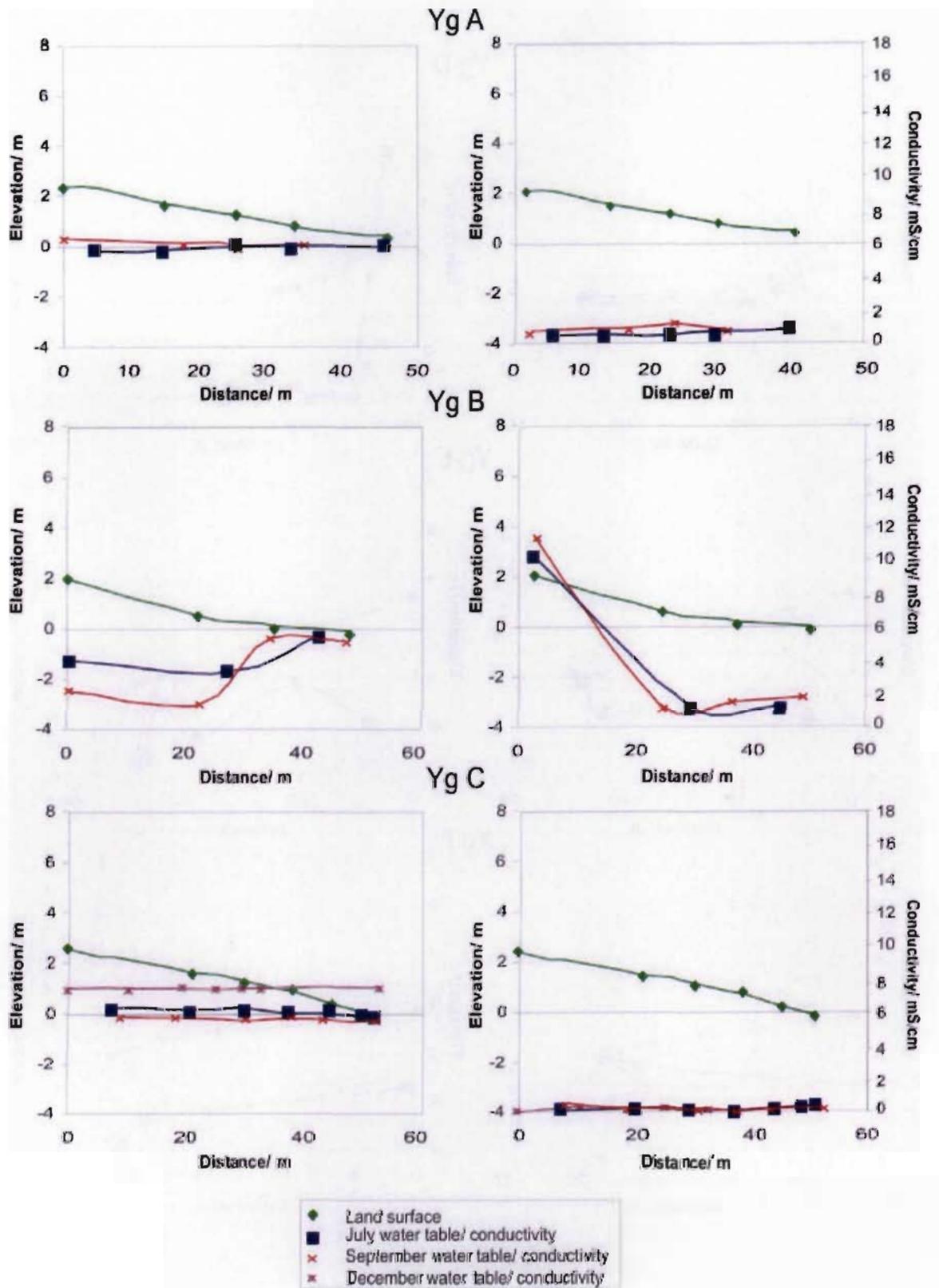
#### 4.4.4. Surface water-groundwater interactions in the Yengweni Drainage Line

A similar north-south pattern of variation in water table elevation of groundwater to that found in the Totweni Drainage Line was evident in the Yengweni Drainage Line, with groundwater stasis and discharge conditions in the north at Yg A to C, while groundwater recharge conditions were found in the south at Yg D to G (Figure 4.4.6). The exception to the observed conditions was at Yg B, which is better grouped with the groundwater recharge transects in the south due to the water table sloping away from the valley in this transect.

The difference between the dry season water tables of July and September and the water tables in December due to the flooding during November 2000, was far more marked in the Yengweni transects than in the Totweni transects, with water tables consistently between 0.5 to 2.5 m higher in December than in July or September in the Yengweni Lake. The average water table fluctuation over all seasons was 1.4 m in Yengweni, which exceeds the Totweni average by a factor of 3.3.

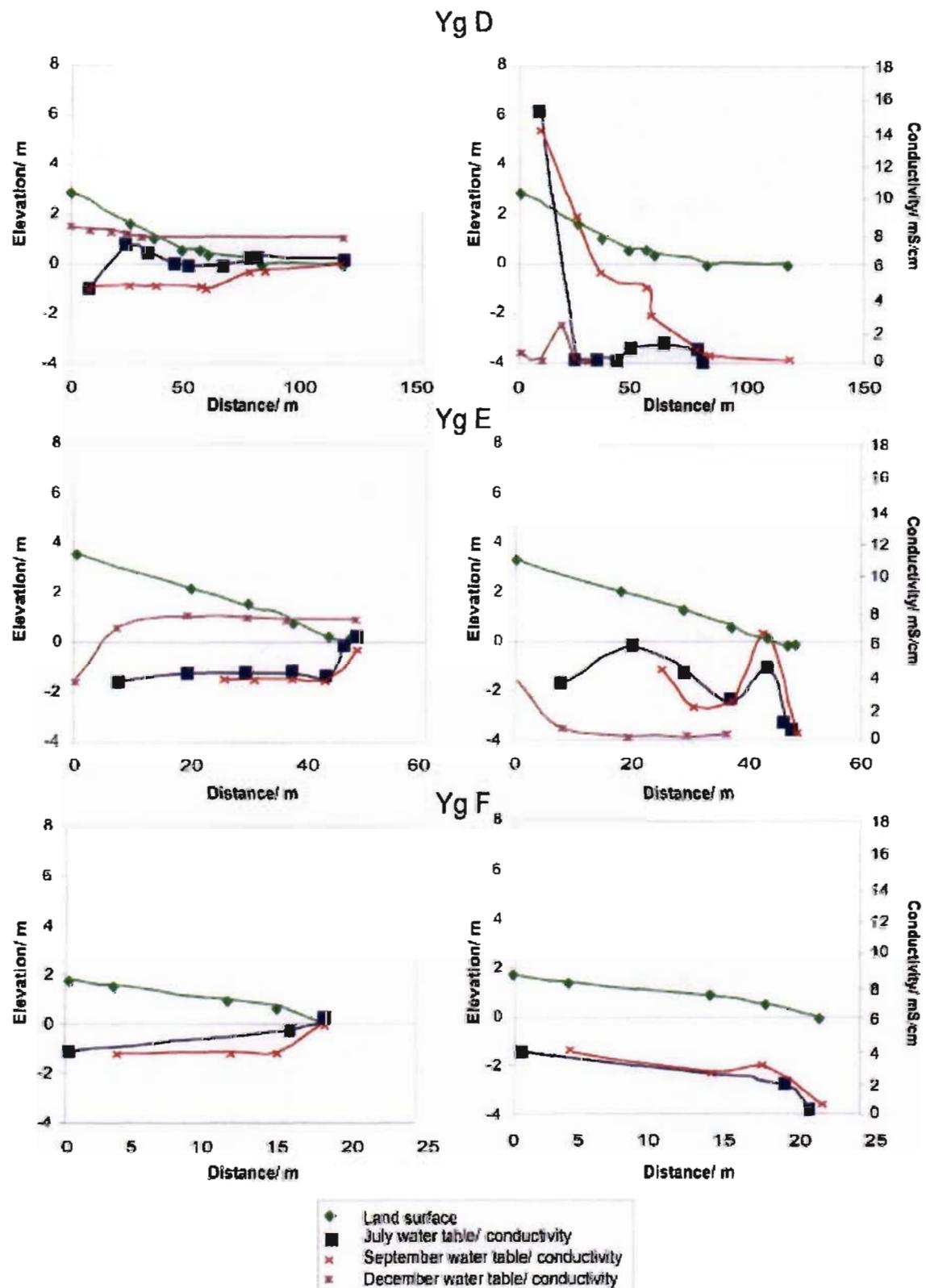
The conductivity profiles were not as easily grouped as the water table characteristics due to considerable variation across the Yengweni transects (Figure 4.4.6). The transects with flat water tables (Yg A and C) did not exceed a conductivity of 1.7 mS/cm, while at the recharge transects, maximum conductivities ranged from 4.2 mS/cm to 16.40 mS/cm.

In all of the recharge transects in southern Yengweni (Yg D to F), there was an increase in conductivity away from the drainage line, which often intensified with the progression of the dry season (from July to September). The conductivity peaks often occurred in the portion of the transect furthest away from the drainage line, as recorded at Yg B, D, E and G. In some cases there was also a high conductivity recorded between the surface water and the end of the transect away from the water's edge (transects Yg E and G).



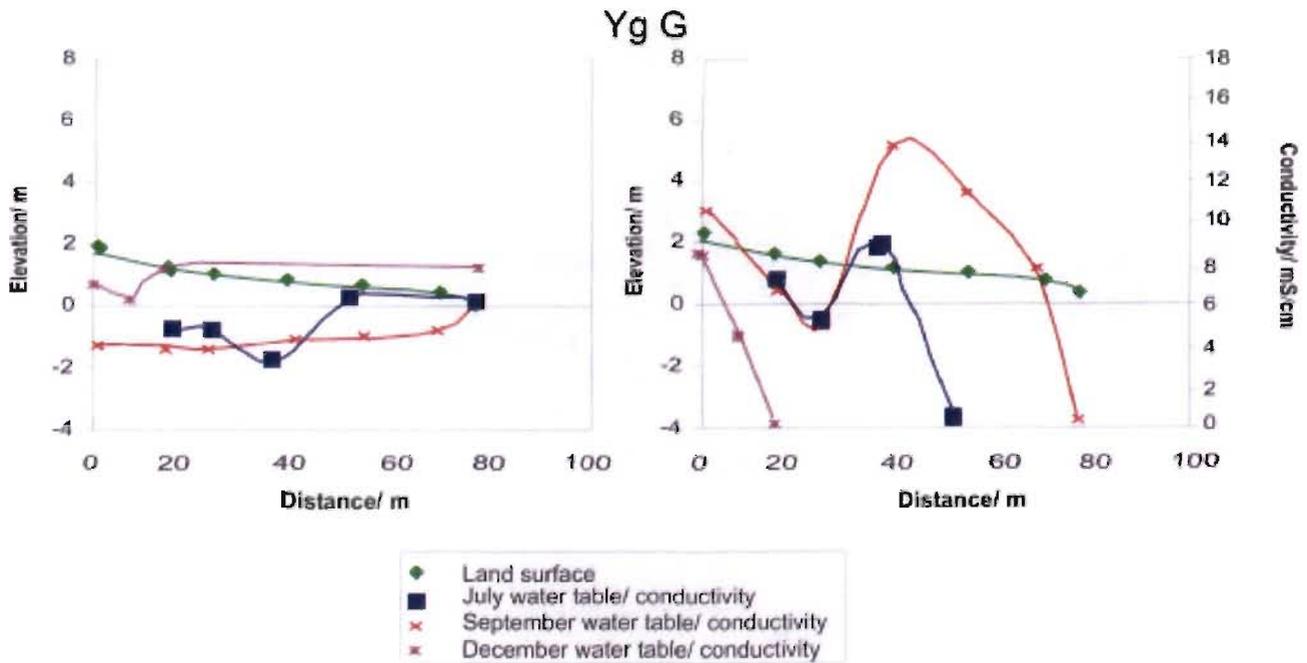
**Figure 4.4.6** Variation in water table elevation (left panels) and conductivity (right panels) of the Yengweni transects A to C.

Note: Water tables have been extended past land surface to highlight differences in surface water level.



**Figure 4.4.6 cont.** Variation in water table elevation (left panels) and conductivity (right panels) of the Yengweni transects D to F.

Note: Water tables have been extended past land surface to highlight differences in surface water level.



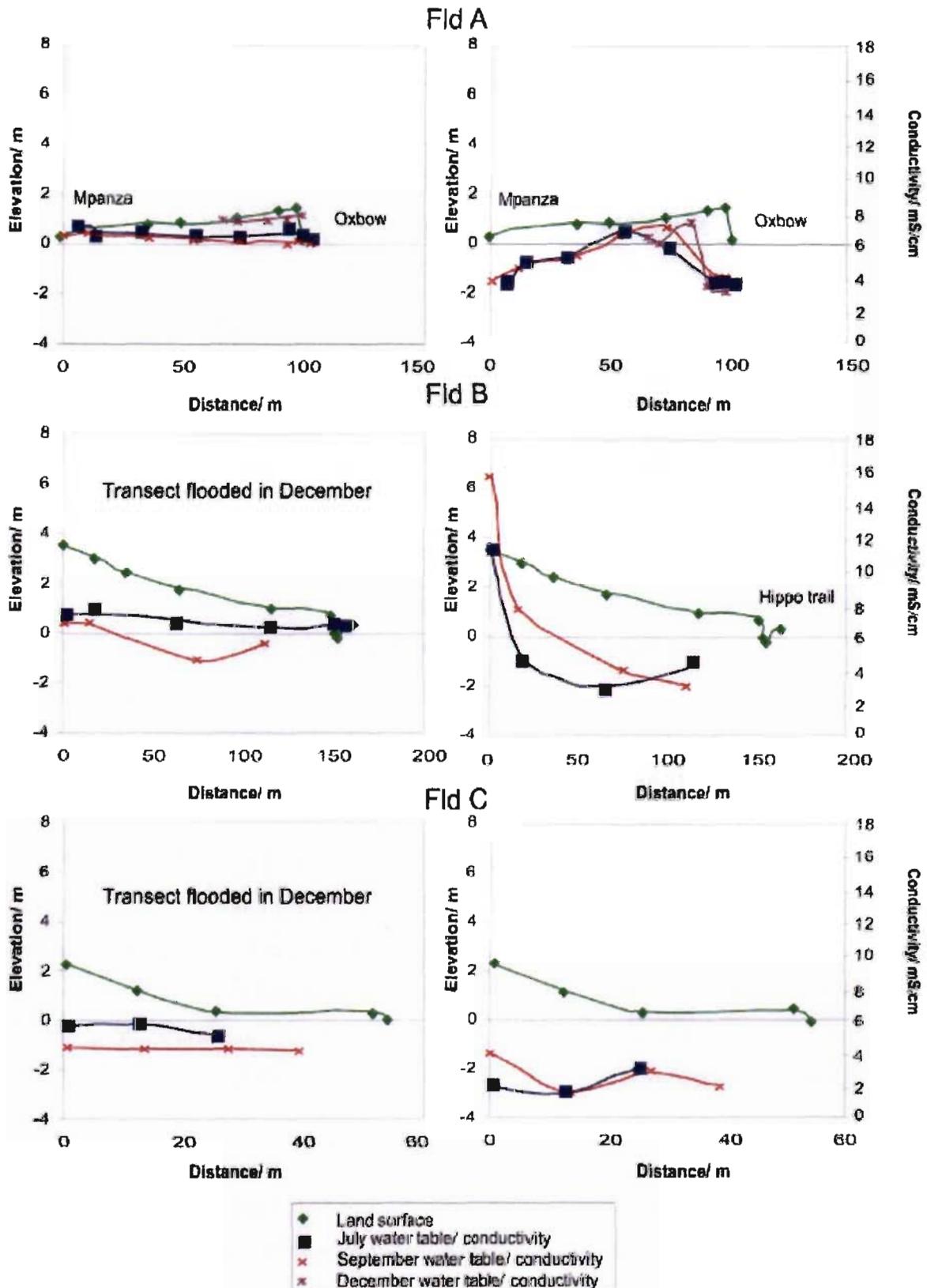
**Figure 4.4.6 cont.** Variation in water table elevation (left panels) and conductivity (right panels) of the Yengweni transect G.

Note: Water tables have been extended past land surface to highlight differences in surface water level.

#### 4.4.5. Surface water-groundwater interactions on the uMkhuze River floodplain

The water table in the three transects on the floodplain margin was relatively flat, and its elevation declined with the progression of the dry season (July to September; Figure 4.4.7). The results suggest slight groundwater discharge from the floodplain margin onto the floodplain in the dry winter months, with indications of groundwater recharge from the oxbow towards the Mpanza Lake in the wet season at Fld A. The fact that Fld B and C were completely inundated during the wet season indicates that at this time groundwater recharge must have been taking place from the floodplain.

The water surface and elevation of the water table rose by 1 m from September to December at Fld A. The water tables varied between July and September at Fld B and Fld C by 1.5 m and 1 m, respectively, and these transects were completely inundated in December.



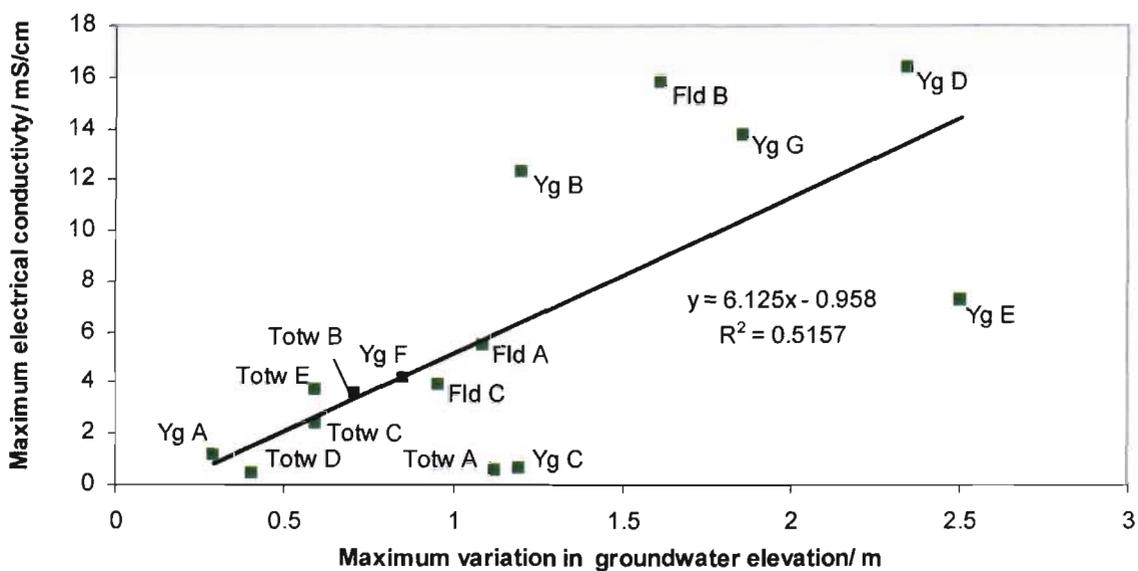
**Figure 4.4.7** Variation in water table elevation (left panels) and conductivity (right panels) of the uMkhuze River floodplain transects Fld A to C.

Note: Water tables have been extended past land surface to highlight differences in surface water level.

Fld A exhibited a wide range of conductivity values with lowest values of 0.7 – 1.0 mS/cm at either end of the transect (oxbow lake on the floodplain and Mpanza Lake) and highest values of 3.0 – 5.2 mS/cm beneath the floodplain. On the other two transects conductivity values increased from the floodplain towards the floodplain margin, with a range of 2.7 – 15.9 mS/cm at Fld B and 1.2 – 4.0 mS/cm at Fld C. The increase in conductivity from the floodplain to the floodplain margin in the case of Fld B was much greater than for Fld C. There was not a particularly striking pattern of change in conductivity with season, as some values increased with progression of the dry season while some values decreased, and *vice versa* for the wet season. However, the overall pattern of variation in conductivity at each transect is similar from season to season.

#### 4.4.6. Relationships between groundwater elevation and electrical conductivity

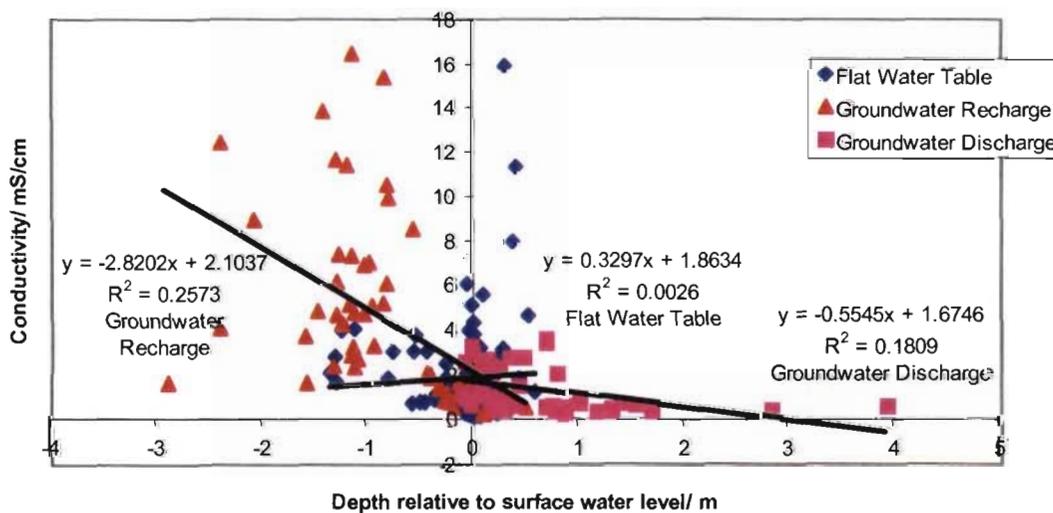
In examining the change in groundwater elevation seasonally for each transect, it was noted that in many transects there was a general trend of increasing electrical conductivity in the groundwater associated with a decline in groundwater elevation and *vice versa*. In Figure 4.4.8 the maximum range in the water table elevation at each transect over four sampling periods is plotted against the maximum conductivity measured over all sampling periods. The general trend incorporating all transects and sampling periods, is one of increasing conductivity values with large fluctuations in water table elevation ( $R^2 = 0.52$ ;  $p < 0.005$ ).



**Figure 4.4.8** The relationship between maximum range in groundwater elevation and maximum electrical conductivity at each transect.

The Yengweni transects showed a more dramatic response to the November flooding than transects in the other regions. In December, all water tables were recharged by floodwaters as the elevation of the water table increased and there was generally a decrease in electrical conductivity. For sites where there was a large increase or a large decrease in groundwater elevation, groundwater conductivities were typically high. The Totweni transects that had flat and groundwater discharge water table surfaces, had low electrical conductivity values across all seasons, with low variation in water table elevation. The floodplain transects Fld A and Fld C, that are typified by flat water tables have intermediate conductivities, while the remaining floodplain transect, Fld B had groundwater recharge characteristics and had high electrical conductivities in the groundwater.

Groundwater elevation relative to surface water level was plotted in relation to electrical conductivity in groundwater samples (Figure 4.4.9). The best correlation was obtained for groundwater recharge samples, which showed a general increase in electrical conductivity with increasing depth below the surface water level. The majority of samples from both groundwater discharge and hydrological equilibrium (flat water table) conditions did not exceed 6 mS/cm, and showed very poor correlations between electrical conductivity and depth below surface water level. The high electrical conductivities among the samples were from Fld B (horizontal water table) at locations furthest from the wetland where the water table was 3 – 4 m below the land surface.

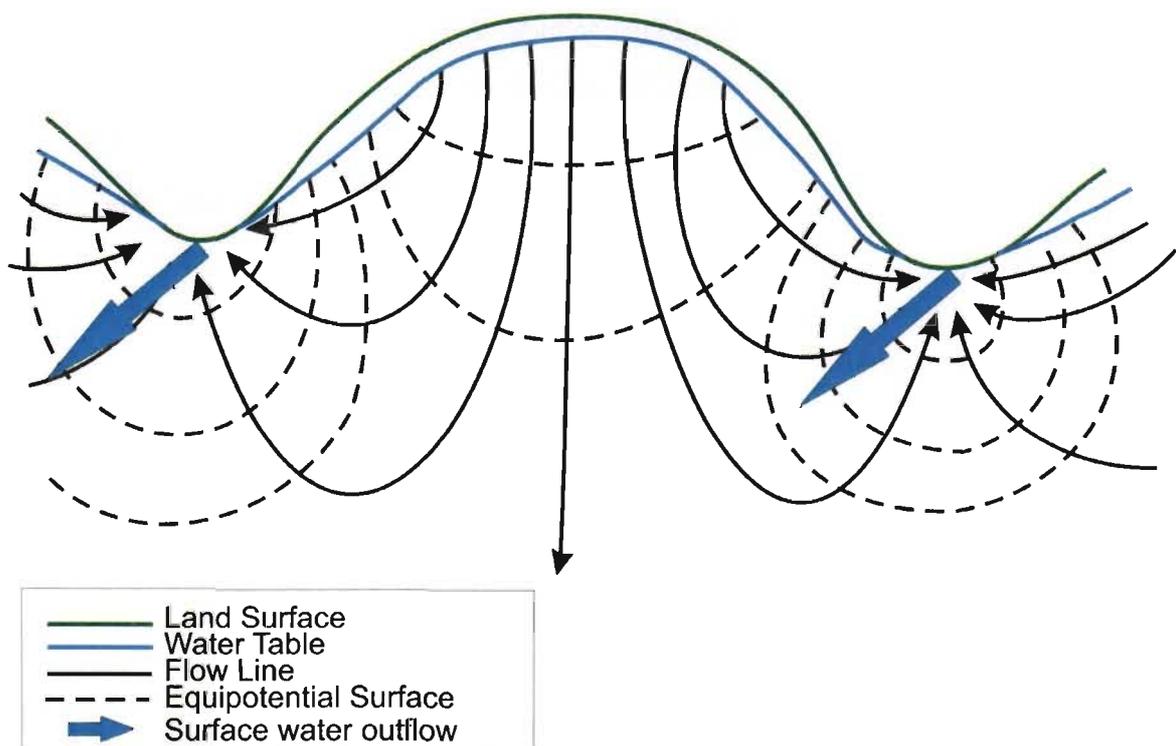


**Figure 4.4.9** Relationship between groundwater elevation relative to surface water level of lake and electrical conductivity of groundwater

#### 4.5. Discussion: Hydrological processes in the Totweni and Yengweni Drainage Lines

##### 4.5.1. Intermediate flow systems

The gently undulating topography and ubiquitous presence of fine- to medium-sand on the coastal plain of Maputaland should produce intermediate flow systems in which the water table mimics topography such that areas of high elevation constitute groundwater divides while depressions are regions of groundwater discharge and surface water outflow (Figure 4.5.1; Kellman and Roulet, 1990). Equipotential isolines, indicated as dashed lines in Figure 4.5.1, depict zones of equal water pressure (hydraulic head) such that flow is perpendicular to areas of equal hydraulic pressure as indicated by the solid lines. Therefore, flow occurs from regions of high elevation to those of low elevation in a curvilinear fashion. Any irregularities or discontinuities in the hydraulic characteristics of the substratum will affect the water pressure distribution and therefore the flow path of water. For example, the hydraulic conductivity of soils will affect the elevation of the water table in areas of high elevation such that the less permeable the soils the greater will be the elevation of the water table above the zones of groundwater outflow as surface flow.



**Figure 4.5.1** Intermediate groundwater flow system in hummocky terrain in homogeneous sediments.

Modified after: Domenico and Schwartz, 1990

Worthington (1978), reported in (Stormanns and Breen, 1987), conducted a hydrogeological survey of the coastal plain of northern KwaZulu-Natal in the vicinity of Richards Bay and found that the water table was generally similar to the topography as illustrated in Figure 4.5.1.

The results from this study suggest that this generalised pattern of groundwater flow applies to much of the Totweni and Yengweni drainage systems. Surface flow occurs from north to south along the drainage lines, with lateral input of groundwater from the adjacent elevated terrain to the west and east of each surface water drainage system.

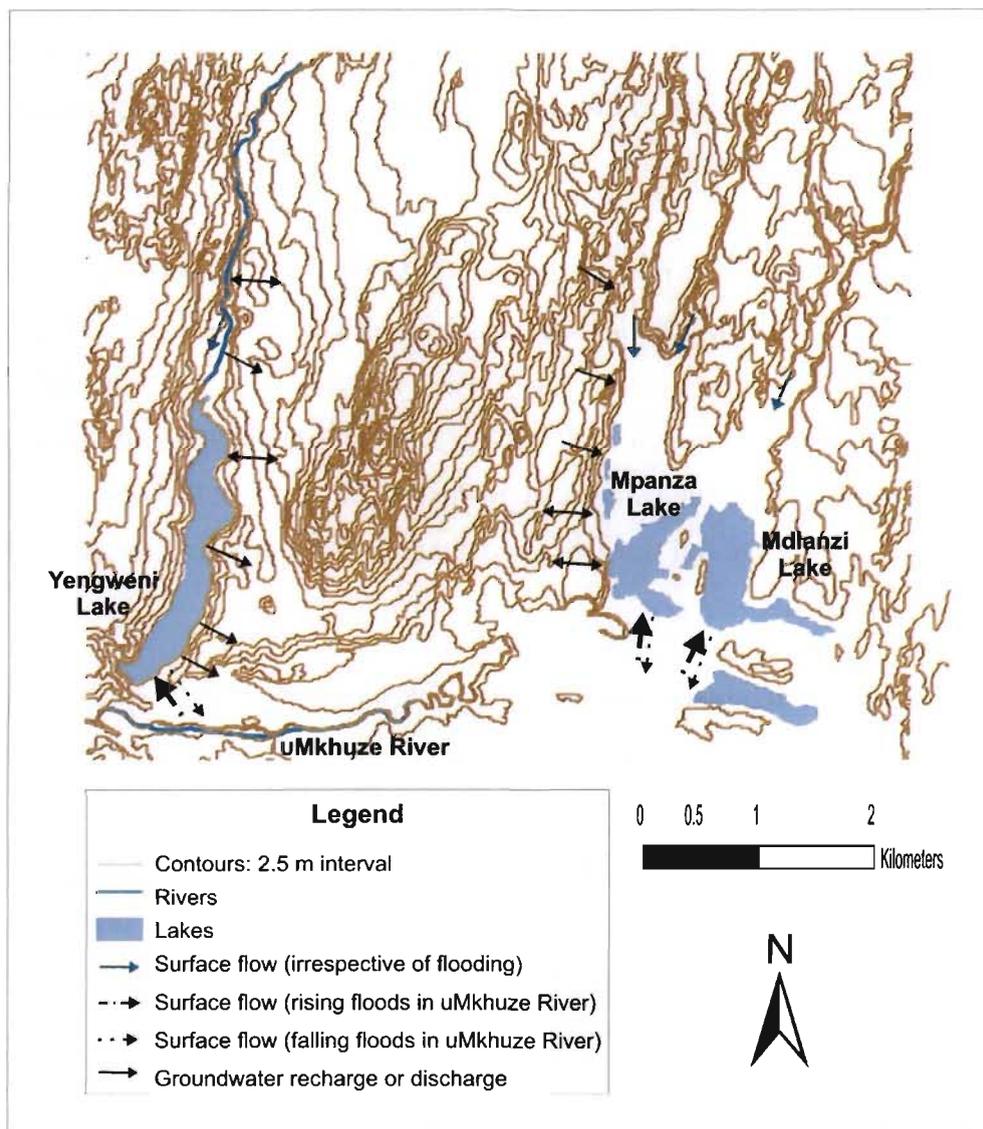
Intermediate flow systems are produced by the undulating topography and constitute sub-components of the regional flow system. Intermediate flow systems respond to smaller hydrological inputs than regional systems due to their smaller capacity (Domenico and Schwartz, 1990). The behaviour of such intermediate flow systems assumes that there is no restriction on surface water outflow such that the difference in hydraulic head between the groundwater divide and the point of surface water outflow is maintained, at least in the fact that the water table is always at a higher elevation than the point where groundwater discharges onto surface. This is likely in areas of high and/or continuous rainfall where the hydraulic conductivity is generally higher than rainfall intensity. In the case of the coastal plain of Maputaland, these conditions are generally met with the exception that surface water flow from the toe of these drainage lines is limited by the presence of alluvial fill on the uMkhuze Floodplain, giving rise to fairly complex hydrological systems.

A surprising feature of the topographic data collected to inform the hydrological component of this study was the complexity of the topography between the uMkhuze River (levee) and the lakes at the southern ends of the Yengweni and Totweni Drainage Lines. It is extremely difficult to explain the mounds at the southern end of the two drainage systems that separate the lakes from the adjacent floodplain and their origin deserves investigation. Nevertheless, these mounds restrict the free flow of water from the drainage lines onto the floodplain, making them more complex than might be first imagined.

#### **4.5.2. Hydrological characteristics of the Yengweni and Totweni Drainage lines**

Based upon the data collected in this study, hydrological processes in the Totweni and Yengweni Drainage lines are summarised in Figure 4.5.2. The northern Totweni drainage line is a groundwater discharge zone, sustaining permanently wet conditions that favour peat formation.

Flow of surface water down the Totweni Drainage Line, in association with aggradation of the uMkhuze Floodplain sustains two lakes at the southern end of this drainage line. The efficiency of surface water flow southwards along the Totweni Drainage system is such that at the southern end of the drainage line there is adequate surface water to maintain a situation of limited groundwater discharge or recharge.



**Figure 4.5.2** Groundwater and surface water flows in the Yengweni and Totweni Drainage Lines, as measured and observed in the field.

However, the Yengweni drainage system is more complex. The longitudinal slope of the northern Yengweni drainage system is somewhat irregular, with areas of relatively high slope and areas of

relatively low slope. In the far northern part of this system there is groundwater discharge while further south (but still north of Yengweni Lake) there is a zone of groundwater recharge. Surface water – groundwater interactions in this part of the system seem to be determined by differences between rates of surface water and groundwater flow. The southward longitudinal slope on the bed of the valley to the north of the lake is low, particularly in the region of Yg B, which reduces the efficiency of surface flow to the south and thus promotes groundwater recharge in this area. With respect to those sites adjacent to Yengwini Lake, with the exception of Yg C, which had a flat water table over the period of sampling, the remaining Yengweni transects exhibited groundwater recharge characteristics, except during December when gradients on the water table at the southernmost sites were reversed due to exceptionally high water levels in the Yengweni Lake following flooding in late November.

The rate and pattern of groundwater recharge following the flood in November for the sites adjacent to Yengweni Lake was dependant upon hydraulic characteristics of the soils. In the case of sediments with high hydraulic conductivity (Yg D) there was significant input of surface water to the local groundwater. The rapid decline in the water level in the lake following flooding led to a degree of return flow from the groundwater back to the lake in this case. However, in a case where the hydraulic conductivity of the soil was low (Yg E) there was limited groundwater recharge and return flow was also limited.

Surface water inputs to the floodplain and its tributary lakes from the uMkhuze River are large during flood events, particularly in the Yengweni Lake, since the levee of the uMkhuze River is elevated well above the floodplain and tributary stream lake. Return flow of surface water from tributary lakes to the floodplain during receding floodwaters is restricted to the floodplain margin where minor channels and hippo trails accommodate flow. Hippo trails connecting the floodplain with the tributary lakes clearly determine the maximum retention level of the lakes such that return flow from the lakes following a flood event does not drain the lakes completely.

Although the observational period is limited, flood events are a regular occurrence in the system and at the rate of aggradation of the uMkhuze River and progradation of the floodplain, the hydrological functioning mentioned above has probably persisted over the last few decades as indicated by aerial photography. However, the aggradation of the channel bed of the uMkhuze River means that the system is increasingly vulnerable to channel avulsion of the uMkhuze River.

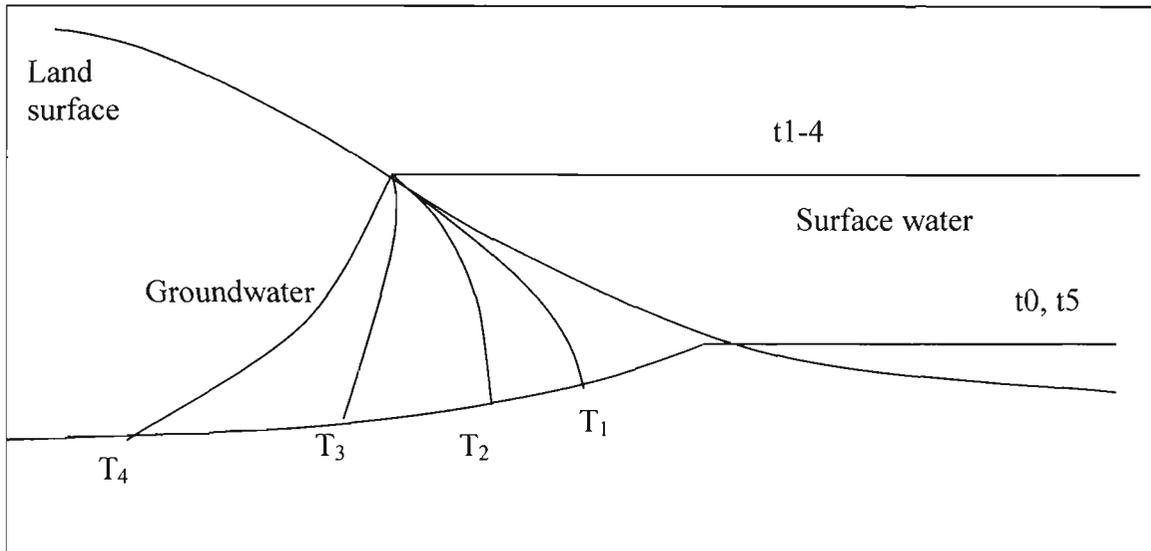
### 4.5.3. Local-scale interactions of surface water and groundwater

The electrical conductivity data collected in this study sheds some light on the mechanisms of groundwater recharge from surface waters. Both Yg E and Yg G are groundwater recharge situations, and both show a decline in electrical conductivity during large flood events. This suggests that surface water enters groundwater by flowing over existing groundwater, which therefore seems to be buried by the addition of surface water.

This contrasts with islands in the Okavango Delta, where a rise in the elevation of surface water causes a rise in the elevation of groundwater without causing any change in the electrical conductivity of groundwater in spite of a steep persistent gradient of groundwater recharge from swamp to island (McCarthy and Ellery, 1994; Wolski and Savenije, 2006). Therefore, it seems that the hydraulic head generated by a rise in the elevation of surface water causes the water table beneath islands to rise, without significant penetration of surface swamp water into island groundwater.

The reason for the differences in the observed patterns between these 2 systems may be due to the dramatic nature of flood events in the uMkhuze System compared to the Okavango, which experiences a gradual rise in surface water level over a period of weeks to months due to the arrival of floodwaters from the catchment in Angola (McCarthy, 2006). Once the Okavango flood wave has passed, water levels decline gradually over a period of months. Furthermore, variation in the elevation of surface water in the permanent swamps of the Okavango Delta is of the order of 15 –20 cm (McCarthy 2006).

In contrast, variation in the elevation of surface water in the uMkhuze Floodplain is of the order of 2 – 3 m, the arrival of the flood takes place over a period of hours to days, the flood wave persists for days and then declines rapidly over a period of days – or perhaps 1-2 weeks. This allows for penetration of surface water in the zone beneath the flooded area in a progressive fashion as illustrated in Figure 4.5.3, which assumes flooding takes place between  $t_0$  and  $t_1$ , and that it remains there over the period from  $t_1$  to  $t_4$ , following which it returns ( $t_5$ ) to the elevation at or close to  $t_0$ . This is the extent of groundwater recharge due to flooding, following which the groundwater wave created by flooding must dissipate by a combination of return flow to surface water and by flow of water to groundwater ( $T_1 - T_4$ , corresponding to  $t_1 - t_4$ ).



**Figure 4.5.3** Illustration of surface water infiltration into groundwater following flooding, where  $t_0$  represents the period prior to flooding, and  $t_5$  the time at which surface water levels return to pre-flood levels.

Figure 4.5.3 represents the nature of predicted surface water-groundwater interactions in the Totweni and northern Yengweni Drainage Lines in response to flooding. The sediments of these regions were found to be largely unmodified through pedogenesis associated with wetland processes, remaining reworked marine sands typical of the Maputaland Coastal Plain. Therefore high infiltration rates at least initially following flooding will occur.

However, observations in the field as well as chemical and mineralogical analyses of sediments presented in Chapter 6, indicate that the sediment of the southern Yengweni consists of a marine sand of high hydraulic conductivity typical of the Maputaland Coastal Plain as well as fine clay-like material of low hydraulic conductivity at depth in proximity to the water table, such that clayey sand is the best description of southern Yengweni sediment. The floodplain sediments, being composed of alluvial silts and clays of the uMkhuze River, also differ in hydraulic properties from the sands on which the wetland is founded. It is therefore probable that the rate of surface water infiltration is retarded in the southern Yengweni and floodplain regions.

Floodwaters will therefore modify the groundwater chemistry of the northern Yengweni and Totweni Drainage Lines, with the degree of modification dependent on the local capacity of the drainage lines, which is in turn influenced by groundwater flows to these regions and evapotranspiration of riparian vegetation. In this way, the Totweni and northern Yengweni systems function similarly to the Okavango Delta, Botswana where surface water infiltration accounts for 80

– 90 % of surface water inflow (Ramberg *et al.*, 2006). The groundwater chemistry of the uMkhuze floodplain is modified to a lesser degree due to restricted infiltration through alluvial silts and clays of lower hydraulic conductivity, with correspondingly higher evapotranspirative loss from the floodplain surface. The southern Yengweni is likely to be the least modified by surface water infiltration, due to slow infiltration rates into the groundwater in this region as a result of highly modified clay-like sediments. This degree of retardation concerning surface water infiltration is suggested by the rapid rise in groundwater level, after puncturing of the clay-like layer during augering, to reveal sandy sediments beneath. This latter case of restricted infiltration of surface water is more common in floodplain wetland systems where an alluvially-defined confining layer restricts infiltration of surface water as observed in the Everglades and Murray River floodplain wetlands (Ramberg *et al.*, 2006).

#### **4.5.4. Inferring hydrological processes based on electrical conductivity of surface and groundwater**

Net changes in water table elevations over a number of months are the result of many inflow and outflow events or processes. Generally there is an increase in the elevation of the water table during the wet season, and a decline in the water table during the dry season. Variation in the elevation of the water table was generally less in the Totweni transects than both the floodplain and Yengweni transects. A further noticeable feature was that variation in the elevation of the water table was greatest in groundwater recharge settings than in groundwater discharge or equilibrium settings.

This negative relationship between electrical conductivity and water table elevation (electrical conductivity increases with a decrease in the relative elevation of the water table compared to surface water elevation at the time of sampling), as illustrated in Figure 4.4.8, suggests a process by which groundwater is removed while concentrating solutes. The trend is strongly seasonal, with lowered water tables and increased conductivities in the dry season, while precipitation inputs in the wet season (summer) result in elevated water tables and more dilute groundwater.

The concentration of groundwater up to 16 mS/cm at Yg D on the Yengweni cannot be attributed to solute additions, as the most concentrated possible addition is uMkhuze River water with a conductivity of approximately 1.5 mS/cm. The very high electrical conductivity values are all associated with large variations in water table in both the dry season (July to September) and under flooded conditions (September to December). At transects where large volumes of water are

removed, which is indicated by increasing groundwater electrical conductivities and declining water table elevations away from the lake margin. Therefore, these areas are characterised by a large variation in water table elevation as measured after flooding events. The other factor resulting in a large variation in water table elevation is the larger volume of floodwater that enters the Yengweni Drainage Line because of surface water inputs from the uMkhuze River, than is the case in the Totweni Drainage Line.

Furthermore, it seems that the concentration mechanism is increasingly effective at greater depths below the land surface (Figure 4.4.9). The increase in conductivity with depth is restricted to groundwater recharge and to some extent flat water tables, where groundwater residence times are likely to be longer than in discharge situations, thereby allowing greater concentration of solutes in the groundwater. Research in the Okavango Delta and the prairie potholes of North and South Dakota suggest that chemical transformations are affected largely by the ratio of recharge to discharge waters within the groundwater, as governed by regional factors such as climate, geology, groundwater gradients and landforms, as well as local conditions of substrate composition and hydraulic conductivity (Dahm *et al.*, 1998; Euliss *et al.*, 2004; McCarthy *et al.*, 1993; Stein *et al.*, 2004). The higher the proportion of recharge water, the greater is the potential for its modification. Research in south central Saskatchewan indicates that this phenomenon may not be generally applied, as saline soils are associated with groundwater discharge in this region, due to the outflow of highly mineralised deep groundwater of a regional system into local depressions (Domenico and Schwartz, 1990).

Although this process of groundwater concentration may be detected in all transects, it is most marked in areas of groundwater recharge or flat water tables, where the most concentrated samples occur at a depth of 2 m or more below the land surface. The process of removing groundwater in such a way as to cause solute concentrations to increase, maintains very steep recharge gradients in the southern Yengweni, where concentration of solute concentrations in groundwater has been most marked. These findings indicate that the chemical transformations are governed by factors other than purely atmospheric water demand at the soil surface and sediment leaching by infiltrating water.

#### **4.5.5 Conclusion: Hydrological insights into chemical evolution of uMkhuze Wetland System water**

In spite of the common origin of the Totweni and Yengweni Drainage Lines on the Maputaland Coastal Plain, the drainage lines differ hydrologically. Given the high hydraulic conductivity sediments of the uniform reworked marine sands of the coastal plain, expected intermediate flow systems in the undulating topography of old dune fields is encountered on the Totweni Drainage Line, and mostly on the northern Yengweni Drainage Line. In contrast, prolonged recharge conditions were documented for the southern Yengweni, which were also regions of elevated electrical conductivity values. Not only were these regions of high electrical conductivity but also where the largest fluctuations in groundwater level were recorded. The floodplain regions had electrical conductivity values intermediate between the conductivities of the discharge transects of the Totweni and northern Yengweni, and the highest conductivity values of the recharge transects of the southern Yengweni. The strong relationship between fluctuations of the water table and electrical conductivity values indicated that the larger variation in water table on the southern Yengweni relative to the rest of the study area, was not only due to the greater input of uMkhuze River water but also due to a process whereby water was removed, while allowing solutes to concentrate in the groundwater. The degree to which this process is still occurring in parts of the southern Yengweni, where a low hydraulic conductivity clay layer was observed, is addressed in Chapter 7. Furthermore, this process occurred at depth in the groundwater recharge regions, such that concentration of the groundwater cannot be attributed to capillary rise and evaporation from the soil surface. A mechanism of evapotranspiration by vegetation rooted at or near the water table must therefore account for such elevated conductivity values and the removal of water at depth, all of which is further discussed in Chapters 5 and 6.



**CHAPTER 5**  
**SURFACE WATER-GROUNDWATER INTERACTIONS:**  
**CHEMICAL EVOLUTION**

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### **5.1. Introduction**

This chapter examines chemical evolution of groundwater in the uMkhuze Wetland System. The wetland is founded on reworked marine sand composed predominantly of quartz, which is inert and does not play a major role in either solute additions or removal. The uMkhuze Wetland System therefore, presents an ideal setting in which to trace chemical evolution of wetland waters.

During the Quaternary Period (the last 2 million years), sea levels fluctuated and have since receded, exposing the sandy strip from the Lebombo Mountains to the current shoreline by around 6500 years ago (McCarthy and Hancox, 2000; Stormanns and Breen, 1987). Therefore, thousands of years of flushing by percolating rainwater through the high hydraulic conductivity sediments of the coastal plain, should have removed any aragonite ( $\text{CaCO}_3$ ) shell fragments (Alcock, 1999; Warren, 1989). This view is supported by the high silica content of sediments of the coastal plain (> 90 % silica). Consequently, waters within the system should be negligibly modified by the pre-existing wetland sediment.

In addition, expected solute additions to the groundwater system are low, with the main sources identified as precipitation and uMkhuze River water. The uMkhuze River is potentially an important source of solutes to the wetland and adjacent groundwater, as weathering of sedimentary and (particularly) igneous rocks in the catchment should result in greater solute loads than other inputs. Based on the previous chapter it should be clear that the uMkhuze River is an important source of water to the Yengweni, which also receives surface and groundwater inputs from the north. In contrast, the Totweni is largely driven by groundwater inputs from the north, with occasional input of water into the southern part of the drainage line from the uMkhuze River from the south. The floodplain and floodplain margin mainly receive inputs from the uMkhuze River. Groundwater inflows from the sandy coastal plain are likely to be rainfall-derived from the north of the system draining along the expected water table slope, which mirrors the slight southward slope allowing drainage towards Lake St Lucia. Solutes derived from weathering processes as well as dissolution of secondary minerals will be minimal in such a setting.

Due to the low background chemical concentrations from both the sediment and recharging waters of the system, and the more humid climate where rainfall exceeds evapotranspiration in most months of the year, chemical processing should be limited. However, as discussed in Chapter 4, surprising variations of the wetland hydrology combined with elevated electrical conductivity readings within the groundwater, indicate that a concentration process is modifying wetland source waters to a large extent. Chemical evolution of the shallow groundwater will be considered in greater depth in this chapter.

Chemical evolution of groundwater is the subject of much research due to the recognised value of groundwater as an important resource, and the insights gained into flow paths, chemical processing and geological formations (Armenteros *et al.*, 1995; Arndt and Richardson, 1989; Arndt and Richardson, 1993; Barbiéro *et al.*, 2002; De Mars and Garritsen, 1997; Jørgensen, 2002; Katz *et al.*, 1995; Logan *et al.*, 1999; Rademacher *et al.*, 2001; Salama *et al.*, 1993; Spears, 1986). It is widely accepted that the solute load of groundwater increases with increasing distance from the recharge area, primarily due to mineral dissolution of the geological strata with which the groundwater is in contact (Domenico and Schwartz, 1990; Schwartz *et al.*, 1981; Wallick, 1981). The focus of this study is shallow groundwater, which occurs at a maximum depth of 4-5 m below surface, in a wetland area where water tables are generally high. Although the scope for groundwater processes in terms of solute inputs and subsequent reactions is relatively limited, the surface water-groundwater interface is known to be an active site of chemical transformations (Dahm *et al.*, 1998).

## 5.2. Methods

Chemical evolution of water in the uMkhuze Wetland System was investigated by classifying water samples based on their chemical composition using multivariate methods. In this way solute source and likely evolutionary paths may be identified (Domenico and Schwartz, 1990; Eugster and Jones, 1979; Langmuir, 1997; Ortí *et al.*, 2003; Salvany *et al.*, 1994; (Yechieli and Wood, 2002). The process of evaporative concentration was described by use of a concentration tracer such as chloride, which is widely employed to track solute behaviour during concentration due to its conservation during an evaporation process as a result of its solubility over an extremely wide range of concentrations and limited interactions with biota. Possible mineral saturation and subsequent precipitation were considered by calculating saturation indices of predicted minerals.

### **5.2.1. Field sampling and preliminary measurements**

Field sampling was described in Chapter 4. Conductivity and pH were measured in the field on unfiltered samples. Rainwater samples were taken in 1999, using large funnels feeding into polyethylene sample bottles. uMkhuze River samples were taken at least a metre from the river bank, at a depth of 20 – 30 cm below the surface.

### **5.2.2. Chemical analyses**

#### **5.2.2.1. Sample preparation**

Chloride concentrations of free or weakly complexed chloride were measured on unfiltered samples by ion-selective electrode. Although filtering would not affect the measured chloride concentration, the chloride analyses were performed on the unmodified samples to reduce the risk of sample contamination. Thereafter each sample was filtered to 0.22  $\mu\text{m}$  to exclude sediment and colloidal material in order to analyse solutes only. Total chemical analyses were conducted for the solutes calcium, iron, magnesium, potassium, silicon and sodium. Due to the rural and undeveloped nature of the catchment, these solutes do not reach levels at which they may be described as pollutants in the wetland source waters, and are considered to reflect a natural system. However, conductivity readings in the uMkhuze Wetland System differed by over two orders of magnitude and instrumental techniques were selected that could accommodate a wide range of concentrations with reliable results.

#### **5.2.2.2. Chloride analysis by ion-selective electrode**

Due to the coastal location of the uMkhuze Wetland System high chloride concentrations were expected. Potentiometry using an ion-selective electrode was employed as this technique affords accurate measurement of a wide concentration range and low sample preparation time (Marr and Cresser, 1983).

Potentiometry by ion-selective electrode is the measurement of potential generated on either side of a phase boundary between an electrode and the solution being measured. A charge imbalance develops due to ion diffusion across the phase boundary (Cammann *et al.*, 2001). The phase boundary may be glass, solid state (such as the  $\text{LaF}_3$  crystal of fluoride ISE's or a sparingly soluble salt within a polymer, such as  $\text{AgCl}$  in a silicon rubber polymer) or liquid attached to or embedded

within a polymer (Marr and Cresser, 1983). A calibration of potentials generated by a range of standards of known concentrations allows analysis of sample solutions. The analysis is restricted to free ions in solution, and is non-destructive.

A Jenflow Plus Chloride Combination Ion-Selective Electrode (ISE) with a solid-state membrane was employed. This electrode has a range of 1 to 35 500 ppm chloride (Spectronic, 2003). Calibration standards of 1, 10, 100 and 1000 ppm chloride were used. Samples with concentrations in excess of 1000 ppm were diluted accordingly. Five mL of an ionic strength adjustment buffer (ISAB) (5 M sodium nitrate) was added to 50 mL of each standard and sample (USEPA OSW Methods Team, 2003). No further reagents were used as negligible concentrations of interferents; including bromide, cyanide, iodide and sulfide were expected. Iron and aluminium at concentrations greater than 300 ppm form complexes with chloride that prevent detection by the ISE (USEPA OSW Methods Team, 2003). Although aluminium was not analysed, groundwater in quartzitic sediment is unlikely to have high aluminium concentrations and the maximum iron concentration measured was 145 ppm. Three sample replicates were run after every thirty samples, which produced an average RSD of 7 %.

### **5.2.2.3. Atomic emission spectroscopy**

Calcium, iron, magnesium, potassium, silicon and sodium were analysed using atomic emission techniques. The basis of atomic emission spectrometry is that atoms in their ground (lowest energy) state subjected to thermal energy from a heat source, absorb energy, causing atoms to exist for a brief period in an excited state (Broekaert and Evans, 2001). Transition to the excited state involves the promotion of electrons surrounding the nucleus into higher energy levels within each atom. On relaxation to the ground state, energy is emitted as electromagnetic radiation. Each element has specific energy levels, such that the energy difference between levels differs across the elements. As electrons return to lower levels, specific or quantised amounts of energy are released. The wavelengths emitted, related to energy by the equation  $E = hv$ , is therefore typical of the excited element (Skoog *et al.*, 1996). Choice of excitation method depends on the element to be analysed and the accuracy required. For the alkali elements potassium and sodium, a relatively low energy is required for excitation, so that the use of a low temperature heat source, such as an air/ acetylene flame, excites few other elements and restricts interferences (Marr and Cresser, 1983). In a higher flame temperature, such as that generated by a nitrous oxide/ acetylene flame, stable compounds

may be formed that interfere with the relationship between intensity of emission and analyte concentration (Broekaert and Evans, 2001).

An air/acetylene flame, reaching temperatures of 2300 °C, was used as the heat source on the AAnalyst 100 AA Spectrometer using standard conditions recommended by Perkin Elmer (1996). Calibration standards for potassium were 0.05, 0.1, 0.2, 0.5 and 1 ppm, while the sodium calibration included the standards 5, 10, 15, 20 and 25 ppm. Sample concentrations in excess of the standards were diluted accordingly.

In the technique inductively coupled plasma optical emission spectrometry, an argon plasma (a partially ionized gas) is the heat source (Broekaert and Evans, 2001). The inert argon atmosphere and very high flame temperatures (up to 6 000 °C) reduce interference due to refractory compounds and cause most elements to be excited (Broekaert and Evans, 2001). These features allow analysis to trace levels (ppb) of most elements, while still retaining a wide linear range (Thompson and Walsh, 1983).

The Jobin Yvon 24 ICP-OES Spectrometer was used for elemental analyses of calcium, iron, magnesium and silicon. Five multielement standards constituted the calibration, which were 0.05, 5, 12.5, 25 and 50 ppm for calcium and magnesium, 0.02, 2, 5 10 and 20 ppm for silicon and 0.01, 1, 2.5, 5 and 10 ppm for iron. Wavelengths were selected both for their sensitivity and lack of interferences.

Typical RSD's obtained were 16.8 and 12.3 % for potassium and sodium respectively. These RSD's are comparable to those obtained by flame photometer by the WHO (Ballance, 1996). Calcium, magnesium and silicon returned average RSD's of 12.8, 19.8 and 14.8 % respectively. These RSD's are considered satisfactory to determine trends in chemical evolution in the uMkhuze Wetland System. Iron analysis produced an average RSD of 101.7 %. The difficulties of iron analysis are considered in Section 5.2.3.

#### **5.2.2.4. Total alkalinity by titration**

Samples collected in July 2002 were also analysed for total alkalinity by titration using phenolphthalein and screened bromocresol green – methyl red as indicators (Csuros, 1997). The mixed indicator is used as a substitute for the more common methyl orange, as the endpoint is

sharper at pH 4.5. The phenolphthalein endpoint at pH 8.3 is attributed to alkalinity due the carbonate ion ( $\text{CO}_3^{2-}$ ) (Broekaert and Evans, 2001). The bromocresol green – methyl red endpoint at pH 4.5 accounts for most alkaline substances, predominantly carbonate and bicarbonate, and to a lesser extent hydroxide, in natural waters. The bromocresol green – methyl red value is referred to as total alkalinity. Other species that may contribute to alkalinity such as silicates, phosphate, and sulfate were considered to have a negligible contribution as confirmed for sulphate and phosphate by anion chromatography (Rowland and Grimshaw, 1989). The total alkalinity at the pH 4.5 endpoint is reported as ppm  $\text{CaCO}_3$  according to convention, unless otherwise stated.

It must be noted that total alkalinity is usually overestimated by the above method. Organic acid anions such as acetate may play an important role in groundwater systems (Palandri and Reed, 2001). The omission of such analyses may lead to an overestimation of the bicarbonate ion concentration.

#### **5.2.2.5. Anion analysis by ion chromatography**

Selected samples taken during July 2002 were analysed for the anions sulphate, phosphate, nitrate and fluoride using the Dionex ICS-90 Ion Chromatography System. Ion chromatography involves the separation of ions on an ion-exchange material by virtue of their size and charge. The differing intensities of adsorption to the column packing results in an elution sequence (Marr and Cresser, 1983).

The sample solution was first run through a guard column (IonPac AG14) to remove any organic contaminants, before passing through the separation column. The eluent employed was a dilute solution of 3.5mM  $\text{Na}_2\text{CO}_3$ / 1.0 mM  $\text{NaHCO}_3$  at a flow rate of 1.2 mL/min (Dionex Corporation, 2002). The separation column used was an IonPac AS14. The packing of the column supports alkyl quaternary ammonium groups that exert differing degrees of electrostatic influence on the sample anions (Dionex Corporation, 2002). Thereafter, the sample was passed through a suppressor column (a strong cation exchanger, AMMS III anion micromembrane suppressor) with dual purpose to form higher conductivity acids of each anion, that may then be measured by a conductivity detector, and to suppress the conductivity of the eluent by forming the non-conducting  $\text{H}_2\text{CO}_3$  (Lemke *et al.*, 2001). The suppressor is then regenerated by a dilute sulfuric acid solution.

The Dionex anion stock solution was diluted to give three multielement standards, by which the response of the conductivity detector was calibrated to three different concentrations of each anion (Table 5.2.1).

**Table 5.2.1** Multielement standards for ion chromatography

<b>Anion</b>	<b>Standard 1</b>	<b>Standard 2</b>	<b>Standard 3</b>
<b>Fluoride</b>	0.745	3.88	20
<b>Nitrate</b>	3.73	19.38	100
<b>Phosphate</b>	5.59	29.06	150
<b>Sulphate</b>	5.59	29.06	150

The analyses of samples collected in April, July, September and December 2000 as well as July 2002 for all analytes mentioned above, generated around 2 800 data points.

#### **5.2.2.6. Constraints on accuracy of chemical analyses**

Ideally, groundwater should be sampled into a sealed evacuated container at the water table, such that the sample composition remains unchanged, with no solute additions or removals and preventing carbon dioxide degassing. In this way the sample is never exposed to conditions other than its natural state, assuming that the sample container is perfectly isolating. However, conditions in the field are far from ideal. In augering a borehole to the water table, the groundwater becomes exposed to an atmosphere of different composition to that at the water table; most significantly higher oxygen concentrations. Surface soil and material enter the borehole and may change the groundwater chemical composition. Furthermore, in the fine sand of the Totweni Drainage Line, sand collapses into the hole at the water table forming a slurry. This slurry was poured into beaker and allowed to settle in order to pour off any supernatant groundwater. As such, the redox status of the sample was probably highly modified.

The polyethylene sample containers are also microporous, and allow oxidation as was evident from red iron precipitates in some sample bottles as well as carbonate precipitation. Later analyses of calcium as replicates found markedly different values that were corrected on acid addition to dissolve the calcite precipitates.

In view of the altered state of the samples, they were not acidified in order to retain reduced solutes, as field filtering required prior to acidification would have been too lengthy. Thereby the samples

would have been subject to many sources of contamination. Initially, samples were filtered in the lab under an inert nitrogen atmosphere to maintain the prevailing redox conditions at the time of sampling. However, this proved to be impractical, partly due to the very long filtration times as a result of fine sediment in the samples, and probably unnecessary due to errors introduced during sampling and sample storage.

Due to alteration of redox conditions during and after sampling, reported iron values are used with caution. Iron mottling in the oxidised sediment of the southern Yengweni and floodplain suggests that it should be a more important component of the groundwater than elsewhere, but this is not evident in the data. It was thus considered unnecessary to increase analytical accuracy of the iron analysis using the very sensitive method of GF-AAS (graphite furnace atomic absorption spectroscopy) due to the problems of oxidation. Further research into redox-sensitive solutes, such as iron and manganese, their role in chemical cycling and sedimentation, as well as possible interactions with organic compounds, is required in the uMkhuze Wetland System.

### **5.2.3. Data analysis**

#### **5.2.3.1. Multivariate statistics**

Complex data sets of many variables, the measurement of which may cover long time periods, are unlikely to exhibit simple trends detectable by simultaneous analysis of two or three variables at a time. Multivariate methods allow the combination of variables into a simplified output that may be interpreted in the context of the dataset as a whole and even in comparison to other datasets.

Two different techniques were employed. The first was classification by cluster analysis in which samples were grouped according to their similarity in solute concentrations, and the second was ordination. Both the classification and the ordination were performed using the statistical package SPSS for Windows, Version 11.0 (2001).

Cluster analysis is a general description for a large number of techniques that group samples based on the similarities identified from the variables measured on each sample. Hierarchical clustering is the most common classification technique, particularly in the environmental sciences (Swanson *et al.*, 2001).

Hierarchical cluster analysis was used to group the samples along one axis based on the water chemistry variables: pH, conductivity, chloride, sodium, potassium, silicon, magnesium and calcium. Iron was excluded due to problems with analysis. A hierarchical cluster analysis was run for each sampling period. Groups were defined at a rescaled cluster distance of greater than 2.5, as a satisfactory grouping was obtained in terms of identifying a small number of groups while adequately accounting for heterogeneity in uMkhuze Wetland waters. As April 2000 sampling was only conducted in the Totweni and a limited number of samples were collected in July 2002, these data were not included.

Initially, all water samples were included in a single cluster analysis. However, this only served to highlight that seasonal variation is a dominant influence in the uMkhuze Wetland System, with no clear grouping of wetland waters discernible. This is not surprising considering the widely varying sampling conditions from flooding in December 2000 to drought in July 2002. Therefore, separate cluster analyses were run on each sample set excluding April 2000 and July 2002 due to the small number of samples in these groups. Dendrograms were analysed according to both a hydrological grouping of recharge, discharge and flat water tables, as well as a geographical grouping of Totweni, northern Yengweni, southern Yengweni, floodplain and lake and uMkhuze River samples. In all cases the geographical grouping produced the better separation of sample groups and is presented in section 5.3.1.

Drawbacks of hierarchical cluster analysis are that the variation between samples is projected onto a two dimensional plane, which may under-represent the interaction between samples based on all variables, and outliers may not be detected within the analysis (Johnson and Wichern, 1992). In addition, no internal audit procedures are in place to ascertain the accuracy of group assignment, and therefore results should be carefully considered (Davis, 1986). An ordination technique will augment a cluster analysis, as the number of planes onto which the sample groupings are projected is only restricted by the number of variables. Furthermore, not every resulting plane is generally required in the analysis to account for most variation within a dataset, thereby simplifying the output.

Factor analysis was chosen as an ordination method, with an extraction method of principal components. Values for all of the variables were standardized to a mean of 0 and standard deviation of 1.

The number of orthogonal principal components or factors produced is equal to the number of variables, although the independent components cannot be directly described by inspection of the data (Suk and Lee, 1999). Each successive component or factor accounts for as much of the residual variance in the dataset as possible, the proportion of which is described by an eigenvalue (Johnson and Wichern, 1992). Each sample is then projected onto the principal axes or components, and principal component scores for each axis are derived from these projections locating the samples in  $m$ -dimensional space (Davis, 1986). The component scores of each variable provide an indication of the contribution of that variable to the variance in the data, and to each dimension of the ordination. Each group (and any outliers) can therefore generally be described in terms of their water chemistry. The component scores for each axis may then be plotted relative to each other to gain a two or three-dimensional depiction of the similarity between samples. The factor loadings attributed to each variable, when plotted on the same graph, give an indication of the contribution of the variables to each of the principal axes and therefore the relative importance of each variable to the sample groups (Suk and Lee, 1999). In this way, sample groups identified by cluster analysis were compared to the ordination sample groups, and a reasonable picture of the dataset based on chemical composition was derived. The differences in chemical composition between groups were then attributed to certain variables based on the position of the variable factor loadings. Once distinct, relatively homogeneous groups were identified, the chemical evolution of each separate water chemistry group was considered using bivariate regression, with chloride as a concentration tracer.

#### **5.2.3.2. Tracing chemical evolution in the uMkhuze Wetland System**

As indicated in the previous chapter, it seems that the groundwater chemistry in the uMkhuze Wetland System is influenced by a concentration mechanism. In order to both verify and track this mechanism, solutes were plotted relative to a concentration tracer that is conserved in solution over a large concentration range. Either chloride or sodium is generally employed as a concentration tracer, and in some cases salinity or the concentration of total dissolved salts (TDS). Due to the conservative nature of these solutes or measures of total solute concentrations, they are reliable indicators of hydrologic processes (Dahm *et al.*, 1998; Eugster and Jones, 1979; Logan and Rudolph, 1997; Love *et al.*, 1993; Mandel and Shifftan, 1981; Weber, 2001). Many studies have taken advantage of these groundwater tracers, allowing description of flow paths and groundwater history based on some knowledge of hydrogeological conditions (Barbiéro *et al.*, 2002; De Mars and Garritsen, 1997; Genereux, 2004; Genereux *et al.*, 2002; Katz *et al.*, 1995; Logan *et al.*, 1999;

Love *et al.*, 1993; Salama *et al.*, 1993; Schwartz *et al.*, 1981; Stallard and Edmond, 1983; Szikszay *et al.*, 1981; Wallick, 1981).

Although the compounds of sodium have high saturation limits, the singly charged cation is consumed by cation exchange reactions such as substitution into clay mineral lattices, or purely by adsorption onto negatively charged clay surfaces (Matthess, 1982). The usefulness of chloride as a concentration tracer is limited only by the saturation solubilities of its compounds, as chloride is largely unaffected by other geochemical reactions (Love *et al.*, 1993). However, there are no perfect concentration tracers as a proportion of each solute is lost during a concentration process. Sodium is often useful in continental locations where chloride concentrations are low, such as in the Okavango Delta, Botswana and in the Pantanal of Mato Grosso, Brazil (Barbiéro *et al.*, 2002; McCarthy and Ellery, 1995). Furthermore, natural systems undergoing concentration processes cannot be isolated from their environments such that additions of these tracers are excluded. In coastal regions where chloride concentrations are higher, it is the better conserved element, although chloride additions by seawater intrusion or flow, as well as by windblown material of marine origin may reduce its usefulness.

Eugster and Jones (1979) have investigated behaviour of solutes under a concentration process in closed basins using a concentration tracer. Trends found in the uMkhuze Wetland System will be compared to those described by Eugster and Jones (1979) within closed basin brines and other appropriate work. Plots of concentration tracer versus conserved solute were plotted on a log scale. Samples were grouped by their distribution in the study area as presented in Figure 5.3.1. The data were interpreted based on the assumption that all inputs had the same solute: chloride (conserved solute) ratio at the beginning of the concentration process. It was further assumed that the starting solute concentrations were low. Based on observations in the uMkhuze Wetland System through the dry season and times of flood, it was assumed that the predominant input to the Totweni drainage system is rainfall and rainfall-derived groundwater, while the Yengweni and more frequently the floodplain region is influenced to a greater extent by uMkhuze River water.

Lake samples were also considered separately with uMkhuze River water as the lakes are expected to exhibit uMkhuze River water evolution, particularly on the Yengweni and the floodplain. The northern Yengweni sample Yg B1 taken in September was ignored as an outlier in this analysis, due to its chloride concentration of 4164 ppm, which is almost a factor of three greater than the next most concentrated sample of its group.

### 5.2.3.3. Investigating mineral saturation

In order to address mineral saturation in the uMkhuze Wetland System, activities were calculated from the measured molar concentrations using activity coefficients. The Davies equation, derived from the Debye-Hückel limiting law, was used to calculate activity coefficients, due to its recommended use in solutions with ionic strengths up to 0.5 accounting for the more concentrated water samples of the uMkhuze Wetland System (Stumm and Morgan, 1981):

$$\text{Log } \gamma_A = -Az^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \quad \text{where } A = 1.82 \times 10^{-6} (\epsilon T)^{-1.5} = 0.509 \text{ at } 25 \text{ }^\circ\text{C}$$

$\epsilon$  = dielectric constant

$z$  = charge on ion

Operational solubility products ( $K'_{sp}$ ) were calculated for each sample according to its ionic strength, as illustrated for halite below:



$$K_{sp} = \{ \text{Na}^+ \} \{ \text{Cl}^- \}$$

$$= \gamma_{\text{Na}^+} [\text{Na}^+] \gamma_{\text{Cl}^-} [\text{Cl}^-]$$

$$\log K_{sp} = \log \gamma_{\text{Na}^+} + \log \gamma_{\text{Cl}^-} + \log [\text{Na}^+] + \log [\text{Cl}^-] = 1.54$$

$$\log [\text{Na}^+] + \log [\text{Cl}^-] = 1.54 + 2A \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) = \log K'_{sp}$$

Where  $\{x\}$  denotes activities,  $\gamma$  activity constants and  $[x]$  molar concentrations.

Saturation indices (SI) were calculated by the following equation:

$$\log \left( \frac{\text{IAP}}{K'_{sp}} \right) = \text{SI}$$

IAP is the ion activity product to be calculated for each sample, although in this case molar concentrations of the participating ions were used to calculate the IAP, as operational solubility products for each mineral were substituted for the standard  $K_{sp}$  values. If the SI is greater than -0.1 the solution is saturated, and if less than -0.1, it is undersaturated in that particular mineral (Arndt and Richardson, 1993).

Due to the limited data set, the full ionic strength could not be calculated. Therefore, this investigation of mineral saturation should be viewed as a first approximation. Furthermore, ion pairings such as  $\text{CaCl}^+$  in solution that also reduce the free ion concentrations will be ignored.

Mineral saturation was calculated for all water chemistry data regarding the minerals halite ( $\text{NaCl}$ ), quartz and amorphous silica. The July 2002 water samples were also analysed for total alkalinity and sulfate. Possible saturation of calcite, gypsum and trona were also considered. Table 5.2.2 presents the  $\log K_{sp}$  values employed.

**Table 5.2.2** Equilibrium solubility products for selected minerals

Mineral	Formula	Log $K_{sp}$	Reference
Halite	$\text{NaCl}$	1.54	(Domenico and Schwartz, 1990)
Quartz	$\text{SiO}_2$	-3.7	(Stumm and Morgan, 1981)
Amorphous silica	$\text{SiO}_2$	-2.7	(Stumm and Morgan, 1981)
Calcite	$\text{CaCO}_3$	-8.22	(Stumm and Morgan, 1981)
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-4.60	(Stumm and Morgan, 1981)
Trona	$\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$	-0.24	(Doner and Lynn, 1977)

It must be noted that a simple thermodynamic approach, using solubility products to predict mineral phases in solution, has limited usefulness. Literature values for equilibrium constants and solubility products are generally reported for standard conditions ( $25^\circ\text{C}$  and 1 atmosphere) at an initial ionic strength of 0 (a condition of infinite dilution), although values do exist for seawater in some cases (e.g. aragonite and calcite) (Stumm and Morgan, 1981). In addition, these thermodynamic properties are experimentally determined in a single component system for a pure compound. Naturally-occurring compounds are seldom pure and often poorly crystalline (Langmuir, 1997). As such, interactions between species such as ionic pairs that reduce the free ion concentration, co-precipitation with a saturated mineral phase, and inhibition of precipitation due to a shared ion between two compounds of which the least soluble precipitates, are unaccounted for in this simple model.

Preliminary equilibrium water chemistry modeling was conducted on the July 2002 data set using Visual MINTEQ. Visual MINTEQ is available as freeware on the internet, and is based on the

Fortran-formulated MINTEQA2 developed by the US Environmental Protection Agency (Gustaffsson, 2003). The programme and its predecessors have been widely used in the field of geochemistry and have an extensive thermodynamic database (Domenico and Schwartz, 1990). Although equilibrium modeling does correct some shortcomings of the simple thermodynamic approach, there are limitations in its application in the natural environment. These are discussed in Stumm and Morgan (1981) and Langmuir (1997). Dilute source waters of each group were subjected to a concentration process within the model, concentrating the waters to the maximum chloride value in each water chemistry group. Preliminary water chemistry modeling indicated a large under-estimation of anions within the analyses, which is probably largely due to carbon dioxide degassing during removal of groundwater samples, as well as storage and transport to the laboratory, as noted by Palandri and Reed (2001). Other solute concentrations roughly mimicked their 'real' counterparts, while calcium concentrations were vastly over-estimated, supporting the above suggestion of CO<sub>2</sub> degassing. Simply accounting for the lack of anion charge with speciated carbon dioxide for the pH of the water sample produced surprisingly high bicarbonate values. It is expected that organic acid anions play a larger role in the alkalinity of uMkhuze Wetland System water than previously thought. Additional analyses should include acetate as an analyte, as Palandri and Reed (2001) discovered that acetate is generally the most important organic anion, although the range of organic anions in the uMkhuze Wetland System should be assessed first. Furthermore, aluminium was not included in the cation analysis. Therefore, water chemistry modeling will not be presented, and calculation of mineral saturation by a simple calculation will suffice, although it is expected that calcite saturation will be underestimated. Further work in the uMkhuze Wetland System was planned to incorporate water chemistry modeling as the next step in understanding chemical transformations in the system (Humphries, 2007).

### **5.3. Results**

#### **5.3.1. Variation in water chemistry in the study area**

The intention of this section is to relate processes identified in the hydrology chapter (Chapter 4), to variation in chemical composition of surface and groundwater.

##### **5.3.1.1. Classification**

###### **July 2000**

Classification of the July 2000 samples resulted in Groups 1 – 3 being distinguished from the rest of the samples at a rescaled cluster distance of approximately 7.5 (Appendix C). These samples were

generally more similar to each other than the remaining samples within Groups 4 – 8, which were mainly differentiated at rescaled cluster distances of greater than 7.5. Groups 6 – 8 were most different from the rest of the samples with rescaled cluster distances of 10 and more, as well as from each other, being grouped singly or in pairs.

Group 1 comprised surface water samples throughout the study area as well as some groundwater samples from the Totweni and northern Yengweni margins. Most of the groundwater samples in Group 2 of the classification were from the floodplain margin, which also had some samples in Group 3 of the classification. The samples from the southern Yengweni were mostly from Group 4. Groups 5 – 8 predominantly contain floodplain samples, with a single sample from the southern Yengweni in Group 7, and three Totweni samples in Groups 6 and 7.

Overall, surface waters throughout the study area were similar to each other, while samples from the Totweni and northern Yengweni margins were similar in some cases to surface water and in other cases formed a distinct group. Floodplain margin samples were distinct, and so were samples from the margin of southern Yengweni.

**Table 5.3.1** Classification groups of the July 2000 samples by sampling region

Sampling Region	Classification Group									Total
	1	2	3	4	5	6	7	8	9	
uMkhuze River	1									1
Yengweni Lake	4									4
Totweni Surface Water	4									4
Floodplain Lake	3	1								4
Northern Yengweni Margin	11		6							17
Totweni Margin	3	1	8			1	2			15
Floodplain Margin	2	9		1	5			1	2	20
Southern Yengweni Margin	2	1	1	5			1		1	11
<b>Total</b>	30	12	15	6	5	1	3	1	3	76

### September 2000

Classification of samples taken in September 2000 produced eleven groups, of which Groups 1 – 5 were separated from the rest of the samples at a rescaled cluster distance of approximately 5, being more closely related to each other than the samples of Groups 6 – 11. Group 6 was most closely related to the samples of Groups 1 – 5 being differentiated at a rescaled distance of 10. All other groups were distinguished at rescaled cluster distances of greater than 15, illustrating their dissimilarity with the samples of Groups 1 – 6. Furthermore, Groups 7 – 11 were generally differentiated from each other at rescaled distances greater than 15, and were therefore less internally coherent than those samples in Groups 1 – 6. Group 1 accounted for most of the Totweni and northern Yengweni samples, while the closely associated Group 2 was mainly composed of floodplain and lake samples (Table 5.3.2). The sample in Group 3 (northern Yengweni) was intermediate between Groups 1 and 2, and Groups 4 and 5. Groups 4 and 6 both contained mostly lake samples, with predominantly Yengweni Lake samples in Group 4 and Mpanza Lake samples in Group 6. Groups 7 – 11 contained mostly southern Yengweni and floodplain samples, with the most dissimilar samples being those taken from upper transect positions, which occurred in the Groups 10 and 11.

**Table 5.3.2** Classification groups of the September 2000 samples by sampling region

Sampling Region	Classification Group											Total
	1	2	3	4	5	6	7	8	9	10	11	
Totweni Margin	14	1			1	3		1	1			21
Northern Yengweni Margin	10		1						1		1	13
Floodplain Margin		5			3		1	1		2		12
Floodplain Lake		1		1		1						3
Yengweni Lake		1		4								5
uMkhuze River					1							1
Totweni Surface Water	1	1				3						5
Southern Yengweni Margin		1			8					9		18
<b>Total</b>	25	10	1	5	13	7	1	2	2	11	1	78

### December 2000

Classification of water samples collected in December 2000 differed from the previous sample periods. Group 1 comprised samples from throughout the study area (Table 5.3.3). Groups 2 – 4 mostly constituted upper transect samples of the Totweni, southern Yengweni and floodplain regions. These areas were possibly not affected by flooding to the same degree as other sampling locations. Totw B was once again differentiated from the other Totweni samples and constituted Group 2. Group 5 was the most dissimilar to the other Groups and consisted of one Mpanza (Totweni) Lake sample.

**Table 5.3.3** Classification groups of the December 2000 samples by sampling region

Sampling Region	Classification Group					Total
	1	2	3	4	5	
uMkhuze River	1					1
Yengweni Lake	4					4
Totweni Surface Water	3					3
Northern Yengweni Margin	5					5
Totweni Margin	14	4	1			19
Southern Yengweni Margin	8			2		10
Floodplain Margin	1			2		3
Floodplain Lake	2				1	3
<b>Total</b>	<b>38</b>	<b>4</b>	<b>1</b>	<b>4</b>	<b>1</b>	<b>49</b>

#### 5.3.1.2. Grouping of uMkhuze Wetland System waters based on the classification analysis

The results of the classification of each sample set revealed that the Totweni margin and northern Yengweni groundwaters had similar chemical compositions. The groups other than those of the Totweni and northern Yengweni samples were less well defined, although the floodplain samples were mostly associated with one another. For both the floodplain and southern Yengweni, samples were differentiated from each other at higher rescaled distances than those of the Totweni and

northern Yengweni. Surface water samples were not often included in the same groups as samples from their margins. Samples from the margin of the Totweni were more often grouped separately from Totweni surface samples. The southern Yengweni and floodplain lake samples were more often grouped in close proximity to their local groundwater samples, although in different groups. uMkhuze River samples were most closely associated to floodplain samples in July, but with the southern Yengweni group in September and December.

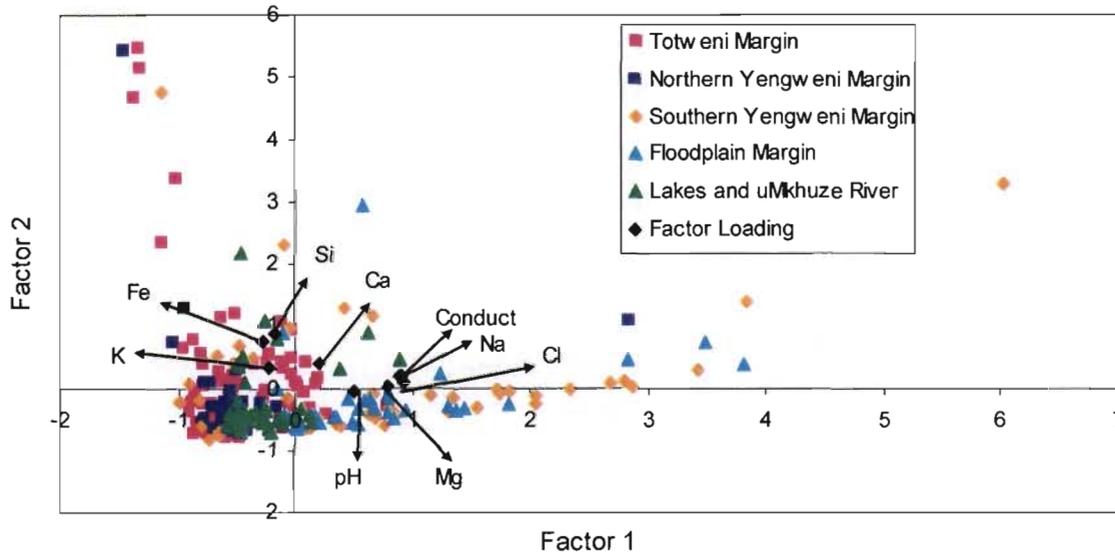
### 5.3.1.3. Ordination

The results of principal components analysis of the full sample set produced only three factors with eigenvalues greater than one, and these three factors were included in the analysis (Table 5.3.4). The factors combined accounted for 77 % of the variance in the data set. The factor scores are presented in Appendix D, and the ordination plot of Factor 1 and Factor 2 is presented in Figure 5.3.1.

**Table 5.3.4** Factors produced by factor analysis of the water samples from April, July, September and December 2000, and July 2002

Component/ Factor	Eigenvalue	Variance/ %	Cumulative Variance/ %
1	3.32	41.5	41.5
2	1.70	21.2	62.7
3	1.14	14.2	76.9

Totweni and northern Yengweni samples including their lake counterparts typically had negative Factor 1 scores and low Factor 2 scores (Figure 5.3.1). The majority of southern Yengweni and floodplain samples had positive Factor 1 scores. Samples with positive Factor 1 scores had high conductivity, chloride, sodium and magnesium concentrations, as well as high pH values. The mean values for chloride, sodium, magnesium and conductivity for samples from the southern Yengweni margin exceeded those of the Totweni and northern Yengweni margins by factors of 3.0, 4.5, 2.8 and 3.1 respectively. Similarly, floodplain values exceeded those of the Totweni and northern Yengweni margin by the factors 2.4, 2.7, 2.5 and 2 for the same elements respectively. Southern Yengweni and floodplain samples in the positive region of Factor 1 showed the influence of higher pH values, with an average of 7.5. Totweni and northern Yengweni samples were located in the negative Factor 1 region that indicated lower pH values, with an average of approximately 6.5. Totweni and northern Yengweni samples had low pH values with a minimum value of 3.7.



**Figure 5.3.1** Ordination plot of full sample set, displaying factor loadings for variables included in the analysis

Calcium and potassium generally had low Factor 1 scores. Potassium values were greater in the Totweni and northern Yengweni, with an average of 9.3 ppm and a maximum of 32 ppm, while the southern Yengweni and floodplain averages were 5.2 and 4.9 ppm respectively. Although the uMkhuze River calcium average of 83 ppm approximated that of the floodplain samples at 85 ppm, the uMkhuze River samples were grouped with the Totweni and northern Yengweni samples which had an average calcium concentration of 44 ppm.

Iron and silicon had low negative Factor 1 scores and positive Factor 2 scores. Groundwater in the Totweni and northern Yengweni typically had high concentrations of iron and silicon. The outlier at high positive Factor 1 and 2 scores was a southern Yengweni sample taken in July 2002, and had unusually high chloride, sodium and magnesium concentrations that distinguished it from the remaining samples.

The Factor 3 plots are not presented here as they display similar characteristics to the Factor 2 plots described above, but provide greater differentiation of samples along Factor 3. This differentiation is attributed to potassium and calcium in the positive region, which distinguishes Totweni (Totw B and Totw samples taken in July 2002 under severe drought conditions) and surface water samples, as well as a few southern Yengweni (taken in July 2002) and floodplain samples.

### 5.3.2. Variation in chemistry of water sources

Rainwater sampled in the uMkhuze Wetland System had a pH of approximately 5.46 (Table 5.3.5), which is similar to that of groundwater in the Totweni and northern Yengweni. All other solute concentrations fell below the minimum groundwater concentrations by the factors reported in Table 5.3.5.

**Table 5.3.5** Chemical composition of rainwater from the uMkhuze Wetland System

Analyte/ units	Value	Ratio of groundwater minimum concentrations to rainwater concentrations
<b>pH</b>	5.46	
<b>Conductivity/ mS/cm</b>	0.065	1.8
<b>Chloride/ ppm</b>	3.66	3.8
<b>Sodium/ ppm</b>	0.80	22
<b>Potassium/ ppm</b>	0.60	2.0
<b>Silicon/ ppm</b>	0.00	-
<b>Iron/ ppm</b>	0.00	-
<b>Magnesium/ ppm</b>	0.00	-
<b>Calcium/ ppm</b>	0.00	-

Water chemistry data for the uMkhuze River is presented in Table 5.3.6. The pH was consistently neutral to slightly alkaline which was typical of the southern Yengweni and floodplain samples. The conductivity ranged from 0.612 mS/cm in the December floodwaters to 1.456 mS/cm in July and September 2000, which indicated that in terms of conductivity values uMkhuze River water was similar to dilute groundwater samples in the wetland system. All chloride and sodium values were less than 350 ppm, again comparable to groundwater samples with low sodium and chloride concentrations. Potassium ranged from 4.2 to 6.3 ppm, which was about five times less concentrated than the groundwater maximum. Only two samples exceeded 25 ppm silicon. The iron values were low at less than 0.5 ppm, which fell into the lowest class of groundwater iron values. All magnesium concentrations, except July 2002, were greater than calcium values. Again, uMkhuze River water was classified with the most dilute groundwater samples in terms of both calcium and magnesium concentrations.

**Table 5.3.6** Chemical composition of uMkhuze River water, 2000 – 2003

Analyte/ Units	May 2000	July 2000	August 2000	September 2000	December 2000	July 2002	June 2003
<b>pH</b>	8.06	7.90	7.67	8.35	7.23	7.29	7.66
<b>Conductivity/ mS/cm</b>	0.925	1.354	1.456	1.456	0.612	1.033	1.074
<b>Chloride/ ppm</b>	81	279	235	331	109	65	99
<b>Sodium/ ppm</b>	111.8 (2.53)	182.6 (2.35)	209.3 (1.58)	214.4 (1.93)	70.51 (0.61)	182.2	294.5
<b>Potassium/ ppm</b>	4.15 (0.03)	4.78 (0.07)	5.34 (0.05)	6.32 (0.07)	5.97 (0.02)	5.80	7.37
<b>Silicon/ ppm</b>	26.4 (2.14)	22.8 (1.01)	22.4 (1.63)	19.31 (1.86)	13.37 (0.47)	56.5 (0.66)	3.19
<b>Iron/ ppm</b>	0.43 (0.01)	0.42 (0.01)	0.21 (0.03)	0.22 (0.03)	0.21 (0.02)	0.065 (0.01)	0.16
<b>Magnesium/ ppm</b>	49.2 (4.43)	68.9 (1.41)	75.9 (3.94)	72.99 (4.75)	28.54 (1.06)	25.0 (0.40)	2.89
<b>Calcium/ ppm</b>	29.3 (2.58)	16.9 (1.72)	38.9 (1.53)	31.7 (2.82)	23.16 (2.10)	42.3 (1.05)	17.9
<b>Total Alkalinity/ ppm</b>						160	184

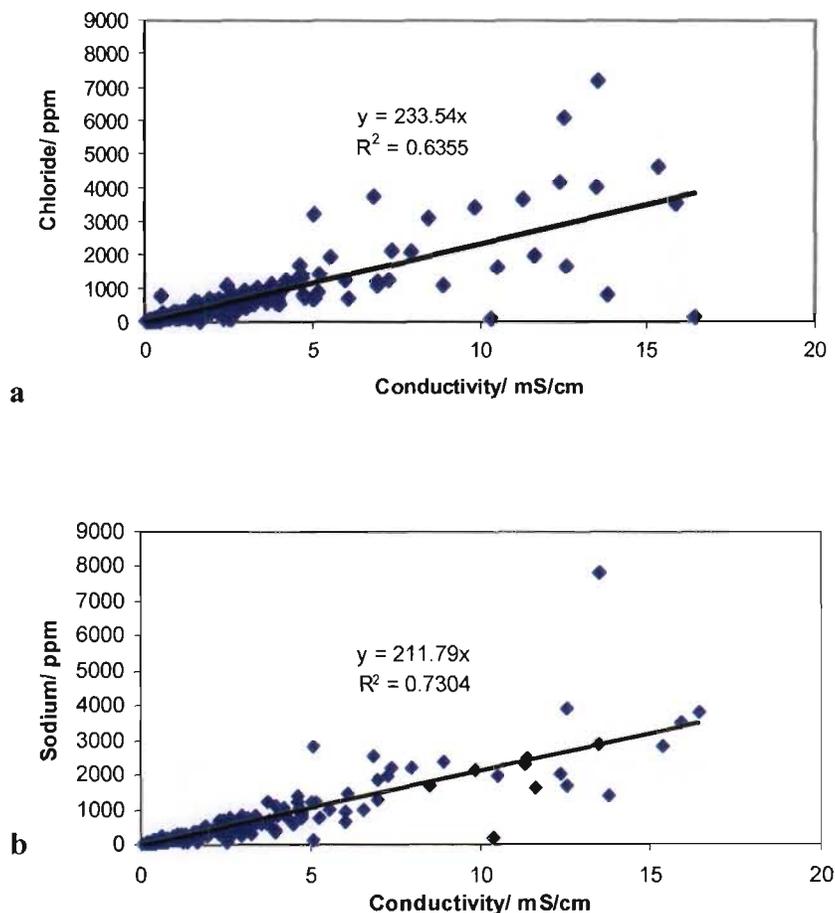
(Standard deviation in brackets)

Generally, rainwater and uMkhuze River water was grouped with the most dilute groundwater samples in the classification. The pH values were the distinguishing variable in assigning rainwater and uMkhuze River water into a geographical grouping. The rainwater pH was similar to the pH of the Totweni and northern Yengweni samples, while the uMkhuze River water had similar pH values to groundwater of the southern Yengweni and floodplain. Rainwater constitutes the most dilute input to the uMkhuze Wetland System.

### 5.3.3. Relationships between solutes in uMkhuze Wetland System waters

As presented in Chapter 4, groundwater electrical conductivity values indicated that a concentration process was modifying the relatively dilute chemical inputs, producing conductivities as high as 16.40 mS/cm from sources with conductivities of less than 1.5 mS/cm. In order to identify a suitable concentration tracer, conductivity was plotted relative to chloride and sodium, which were both well correlated with conductivity, producing  $R^2$  values (and significance) of 0.64 ( $p < 0.05$ ) and 0.73 ( $p < 0.05$ ) respectively (Figure 5.3.2 a and b). Although the  $R^2$  values indicated that the variation in conductivity was more closely related to variation in sodium concentration than in

chloride concentration, the increase in chloride concentration was more closely related to the amount of water lost by evaporation indicated by the increase in conductivity. This was seen from the trendline equation where the slope of the relationship between sodium and chloride, and electrical conductivity was lower for sodium (212) than for chloride (234).

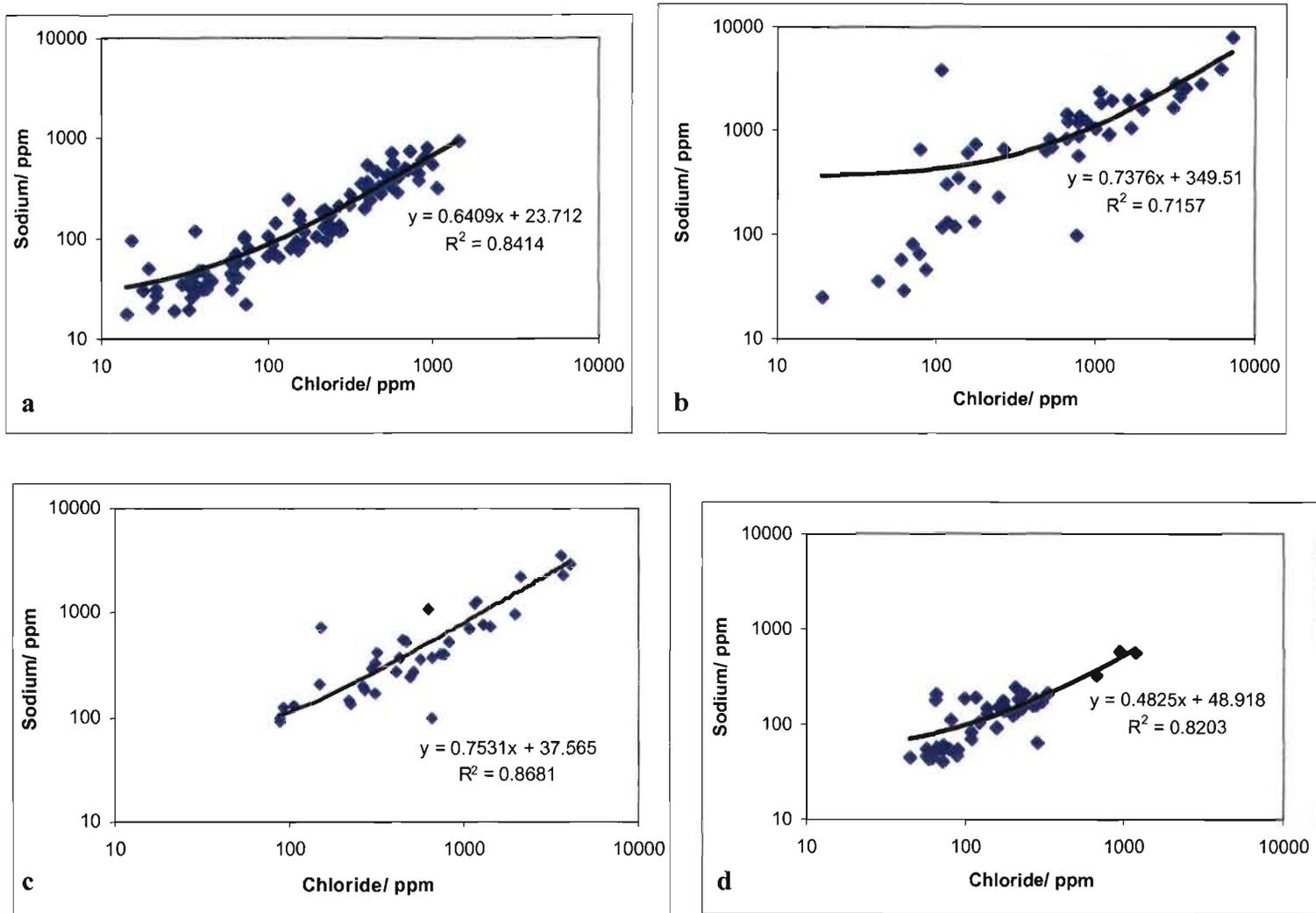


**Figure 5.3.2** The relationship between (a) chloride and conductivity and (b) sodium and conductivity in the uMkhuze Wetland System

### 5.3.3.1. Sodium

Sodium concentrations of all groups increased with chloride concentrations. In comparing sodium to chloride, the sodium values that most closely followed the behaviour of chloride were those of the floodplain samples, which probably indicated that inputs to this region were relatively constant in terms of chloride and sodium concentrations (Figure 5.3.3 a, b, c, and d). The range of

concentrations for both sodium and chloride varies between groups, with Totweni and northern Yengweni samples being in the range 10 – 1000, with the southern Yengweni and floodplain at high values (100 – 10 000) and lake and uMkhuze River samples at intermediate concentrations (100 – 1 000).

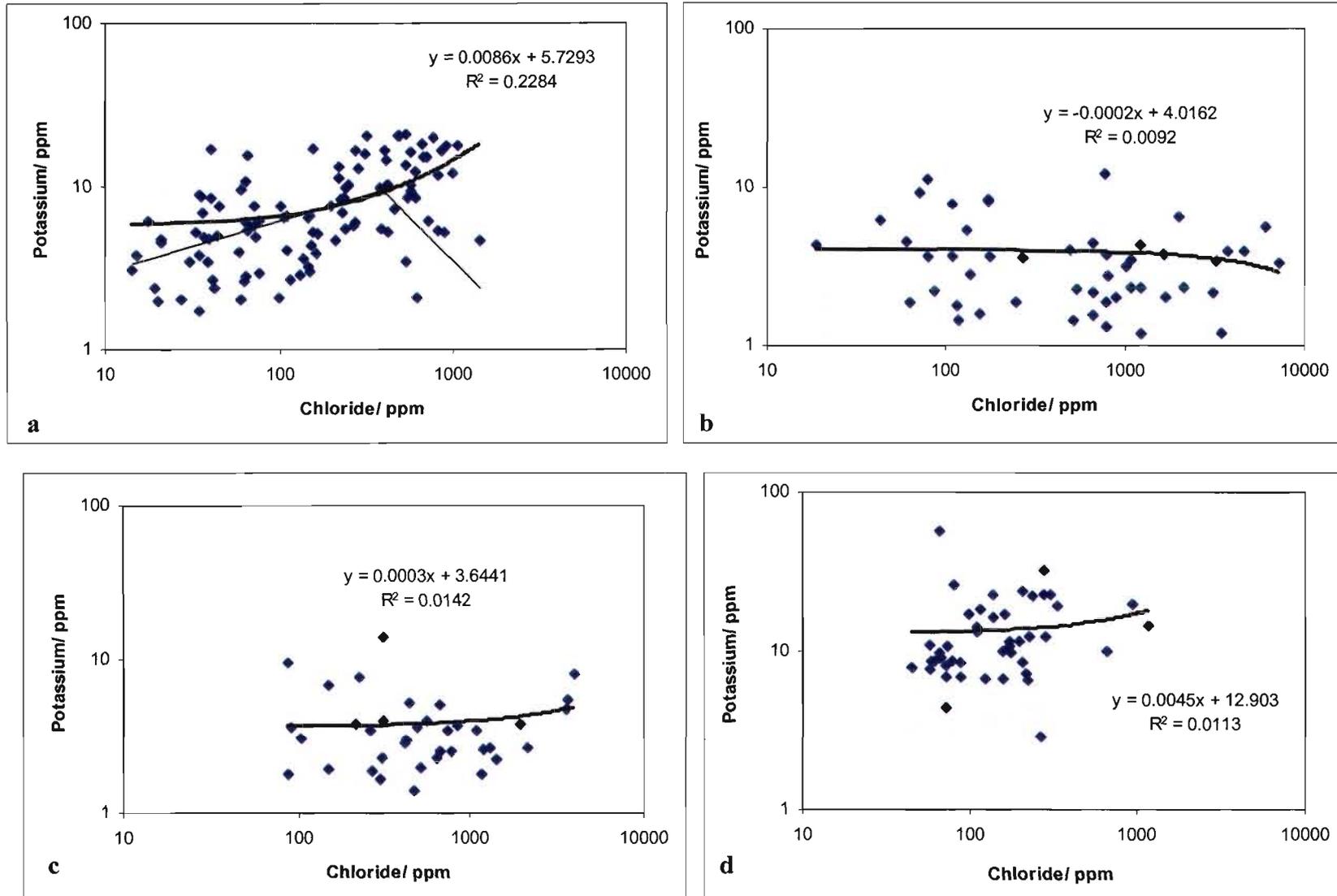


**Figure 5.3.3** The relationship between sodium and chloride concentrations in (a) Totweni and northern Yengweni (b) southern Yengweni (c) floodplain and (d) lake and uMkhuze River

### 5.3.3.2. Potassium

Potassium concentrations in all four groups were poorly correlated to chloride values, with only the Totweni and northern Yengweni samples showing something of a decrease in potassium concentrations with increasing chloride concentrations (Figure 5.3.4 a, b, c and d). This trend may be described in a general way in spite of large variation within the sample group. The point of saturation (point after which a decrease in potassium concentration with increasing chloride concentration is noticeable) in relation to chloride concentration for the Totweni and northern Yengweni samples was approximately 300 ppm. Other points of saturation were less clear, and may be present at approximately 300 ppm for floodplain samples, 250 ppm for the surface water samples and around 150 ppm for the southern Yengweni samples.

It seems that chemical interactions in the southern Yengweni had a greater limiting effect on potassium concentrations. This was shown in the distribution of potassium concentrations, with 72, 83 and 96 % of values greater than 5 ppm in the Totweni and northern Yengweni, the floodplain as well as the lake and uMkhuze River samples respectively, while only 39 % of the southern Yengweni samples exceeded 5 ppm potassium.

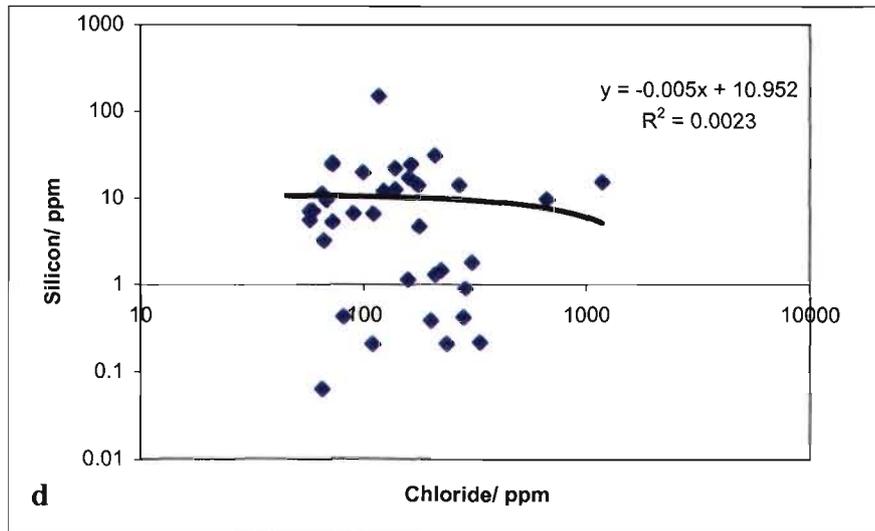
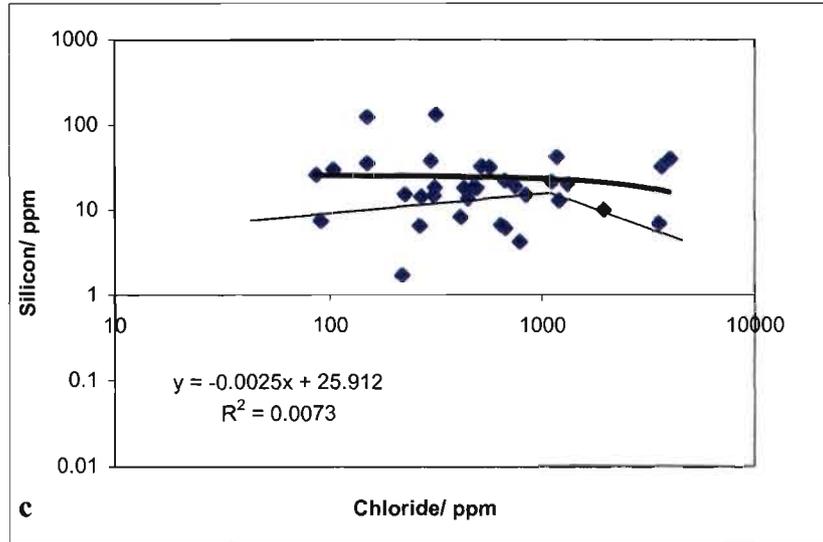
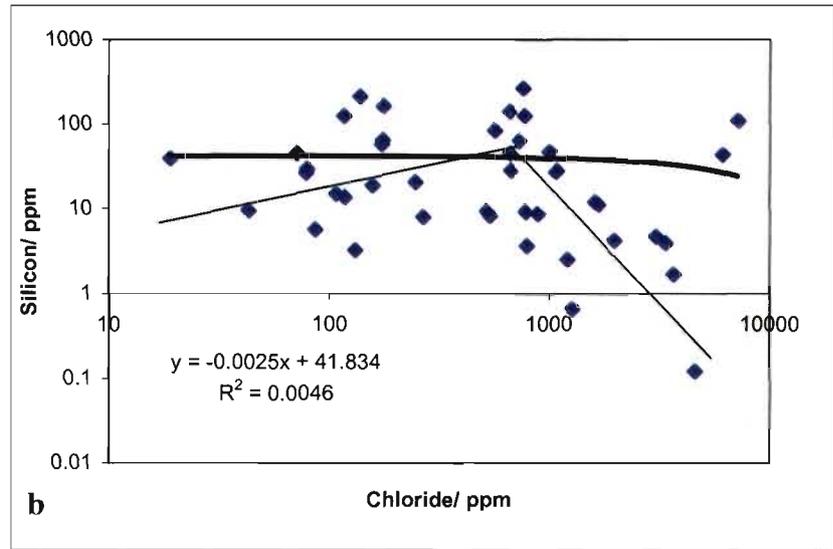
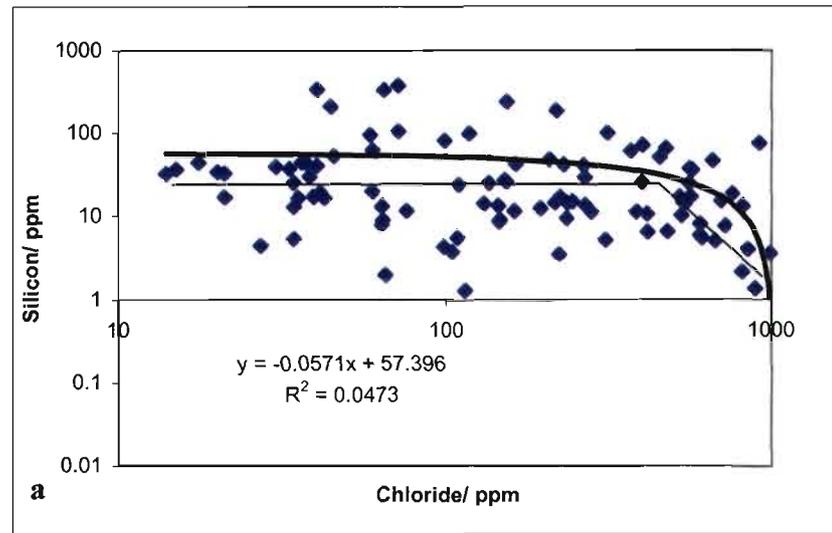


**Figure 5.3.4** The relationship between potassium and chloride concentrations in (a) Totweni and northern Yengweni (b) southern Yengweni (c) floodplain and (d) lake and uMkhuze River

Note: thin trendline in plot (a) depicts the approximate saturation point in potassium concentration

### 5.3.3.3. Silicon

An initial increase in silicon with increasing chloride concentration was followed by a decrease in silicon concentration with increasing chloride values (5.3.5 a, b, c and d). Silicon values were generally restricted to less than 20 ppm at chloride concentrations greater than 1 000 ppm in all regions, with points of saturation in each region at roughly 450 ppm chloride for the Totweni and northern Yengweni samples and 400 ppm for the southern Yengweni region, approximately 300 ppm on the floodplain and possibly 200 ppm for the lake and uMkhuze River samples.

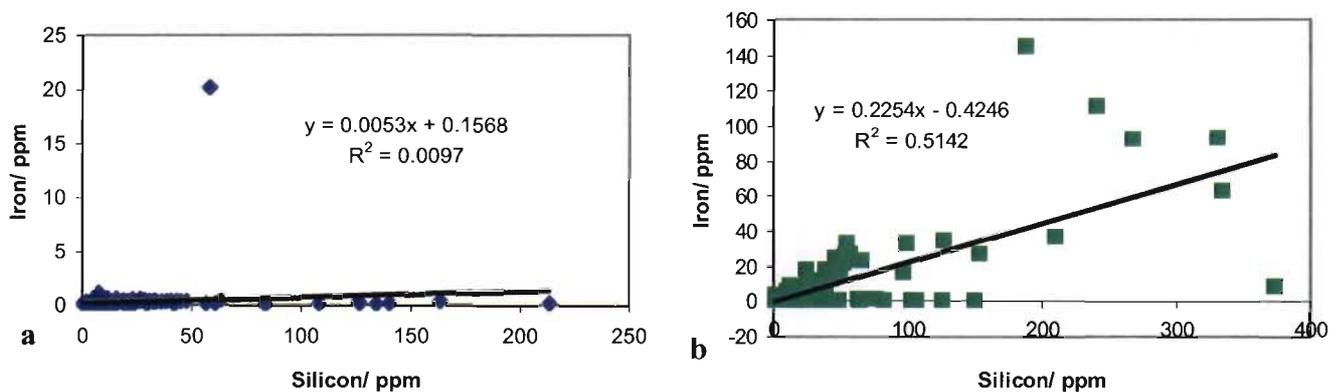


**Figure 5.3.5** The relationship between silicon and chloride concentrations in (a) Totweni and northern Yengweni (b) southern Yengweni (c) floodplain and (d) lake and uMkhuze River  
 Note: thin trendlines in plots (a) – (c) depict the approximate saturation points in silicon concentration

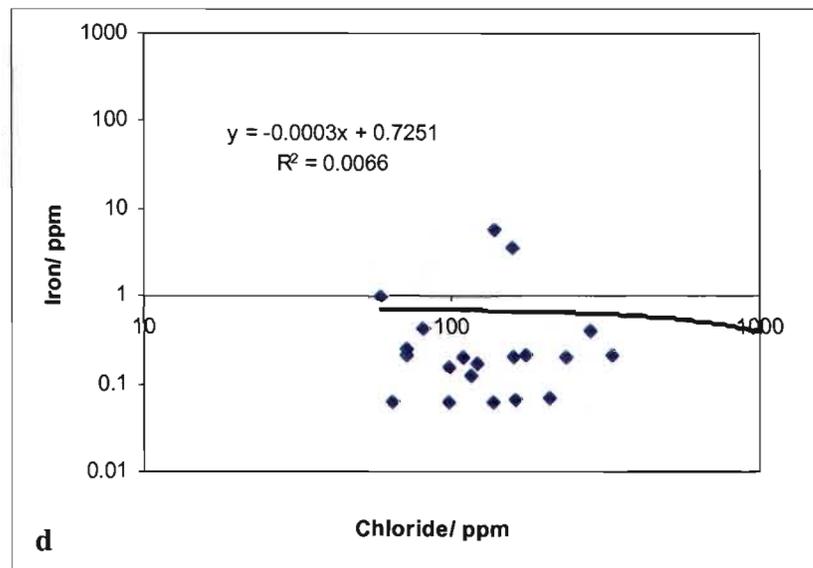
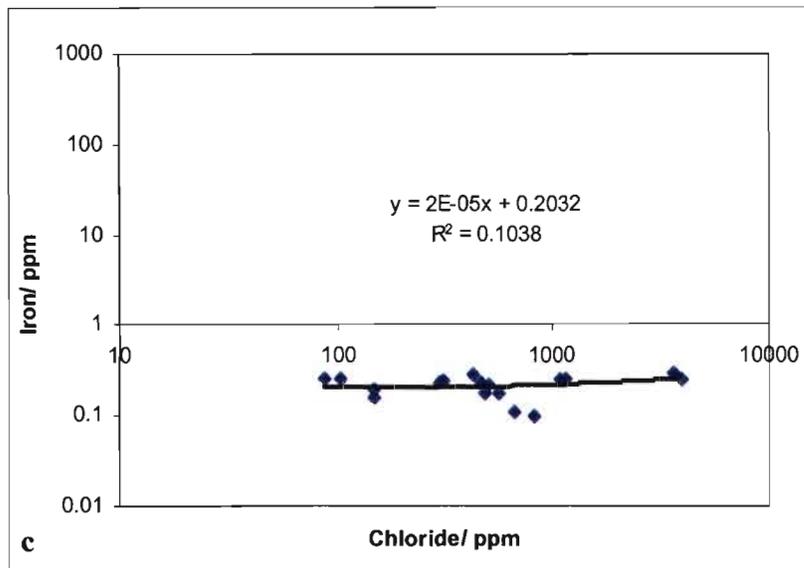
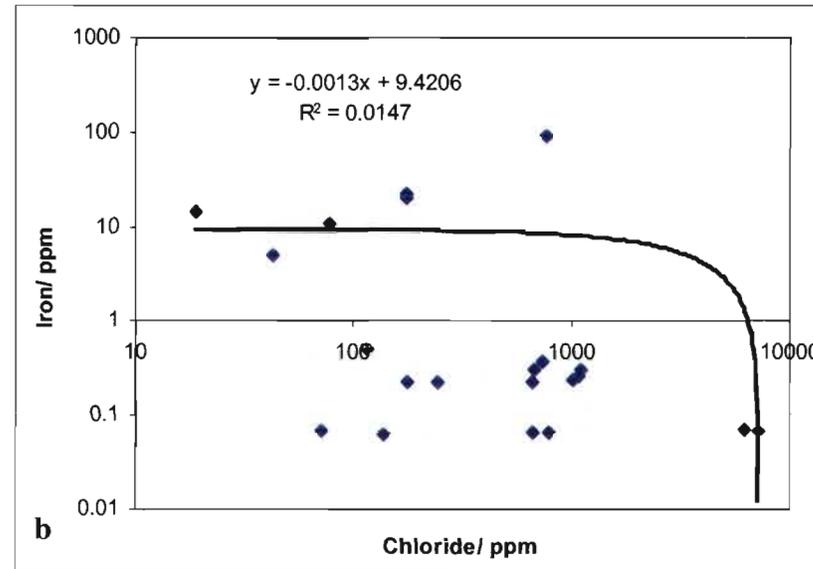
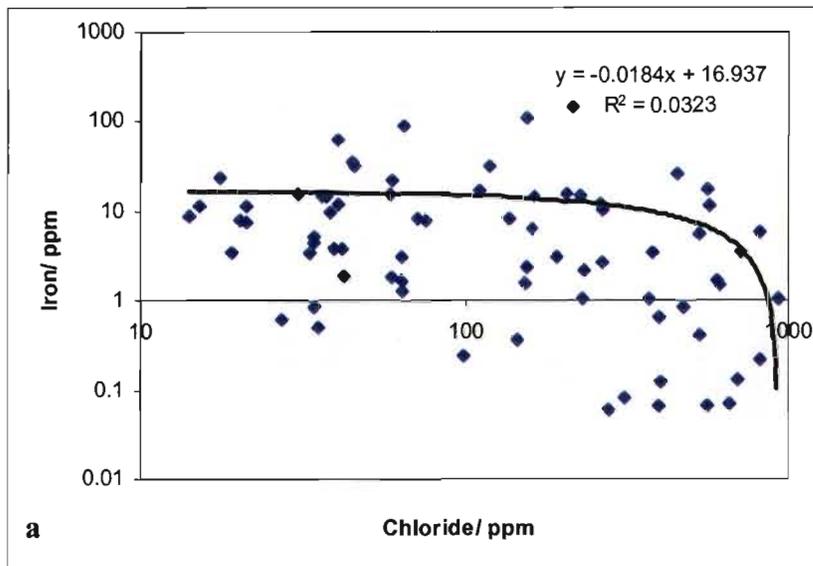
### 5.3.3.4. Iron

A similar relationship between iron and chloride as seen between silicon and chloride was evident on the Totweni and northern Yengweni, with high iron values, those in excess of 5 ppm, generally confined below 300 ppm chloride (Figure 5.3.6 a, b, c and d). On the southern Yengweni and floodplain, iron concentrations less than 1 ppm remained constant over the entire concentration range with only a Yg D and E southern Yengweni series that increased uniformly with chloride. Lake and uMkhuze River samples generally had iron concentrations less than 1 ppm.

In Figure 5.3.7 a it can be seen that there was no relationship between iron and silicon in the southern Yengweni and floodplain regions ( $R^2 = 0.01$ ;  $p < 0.05$ ), with only a Yg E sample taken in September having an iron concentration greater than 2 ppm. Although the Yg D transect midway along the Yengweni Drainage Line was classified with the southern Yengweni samples, in terms of the relationship between silicon and iron it was better grouped with transects Yg A to C of the northern Yengweni. Plots of the relationship between silicon and iron confirmed that iron and silicon are closely associated in the Totweni and northern Yengweni, with a relatively high  $R^2$  value of 0.51 ( $p < 0.05$ ; Figure 5.3.7 b). Those samples with higher iron values (above 5 ppm) were mostly those sampled in April and December 2000 after flooding, as well as those taken during an extended drought in July 2002. Totweni samples taken in July and September 2000 are also well represented in this group. Samples with no or limited concentrations of iron were predominantly northern Yengweni samples taken in July or September 2000.



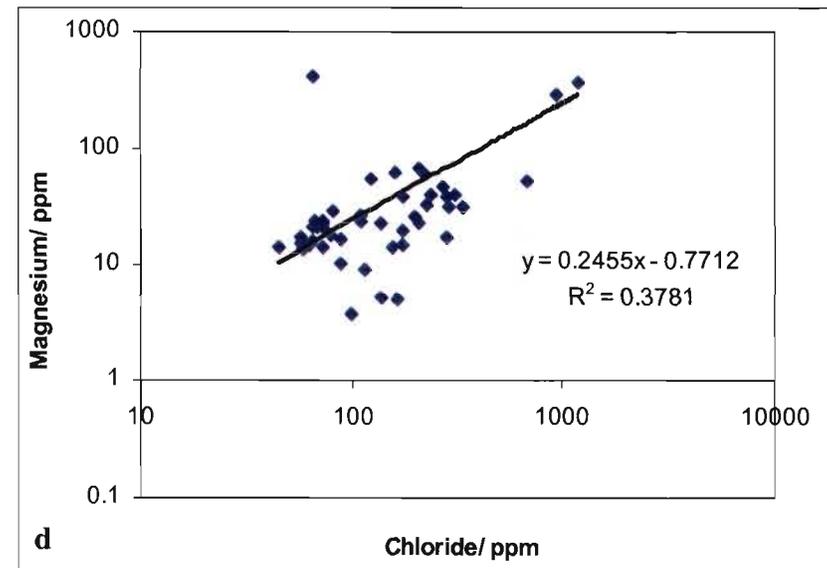
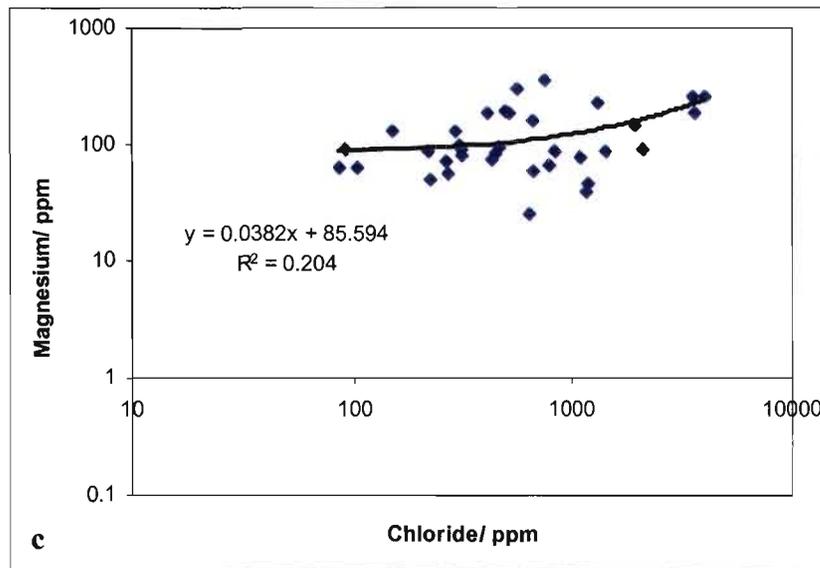
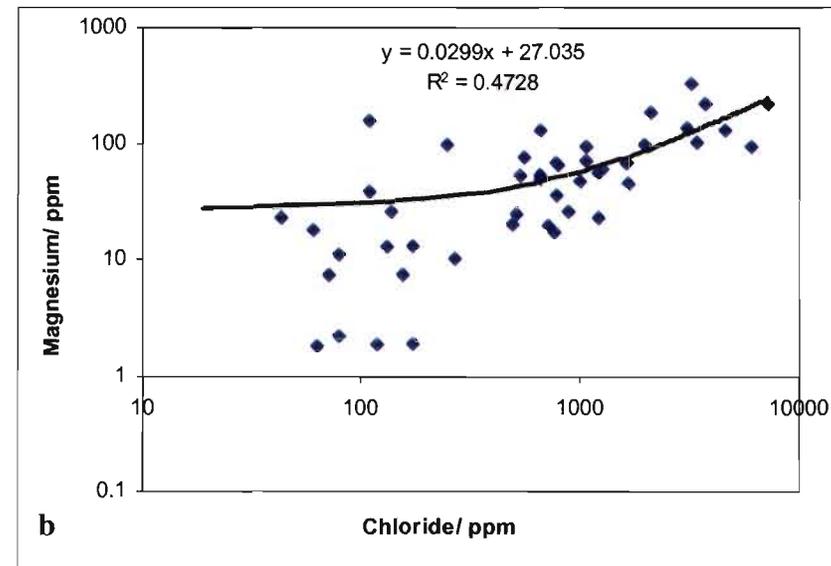
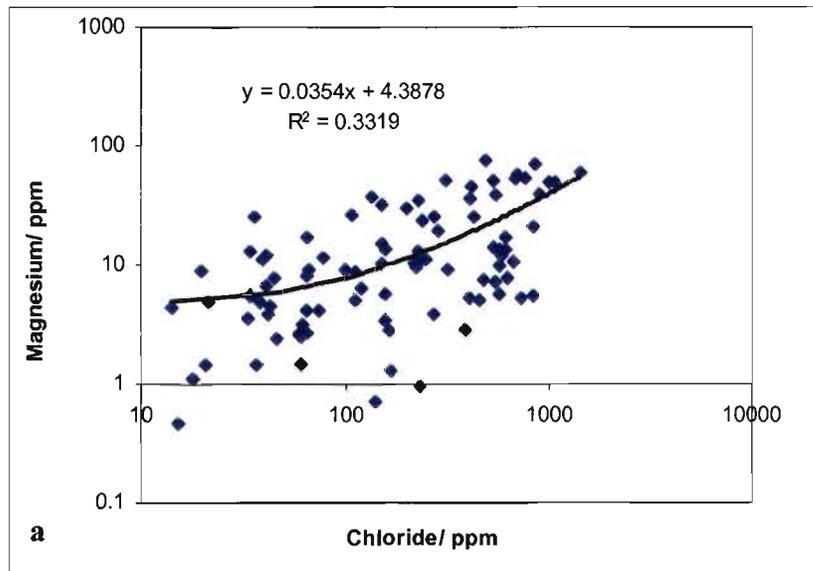
**Figure 5.3.7** The relationship between iron and silicon for (a) southern Yengweni and floodplain samples and (b) Totweni and northern Yengweni (including Yg D) samples



**Figure 5.3.6** The relationship between iron and chloride concentrations in (a) Totweni and northern Yengweni (b) southern Yengweni (c) floodplain and (d) lake and uMkhuze River

### 5.3.3.5. Magnesium

Generally, magnesium increased in concentration as chloride concentrations increased (Figure 5.3.8 a, b, c and d). The best correlation was found in the southern Yengweni group with  $R^2 = 0.47$  ( $p < 0.05$ ). Magnesium concentrations for the lake and uMkhuze River waters were reasonably well correlated with chloride concentrations at an  $R^2$  of 0.38 ( $p < 0.05$ ), while Totweni and northern Yengweni samples as well as the floodplain were slightly less well correlated at  $R^2$  values of 0.33 ( $p < 0.05$ ) and 0.20 ( $p < 0.05$ ) respectively.



**Figure 5.3.8** The relationship between magnesium and chloride concentrations in (a) Totweni and northern Yengweni (b) southern Yengweni (c) floodplain and (d) lake and uMkhuzi River

5.3.3.6. Calcium

Calcium and chloride concentrations were poorly correlated with a maximum  $R^2$  value of 0.14 ( $p < 0.05$ ) for the southern Yengweni samples (Figure 5.3.9 a, b, c and d). The calcium concentrations of the floodplain and southern Yengweni as well as the Totweni and northern Yengweni waters displayed the trend encountered with both potassium and silicon, where there is an initial increase in calcium concentration, but beyond a certain chloride concentration calcium values no longer increased. Such saturation points were 550 ppm for floodplain samples, 200 ppm for surface water samples and approximately 450 ppm for the Totweni and northern Yengweni samples respectively.

Although calcium concentrations in general exceed magnesium concentrations, it is evident from the relationship between the magnesium to calcium ratio and chloride concentration in Figure 5.3.10, that magnesium concentrations decrease faster in some regions than do calcium concentrations, with increasing chloride concentration. This is particularly noticeable for Totweni and northern Yegweni samples and to some extent for southern Yengweni samples.

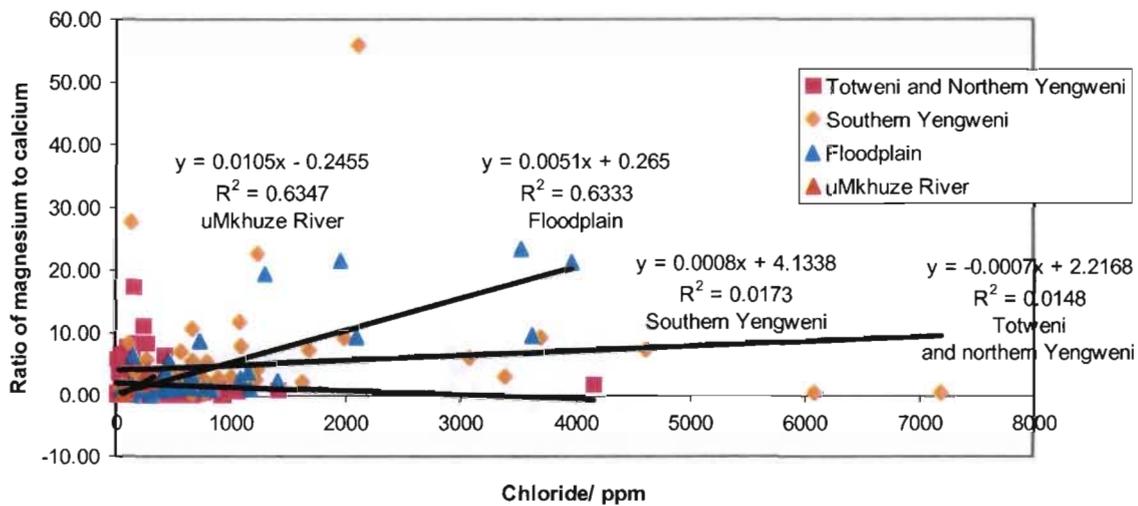
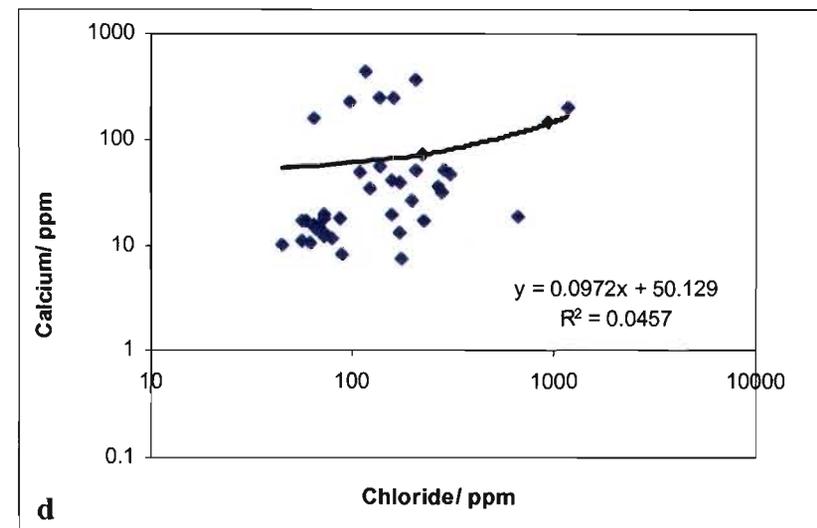
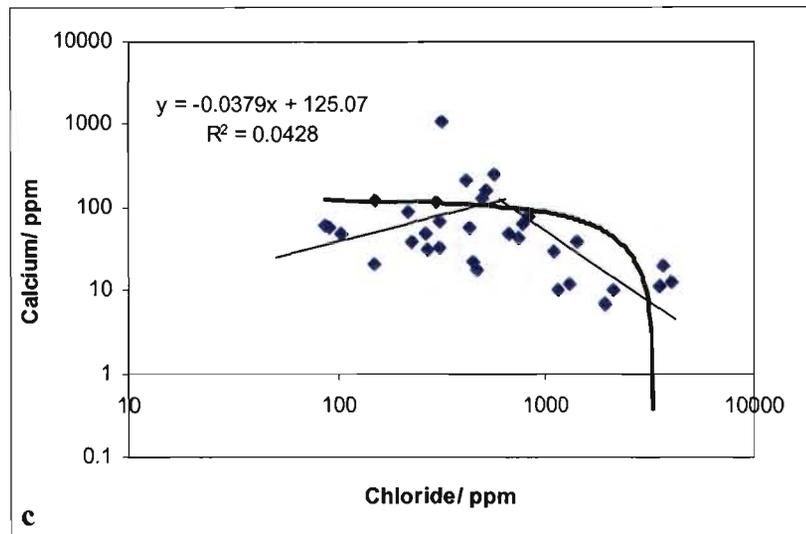
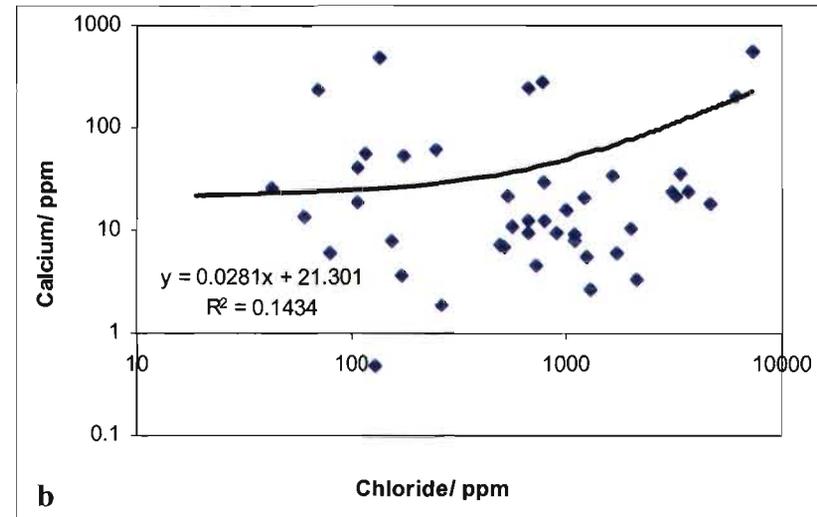
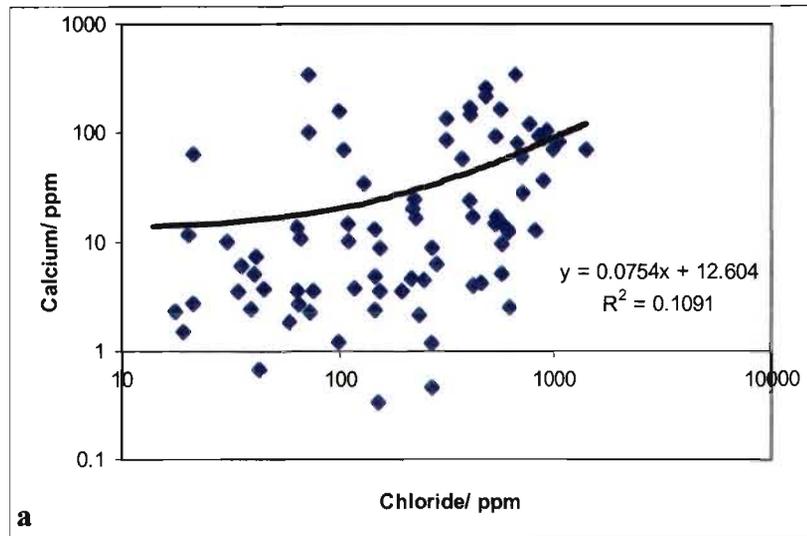


Figure 5.3.10 The relationship between the magnesium to calcium ratio with increasing chloride concentration.



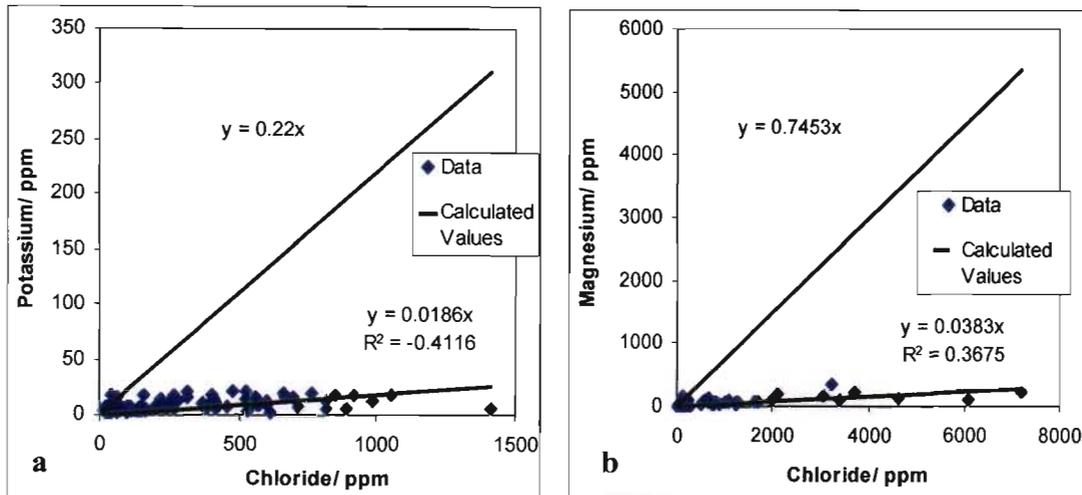
**Figure 5.3.9** The relationship between calcium and chloride concentrations in  
 (a) Totweni and northern Yengweni (b) southern Yengweni (c) floodplain and (d) lake and uMkhuze River  
 Note: thin trendline in plot (c) depicts the approximate saturation point in calcium concentration

### **5.3.3.7. Variation in solutes in relation to chloride concentration in the uMkhuze Wetland System**

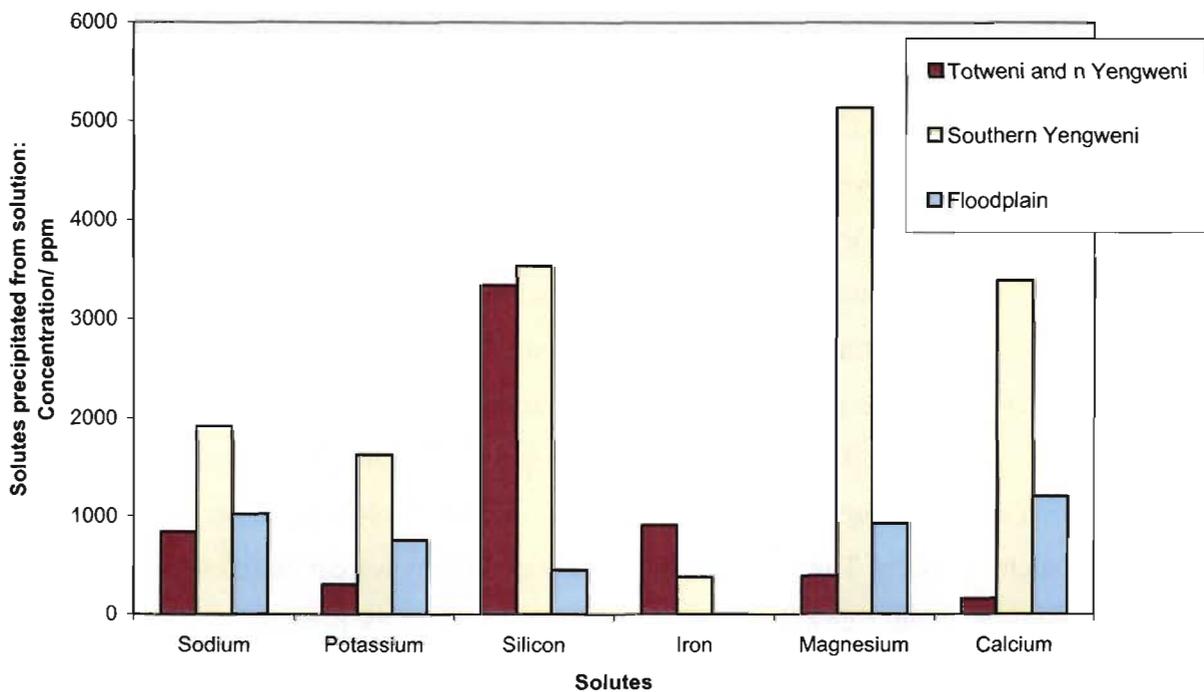
Most solutes showed a positive relationship with chloride at low chloride concentrations. However, as chloride concentration increased, the concentration of many solutes decreased. The point at which solute concentration declined with increasing chloride concentration, was generally not consistent within different areas of the study site, and was generally indistinct. This was probably due to heterogeneity in solute to chloride ratios of the hydrological inputs, as well as the interference of marine chloride additions in this coastal setting. Sodium and magnesium differed from all other elements in that their concentrations increased consistently with increasing chloride concentration.

### **5.3.4. Chemical evolution of groundwater in the uMkhuze Wetland System**

Under an ideal concentration process, solutes progressively concentrate in proportion to the amount of water lost by evaporation until no solvent remains, causing the precipitation of all solutes. If it is assumed that with evaporative water loss the individual ions exert no influence over each other through electrostatic forces or bonds of any kind, being involved in compound formation only, the concentration of solutes should be directly proportional to the amount of solvent evaporated. The position of the ideal concentration line is dependent on the choice of starting point. In each water body, the most dilute sample was selected as representing inputs to the water body on which chemical evolution may act. This method allows comparison of the efficiency of the concentration process for each sample grouping, and is not intended to give absolute values of amounts of solute 'lost' during such a process. The predicted solute concentrations were plotted over the entire concentration range of chloride measured in the study; examples for potassium and magnesium are presented in Figure 5.3.11 a and b. The observed values for both potassium and magnesium are lower than suggested by the predicted concentration with a ratio of solute to chloride of 0.02 for potassium and 0.04 for magnesium, which indicates the precipitation of these solutes in the solid phase as evaporation takes place. Using chloride as the conserved solute it was possible to calculate an amount removed from solution for each solute analysed in the uMkhuze Wetland (Figure 5.3.12).



**Figure 5.3.11** The effect of concentration on (a) potassium in the Totweni and northern Yengweni and (b) magnesium in the southern Yengweni



**Figure 5.3.12** Solutes precipitated from solution during a concentration process according to water chemistry groups in the uMkhuze Wetland System waters, as calculated from the difference between the ideal solute trendlines and observed solute concentrations

Given this conceptual approach it is expected that the group with the largest range of chloride concentration would result in the greatest quantity of chemicals removed from solution. This is indeed the case, with the southern Yengweni having a 7 000 ppm chloride concentration range

which translates to a factor of about 380 between minimum and maximum chloride values (Table 5.4.2). This is equivalent to 1000 litres of water being evaporated to less than 3 litres. It can be seen in Figure 5.4.2 that solute removal is most active in the southern Yengweni, with only the removal of iron being greater in the Totweni and northern Yengweni group. Magnesium, silicon and calcium are removed in large quantities from the waters of the southern Yengweni, with 5 139, 3 539 and 3 390 ppm unaccounted for respectively during the concentration process.

**Table 5.3.7** A summary of chloride concentrations in the three water chemistry groups

	<b>Totweni and northern Yengweni</b>	<b>Southern Yengweni</b>	<b>Floodplain</b>
<b>Minimum chloride/ ppm</b>	14	19	57
<b>Maximum chloride/ ppm</b>	1413	7188	3969
<b>Maximum: Minimum</b>	101	378	69.6

Although the floodplain samples have a maximum of 3 969 ppm chloride, the concentration factor is only 69.6 due to the relatively high minimum chloride concentration of 57 ppm. The solutes that seem to be most effectively removed on the floodplain are calcium, sodium and magnesium, while silicon is being lost in large quantities in the Totweni and northern Yengweni.

As noted in Section 5.3.3, most solutes increase in concentration with increasing chloride up to a certain turning point, decreasing rapidly thereafter. However, there is no discernible relationship between iron and chloride concentrations. The approximate chloride concentration at which the sample trendline becomes negative is presented in Table 5.4.3 for all three sample groups. It must be noted that these values give a general sense of chemical processing and that distinct turning points as noted by McCarthy *et al.* (1991) and Eugster and Jones (1979) for the Okavango Delta and lakes in Kenya, USA and Canada respectively, are absent in the uMkhuze Wetland System, possibly due to the interference of marine chloride additions.

**Table 5.3.8** The chloride concentration at which a saturation point in solute concentration is discernible, derived from Figures 5.3.4 – 5.3.9

	<b>Totweni and Northern Yengweni</b>	<b>Southern Yengweni</b>	<b>Floodplain</b>	<b>uMkhuze River and lake water</b>
Calcium	450	-	550	200
Iron	-	-	-	-
Magnesium	-	-	-	-
Potassium	300	150	300	250
Silicon	450	400	300	200

### 5.3.5. Mineral saturation

The above results naturally led to the question: are minerals saturating in the water of the uMkhuze Wetland System under the influence of a concentration mechanism? Due to the lack of complete anion analysis, the answer was limited to the minerals NaCl (halite), quartz (SiO<sub>2</sub>) and amorphous silica (SiO<sub>2</sub>) for all samples. CaCO<sub>3</sub> (calcite), gypsum (CaSO<sub>4</sub>), and trona (NaHCO<sub>3</sub>. Na<sub>2</sub>CO<sub>3</sub>.2H<sub>2</sub>O) was considered for the July 2002 samples only, which were also analysed for total alkalinity and sulfate among other anions.

All waters sampled in the uMkhuze Wetland System were undersaturated with respect to halite, with saturation indices (SI's) ranging from -8.5 to -3.8. The southern Yengweni and floodplain samples in July and September 2000, as well as July 2002 were typically in the range of -5.0 to -3.8. The two most concentrated samples were collected on the southern Yengweni in July 2002, which was an unusually dry period.

Water in the study area was more saturated in both quartz and amorphous silica across most samples, with an SI range of -3.6 to +0.07 for quartz and -4.6 to -0.9 for amorphous silica. These values indicated that silica was saturated in some uMkhuze Wetland System waters with saturation SI values from -0.1 to 0.1 for quartz recorded in the Totweni, the Yengweni transects Yg C and Yg D, as well as floodplain samples.

For the July 2002 samples, saturation indices ranged from -3.3 to 0.1 for calcite, -2.6 to -0.01 for gypsum and -14.5 to -6.9 for trona. It was therefore expected that both calcite and gypsum were saturated or approach saturation. Due to the lower solubility of calcite with a log K<sub>sp</sub> of -8.22 compared to -4.6 for gypsum, calcite will have precipitated first, followed by gypsum if sufficient

calcium remained in solution. Southern Yengweni samples were consistently among the most concentrated, followed closely by floodplain samples.

Preliminary water chemistry modeling thus indicated calcite saturation, as well as saturation of a number of silica compounds in the southern Yengweni. Quartz saturation seems to be typical of uMkhuze Wetland water with Totweni samples generally having the highest silica concentrations. Although quartz precipitation was not expected due to kinetic limitations, it was possible that other silica compounds did precipitate.

## **5.4. Discussion**

### **5.4.1. Grouping of water samples according to water chemistry**

The hydrological grouping of groundwater as identified in Chapter 4, was on the basis of the hydrological status and it was suggested that it might be an important factor determining water chemistry (Table 5.4.1.). It was expected that groundwater discharge areas would resemble rainwater due to only slight modification after leaching of reworked marine sands. In contrast, groundwater recharge areas should reflect the water chemistry of surface water (lake water) that enters the groundwater. Due to evaporation and differing solute inputs from uMkhuze River water, these waters should be more concentrated than the discharge situations. Groundwater in a hydrostatic condition (flat water table) is expected to be of an intermediate composition reflecting mixing of rainwater-derived groundwater with surface water inputs.

The differentiation of samples according to water chemistry by both classification and ordination suggested that the source of water was of greater significance in determining the water chemistry than the hydrological status of the transect (Table 5.4.1). Samples dominated by rainwater inputs formed a single group (Totw A, C, D and E, and Yg A, B and C), while the recharge areas of the southern Yengweni formed a single group receiving rainfall, surface water inputs from the north and uMkhuze River inputs from the south. Although the hydrological regime of the floodplain was similar to the northern Yengweni and southern Totweni, the greater influence of the uMkhuze River was evident in the water chemistry of these transects. Totw B could not simply be explained by geographical position or hydrology. Although distinguished as a separate group in terms of water chemistry, Totw B was included in the Totweni and northern Yengweni group due to the small number of samples involved and its geographical location and predominant hydrological process.

**Table 5.4.1** Grouping of water samples based on hydrological and water chemistry data

<b>Hydrological Grouping</b>			
<b>Groundwater Discharge</b>	<b>Hydrological Equilibrium</b>		<b>Groundwater Recharge</b>
Totw A Totw B Totw C	Totw D Totw E Yg A Yg C Fld A Fld B Fld C		Yg B Yg D Yg E Yg F Yg G
<b>Water Chemistry Grouping</b>			
<b>Totweni and Northern Yengweni</b>	<b>Southern Yengweni</b>	<b>Floodplain</b>	<b>Outlier</b>
Totw A Totw C Totw D Totw E Yg A (Yg B)* Yg C Rainwater-derived	Yg D Yg E Yg F Yg G Yengweni Lake-derived (rainwater and uMkhuze River water)	Fld A Fld B Fld C uMkhuze River- derived	Totw B

\*Although the water table at Yg B displayed a groundwater recharge slope, the inputs to the groundwater at this point will be predominantly rainwater (very rarely uMkhuze River water during floods), and therefore is comfortably grouped with the remaining northern Yengweni samples.

Further multivariate analysis by ordination was not only useful in confirming group assignments of the classification, but as Suk and Lee (1999) suggest, the ordination provided insight into chemical processing. The Factor 1 axis of the ordination seemed to represent a concentration sequence with increasingly concentrated samples (particularly southern Yengweni and floodplain samples) having positive Factor 1 scores, and more dilute samples (especially those from the Totweni and northern Yengweni Drainage Lines) having negative Factor 1 scores (Figure 5.3.1). Samples taken after extensive flooding also had negative Factor 1 scores irrespective of their geographic location. The uMkhuze River samples, representing the most concentrated source of solutes to the wetland were scattered around the origin. It seems that the dominant features of the ordination were the processes of concentration during dry spells, dilution during floods and the source of water. These features are consistent with trends detected in the electrical conductivity and water table data in Chapter 4.

#### 5.4.2. Chemical evolution of groundwater in the uMkhuze Wetland System in an evaporation sequence

In considering evaporation as a possible mechanism of solute concentration in the uMkhuze Wetland System, solutes were plotted relative to chloride as a concentration tracer as presented in section 5.3.4. The chloride concentrations in the groundwater of the wetland far exceed the chloride concentrations of inputs to the wetland. It is unlikely that a concentration of 7 188 ppm chloride would be produced in the short term (one or a few seasons) considering initial concentrations of around 4 ppm in rainwater. Therefore solute concentrations measured in the groundwater represent the cumulative process of chemical evolution in the uMkhuze Wetland System from initial groundwater inputs to the present day. This process includes both additions in terms of water and solutes driven by the hydrological regime, which may increase or decrease solute concentrations, as well as hydrological outflows. Groundwater discharge may remove solutes, while evaporation and transpiration will concentrate solutes. Chapter 7 will address chemical evolution in more detail.

In a solution undergoing evaporation, solutes do not exist in isolation but begin to form ion-pairs and aqueous compounds as the solvent to solute ratio decreases. The associations between solutes are governed by both thermodynamic and kinetic factors, with certain reactions and equilibria favoured over each other. As water is removed compounds start to saturate and precipitate out of solution. The sequence of precipitation is defined by solubility, with the least soluble mineral precipitating first.

Chloride was selected as a concentration tracer as the graphs of chloride and sodium versus conductivity (Figure 5.3.2 a and b) demonstrate the preferential concentration of chloride over sodium in the uMkhuze Wetland System, confirming the findings of a previous study in the wetland (Barnes *et al.*, 2002). The chloride concentrations in the uMkhuze Wetland System range from 3.66 ppm in rainwater to 7 188 ppm on the southern Yengweni. Although the coastal location of the wetland system is likely to result in a larger chloride input than might occur in similar inland wetlands, the concentrations expected from the higher chloride concentration in rainwater and from windblown aerosol material are orders of magnitude less than the chloride concentrations encountered in the groundwater of the uMkhuze Wetland System. Therefore, the wide range of chloride concentrations can only be attributed to evaporation and/ or transpiration, which would progressively remove water, leaving solutes to concentrate (Love *et al.*, 1993). In the evaporation of seawater, which has a chloride concentration at least 2.6 times the most concentrated sample

measured and around 5 000 times the concentration of rainwater, the first chloride compound to saturate and precipitate out of solution would be halite, which would only occur after evaporating 90 % of the seawater (Sonnenfeld, 1984; Warren, 1989). The saturation indices demonstrate that the waters of the uMkhuze Wetland System sampled during July 2002 were undersaturated with respect to halite, in spite of the severe drought of two years duration in northern KwaZulu-Natal at the time of sampling. Therefore, chloride is an effective concentration tracer for the uMkhuze Wetland System. Other regions in which chloride has been employed as the concentration tracer include Lake Magadi, Kenya, Little Lost Man Creek in California, USA, and the La Plata coastal wetland in Argentina (Bencala *et al.*, 1984; Eugster, 1980; Logan and Rudolph, 1997).

Contrary to Eugster and Hardie's (1978) model of closed-basin brine evolution, silicon and potassium are consistently among the first solutes removed from solution in the concentration sequences. Similar results for silicon were obtained from groundwater beneath islands in the Okavango Delta, Botswana (McCarthy *et al.*, 1991). The sequence of solute removal from wetland waters derived from Table 5.4.2 is the following: potassium, silicon and calcium on the Totweni and northern Yengweni; silicon and potassium for southern Yengweni samples; and silicon and potassium, followed by calcium on the floodplain. It must be noted that solutes may be removed throughout the concentration process, particularly in co-precipitation reactions such as the incorporation of magnesium into calcite.

The removal of solutes from the shallow groundwater of the uMkhuze Wetland may have two possible mechanisms: the first is the precipitation of saturated mineral phases and the second is density-driven downward flux of solutes to deeper groundwater. Both mechanisms have been described in the Okavango Delta: the first leading to precipitation of solutes that are insoluble over the range of solute concentrations caused by evapotranspirational water loss, the second for solutes that remain in solution over this range. This second mechanism has been described in the Okavango Delta by Bauer-Gottwein *et al.* (2007) as an important mechanism in sequestering solutes within the system that maintains fresh surface water and stable concentrations of solutes in the shallow groundwater, with highly concentrated deep groundwater underlying the Delta. The first mechanism will be the focus of further analysis in this study due to the lack of data concerning deep groundwater. The investigation of possibly density-driven flow of solutes is necessary to understand the nature and longevity of solute retention in the uMkhuze Wetland System.

### 5.4.2.1. Silicon

Silicon is consistently the first to precipitate from solution in the evaporation sequence occurring at similar chloride concentrations on both Totweni and Yengweni (northern and southern), while a factor of two increase in chloride concentration is required for the precipitation of silicon on the floodplain. Silicon concentrations of 0 to 373.0 ppm were recorded for uMkhuze Wetland System waters, which translate into activities giving quartz saturation and approaching amorphous silica saturation as reported in Section 5.3.4. Most natural surface waters, with silicon concentrations of 0.5 – 14 ppm are therefore under-saturated with respect to amorphous silica and saturated with respect to quartz (Matthess, 1982; Wilding *et al.*, 1977). However, groundwater systems with higher carbonic acid concentrations and greater contact with sediment have typical silicon ranges of 0.5 to 43 ppm (Langmuir, 1997). Therefore, uMkhuze Wetland System silicon concentrations far exceed expected values. However, on evaporation of wetland waters it is possible under natural conditions of pH, temperature and pressure to record elevated silicon concentrations, as found in the uMkhuze Wetland System and the Okavango Delta, Botswana (Langmuir, 1997; McCarthy *et al.*, 1991; Wilding *et al.*, 1977). Silicon groundwater concentrations beneath islands in the Okavango Delta, Botswana reach values of around 930 ppm, which is around 2.5 times more concentrated than the maximum uMkhuze value (McCarthy *et al.*, 1991). As noted by Eugster and Jones (1979) for lakes in East Africa and the USA, in both the Okavango Delta and uMkhuze Wetland System data show a further increase in silicon after 2000 ppm chloride in the uMkhuze Wetland System and around 4000 ppm sodium in the Okavango (McCarthy *et al.*, 1991). This trend is discernible in the southern Yengweni and floodplain datasets, but not in the Totweni and northern Yengweni group. McCarthy *et al.* (1991) attribute the removal of silicon in the Okavango Delta partly to the precipitation of amorphous silica and partly to buffering by an amorphous mineral such as allophane.

The solubility threshold for amorphous silica is 56 ppm silicon and 5.6 ppm silicon for quartz, as calculated from solubility products reported in Stumm and Morgan (1981) as  $\text{Log } K = -2.7$  and  $\text{Log } K = -3.7$ , respectively. Therefore, in order for an equilibrium to exist between silicic acid ( $\text{H}_4\text{SiO}_4$ ) and either solid phase (quartz or amorphous silica), a concentration of around 5.6 and 56 ppm respectively is required. The preliminary thermodynamic modeling indicated that most samples from all three sample areas (Totweni, Yengweni and the floodplain) attain quartz saturation. However, the slow kinetics of quartz formation may allow other silicon compounds to precipitate first. It must be noted that although quartz precipitation might be thermodynamically favoured, the

kinetics of such a process are extremely slow such that precipitation is negligible (Stumm and Morgan, 1981; Wilding *et al.*, 1977). Matthes (1982) reports that co-precipitation of silica with other colloids can occur during an evaporation sequence. This has been documented between silicon and aluminium at high ionic strengths to produce the amorphous clay mineral allophane.

Various authors have reported the presence of smectite group minerals, in particular montmorillonite ( $\text{Si}_4\text{Al}_{1.5}\text{Mg}_{0.5}\text{O}_{10}(\text{OH})_2\text{Ca}_{0.25}$ ) both as a weathering product and as a neo-formed compound (Barbiéro *et al.*, 2002; Borchardt, 1989; Mees, 2001; Ware *et al.*, 2003). The *in situ* post-depositional formation (neof ormation) of smectites requires a basic magnesium-rich environment in addition to silica saturation. However, most databases do not include thermodynamic data for the smectites (Palandri and Reed, 2001).

#### 5.4.2.2. Potassium

In complete contrast to evaporation experiments on both seawater and continental waters, potassium is generally precipitated from solution next in the sequence of increasing chloride concentrations (Eugster and Jones, 1979; Warren, 1989). However, complex natural environments do not follow simple ‘laboratory beaker’ evolution of waters and other processes may have a profound effect on the chemical composition of wetland waters.

Highly soluble potassium-bearing phases should only precipitate after halite saturation at 98.7 % loss of solvent by evaporation (Warren, 1989). However, Eugster and Jones (1979) reported that at Lake Magadi and Abert, Summer and Goose lakes in Oregon (USA), potassium depletion occurred at intermediate chloride values. Eugster and Maglione (1979) documented similar behaviour in the Lake Chad basin, central Africa. The authors attributed this loss to potassium adsorption onto the charged surfaces of volcanic glass in the case of Lake Magadi and unconsolidated clays for the Oregon lakes. It is well documented that potassium is involved in cation exchange reactions with clay minerals, within the lattice itself or the interlayer region between silicate sheets (Mandel and Shiftan, 1981; Matthes, 1982; Rowland and Grimshaw, 1989). In addition, plants are sinks for potassium as it is essential in biochemical functions, being required as a macronutrient in plants (Rowland and Grimshaw, 1989).

In the predominantly sandy substrate of the uMkhuze Wetland System, the uncharged surface of inert quartz granules cannot immobilize or even briefly retain potassium. The reduction in

potassium cannot be attributed to groundwater or surface outflow as the highly mobile chloride would be equally well removed due to undersaturation in halite. Observations and subsequent analyses in the southern Yengweni have identified clay minerals at depth, and floodplain sediment is partly alluvial clays of the uMkhuze River catchment. However, potassium removal is still important in the sandy Totweni and northern Yengweni, although potassium concentrations in these areas are higher than in other groups. Vegetation provides the only possible mechanism of removal. McCarthy *et al.* (1991) have also suggested that vegetation is partly responsible for potassium removal in the Okavango Delta, Botswana.

### 5.4.2.3. Iron

Unlike silicon and potassium concentrations, which are independent of pH- and redox potential under the limited pH range encountered in the uMkhuze Wetland System, the presence and mobility of iron is dictated largely by the redox environment. Most samples have very low iron concentrations, particularly in the southern Yengweni and floodplain areas. As it was not possible to sample under vacuum into a sealed container at the water table, it is likely that any reduced iron was oxidized and precipitated out of solution after sampling. In spite of sampling constraints, the Totweni and northern Yengweni show distinctly different iron chemistry, with concentrations reaching 145 ppm with increasing chloride concentration. A further irregularity in the iron chemistry is the series of samples collected mostly at Yg D and E on the southern Yengweni, which display a strong relationship with chloride. The lower chloride values are due to a dilution of groundwater by November floods, while the two most concentrated samples were collected during the dry season in July.

Iron and silicon concentrations were well correlated on the Totweni and northern Yengweni. Possibly colloidal iron-silica complexes account for the relatively high iron values obtained in spite of exposure to high oxygen conditions on sampling, as reported by Pokrovski *et al.* (2003). If iron-silica colloids were present, iron and silicon solute concentrations may be overestimated if colloidal particles of less than 0.22  $\mu\text{m}$  diameter were present in the samples, which were filtered to 0.22  $\mu\text{m}$ .

It is possible that organic matter-iron (III) complexes allow the oxidised state to remain in solution (Matthess, 1982). Other possible iron (III) complexes include chloride, fluoride, sulfate and phosphate (Stumm and Morgan, 1981). Fluoride and phosphate are present in low concentrations

and are unlikely to play a major role in complexing iron, while sulfate and chloride values suggest that these compounds might be present.

#### 5.4.2.4. Calcium and Magnesium

The alkaline earth elements calcium and magnesium are the next solutes to precipitate from solution in the evaporation sequence, with calcium probably precipitating as calcium carbonate ( $\text{CaCO}_3$ ) as indicated by the saturation indices. In most studies, these elements have been shown to be the first to precipitate from solution in the concentration sequences (Eugster and Jones, 1979; Warren, 1989). Where sulfate is an important component of groundwater, gypsum may also precipitate. However, as gypsum saturation was not detected in any samples collected in July 2002 when sulfate was measured, it is likely that insufficient calcium remains after calcite precipitation to allow gypsum to saturate (Eugster and Jones, 1979).

In continental waters, magnesium carbonates are the predominant magnesium precipitates of which dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) and magnesite ( $\text{MgCO}_3$ ) are most common (Matthess, 1982). Although magnesite is more soluble, it will not precipitate under normal groundwater conditions where calcium is an important component (Matthess, 1982). Although dolomite is poorly soluble, calculations indicate that saturation is not reached in the study area, possibly due to the preferential precipitation of calcium compounds (Matthess, 1982). However, in chloride-rich waters magnesium is better conserved than calcium, and magnesium concentrations increase steadily with chloride concentrations due to the soluble ionic complex  $\text{MgCl}_2$  (Eugster and Jones, 1979).

In spite of magnesium remaining in solution over a large chloride range, Figure 5.3.10 illustrates that, particularly for the Totweni and northern Yengweni samples, magnesium concentrations decrease faster than those of calcium. It does not seem that magnesium carbonates are saturating, although if calcite does precipitate in these areas, there may be increasing amounts of magnesium incorporated in the precipitates as the available calcium is depleted, which has been identified in the Okavango Delta and the Pantanal of Brazil (Barbiéro *et al.*, 2002; Eugster and Jones, 1979; McCarthy *et al.*, 1991). It is more likely in the Totweni and northern Yengweni however, that magnesium is simply transported into the drainage line where it is retained in solution or in complexes with the organic matter of the peat deposit. Alternatively, magnesium silicates may account for the decrease (Barbiéro *et al.*, 2002; Eugster and Jones, 1979). This explanation is most likely on the southern Yengweni where relatively high silicon concentrations are correlated with

high magnesium concentrations. The floodplain, lake and uMkhuze River samples behave as would be expected, where increasing chloride concentrations result in increasing magnesium to calcium ratios as magnesium is retained in solution to a greater degree than calcium.

#### **5.4.2.5. Summary**

Mineral saturation sequences may take many forms dependent on the chemical composition of waters on which a concentration process acts. Although the trajectory of the sequence is dictated by the initial chemical composition of the water body, the resulting suite of minerals is dependent on the degree of concentration to which waters are subjected (Eugster and Hardie, 1978). In systems where inputs regularly dilute the water body, the chemical evolution of the water body will be retarded at early stages of the mineral saturation sequence (Sanford and Wood, 1991). The more dilute groundwaters of the Totweni and northern Yengweni regions have shorter residence times than those of the southern Yengweni and floodplain regions, due to the prevailing discharge regime in the Totweni and northern Yengweni. In this way, the concentration process has limited time in which to act on the groundwater and few, if any, minerals attain saturation in these regions. The longer groundwater residence times in the southern Yengweni and floodplain areas, as inferred from the water table characteristics, allow a greater degree of concentration of the groundwater, resulting in saturation of a greater variety of minerals. The subtropical climate of the region prevents the formation of evaporite minerals towards the end of the sequence, due to regular dilution by rainfall.

#### **5.5. Conclusion: Solute concentration in the uMkhuze Wetland System as the first step in solute retention?**

It is evident that the groundwater of the uMkhuze Wetland System has been highly modified over time from its suspected dilute origins. The maximum chloride concentrations are now ~26 times more concentrated than the maximum uMkhuze River chloride concentration, although this concentration represents uMkhuze River discharges at which river water will not enter the Totweni or Yengweni Drainage Lines. The magnitude of the concentration factor suggests that these elevated concentrations have evolved over long time periods, while the water chemistry compositions indicate that a concentration process is occurring, with some expected features of mineral saturation.

Although the Totweni and northern Yengweni waters do seem to be influenced by a concentration process, the waters remain relatively dilute and are typified by high silicon, potassium and iron concentrations. It is possible that in the case of discharge and flat water tables that may seasonally become discharge regimes, the potential mineral saturation sequence as recorded for semi-arid continental settings by Sanford and Wood (1991) is retarded due to short groundwater residence times and dilute inputs.

Both the southern Yengweni and the floodplain samples have a greater contribution of calcium and magnesium, and higher carbonate and bicarbonate concentrations. Saturation or slight undersaturation of calcite is common. The fact that higher chloride values in the southern Yengweni are accompanied by lower silicon concentrations in spite of similar inputs, suggests that silica compound/s have precipitated in large volumes. The floodplain is differentiated by more concentrated inputs, which reflect their uMkhuze River origin. Magnesium removal is also less prominent, with this element being enriched relative to calcium to a greater degree than occurs in the southern Yengweni.

These divergent evolutionary paths must be first attributed to the chemical composition of source waters. Upon concentration the waters reach certain critical points or chemical divides, where the precipitation of minerals induces depletion of one component and increasing concentration in others (Eugster and Jones, 1979; Sanford and Wood, 1991). Silicon participates in the first divide in all water chemistry groups, followed by potassium in all but the Totweni and northern Yengweni group where iron precedes potassium. The proximity of these critical points might indicate interactions particularly for iron and silicon in the Totweni and northern Yengweni. Calcium is depleted thereafter with large amounts precipitated from solution in the southern Yengweni and floodplain areas. Magnesium depletion is only noticeable on the floodplain.

Concentration of solutes in wetland waters can result in retention within the wetland, the duration of which is defined by the hydrological regime. The saturation of minerals within the groundwater of the uMkhuze Wetland System suggests that precipitation may allow immobilisation within wetland sediment. This possibility will be investigated in Chapter 6.

**CHAPTER 6**  
**CHEMICAL SEDIMENTATION**  
**IN THE uMKHUZE WETLAND SYSTEM**

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## **6.1. Introduction**

Pedogenesis or soil formation is the group of processes to which all surface sediments are subjected, affecting all layers of a soil profile. It is expected that over thousands of years the reworked marine sands of the uMkhuze Wetland System would have been modified by such pedogenic processes, *inter alia* by leaching of soluble minerals and shell fragments. In areas of restricted drainage in a wetland, sediments will also be modified by the accumulation of organic matter that will provide complexation opportunities and cation exchange sites for basic cations and hydrogen. Furthermore, due to the high water tables, some solutes may have been retained at the water table for a period of time depending on residence time of the groundwater. Starting with this framework of pedogenesis typical in wetland systems, the chemical composition of uMkhuze Wetland System sediment will be presented and pedogenic processes occurring in the wetland discussed.

## **6.2. Methods**

### **6.2.1. Field Work**

As described in Chapter 4, a number of transects were placed along the length of the Totweni and Yengweni Drainage Lines as well as the floodplain of the uMkhuze River between the two aforementioned drainage lines. During the first sampling period, sediment samples were taken every 0.5 m, or where a noticeable change in sediment properties was evident, until or just below the water table where possible. Sediment properties of matrix colour, colour of any mottling, presence of nodules and texture were described in the field.

### **6.2.2. Sample preparation and analyses**

On returning to the laboratory, samples from each transect were selected at half metre intervals or with a change in colour or texture such that 283 samples were analysed from the ~800 collected and dried at 105 °C. The samples were then crushed using a pestle and mortar.

### 6.2.2.1. Total Elemental Analysis by X-Ray Fluorescence Analysis

X-Ray fluorescence analysis (XRF) is the most commonly applied and generally useful method of elemental analysis for soil, geological and plant samples (Karathanasis and Hajek, 1996). XRF is a method of total chemical analysis, with results normally reported as oxides. The method requires little sample preparation other than grinding to a suitable particle size, and is therefore not likely to introduce errors through modification of the matrix by addition of contaminants or reagents that may occur during dissolution techniques. Samples are fused into a sample disc, which is then subjected to a beam of X-Rays generated by an X-Ray tube consisting of a tungsten filament as the cathode and an anode of suitable material (Fitton, 1997). Electrons are accelerated from the filament on applying a voltage across it, and are halted in their flight by the anode. This abrupt deceleration of the electrons releases energy in the form of X-Rays (Moore and Reynolds, 1989). The replacement of electrons ejected from the inner shell of anode atoms due to the energy generated by the filament electrons, also produces X-Rays. These high energy photons, the primary X-Rays, incident on the sample, are diffracted on interaction with electrons surrounding the sample atoms (Moore and Reynolds, 1989). On relaxation to the ground state, secondary X-Rays characteristic of the sample constituents are released, with their intensity equivalent to the concentration of each element in the sample (Karathanasis and Hajek, 1996). The resulting X-Rays are passed through a detector, allowing the intensity of each wavelength to be measured and a spectrum produced.

XRF was conducted on homogenised milled bulk samples using the fused disc method with platinum-gold crucibles. Spectroflux<sup>TM</sup> was added as a fusion medium, and the samples were analysed using a Philips PW 1404 spectrofluorometer.

All concentrations are expressed as the oxides in units of weight %: calcium as CaO, magnesium as MgO, iron as Fe<sub>2</sub>O<sub>3</sub> and sodium as Na<sub>2</sub>O. Raw soil chemistry data obtained by XRF is presented in Appendix E.

### 6.2.2.2. Mineralogical Analysis by X-Ray Diffraction

As in the case of XRF for total elemental analysis, X-Ray diffraction (XRD) is the most commonly applied and effective method for mineralogical analysis of rock and soil samples (Hughes *et al.*, 1994). The same general principles of X-Ray generation apply as those employed in XRF. X-Rays

incident upon samples, either being randomly oriented powder samples or oriented samples having been allowed to settle out of solution, are diffracted on interaction with electrons surrounding the sample atoms. The diffraction pattern produced is a result of the distribution of electrons around atoms in the sample, as well as the arrangement of atoms within unit cells of the sample, in particular due to the spacing ( $d$  value) between the crystal planes as described by Bragg's equation (Moore and Reynolds, 1989; Schulze, 1989):

$$\frac{d}{n} = \frac{\lambda}{2 \sin \theta}$$

where  $d$  = spacing between the crystal planes

$n$  = order of diffraction

$\lambda$  = wavelength of incident photons

$\theta$  = angle of diffraction

The diffraction patterns produced not only describe the minerals present but their degree of crystallinity with long-range ordered minerals of large particle sizes producing sharp peaks while smaller particle sizes and/ or short-range ordered crystals (low crystallinity) produce broader peaks. Amorphous material may be only visible as very broad peaks just visible above the background signal. Mineralogical analyses were undertaken in order to determine the minerals present and to semi-quantitatively establish their abundance.

Samples were selected for XRD analysis based on the XRF analyses, with the Totweni, northern and southern Yengweni, and the floodplain represented. The mineralogy of these samples was determined by XRD initially on the bulk sample. Those displaying interesting features indicative of modification to the reworked marine sands were selected for XRD analyses on the fine fraction ( $< 2 \mu\text{m}$ ). Further subsamples were sieved to isolate the fine fraction, following which the samples were subjected to the following treatments in order to adequately characterise the clay mineralogy: separate sub-samples were saturated with magnesium and potassium, which were analysed following air-drying. Samples saturated with magnesium were treated with both glycerol and ethylene glycol. Potassium-saturated samples were also heated to  $550^\circ \text{C}$  before further analysis.

X-Ray diffraction analysis was carried out on randomly oriented powder samples using a Philips PW1050 diffractometer with monochromated  $\text{Co K}\alpha$  radiation from  $3^\circ$  to  $75^\circ 2\theta$ . The scanning step employed was  $0.02^\circ$  at  $1^\circ$  per minute. A Sietronics 122D automated microprocessor was used to

capture the diffraction data. In this way the major minerals in the bulk samples, as well as on the fine fraction, were detected.

### 6.2.3. Data analysis

Mineralogical data were obtained from spectra in the following way. Standards were run on the XRD under the same conditions as the samples, in order to get approximate conversion values for quartz, calcite and feldspars. The quartz and calcite conversions have a high degree of accuracy, but due to large variation in feldspar mineralogy, the feldspar content could only be coarsely estimated.

Two quartz standards were employed to roughly quantify quartz in the bulk samples. In the analysis of XRD data on bulk samples, three quartz peaks were identified at d-spacings of 4.26, 3.33 and 1.81 Å. As the peak at 3.33 Å is the most intense, the counts measured in this region were utilised in the analysis. The peak at  $d = 4.45$  Å was used as a general indication of clay content, with the counts (indicating intensity of the instrument signal) used in analysis of mineralogical composition. Similarly two to three feldspar lines in the regions 3.14 – 3.19 Å for plagioclase and 3.21 – 3.26 Å for orthoclase were added and expressed as a percentage of 6250 (Hughes, 2004). A similar empirical method for calcite was used, which entails expressing calcite counts at a d-spacing of 3.05 Å as a percentage of 6600 (Hughes, 2004).

The relationship of oxides of a range of elements to titanium oxide was used to trace the pedogenic trajectory of uMkhuze Wetland System soils. Rutile ( $\text{TiO}_2$ ) is a common titanium mineral found in soils. Due its low reactivity and low solubility, rutile effectively resists weathering, and is therefore unchanged over long time scales (Milnes and Hutton, 1983). It is therefore used as a tracer to track transformation of sediments from the parent material to current state (Langmuir, 1997). However, titanium may occur in many forms depending on the parent rock, and not all are inherited from the catchment geology. Titanium concentration in soils cannot therefore be solely attributed to the inert rutile. Therefore, total elemental titanium concentrations should be employed as a tracer with some caution (Milnes and Hutton, 1983), although in the uMkhuze Wetland System the inert forms of titanium seem to predominate (Hugo, 1993).

## 6.3. Results

### 6.3.1. Soil chemistry

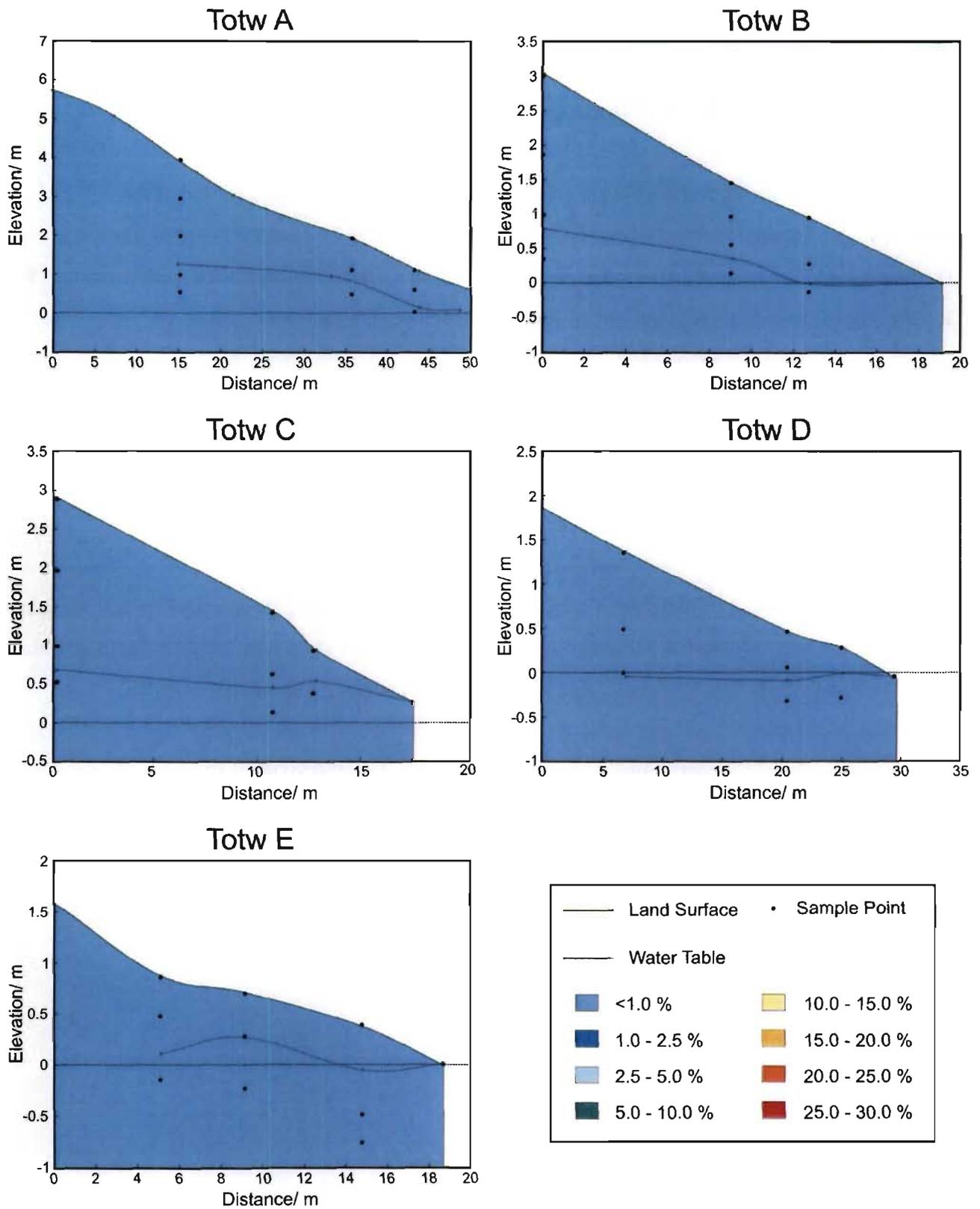
#### 6.3.1.1. The Totweni Drainage Line

Calcium concentrations of the Totweni transects did not exceed 0.71 % recorded at the southernmost Totweni transect (Totw E), with a minimum of 0.3 % for the Totweni transects (Figure 6.3.1). The general pattern was one of increasing calcium concentration with proximity to the drainage line and towards the soil surface for most Totweni transects.

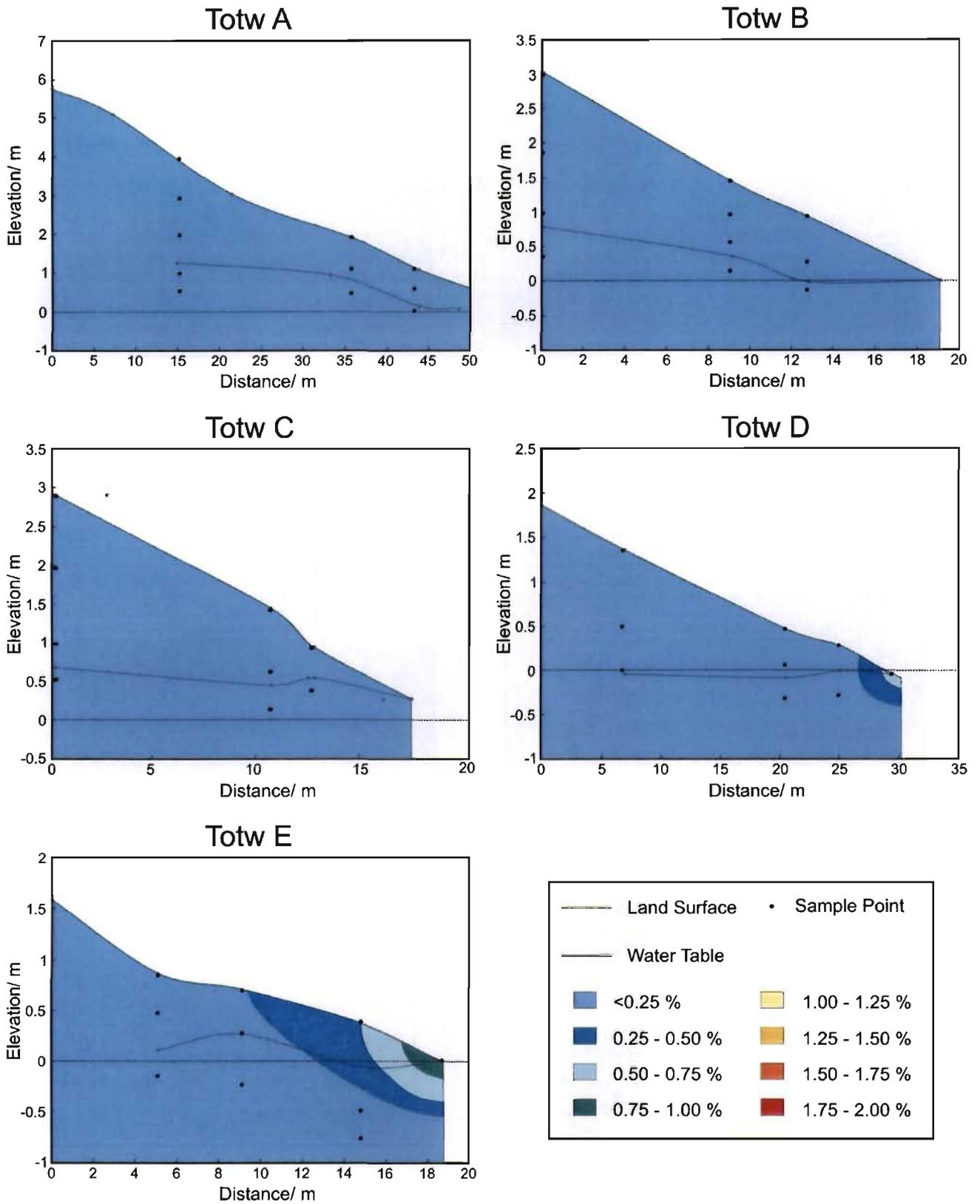
Magnesium concentrations were generally lower than those of calcium, ranging from 0.00 % to a maximum of 1.01 %. The maximum magnesium concentration was again recorded at Totw E (Figure 6.3.2). The trend in concentration was the same as that for calcium concentrations, with magnesium increasing towards the surface and with proximity to the drainage line.

The same general trend of increase in concentration towards the drainage line and the soil surface was found for iron (Figure 6.3.3). The lowest concentration of 0.16 % was found at depth, and the highest value of 7.20 % was recorded for a lake sample of surface sediment at Totw E.

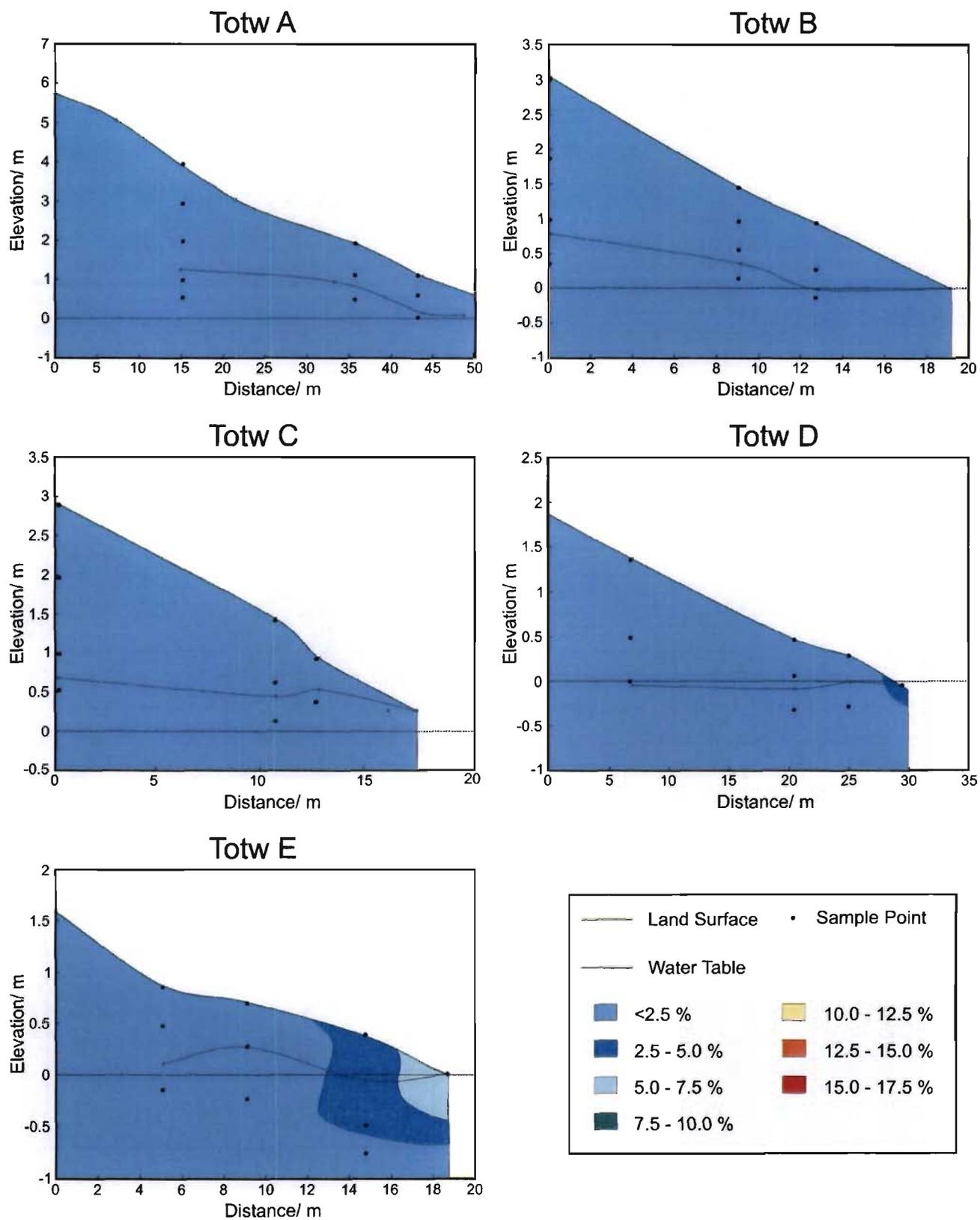
The trend in sodium concentrations was not as clear as for the other oxides, although the maximum of 0.89 % was found at the soil surface at Totw E and the minimum of 0.01 % was recorded for a sample taken at depth (Figure 6.3.4). The two northern Totweni transects differed from the others as the maxima of these two transects occurred either at the water table adjacent to the drainage line at Totw A, or just below the soil surface in mid transect at Totw B.



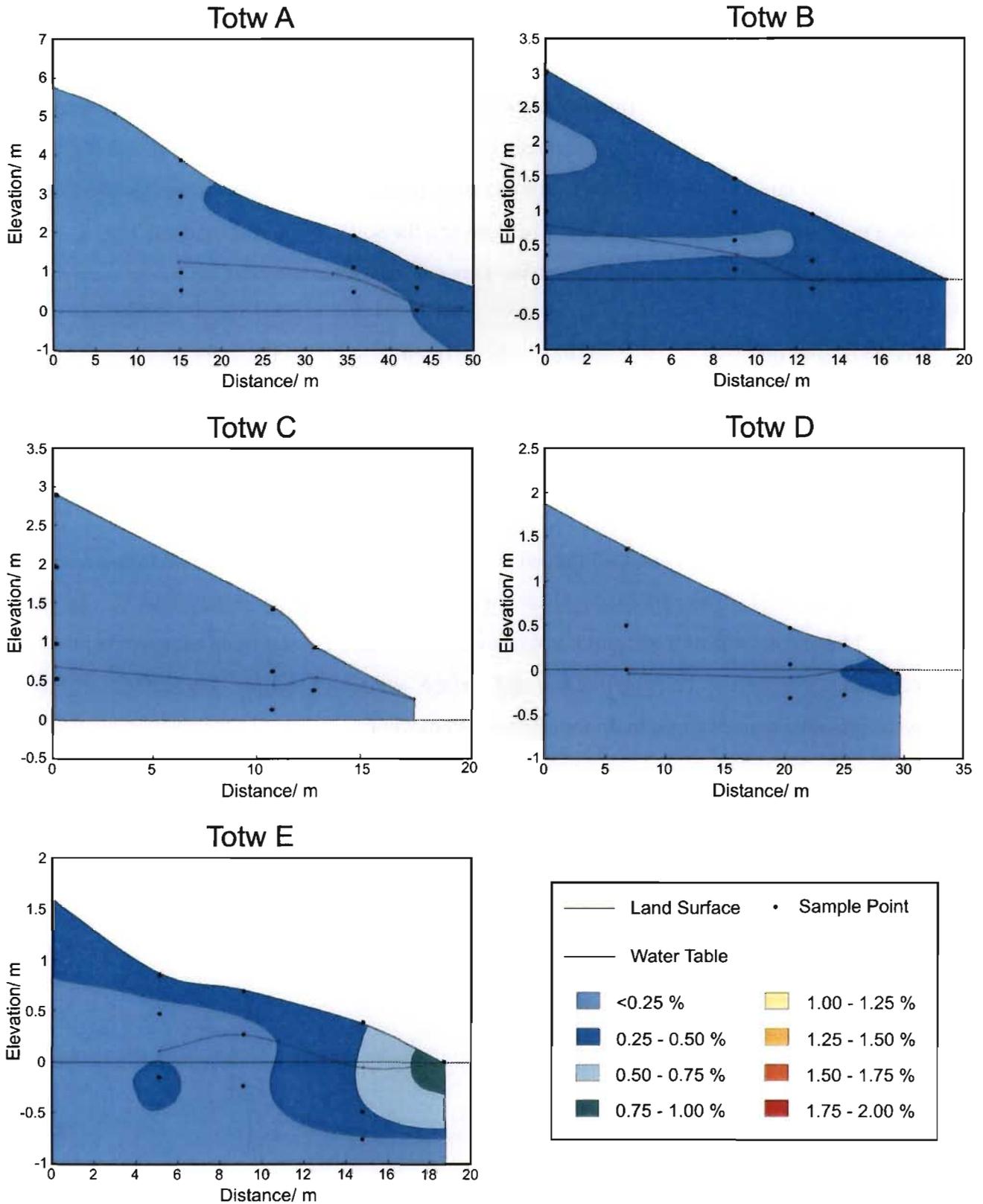
**Figure 6.3.1** Soil CaO concentrations in mass % for Totweni transects A – E



**Figure 6.3.2** Soil MgO concentrations in mass % for Totweni transects A – E



**Figure 6.3.3** Soil Fe<sub>2</sub>O<sub>3</sub> concentrations in mass % for Totweni transects A – E



**Figure 6.3.4** Soil Na<sub>2</sub>O concentrations in mass % for Totweni transects A – E

### 6.3.1.2. Northern Yengweni

Calcium concentrations of the northern Yengweni transects Yg A, B and C were uniformly low with a minimum value of 0.06 %, and a maxima value of 0.54 %, which was recorded at Yg B where the water table suggested groundwater recharge (Figure 6.3.5). Again, a similar trend of an increase in concentration towards the drainage line and the soil surface was evident. The concentrations were comparable to those of the Totweni transects.

Although magnesium values also complied with the trend found in all transects thus far, some samples at the water table at Yg A and C showed elevated values (Figure 6.3.6). Magnesium concentrations ranged from 0.02 % to 1.06 %, with the highest value again recorded at Yg B. These concentrations were similar to those encountered on the Totweni Drainage Line.

Iron values on the northern Yengweni ranged from 0.25 % to 6.49 %, with the maximum recorded at Yg B (Figure 6.3.7). Iron concentrations at Yg A reached a maximum of only 1.34 %, compared to the 5.27 % and 6.49 % of Yg C and B respectively. The same general trend of increase in concentration towards the drainage line and soil surface, as found for oxide concentrations in the Totweni was seen concerning iron on the northern Yengweni.

Sodium concentrations did not follow the general trend exhibited by other oxides, with some elevated concentrations at the water table in all three transects (Figure 6.3.8). The range of sodium concentrations on the northern Yengweni was 0.10 % to 0.57 %, the highest sodium concentration again located at Yg B.

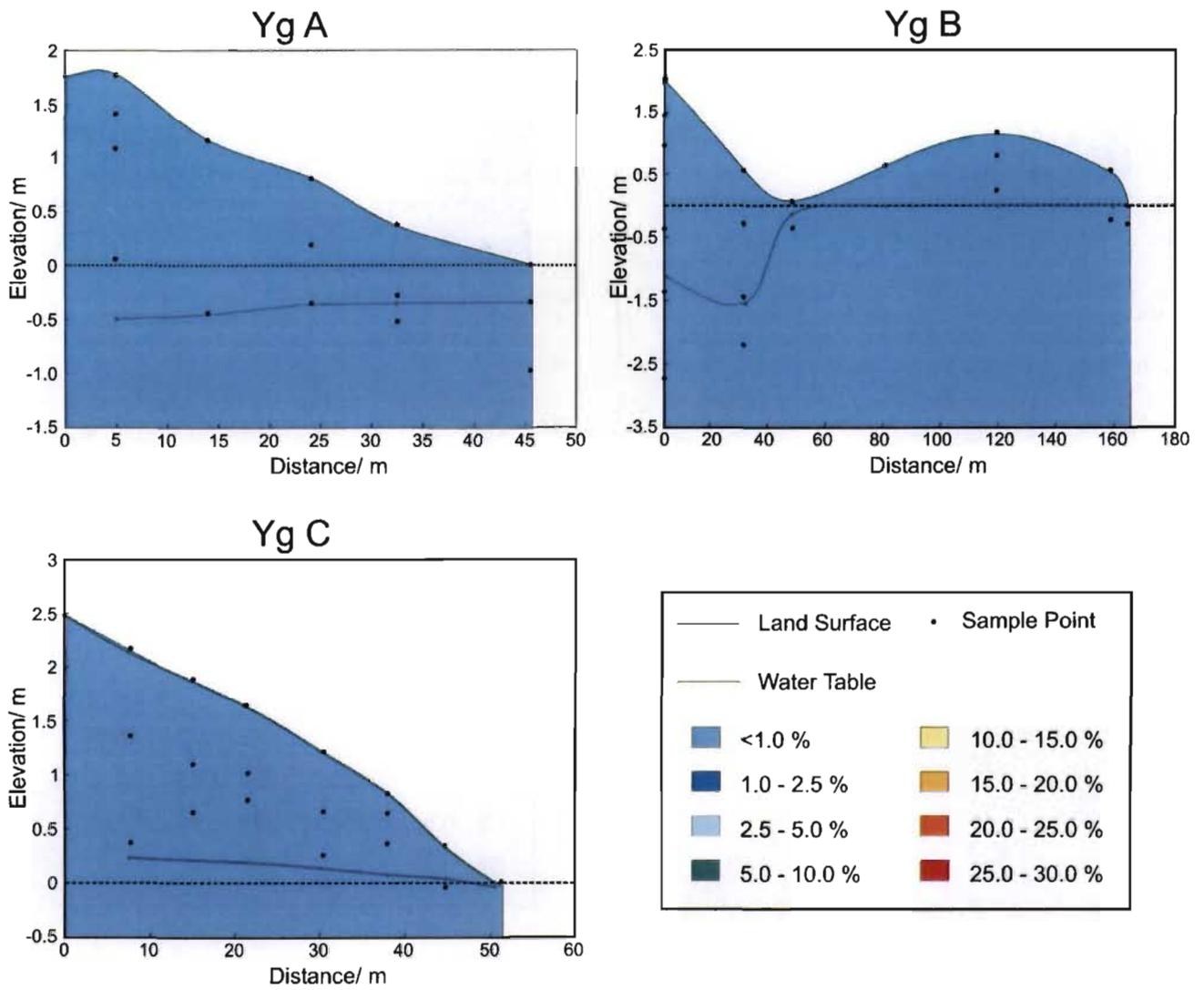
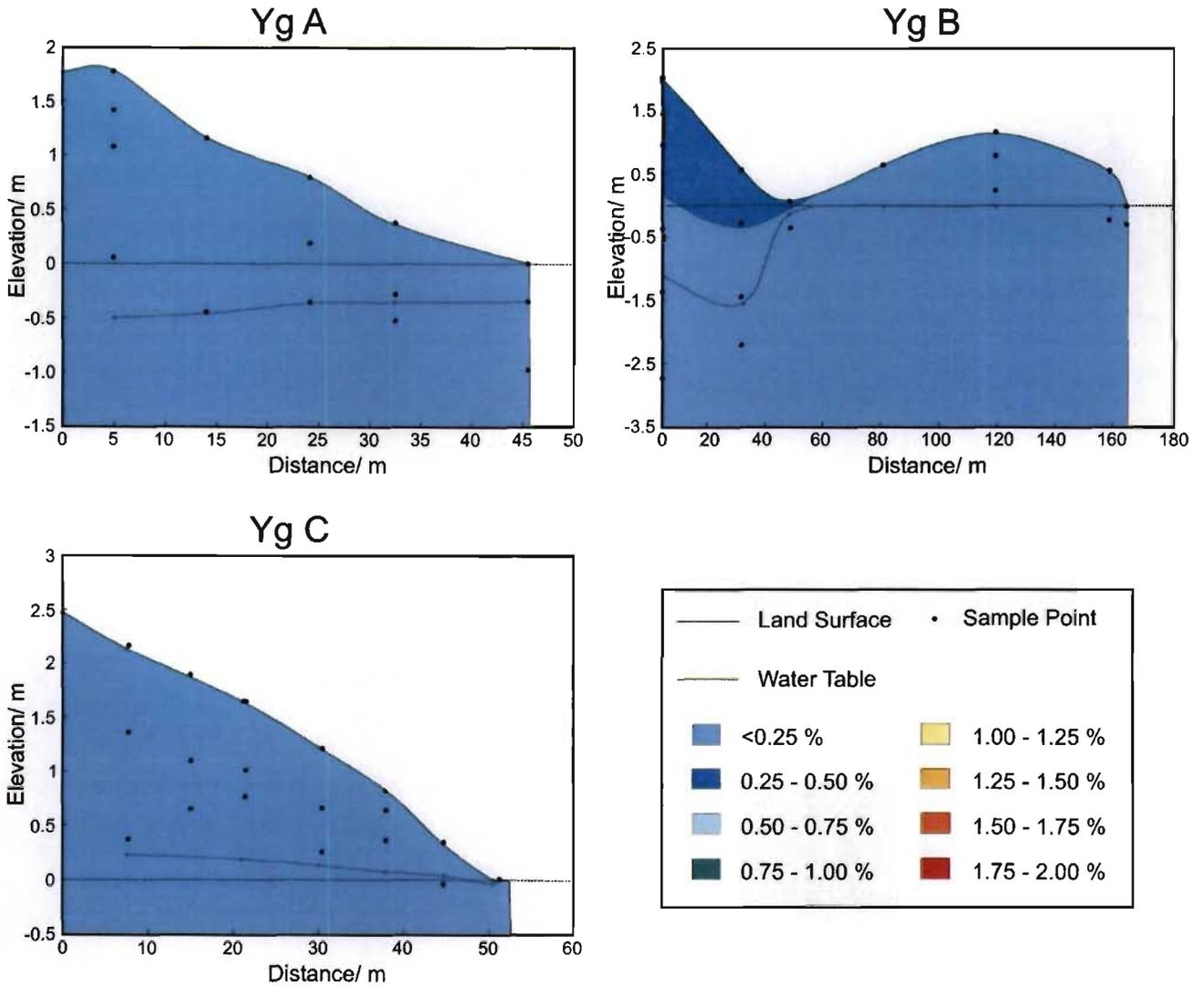
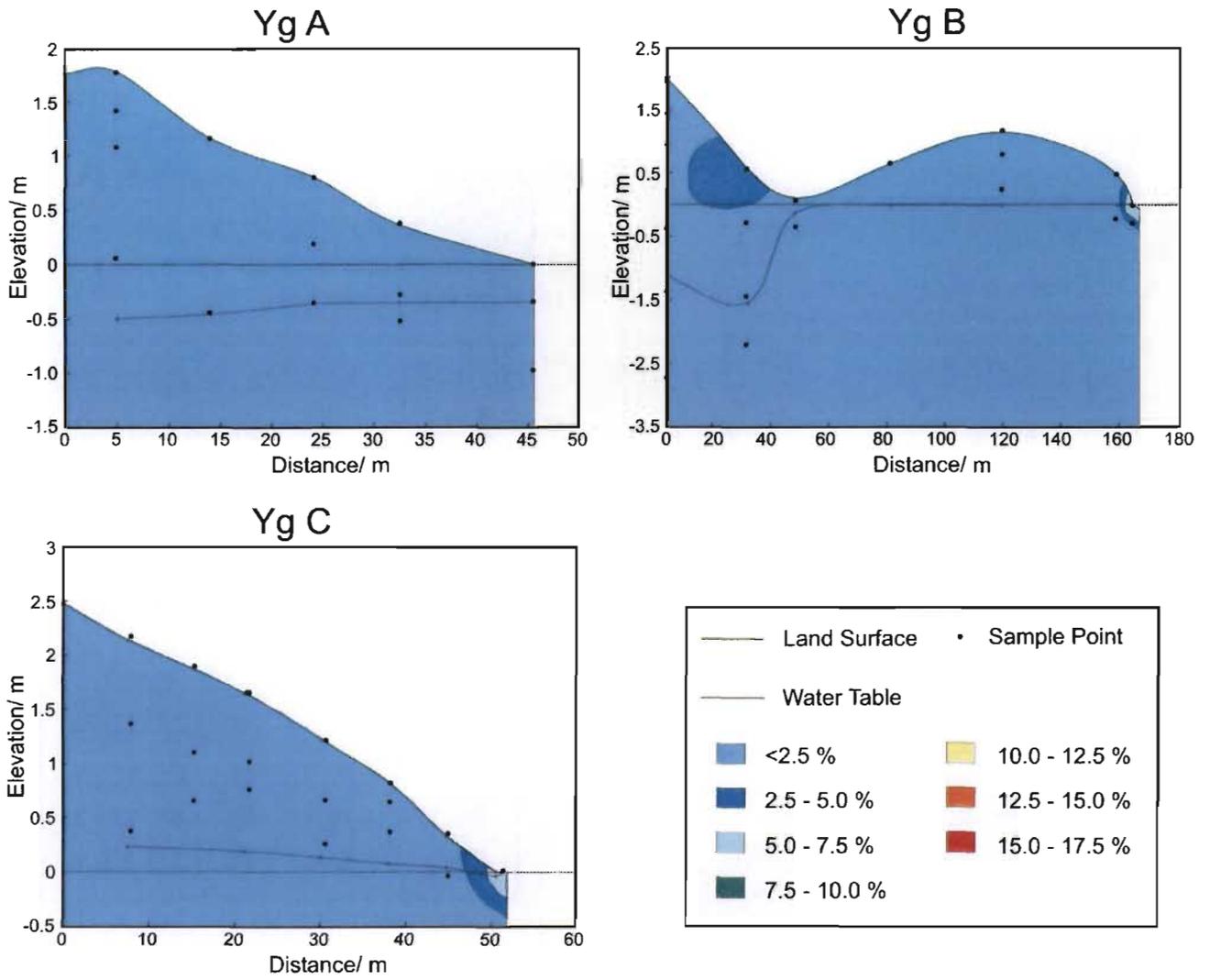


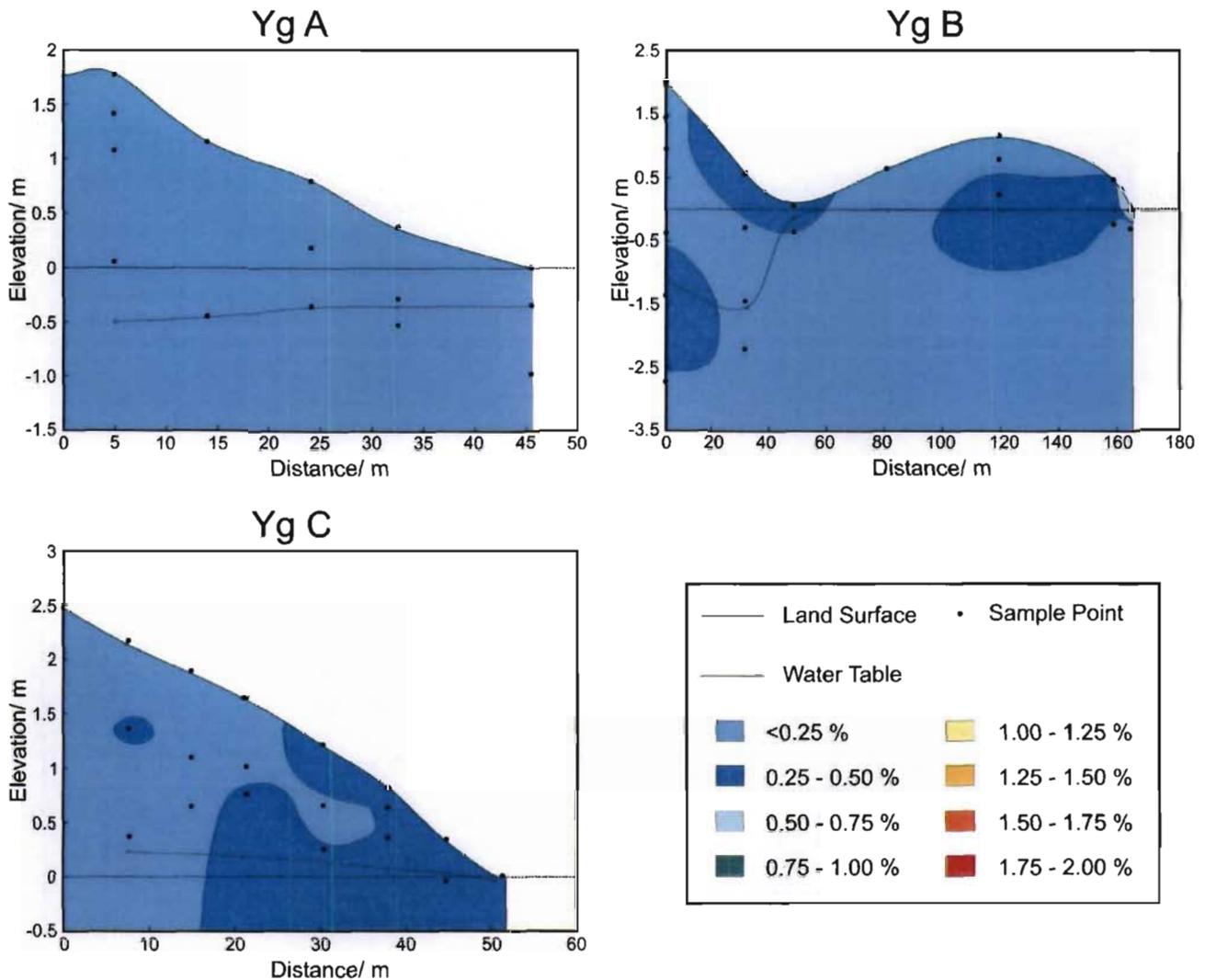
Figure 6.3.5 Soil CaO concentrations in mass % for northern Yengweni transects A – C



**Figure 6.3.6** Soil MgO concentrations in mass % for northern Yengweni transects A – C



**Figure 6.3.7** Soil Fe<sub>2</sub>O<sub>3</sub> concentrations in mass % for northern Yengweni transects A – C



**Figure 6.3.8** Soil  $\text{Na}_2\text{O}$  concentrations in mass % for northern Yengweni transects A – C

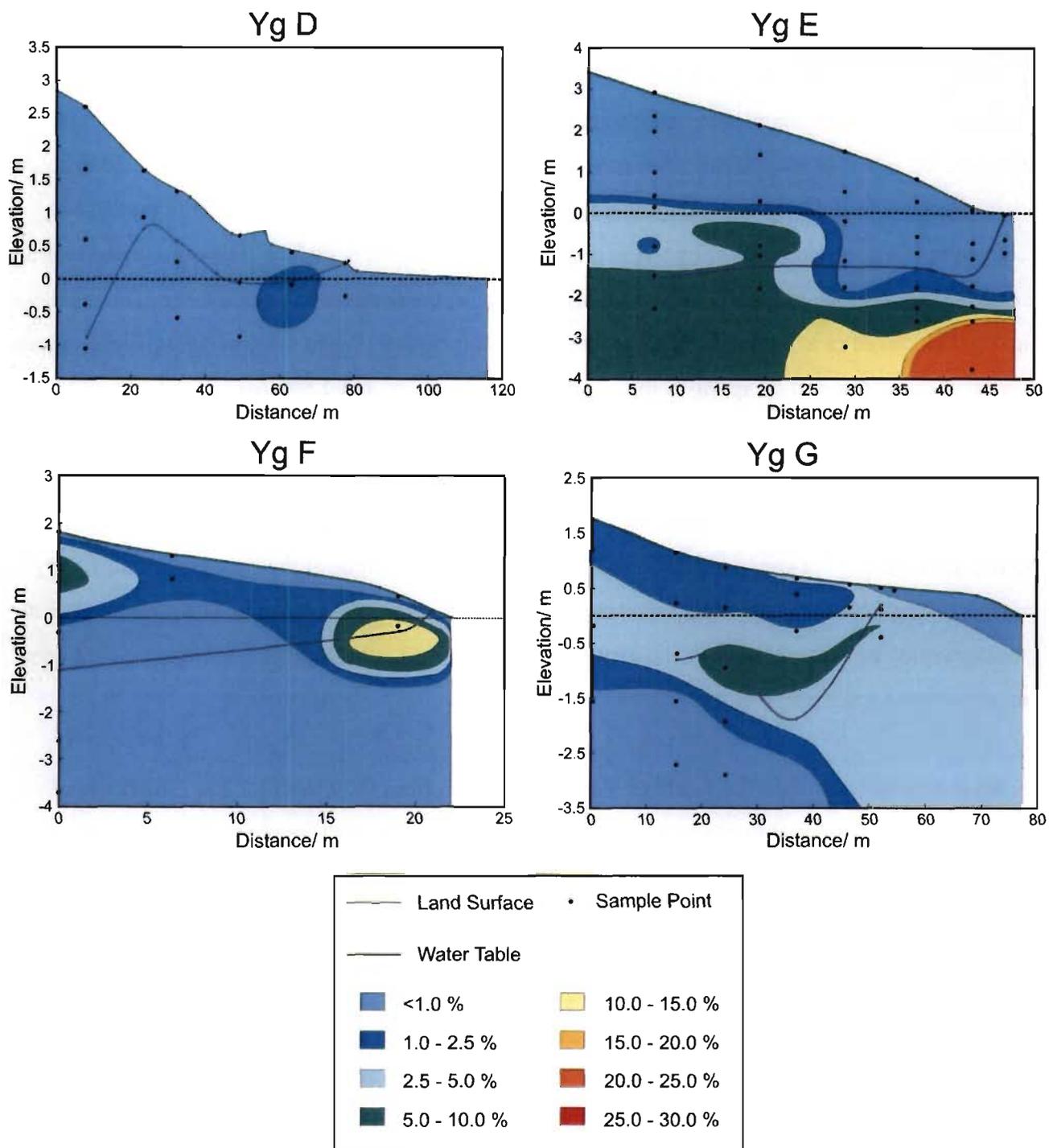
### 6.3.1.3. Southern Yengweni

The pattern and concentration of calcium distribution on the southern Yengweni was distinctly different from elsewhere in the study area (Figure 6.3.9). Calcium concentrations ranged from 0.05 to 24.77 % in transect Yg E and the maximum values in other transects were somewhat lower than this. Calcium distribution at Yg D was most like the other transects in the study area with concentrations generally increasing towards the surface and the drainage line, although the maximum calcium concentration occurred at the water table. Maxima at Yg E, F and G also occurred adjacent to the drainage line below the soil surface. The highest concentrations were all found at or below the water table.

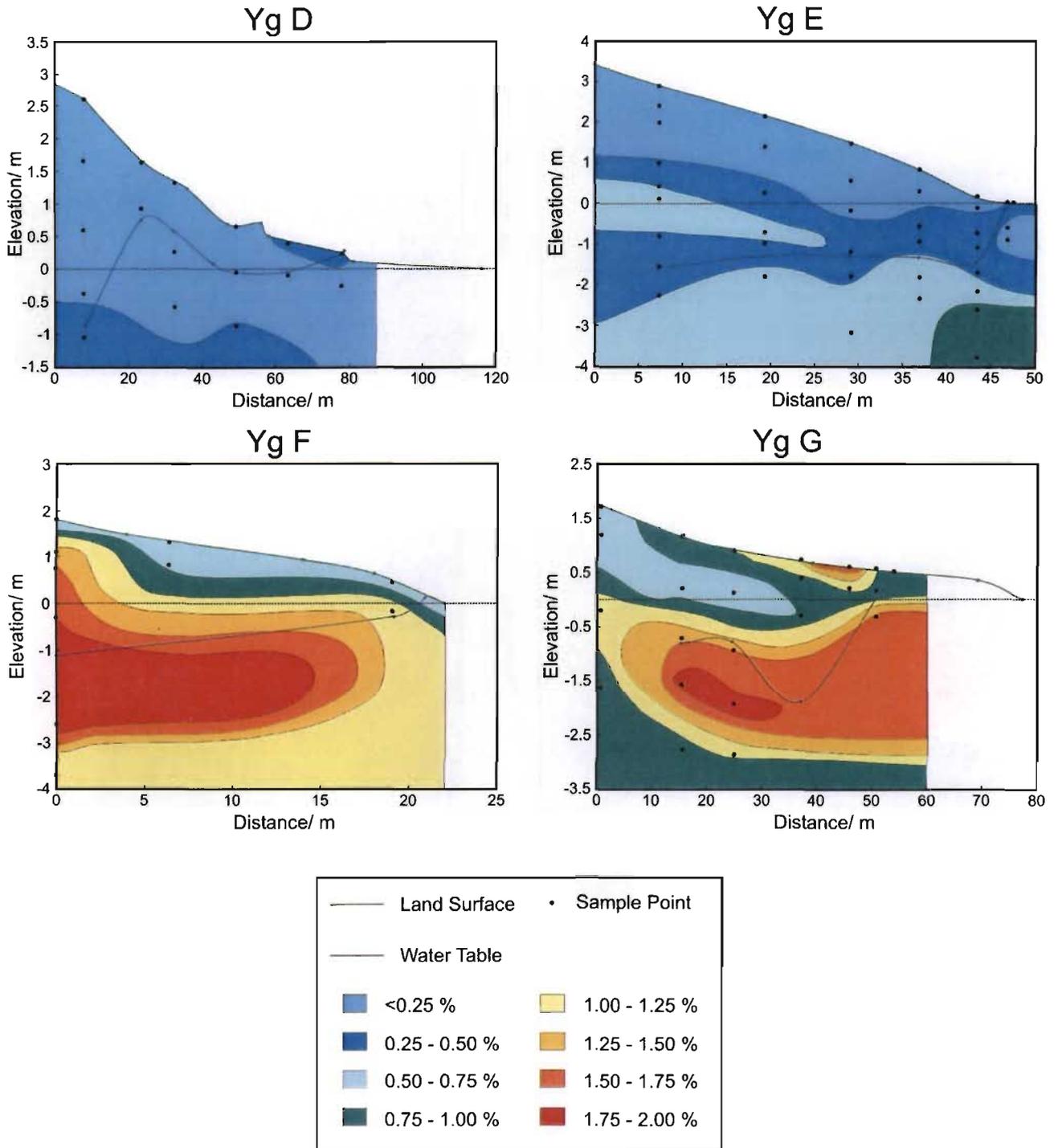
The magnesium minimum of the southern Yengweni was 0.05 %, while the maximum magnesium concentration recorded was 1.88 % at Yg F (Figure 6.3.10). Mid-Yengweni transects Yg D and E had similar ranges of magnesium concentrations to the Totweni and northern Yengweni, while those in Yg F and G were higher. A further trend is evident on the southern Yengweni, other than that identified in the Totweni and northern Yengweni described above, which is the increase in concentration both with proximity to the drainage line and the soil surface. The other trend was the tendency for high magnesium concentrations to occur at the depth of the water table. The maximum at Yg E occurred at a depth of 3 m adjacent to the drainage line, while maxima at Yg F and G were found at upper transect sampling points at depths of about 3 m and 2.5 m respectively.

Iron concentrations on the southern Yengweni ranged from 0.72 % 13.79 % at Yg F (Figure 6.3.11). The range of iron concentrations at the mid-Yengweni transects Yg D and E was comparable to the Totweni and northern Yengweni, while the range at the two southernmost transects (Yg F and G), was higher than the Totweni and northern Yengweni. The dual trend of the 'background' superimposed with elevated concentrations around the water table was evident once more, in transects Yg E, F and G.

Sodium concentrations on the southern Yengweni ranged from 0.00 % to 1.71 %. The range of sodium concentrations at transects Yg D and E was comparable to those of the Totweni and northern Yengweni transects (Figure 6.3.12), while values in Yg F and G exceeded those of the Totweni and the other Yengweni transects. Distribution patterns were once more less distinct than those of the other oxides. The trend of increase in concentration towards the drainage line and the soil surface was discernible to some degree as there was still evidence of surface concentration, but the outstanding feature about the sodium plots was the close association of elevated concentrations with the water table along the length of each transect. Maxima also occurred in similar locations to those recorded for calcium, magnesium and iron.



**Figure 6.3.9** Soil CaO concentrations in mass % for southern Yengweni transects D – G



**Figure 6.3.10** Soil MgO concentrations in mass % for southern Yengweni transects D – G

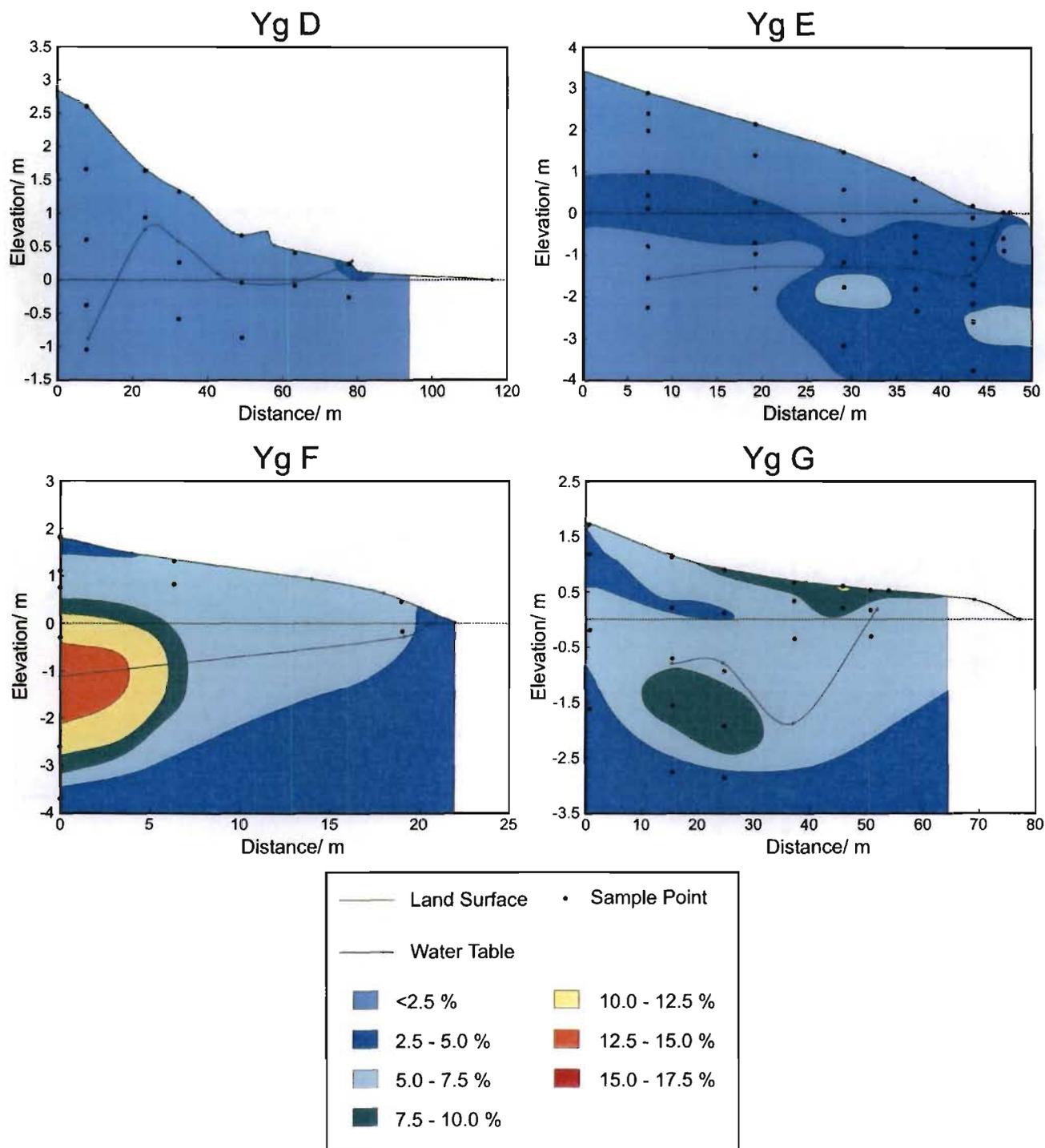
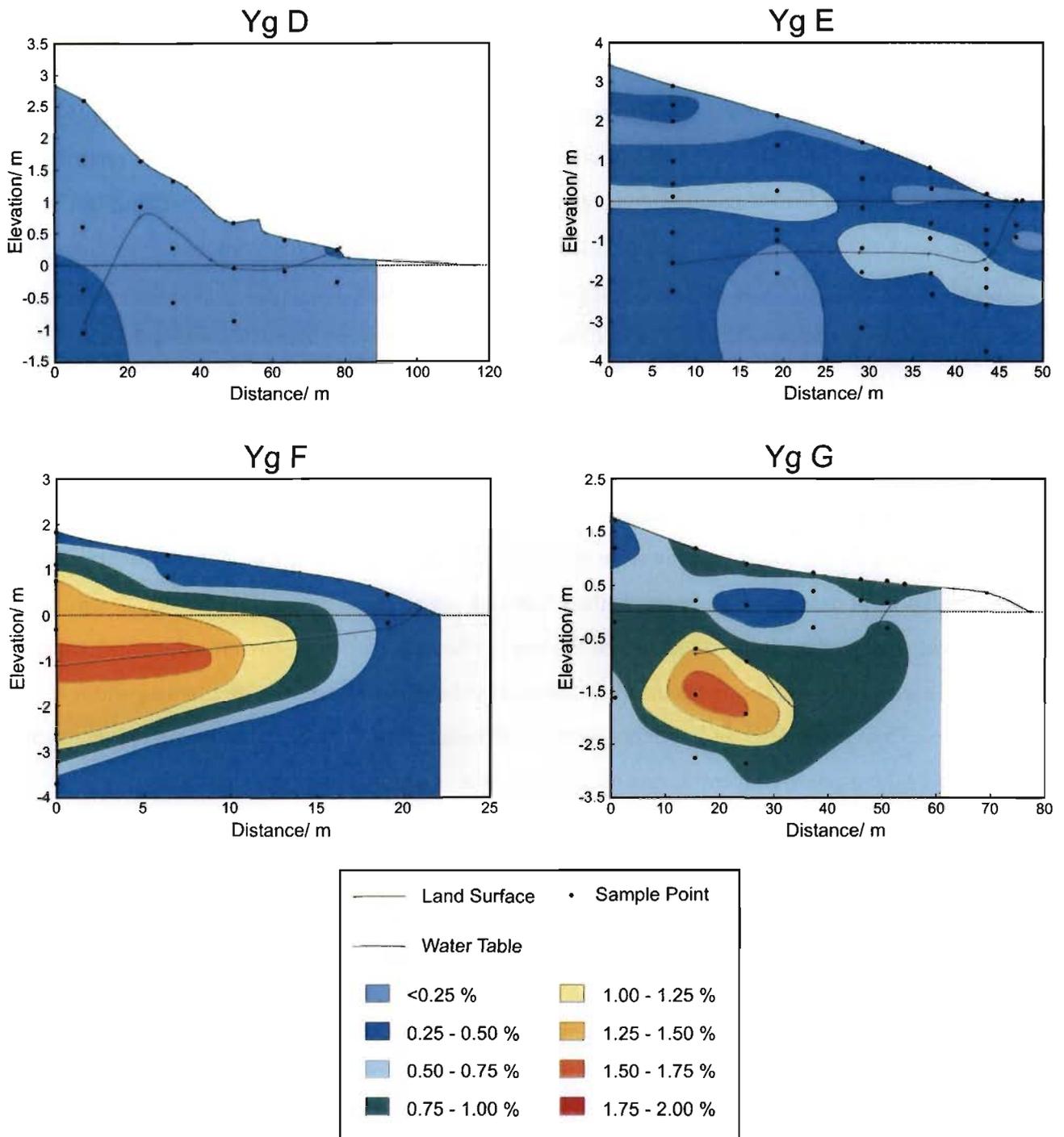


Figure 6.3.11 Soil Fe<sub>2</sub>O<sub>3</sub> concentrations in mass % for southern Yengweni transects D – G



**Figure 6.3.12** Soil Na<sub>2</sub>O concentrations in mass % for southern Yengweni transects D – G

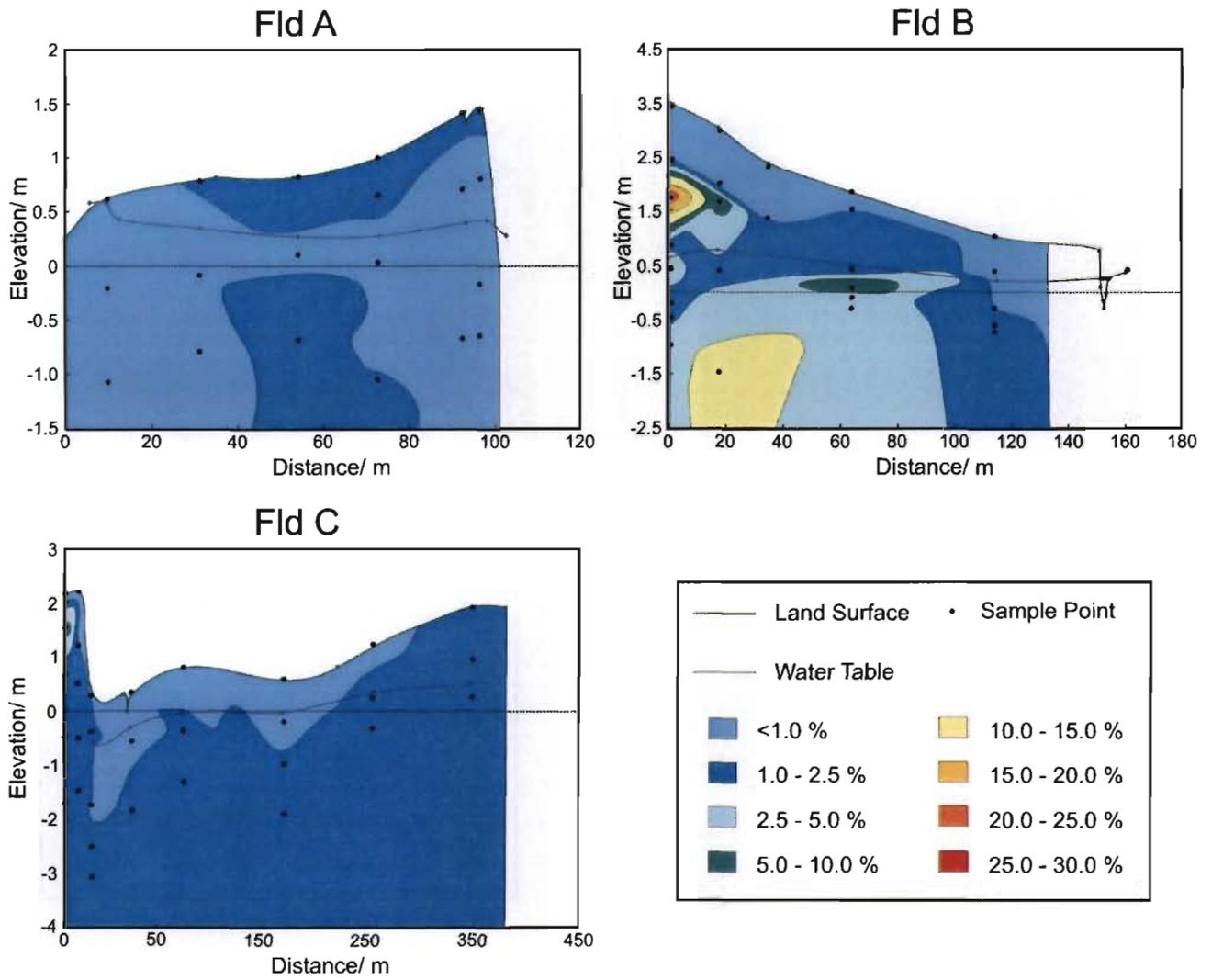
#### 6.3.1.4. Floodplain

Calcium minima found in the floodplain soils were higher than elsewhere in the study area (Figure 6.3.13). The maximum calcium concentration for the floodplain transects was 23.96 % recorded at Fld B. Fld A had the lowest calcium concentrations of the floodplain group with a maximum calcium concentration of 1.30 %. At Fld C the highest concentrations generally occurred at depth although the maximum value was in the upper part of the transect at a depth of less than 1m below the soil surface. In the case of Fld B the highest concentrations were below the water table in the upper part of the transect and at a depth of 2m below the soil surface.

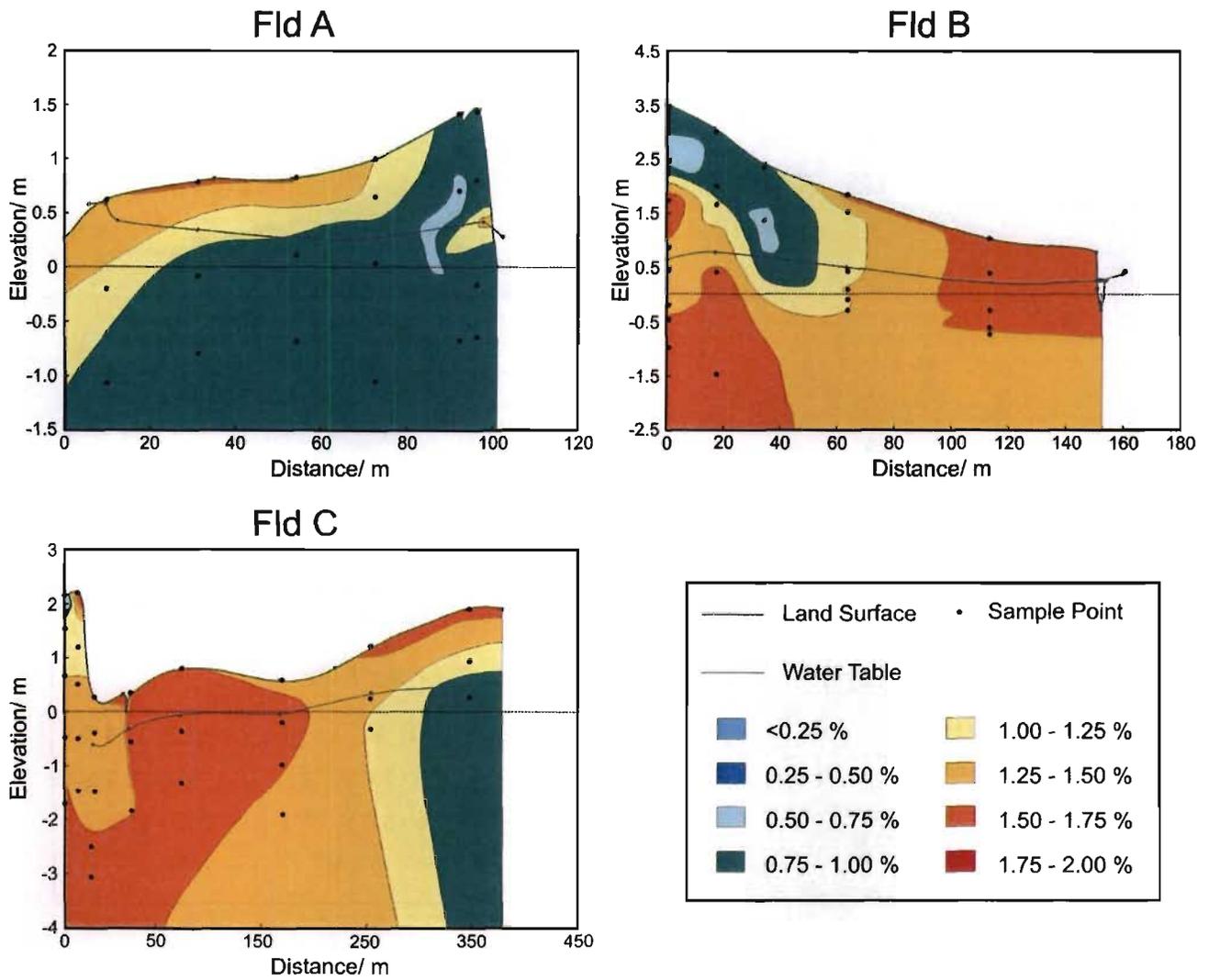
The magnesium concentrations on the floodplain ranged from 0.41 % to 1.81 % at Fld C (Figure 6.3.14). Distribution of magnesium in the sediments of Fld A tended to be lower at depth, increasing towards the surface, away from the oxbow at the southern extent of the alluvial ridge that dams the Totweni drainage line, towards the Mpanza Lake in the north of the transect. A similar pattern was seen in the southern reaches of the Fld C transect. However, towards the upper transect of Fld C, higher concentrations occurred at both the surface and at depth, with the maximum at a depth of ~2.75 m associated with a depression in the water table. The distribution was reversed at Fld B where the highest concentrations mostly occurred at depth below the water table.

The iron minima in the floodplain transects were the highest recorded in the study area ranging from 4.05 to 6.24 % (Figure 6.3.15). Similarly the maximum of 14.86 % recorded at Fld B was the highest iron concentration recorded. The concentration pattern at Fld A showed higher concentrations at the soil surface and towards Mpanza Lake. Iron values at Fld C were higher in the vicinity of a depression on the floodplain and near the soil surface. In the upper transect part of Fld B, higher iron concentrations occurred at depth, while in the lower transect this trend was reversed such that the highest concentrations were near the floodplain surface.

The sodium minima were also the highest recorded in the study area ranging from 0.48 % to 0.81 % (Figure 6.3.16). The maximum at Fld C of 2.01 % was the highest concentration recorded in the study area. At both Fld B and Fld C sodium concentrations generally increased with depth and were highest around the water table, with some exceptions in the upper portion of the transects. At Fld A high concentrations were recorded both at the soil surface in the upper part of the transect and at depth in the lower part of the transect.

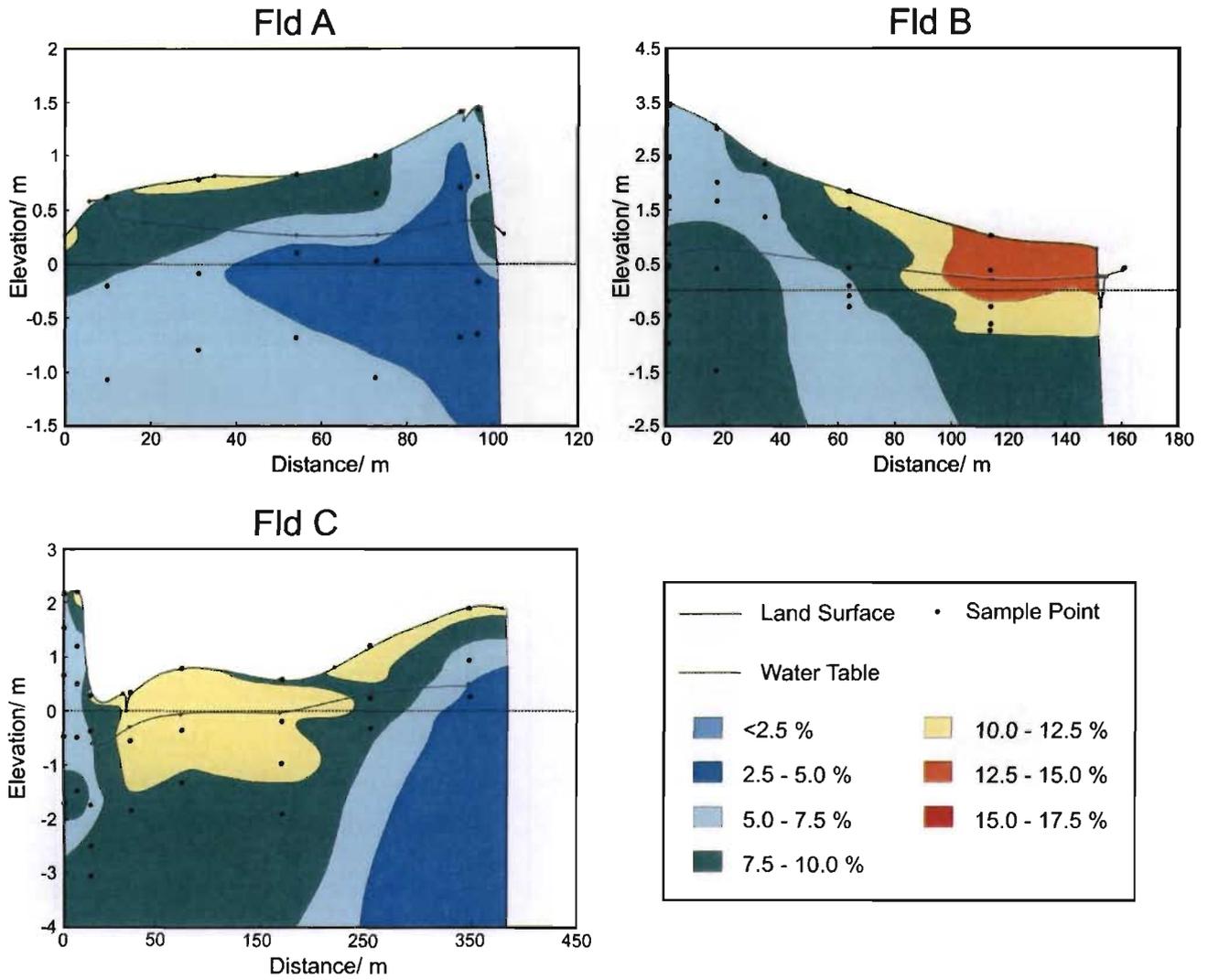


**Figure 6.3.13** Soil CaO concentrations in mass % for floodplain transects A – C  
 Note: All transects plotted from north (left of diagram) to south (right of diagram)



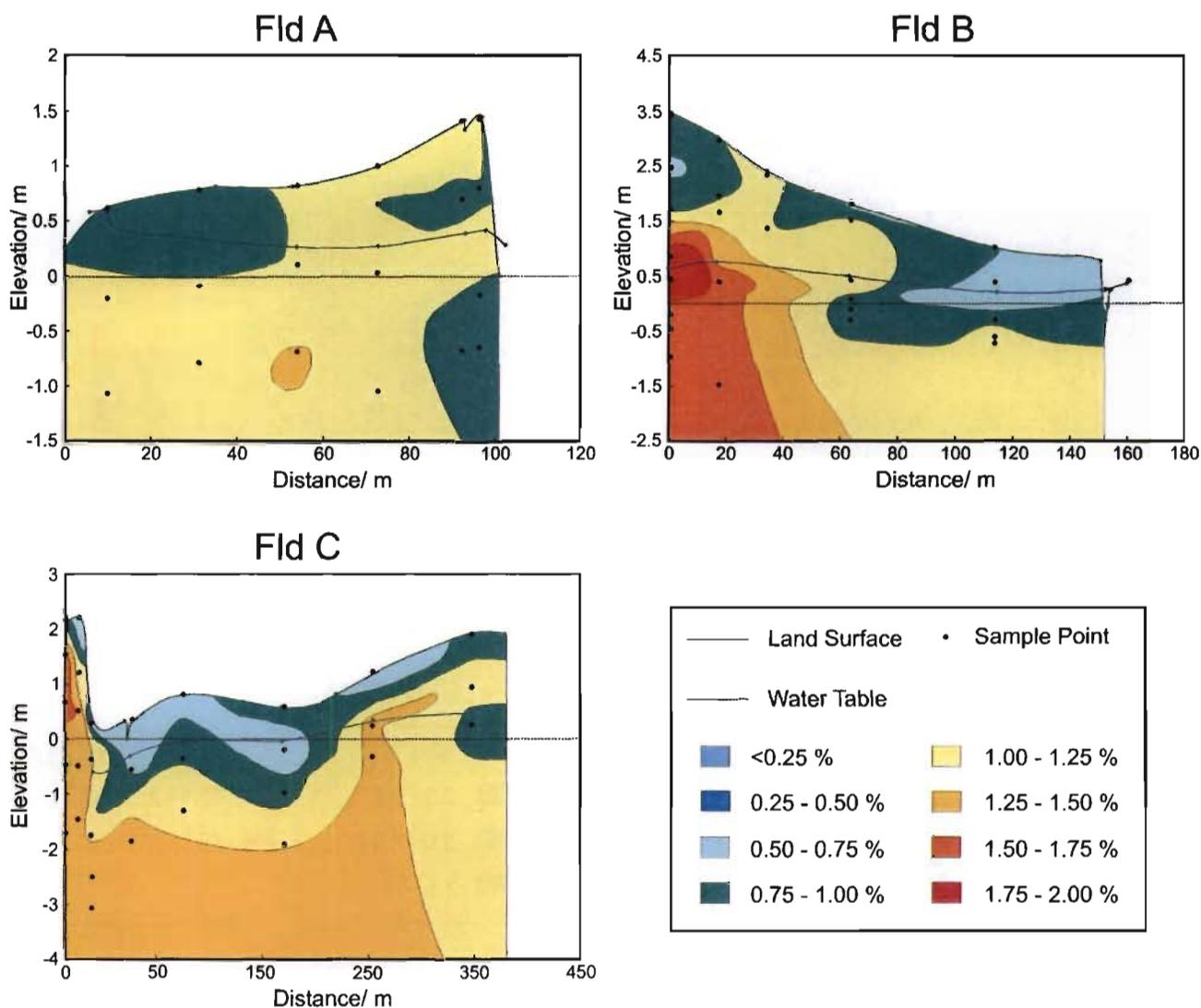
**Figure 6.3.14** Soil MgO concentrations in mass % for floodplain transects A – C

Note: All transects plotted from north (left of diagram) to south (right of diagram)



**Figure 6.3.15** Soil  $Fe_2O_3$  concentrations in mass % for floodplain transects A – C

Note: All transects plotted from north (left of diagram) to south (right of diagram)



**Figure 6.3.16** Soil  $\text{Na}_2\text{O}$  concentrations in mass % for floodplain transects A – C

Note: All transects plotted from north (left of diagram) to south (right of diagram)

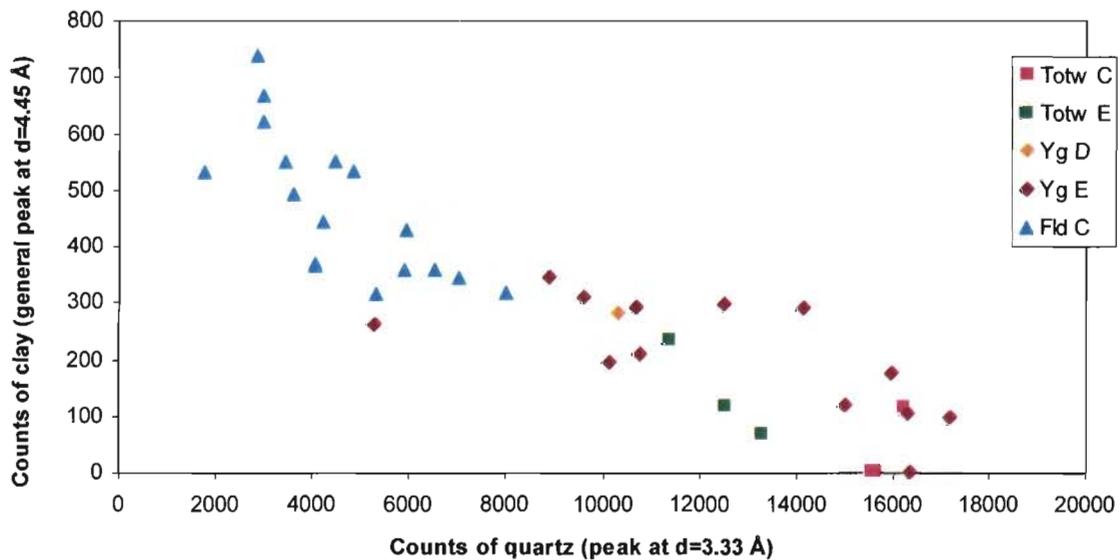
## 6.3.2. Mineralogy

### 6.3.2.1. Bulk sample analysis

XRD on the bulk samples identified strong quartz signals in all samples, particularly in the Totweni and northern Yengweni. Clays, feldspars and calcite were also identified as important minerals (raw data is presented in Appendix F).

The relationship between quartz and clay counts suggested a gradation from quartz-rich, low-clay Totw C, Totw E and Yg E samples (Figure 6.3.17) through intermediate quartz and clay counts at Yg D and Yg E, to the high-clay and low-quartz counts of Fld C. The samples of Fld C represented

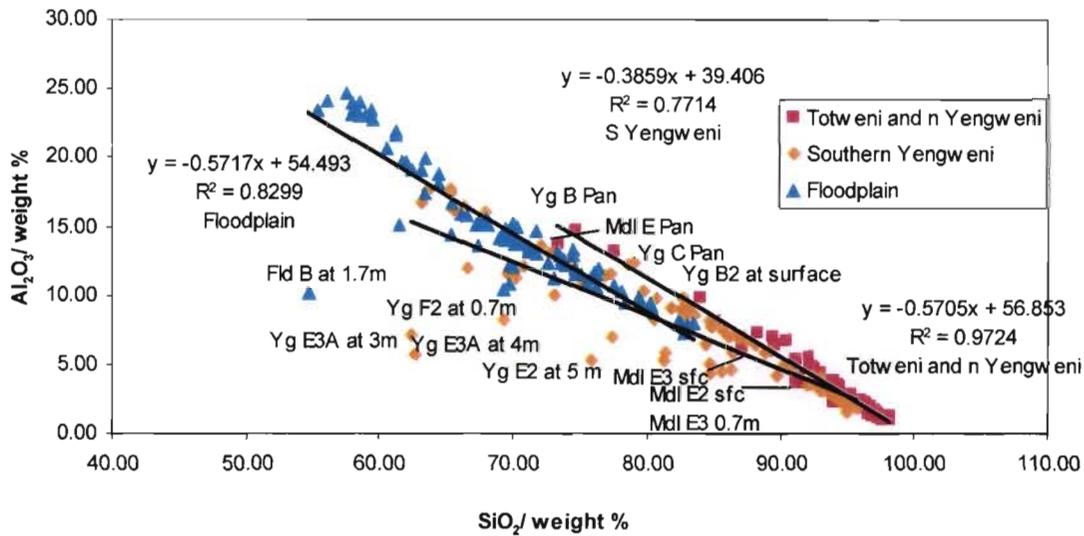
alluvial clay deposits of the uMkhuze River. The intermediate samples were difficult to explain on the basis of fluvial clastic sedimentation alone, given the low uMkhuze River sediment inputs to soils above the maximum retention level of the Yengweni Lake.



**Figure 6.3.17** The contribution of quartz and clays to sediments of the uMkhuze Wetland System based on bulk XRD analyses

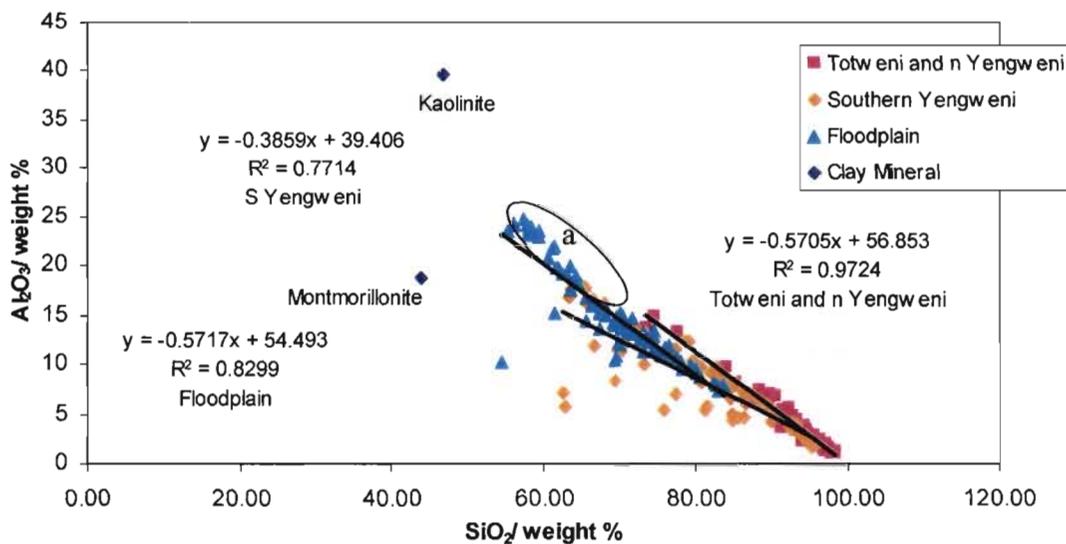
In order to differentiate between the quartz-rich marine sands and the alluvial sediments of the uMkhuze River floodplain,  $\text{SiO}_2$  was plotted against  $\text{Al}_2\text{O}_3$  using XRF data on bulk samples. It revealed distinct differences in terms of alumina and silica composition with respect to geographic location (Figure 6.3.18). In general, the Totweni and northern Yengweni samples had high silica (> 85 %) and low alumina (< 7 %) concentrations, although a few samples in close proximity to the floodplain had higher alumina (10 – 15 %) and lower silica (~70 %) concentrations. There was a decline in silica concentration as alumina concentration increased ( $R^2 = 0.97$ ,  $p < 0.05$ ). In contrast to samples from the Totweni and northern Yengweni, floodplain samples had low silica (< 75 %) and high alumina (> 7 %) concentrations, once again with a significant decline in silica concentration as alumina concentration increased ( $R^2 = 0.83$ ,  $p < 0.05$ ). Samples from southern Yengweni were generally intermediate between those of the Totweni and northern Yengweni, and those of the floodplain. A large proportion of these samples showed a similar pattern of decreasing silica concentration as alumina concentration increases, but many samples had an unexpectedly low silica concentration (60 – 70 %) in relation to the alumina concentration, which suggested dilution

of both silica and alumina concentrations by other sediment components. These samples resulted in the low  $R^2$  value for all southern Yengweni samples of 0.77 ( $p < 0.05$ ).

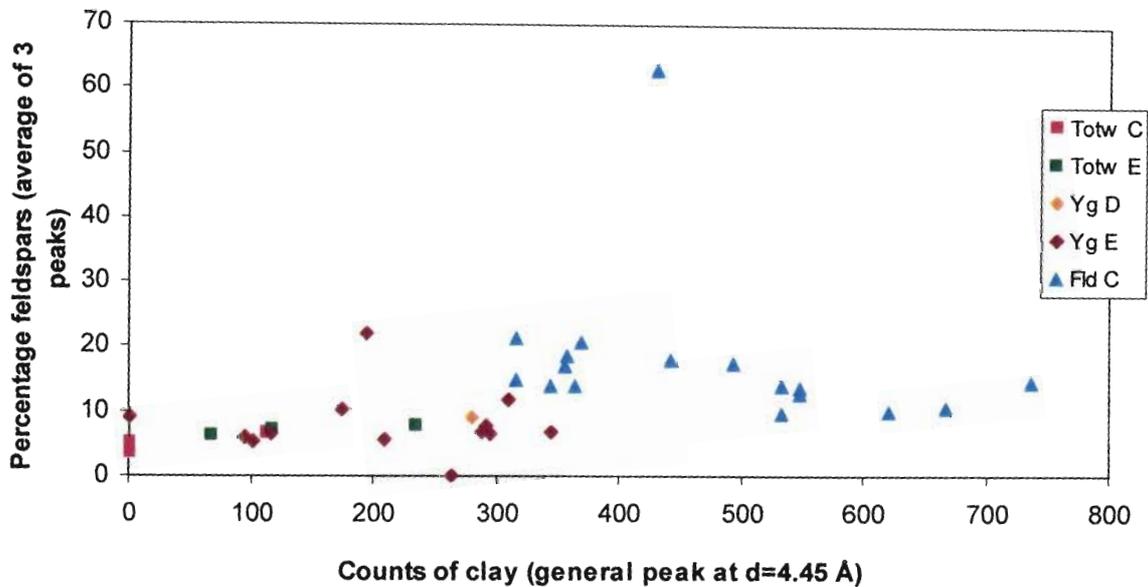


**Figure 6.3.18** The relationship between aluminium and silicon in uMkhuze Wetland System sediments

In Figure 6.3.19, typical kaolinite and montmorillonite values have been included in the plot of silica versus alumina concentrations. The high silica and low alumina concentrations of the Totweni and northern Yengweni samples plot on a trajectory towards the kaolinite data point, while the higher alumina concentrations of the floodplain (indicated by the oval labelled ‘a’) and to some degree the southern Yengweni samples result in dilution of the silica concentration and a greater association with the montmorillonite data point.



**Figure 6.3.19** The relationship between silica and alumina in the uMkhuze Wetland System, including possible clay end members in relation to the variables



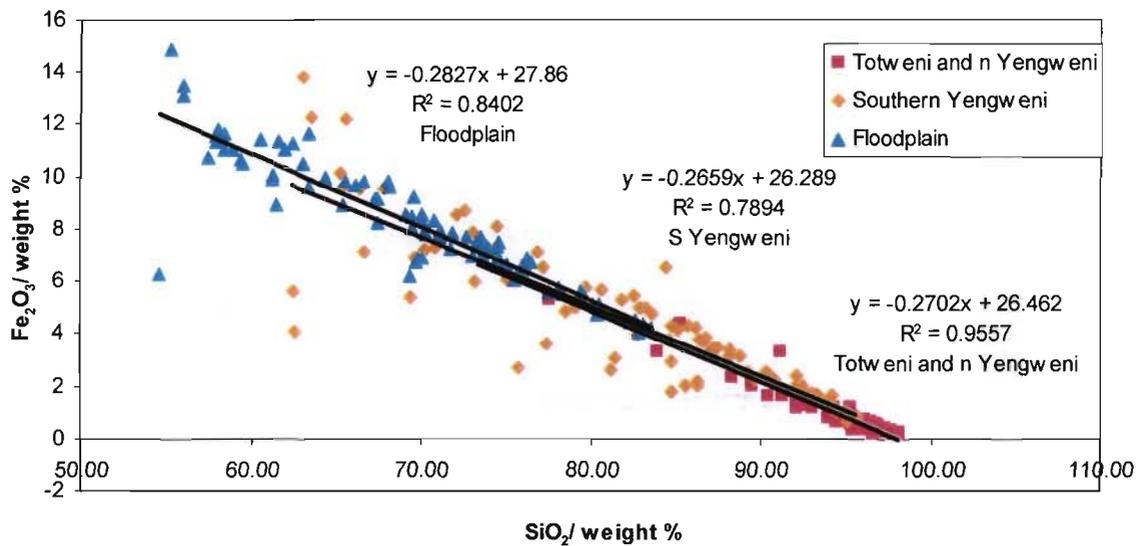
**Figure 6.3.21** The relationship between feldspar and clay content in uMkhuze Wetland System sediments

Except for Totweni E, calcite was detected at all transects included in the analysis (Totw C, Fld C and Yg E). Less than 3 % calcite was present at Totw C, Fld C and samples furthest from the drainage line at Yg E. Lower transect samples (closer to the drainage line) at depth from Yg E produced values of 14.2, 16.9 and 23.5 % calcite.

### 6.3.2.2. Fine fraction analysis

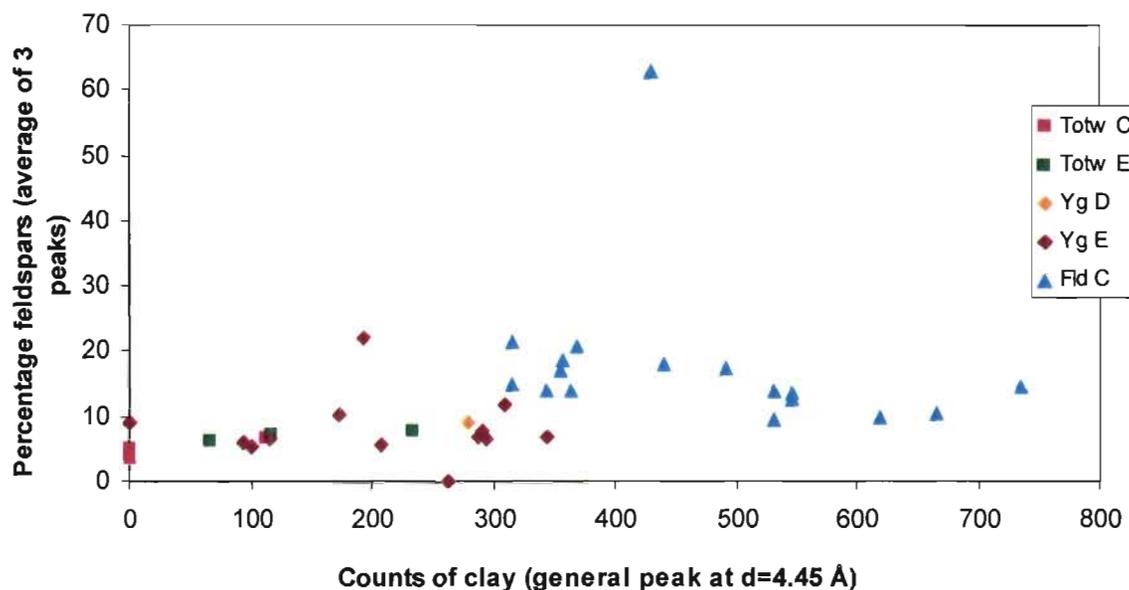
XRD analysis of the fine fraction of selected samples detected the secondary minerals from the decomposition of igneous rocks including mica, potassium feldspar and sodium feldspar, with the most dominant component being mica at a concentration of approximately 60 % (Table 6.3.1). The clay minerals montmorillonite, vermiculite and kaolinite, as well as interlayer minerals montmorillonite-vermiculite and mica-vermiculite were also present in the study area, with montmorillonite and montmorillonite-vermiculite constituting the largest contribution to the fine fraction with concentrations of greater than 60 % in certain samples. The metamorphic mineral talc was found in concentrations up to 10 % of the fine fraction. The iron oxyhydroxide goethite and aluminium oxide gibbsite were present in slightly higher concentrations of up to 30 %. Traces of quartz, calcite, haematite, palygorskite and mica-chlorite were also detected.

A similar pattern was evident for the relationship between silica and iron oxide. There was a general decrease in iron oxide concentration as silica concentration increased. Samples from the Totweni and northern Yengweni with high silica and low iron oxide concentrations were easily distinguished from floodplain samples with low silica and high iron oxide concentrations (Figure 6.3.20). Samples from the southern Yengweni had intermediate silica and iron oxide concentrations, which indicated dilution of both silica and iron oxide concentrations by other sediment components.



**Figure 6.3.20** The relationship between iron and silicon in uMkhuze Wetland System sediments

A weak relationship existed between the clay and feldspar content with an  $R^2$  value of 0.113 ( $P = 0.33$ ,  $p < 0.05$ ; Figure 6.3.21). Feldspars occurred throughout the study area and were slightly more prevalent in samples of high clay content, typified by the floodplain transect Fld C. Feldspar contributed least to sediment in the quartz-rich regions of the Totweni and as noted in some samples of the southern Yengweni transect Yg E.



**Figure 6.3.21** The relationship between feldspar and clay content in uMkhuze Wetland System sediments

Except for Totweni E, calcite was detected at all transects included in the analysis (Totw C, Fld C and Yg E). Less than 3 % calcite was present at Totw C, Fld C and samples furthest from the drainage line at Yg E. Lower transect samples (closer to the drainage line) at depth from Yg E produced values of 14.2, 16.9 and 23.5 % calcite.

### 6.3.2.2. Fine fraction analysis

XRD analysis of the fine fraction of selected samples detected the secondary minerals from the decomposition of igneous rocks including mica, potassium feldspar and sodium feldspar, with the most dominant component being mica at a concentration of approximately 60 % (Table 6.3.1). The clay minerals montmorillonite, vermiculite and kaolinite, as well as interlayer minerals montmorillonite-vermiculite and mica-vermiculite were also present in the study area, with montmorillonite and montmorillonite-vermiculite constituting the largest contribution to the fine fraction with concentrations of greater than 60 % in certain samples. The metamorphic mineral talc was found in concentrations up to 10 % of the fine fraction. The iron oxyhydroxide goethite and aluminium oxide gibbsite were present in slightly higher concentrations of up to 30 %. Traces of quartz, calcite, haematite, palygorskite and mica-chlorite were also detected.

The fine silt and clay fraction in the Totweni Drainage Line was between 3 and 6 % of the bulk sample while in the southern Yengweni the contribution of fine silt and clay was 6 – 16 %, and on the floodplain 8 – 14 %. Mica<sup>1</sup> formed the largest percentage of the fine fraction at 30 – 60 % in surface and near-surface samples in all regions analysed (Table 6.3.1). At greater depths, mica was still present at 10 – 30 % in the southern Yengweni and floodplain transects. Therefore, the concentration of mica was much higher on the floodplain and in the southern Yengweni, with a trend of decreasing concentration with depth (see Table 6.3.2 at the end of this section).

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<sup>1</sup> Although clay-sized mica is often termed illite, 'mica' will be used throughout the text

**Table 6.3.1** Results of XRD analysis of the fine fraction of selected samples

Mineral	Totw C3	Totw E3	Yg D1	Yg E1.3	Yg E1.8	Yg E1.13	Yg E3A.1	Yg E3A.6	Yg E3A.10	Fld C1.1	Fld C1.5	Fld C1.13	Fld C2.1	Fld CSP.1	Fld CSP.13	Fld C10.1	Fld C10.3
Montmorillonite				***	****	****	***	***(*)	****			***(*)			****		
Montmorillonite-Vermiculite	***	***	****				tr			***	***(*)	*	***	**(*)		***	***(*)
Vermiculite										tr					*(*)		*
Mica-vermiculite	**(*)													**(*)	tr	tr	tr
Mica-chlorite				tr													
Mica	**(*)	***	**	**	**	*(*)	***	**(*)	**	***	**(*)	**	**(*)	**(*)	**	***	**
Kaolinite	**(*)	**	**	*	**	*(*)	**	**	*(*)	**	**	*	**(*)	**	*	**	*(*)
Quartz	tr	tr	tr	**	*	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr
K-feldspar		tr		**	**	*(*)	**	tr	tr	*	tr/*	tr/*	*	tr	*	*	*
Na-feldspar				tr		*(*)			tr	*	*	*			*	tr/*	*
Calcite			tr	tr							tr		tr				tr
Haematite	tr			tr	tr		tr	tr	tr/*	tr	tr/*	tr		tr	tr	tr/*	tr
Goethite		*						**	*(*)	**	**	*	*(*)	**	*	**	*
Gibbsite		tr	tr										*		*		**
Talc	*			*					tr		*	*			tr		*(*)
Palygorskite														tr			tr

**Key**

Trace	<5 %	tr
Present	5-10 %	*
Uncommon	10-30 %	**
Common	30-60 %	***
Abundant	>60 %	****

Bracketed entries e.g. \*(\*) intermediate between \* and \*\* abundance

Potassium feldspar was generally most abundant at the surface, comprising 10 – 30 % of the fine fraction of surface sediments on the southern Yengweni and 5 – 10 % of the fine fraction at depth. Surface samples on the floodplain also constituted 5 – 10 % potassium feldspar (Table 6.3.2). Trace amounts (less than 5 %) were present in samples at depth in the southern Yengweni and floodplain as well as the southernmost Totweni transect. No potassium feldspar was detected at either of the transects midway along the Totweni (Totw C) or Yengweni Drainage Lines (Yg D). Given the particle size distribution, potassium feldspar was far more abundant in the southern Yengweni and floodplain than in the Totweni sediments. Potassium feldspar was present in floodplain regions as well as the southern Yengweni and Totweni Drainage Lines, but was absent from the northern reaches of the drainage lines. The general trend was an increase in concentration towards the surface (Table 6.3.2).

Sodium feldspar occurred at low concentrations in the fine fraction, with maximum concentrations of 5 – 10 % on the southern Yengweni and floodplain (Table 6.3.1). Trace amounts were present in other southern Yengweni and floodplain samples. No sodium feldspar was detected on the Totweni or the mid-Yengweni transect (Yg D). There did not seem to be any definite trend in distribution (Table 6.3.2).

The distribution of montmorillonite was the reverse of both mica and potassium feldspar, increasing in concentration with depth in both the southern Yengweni and floodplain (Table 6.3.2). The fine fraction of surface sediments on the southern Yengweni comprised 30 – 60 % montmorillonite, while no montmorillonite was detected in surface samples of the floodplain. Samples at depth had a >60 % concentration in the fine fraction on both the southern Yengweni and floodplain. No montmorillonite was detected on the Totweni Drainage Line or at the mid-Yengweni transect, Yg D (Table 6.3.1). The southern Yengweni had the highest montmorillonite concentrations.

Vermiculite was poorly represented in uMkhuze Wetland System samples, with only trace amounts detected in a surface floodplain sample, while accounting for between 5 – 30 % of the fine fraction in a floodplain sample at depth (Table 6.3.1). It is thus possible that vermiculite increases with depth (Table 6.3.2).

Vermiculite was however present in interlayer minerals, with both mica-vermiculite and montmorillonite-vermiculite detected in the floodplain sediment and in Totweni sediments (Table 6.3.1). Mica-vermiculite was present in trace amounts in both surface sediments and one sample at

depth on the floodplain, and at a concentration of 10 – 60 % in the fine fraction of a floodplain surface sample and surface sediment at the mid-Totweni transect, Totw C. No clear distribution pattern was present (Table 6.3.2). Montmorillonite-vermiculite was most abundant on the floodplain and southern Yengweni, at greater than or roughly equal to 60 % at depths of less than 1m on the floodplain as well as around 5.5 m on the mid-Yengweni transect. The fine fraction of surface samples on the floodplain and the Totweni Drainage Line comprised 30 – 60 % montmorillonite-vermiculite. A few floodplain and southern Yengweni samples had low to trace amounts of the interlayer mineral, with a notable absence of montmorillonite-vermiculite in the remainder of the southern Yengweni samples and a floodplain sample taken at depth. Therefore, although there was a slight increase in near-surface samples, the distribution of montmorillonite-vermiculite was the reverse of mica and potassium feldspar distribution, decreasing towards the surface (Table 6.3.2).

In comparing the distribution of montmorillonite and montmorillonite-vermiculite, where montmorillonite was most abundant at greater than 30 % in the fine fraction, montmorillonite-vermiculite was absent or present in small amounts (Table 6.3.1). In all samples where montmorillonite was absent, montmorillonite-vermiculite was present in concentrations greater than 30 %.

The concentration of kaolinite in the fine fraction reached a maximum of 10 – 30 % in samples collected both on surface and at depth (Table 6.3.1). Surface and near-surface samples of the floodplain and the Totweni generally had kaolinite concentrations between 10 and 30% as did a single sample in the southern Yengweni. Samples collected at greater than 1 m depth from the mid-Yengweni and southern Yengweni also had kaolinite concentrations between 10 and 30 %. Samples with concentrations of 5 – 10 % were found at depth on the floodplain and near the soil surface on the southern Yengweni. It seemed that the trend on the floodplain was one of decreasing kaolinite concentration with depth, while the southern Yengweni did not show a noticeable trend in kaolinite distribution (Table 6.3.2).

Gibbsite was present in trace amounts at depth on the mid-Yengweni and in surface sediments of the southernmost Totweni transect, while two floodplain samples on surface and at depth had concentrations of 5 – 10 % (Table 6.3.1). A near-surface sample on the floodplain had the highest concentration of gibbsite in the fine fraction, of 10 – 30 %. There was no recognisable pattern in gibbsite distribution (Table 6.3.2).

The iron oxyhydroxide, goethite, was present at depth with concentrations of 10 – 30 % on the southern Yengweni, and in surface and near-surface sediments of the floodplain (Table 6.3.1). Abundances of 5 – 10 % in the fine fraction were found at depth on the floodplain and in surface sediments of the southernmost Totweni transect, Totw E. Again, the distribution pattern seemed to be reversed between the southern Yengweni and floodplain, with goethite decreasing with depth on the floodplain and increasing with depth on the southern Yengweni (Table 6.3.2).

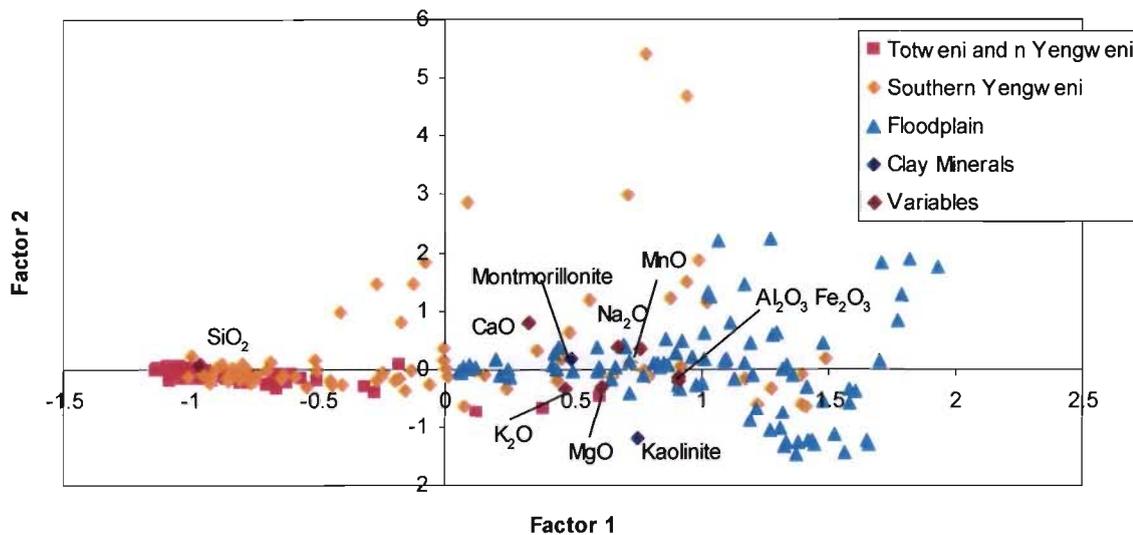
**Table 6.3.2** Distribution of minerals by region and depth

<b>Mineral</b>	<b>Totweni and northern Yengweni</b>	<b>Southern Yengweni</b>	<b>Floodplain</b>
Mica	Lower concentrations at depth	Present in greater amounts Lower concentrations at depth	Present in greater amounts Lower concentrations at depth
Potassium feldspar	Lower concentrations at depth *	Present in greater amounts Lower concentrations at depth	Present in greater amounts Lower concentrations at depth
Sodium feldspar	Not present	Present in some No discernible trend	Present No discernible trend
Montmorillonite	Not present  Higher concentrations at depth	Present in some, most abundant Higher concentrations at depth	Present in some  Higher concentrations at depth
Vermiculite	Not present	Not present	Present Possible higher concentrations at depth
Mica-vermiculite	Present in surface sediment	Not present	Most abundant  No discernible trend
Montmorillonite-vermiculite	Present Higher concentrations at depth	Virtually absent	Most abundant Higher concentrations at depth
Kaolinite	Present	Present in greater amounts No discernible trend	Present in greater amounts Lower concentrations at depth
Gibbsite	Present in some No discernible trend	Present in some No discernible trend	Most abundant No discernible trend
Goethite	Present in some  Lower concentrations at depth	Present in greater amounts Lower concentrations at depth	Present in greater amounts Lower concentrations at depth

\* When considering all bulk samples, this trend is reversed for feldspars in general: there is an increase in concentration with depth.

### 6.3.3. Factor analysis of soil oxide concentrations

A factor analysis of soil oxide concentrations was run including typical oxide concentrations for kaolinite and montmorillonite. Factor 1 versus Factor 2 is plotted in Figure 6.3.22 in order to assess chemical evolution of sediments in the uMkhuze Wetland System. As discussed in detail in Section 6.4.2.2, kaolinite and montmorillonite are possible mineral end members of the chemical evolution process in the system.



**Figure 6.3.22** Factor analysis of soil chemical variables, including montmorillonite and kaolinite as samples.

The Totweni and northern Yengweni samples are mostly clustered around the silica component score with low negative Factor 1 scores and close to 0 on Factor 2. The southern Yengweni samples are scattered along the Factor 1 axis, from grouping with the Totweni and northern Yengweni samples with low negative Factor 1 scores to plotting at some of the highest positive Factor 1 scores. This scatter indicates increasing concentrations of alumina and iron, which have the highest Factor 1 scores of the oxide variables, as well as calcium, magnesium, manganese, potassium and sodium. The spread of southern Yengweni samples into the positive region of Factor 2 is due to higher calcium concentrations in those samples, which were samples collected at depth on the southern Yengweni. The floodplain samples all show a greater influence on their soil chemistry of all the oxides except silica, in contrast to the majority of Totweni and northern Yengweni samples, as well as those from the southern Yengweni. The scatter of floodplain samples above the x-axis with high positive Factor 1 scores is due to higher concentrations of calcium, manganese and

sodium in samples taken at depth, mostly from the Floodplain C transect, with one sample from the Floodplain B transect. Those floodplain samples below the x-axis at high positive Factor 1 scores are surface samples of Floodplain B and C transects and have higher concentrations of magnesium and potassium than the remaining floodplain samples. These floodplain samples plot the closest to the kaolinite point, while the montmorillonite point is most closely associated with both floodplain and southern Yengweni samples from the transects Floodplain A on the southern border of the Totweni drainage line and Yengweni G, the southernmost Yengweni transect.

#### 6.3.4. Oxide concentrations in relation to titanium dioxide

Both the Totweni and northern Yengweni samples had lower titanium and aluminium concentrations than elsewhere in the study area, with relatively good positive correlations between the concentrations of these oxides of  $R^2 = 0.78$  ( $p < 0.01$ ) and  $R^2 = 0.53$  ( $p < 0.01$ ), respectively (Figure 6.3.23 a). Some samples from the northern Yengweni showed very little increase in aluminium concentration over the range of titanium concentrations encountered, while others showed a marked increase in aluminium concentration with increased titanium concentration. The samples of the southern Yengweni covered a wide range of titanium concentrations, and the aluminium concentrations were very well correlated with titanium concentrations with an  $R^2$  of 0.90 ( $p < 0.01$ ). However, two groupings were evident, with the first following the trendline of the Totweni and northern Yengweni samples ((a) in Figure 6.3.23 a), while the second displayed a less pronounced increase in aluminium concentration with an increase in titanium concentration ((b) in Figure 6.3.23 a). The first southern Yengweni group contained samples taken at depth from Yg E, which plotted in similar regions to samples taken from the lake bed of Lake Mpanza in the Totweni and samples from the thalweg of the northern Yengweni. The relationship between aluminium and titanium on the floodplain also produced two distinct groups. The first, comprising samples taken at depth, was similar to the southern Yengweni trend, although aluminium concentrations increased to a lesser degree with increasing titanium concentrations than in the southern Yengweni samples. The second, comprising surface and near-surface samples, was characterised by high aluminium concentrations at intermediate to high titanium concentrations, with evidence of aluminium decreasing with increasing titanium concentration.

The relationships between iron and titanium, and magnesium and titanium were very similar to those for aluminium and titanium concentrations (Figures 6.3.23 b and c). Totweni and northern Yengweni samples were characterised by low iron, magnesium and titanium concentrations, with

lake bed samples showing a marked increase in both iron and magnesium concentration as titanium concentration increased. In contrast, samples from the bank were characterised by relatively little increase in iron and magnesium concentration as titanium concentration increased. Samples from the southern Yengweni exhibited a wide range of concentrations for both iron and magnesium. The southern Yengweni samples with higher iron and magnesium concentrations than the general trend in relation to titanium concentrations were samples taken from the lake margin at depth, with the more southern samples exhibiting higher titanium concentrations. The floodplain samples plotted in two distinct groups in similar fashion to the aluminium plot, again with those samples taken at depth following the southern Yengweni trend of increasing iron and magnesium concentration as titanium concentration increased. However, surface and subsurface samples were characterised by decreasing iron and magnesium concentrations as titanium concentration increased.

The plot of calcium against titanium concentration showed that most samples had low calcium concentrations over the range of titanium concentrations, and a general increase in calcium concentration (Figure 6.3.23 d). However, a number of southern Yengweni samples had high calcium concentrations, which generally occurred at low to intermediate titanium concentrations. In contrast, the floodplain samples with high calcium concentrations occurred at high titanium concentrations and suggest decreasing calcium concentrations as titanium concentrations increased. As a result of this scatter, both the southern Yengweni and floodplain samples displayed poor correlations between calcium and titanium concentrations with  $R^2$  values of 0.0008 ( $p < 0.01$ ) and  $4 \times 10^{-5}$  ( $p < 0.05$ ) respectively. The southern Yengweni and floodplain samples with high calcium concentrations were all taken at depth. Figure 6.3.23 e shows those samples with a calcium concentration of less than 4 %. In contrast to those floodplain samples with high calcium concentrations, a group of floodplain samples with high titanium concentrations had low calcium concentrations ((a) in Figure 6.3.23 e). These samples comprised surface and near-surface material. This was similar to the trend noted for the other soil oxides where surface and near-surface floodplain samples showed decreasing concentrations of oxides with increasing titanium concentrations. However, the Totweni and northern Yengweni samples generally had low concentrations of calcium and titanium with a positive correlation between calcium oxide and titanium concentrations, with the overall pattern in these samples being similar to other oxides.

Both potassium and sodium concentrations showed a similar relationship to titanium concentration as other oxides, with Totweni and northern Yengweni having relatively low potassium, sodium and titanium concentrations, the southern Yengweni samples exhibiting a wide range of concentrations

while the floodplain samples had the highest potassium and sodium concentrations (Figures 6.3.23 f and g). There were two floodplain groups, with one exhibiting an increase in potassium and sodium concentration with increasing titanium concentration, while the other exhibited decreasing potassium and sodium concentrations with increasing titanium concentrations. Similar trends were noted for aluminium, iron and magnesium in relation to titanium concentration. A few southern Yengweni samples displayed higher potassium and sodium concentrations for a given titanium concentration than the remainder of the southern Yengweni samples ((a) in Figures 6.3.23 f and g). The samples with higher potassium concentrations were surface sediments, while the samples with high sodium concentrations were taken at depth. The relationship between potassium and titanium differentiated the Totweni and northern Yengweni samples, with the Totweni samples having higher potassium concentrations than the northern Yengweni samples. The northern Yengweni lake bed samples plotted along a similar trend to the Totweni samples with respect to the relationship between potassium and titanium concentrations.

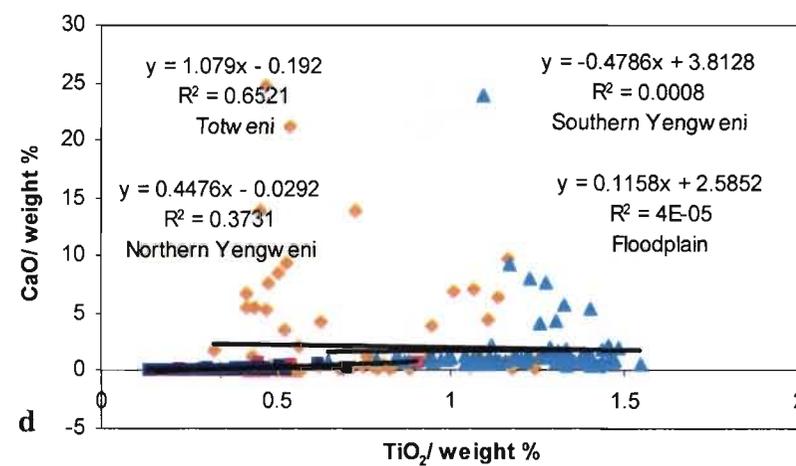
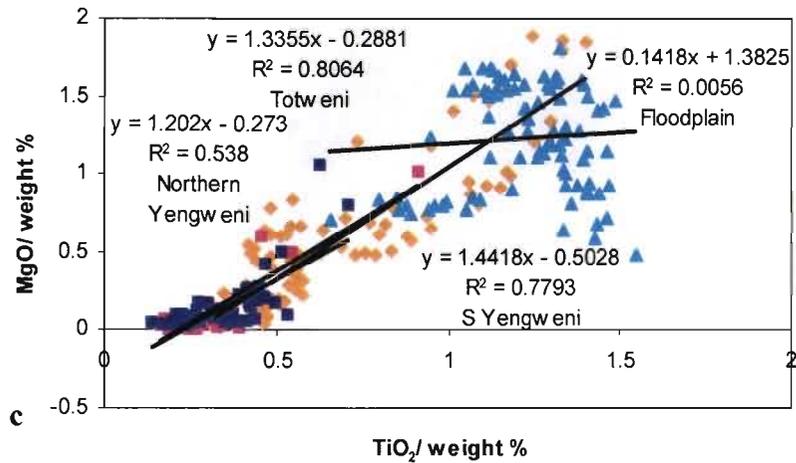
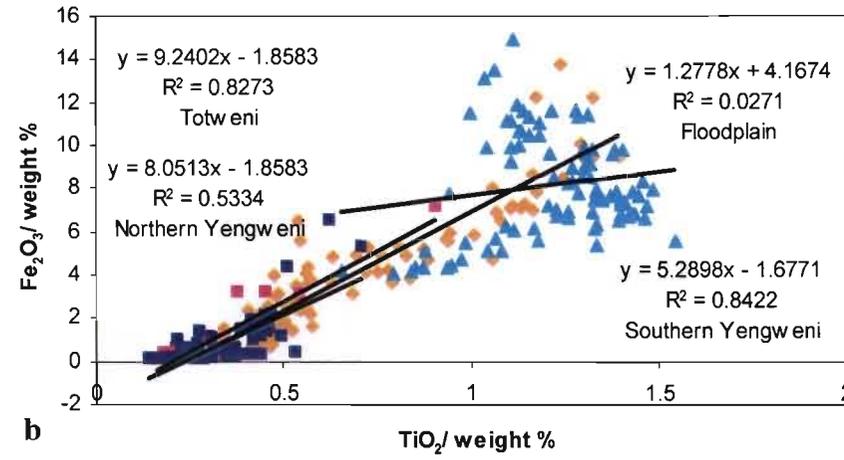
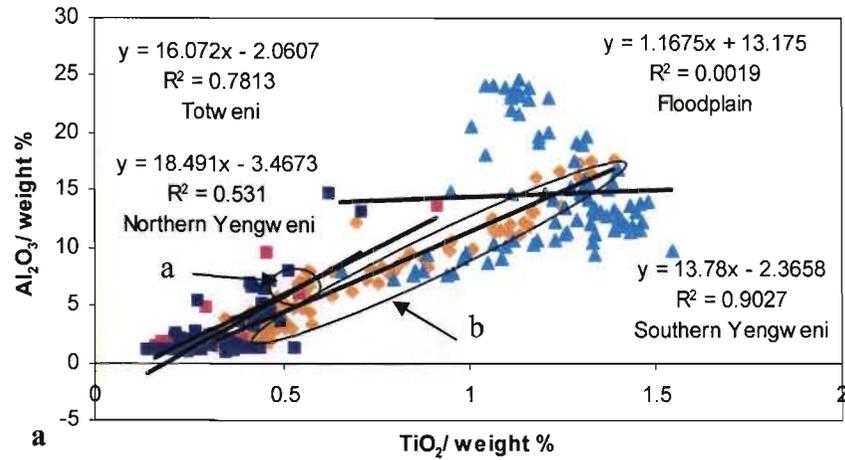
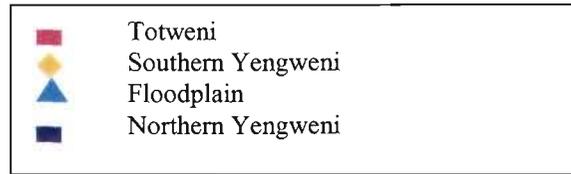


Figure 6.3.23 a – d The relationship between titanium dioxide and other soil oxides

(a) aluminium (b) iron (c) magnesium (d) calcium

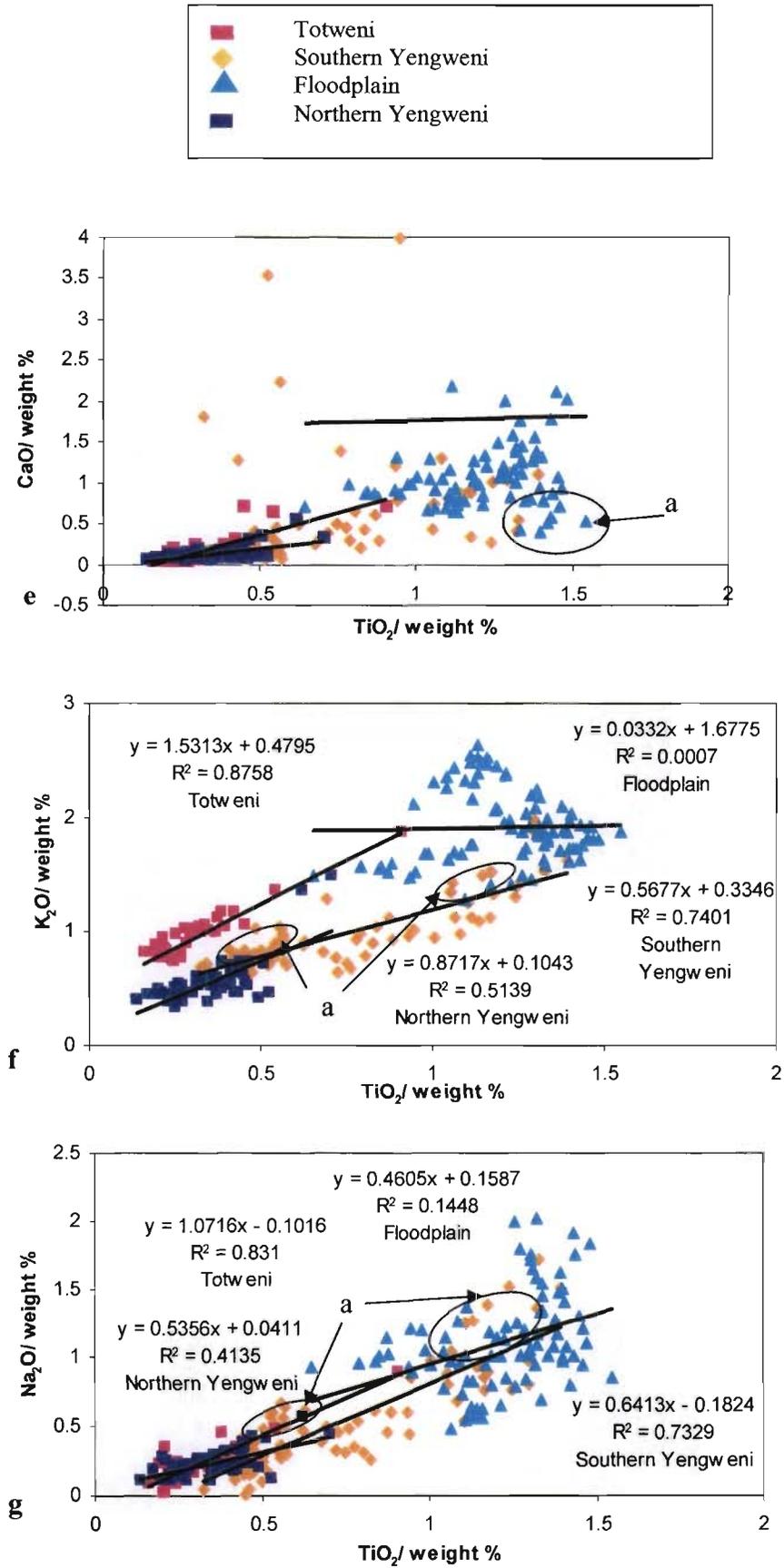


Figure 6.3.23 e – g The relationship between titanium dioxide and other soil oxides (e) expanded calcium (f) potassium and (g) sodium

## **6.4. Discussion**

### **6.4.1. Features of uMkhuze sediments**

Variation in soil chemistry in the uMkhuze Wetland System can be meaningfully related to hydrological processes and water chemistry. The Totweni and northern Yengweni were zones of groundwater discharge in which solute loads of groundwater were low. The southern Yengweni was a region of groundwater recharge in which the groundwater had variable solute loads, and the floodplain margin between the Totweni and Yengweni Drainage Lines was a region of low groundwater-surface water interaction, where groundwater solute loads were high.

#### **6.4.1.1. Totweni and northern Yengweni**

The Totweni and northern Yengweni showed relatively little variation with respect to soil chemistry and mineralogy, with relatively high quartz contents and low concentrations of elemental oxides. Concentrations (as weight %) did not exceed 0.55 % CaO, 7.3 % Fe<sub>2</sub>O<sub>3</sub>, 1.1 % MgO, and 0.90 % Na<sub>2</sub>O. Samples from the southernmost Totweni transect (Totw E) showed evidence of modification through floodplain processes. The soil chemistry of Totw E differed from the rest of the Totweni samples as they had the highest value of the minimum concentrations among the Totweni transects as well as the highest maximum concentrations of soil oxides of the Totweni transects. Totw E samples had higher clay to quartz ratios than other samples along the Totweni Drainage Line, which reflected the fact that deposition of clay material from the uMkhuze River must have taken place in this region.

Relatively minor transformations to the reworked marine sands were seen from patterns of oxide distribution within the soil profiles, which were consistent with evaporation from the soil surface due to capillary rise of groundwater. Higher values were encountered on the surface and towards the drainage line, as increasingly concentrated runoff or vadose water flowed downslope towards the drainage line. In tracing the evolution of the sediments in the Totweni and northern Yengweni group, little modification was evident from plots of titanium versus other soil oxides.

#### **6.4.1.2. Southern Yengweni**

The southern Yengweni samples were variable with respect to soil chemistry and mineralogy, and tended to have intermediate characteristics between Totweni and northern Yengweni samples and

those of the floodplain margin. Samples in the topsoil of the southern Yengweni were similar to those of the Totweni and northern Yengweni, while samples taken at depth (particularly at Yg E, F and G) were more similar to certain floodplain samples taken at depth. The southernmost Yengweni transects (Yg F and G) tended to be most closely related to floodplain samples, possibly reflecting greater interaction with the floodplain and floodplain processes.

Certain samples, particularly those taken from depth at Yg E, could not really be considered intermediate between the quartz-rich Totweni and northern Yengweni nor the clay-rich floodplain samples for all oxides. This was particularly true regarding calcium, which occurred at very high concentrations at depth. Furthermore, some Yg F and G samples at depth showed the same pattern of silicon depletion and calcium enrichment as the Yg E samples taken from depth.

#### **6.4.1.3. Floodplain**

The floodplain sediments had the highest minimum concentrations among all sampling regions for all oxides presented, which, amongst other properties, suggests that the sediment composition was different from that at other sites. Floodplain samples had the highest clay: quartz ratio of all sample groups. Furthermore, floodplain samples had higher aluminium concentrations and lower Si: Al ratios than the Totweni and northern Yengweni, and most of the southern Yengweni samples. The floodplain sediments also had the highest feldspar content, suggesting alluvial deposition of sediments. The highest range of titanium concentrations were also recorded in floodplain sediments, indicating alluvial input of material from the uMkhuze River catchment.

However, the relationship between various oxides and titanium dioxide suggest that there were two distinct floodplain groupings. The first was composed of predominantly samples from depth, which had high titanium concentrations and roughly conformed to the overall trend of uMkhuze Wetland System samples of increasing oxide concentrations with increasing titanium dioxide concentrations. The second group included primarily surface samples, and although it was also located at high titanium dioxide concentrations, the group had lower sodium concentrations and higher aluminium, iron, magnesium, and potassium concentrations than floodplain samples at depth. These features of the surface samples were attributed to the presence of alluvial clays of the uMkhuze River. The lower silicon concentrations of the upper sediments reflected the lower silicon to aluminium ratios of clay deposits, while increased sodium concentrations with depth was probably due to its highly soluble nature, leading to downward leaching in the profile. Although, potassium might be expected

to have a similar distribution as its compounds are also highly soluble, its status as a plant macronutrient may favour its retention within the upper soil zone (Jobbágy and Jackson, 2001). Another possible explanation is the high affinity of mica for potassium, both of which are concentrated in the surface sediments of the uMkhuze Wetland System, as noted for Australian micas by Norrish and Pickering (1983).

Some floodplain samples have had their Si:Al and Si:Fe ratios as well as the titanium to other element ratios diluted by calcium oxide. Other floodplain samples also seem to have been diluted by a mineral not typical of the majority of samples, evident from lower silicon concentrations. The nature of this mineral will be considered in Section 6.4.2.

#### **6.4.2. Chemical sediments in the uMkhuze Wetland System**

Sediments in any environment will be constantly influenced by modifying agents during a group of processes known as pedogenesis. The rate and direction of change is governed by both extrinsic and intrinsic factors. Extrinsic factors include climate, relief, biota (on a scale from large mammals to micro-organisms), nature of parent material and input of material, including water, clastic sediments and solutes, as well as time (Chadwick and Chorover, 2001; Muhs, 1984). Intrinsic factors relate to the nature of the sediments themselves (mineralogy and chemistry), including pH, redox potential, chemical composition of the groundwater and of vadose water (Chadwick and Chorover, 2001). Due to the wide range of variables acting on any profile, the question of provenance of any single sediment type or mineral is often problematic. The two main sources of any material present in a profile are detrital or formed *in situ*. Two *in situ* processes are possible, weathering or neof ormation. Neof ormed minerals are also termed ‘chemical sediments’, which is strictly only applied to inorganic processes resulting in saturation of a mineral in solution (Goudie and Pye, 1983). Inorganic processes that allow fractionation of solutes leading to saturation may include cation-exchange reactions, redox processes, dissolution of minerals, degassing of CO<sub>2</sub> or H<sub>2</sub>S, as well as precipitation of solid phases, which together dictate the chemical composition of the remaining solution (Eugster and Kelts, 1983). However, the influence of micro-organisms on the chemical composition of sediments is often important in dictating the minerals precipitated as well as the rate of precipitation (Gabe *et al.*, 1965; Kappler and Newman, 2004; McCarthy *et al.*, 1989). It is also possible that other sediments, such as clastic sediment or weathering residua, may be incorporated within a chemical sediment, either as a ‘seed’ initiating precipitation or due to the process of inclusion during precipitation (Goudie and Pye, 1983).

Two chemical sediments seemed to be involved in modifying the reworked marine sands on the margin of the uMkhuze Wetland System. The first is nodular or powdery calcite precipitates, and the second is clay-like sediments of the southern Yengweni and floodplain regions. Both of these sediment types are present in the southern Yengweni and floodplain margins.

#### **6.4.2.1. Calcite**

##### **Calcite deposits and their developmental stage**

Terminology describing the geochemical nature and development of calcite deposits within a soil profile is varied and contradictory, with the formulation of many classification sequences according to morphology, development stage of calcite within a soil profile, mineralogy and microstructure, among other variables (Botha, 2000; Netterberg, 1980; Wright and Tucker, 1991). The term calcrete will be used to describe calcite deposits as the most general designation following the definition of Wright and Tucker (1991) who define calcrete as “a near surface, terrestrial, accumulation of predominantly calcium carbonate, which occurs in a variety of forms from powdery to nodular to highly indurated. It results from the cementation and displacive and replacive introduction of calcium carbonate into soil profiles, bedrock and sediments, in areas where vadose and shallow phreatic groundwaters become saturated with respect to calcium carbonate.”

Morphological descriptions follow Netterberg (1980; Table 6.4.1) and stages of development of calcrete will be described using Machette (1995) in Wright and Tucker (1991; Table 6.4.2).

**Table 6.4.1** Morphological classification of calcrete

<b>Calcrete Type</b>	<b>Description</b>
Calcareous soil	Very weakly cemented or uncemented soil with small carbonate accumulations as grain coatings, patches of powdery carbonate including needle-fibre calcite (pseudomycelia), carbonate-filled fractures and small nodules
Calcified soil	A firmly cemented soil, just friable; few nodules. 10 – 50 % carbonate
Powder calcrete	A fine, usually loose powder of calcium carbonate as a continuous body with little or no nodule development
Pedotubule calcrete	All, or nearly all, secondary carbonate forms encrustations around roots or fills root or other tubes (tubules)
Nodular calcrete (syn. glaebular calcrete of Netterberg (1991))	Discrete soft to very hard concentrations of carbonate-cemented and / or replaced soil. Concentrations may occur as laminated coatings to form pisoids
Honeycomb calcrete	Partly coalesced nodules with interstitial areas of less indurated material between
Hardpan calcrete (syn. petrocalcic horizon of Netterberg (1985))	An indurated horizon, sheet-like. Typically with a complex internal fabric, with sharp upper surface, gradational lower surface
Laminar calcrete	Indurated sheets of carbonate, typically undulose. Usually, but not always, over hardpans or indurated rock surfaces
Boulder / cobble calcrete	Disrupted hardpans due to fracturing, dissolution and rhizobrecciation (including tree-heave). Not always boulder grade. (Clasts are rounded due to dissolution)

Source: Wright and Tucker (1991)

**Table 6.4.2** Classification of calcrete by developmental stage

Stage	Gravel content	Diagnostic features	CaCO <sub>3</sub> distribution	Maximum CaCO <sub>3</sub> content
1	High	Thin discontinuous coatings on pebbles, usually on undersides	Coatings sparse to common	Trace to 2 %
	Low	Few filaments in soil or faint coatings on ped surfaces	Filaments sparse to common	Trace to 4 %
2	High	Continuous, thin to thick coatings on tops and undersides of pebbles	Coatings common, some carbonate in matrix	2 – 10 %
	Low	Nodules, soft 5 – 40 mm in diameter	Nodules common, generally non-calcareous to slightly calcareous	4 – 20 %
3	High	Massive accumulations between clasts, fully cemented in advanced forms	Continuous in matrix to form <i>K</i> fabric	10 – 25 %
	Low	Many coalesced nodules, matrix is firmly to moderately cemented	Continuous in matrix to form <i>K</i> fabric	20 – 60 %
4	Low / High	Thin (<2 mm) to thick (10 mm) laminae capping hardpan ( <i>K<sub>m</sub></i> )	Cemented, platy or tabular structure. <i>K<sub>m</sub></i> horizon is 0.5 – 1 m thick	> 25 % in high gravel content. > 60 % in low gravel content
5	Low / High	Thick laminae (> 10 mm); small to large pisoids above. Laminated carbonate may coat fracture surfaces	Indurated, dense, strong, platy to tabular. <i>K<sub>m</sub></i> horizon is 1 – 2 m thick	> 50 % in high gravel content. > 75 % in low gravel content
6	Low / High	Complex fabric of multiple generations of laminae, brecciated and recemented, pisolitic. Typically with abundant peloids and pisoliths in fractures	Indurated, dense, thick, strong tabular structure. <i>K<sub>m</sub></i> horizon is commonly >2 m thick	>75 % in all gravel contents

High gravel content refers to > 50 % gravel, low is < 20 %. The % CaCO<sub>3</sub> refers to the < 2 mm fraction. *K* is a carbonate soil horizon; *m* subscript refers to induration.

Source: Machette (1985) in Wright and Tucker (1991)

Nodular, also sometimes referred to as glaebular, calcrete was found in all the southern Yengweni transects at depth. It was common in the upper transect (furthest from the drainage line) at Yg E, F and G and found in the uppermost sampling point at Yg D, as well as the floodplain transects Fld B and C, again at depth in cores restricted to higher elevations. In most cases, nodule size increased with depth. Powdery calcrete was only evident at Yg E, above nodular calcrete layers. At no point was anything approaching hardpan encountered, with the densest calcrete layer being numerous discrete calcite nodules. These features place calcrete development in the uMkhuze Wetland System at not more than Stage 2 (Table 6.4.2). Stage 1, although not noted in the field, is probably present in the southern Yengweni transects of Yg E, F and G, as well as the floodplain transects Fld B and C. Calcium carbonate contents of greater than 2 % are common in Yg E – G and Fld B and C, occurring in samples at depth. Calcium carbonate is also present at concentrations greater than 4 % in Yg E – G and Fld B, again in samples collected at depth. Most nodules found in the uMkhuze Wetland System were not soft, as noted for Stage 2, and possibly represent further development stage between Stages 2 and 3.

### **Conditions required for calcrete formation**

There are a number of models of calcrete formation. The diverse morphology of calcrete and the varied arrangement of aggregates in a profile suggest that a number of mechanisms are responsible for its formation. However, the long time scales over which calcretes persist and, in the case of multilayer profiles, the long time periods (tens to hundreds of thousands of years) required for them to form, adds further complication of cycles of aggradation and erosion, reworking and re-sedimentation (Goudie, 1973; Goudie, 1983; Milnes and Hutton, 1983; Wright and Tucker, 1991). Interpretation of profiles is therefore difficult. The climatic conditions under which calcretes form are one aspect on which most researchers agree. Although numerous factors have been suggested to define the geographic distribution of currently forming calcretes, the most useful is simply 400 to 600 mm average annual rainfall (Wright and Tucker, 1991). Where calcretes are forming in regions of between 500 and 600 mm per year, maximum monthly rainfall is limited to less than 30 % of the annual rainfall (Table 6.4.3). The uMkhuze Wetland System does not however conform with this as it has a mean annual rainfall of 760 mm and a maximum monthly rainfall of 51.78 % of the annual (Table 6.4.3). As noted above, calcretes are limited in vertical extent in the uMkhuze Wetland System, being one to two metres thick at the most. They are in an immature stage of development. Botha (2000) notes such calcrete profiles may form in areas up to 800 mm mean annual rainfall, which is enhanced by high evaporation rates and moisture deficits in some months of the year.

Estimates of the annual precipitation deficit range from 343 to 800 mm, which according to Buol (1965), places the uMkhuze Wetland System in a semi-arid zone in spite of high rainfall in the area.

**Table 6.4.3** Relationship between calcrete formation and the ratio of monthly maximum to average annual rainfall

<b>Calcrete Area</b>	<b>Mean annual rainfall/ mm</b>	<b>Monthly minimum rainfall/ mm</b>	<b>Monthly maximum rainfall/ mm</b>	<b>% Monthly maximum of annual rainfall</b>
Tunis (Tunisia)	413	2.5	60	14.55
Kimberley (South Africa)	405	0	62.5	15.43
Murcia (Spain)	363	5	48	13.10
Austin (USA)	293	10	40	13.68
Mexico City (Mexico)	570	5	115.0	20.18
Santiago (Argentina)	520	5	115.0	22.12
<i>uMkhuze Wetland System (South Africa)</i>	765.8	0.0	396.5	<b>51.78</b>
<b>Non-calcrete areas</b>				
El Obeid (Sudan)	350	0	112.5	32.14
Kayes (Mali)	728	0	207.5	28.52
Zinder (Niger)	543	0	240.0	44.24
Jaipur (India)	600	10	107.0	34.58

Modified after: Goudie (1973)

### **Calcium sources**

Following the lower sea levels of the Last Glacial Maximum, the current sea level was attained around 6 500 years ago, with minor fluctuations since then up to the present day (Ramsay, 1995; Watkeys *et al.*, 1993). It is highly likely that shell fragments as remnants of marine life would have been dissolved in the modern humid climate of the uMkhuze Wetland System situated on sediments of the coastal plain. Hugo (1993) reports the presence of 'minor shell fragments' for the dunes from Cape St Lucia to Kosi Bay on the Maputaland Coastal Plain. The low calcium concentrations in sediments of the Totweni and northern Yengweni, which do not exceed 0.71 weight %, suggest that these assumptions are correct. Furthermore, it is expected that calcium would have been flushed

from the uMkhuze Wetland System groundwater due to the many thousands of years in which sea level was lower than the present level. In the fine to medium sand of the coastal plain, it is unlikely that groundwater flow would have been restricted and conditions would have favoured flushing of calcium derived from mineral dissolution from the coastal plain (Levy, 1980; Logan *et al.*, 1999). Therefore, calcium must be derived from water and sediment additions to the system. The most concentrated calcium input to the uMkhuze Wetland System is the uMkhuze River water and clastic sediments, as rainfall would contribute very little calcium.

### **Mechanisms of calcrete formation**

Based on the geomorphology and soil chemistry of the uMkhuze Wetland System, it seems there is only one possible mechanism of calcrete formation in this system, which is best described by the *per ascensum* model (Botha, 2000; Goudie, 1973; Goudie, 1983; Wright and Tucker, 1991). The *per ascensum* model involves the concentration of groundwater through capillary rise and evaporation or transpiration, to a point of saturation of calcium carbonate.

Although the validity of this model has been questioned as the cause of many calcrete deposits, conditions in the uMkhuze Wetland System satisfy the model requirements. Many calcrete deposits form close to water tables at many metres in depth, from which evaporation from the soil surface, capillary rise or concentration by transpiration could not account for saturation of calcium carbonate. The high water tables of the uMkhuze Wetland System, as well as the high precipitation deficit causing marked seasonal fluctuations in the elevation of the water table and the dense vegetation of the system, probably cause calcium carbonate to saturate just above the water table.

The same mechanism of transpirative concentration of groundwater seems to account for the neoformation of clay minerals in the uMkhuze Wetland System. Therefore, it is not surprising that calcrete deposits are associated with montmorillonite in the southern Yengweni in particular. It is interesting to note that many calcrete deposits are accompanied by high silica contents, often due to the presence of clay minerals, the magnesian silicates, palygorskite and sepiolite, and in certain cation-poor environments, silcrete (Buol, 1965; Langmuir, 1997; Milnes and Hutton, 1983). Armenteros *et al.* (1995) report that calcrete deposits in a closed basin in northern Spain, were often associated with neoformed clay minerals, of which smectite was the most common. The lower profile at 1.5 to 2.5 m depth of a soil in Arizona was found to be enriched in both carbonate and montmorillonite, as are the sediments of the Hindmarsh River mouth in Australia (Buol, 1965;

Milnes and Hutton, 1983). Other calcretes in Australia show a predominance of illite and kaolinite over montmorillonite (Milnes and Hutton, 1983). Calcrete in association with palygorskite as well as silcrete, was noted in swamps of western Portugal (Armenteros *et al.*, 1995).

#### 6.4.2.2. Clay-like sediment

The origin and developmental path of clay minerals is the subject of many studies in many different environments (Curtis, 1990; Sellwood and Price, 1993). The interaction of parent material, climate, topographic setting, varying hydrological regime and soil or sediment characteristics during pedogenesis, makes clay mineral origin and transformation pathways complex.

There are three possible explanations for the presence of clay minerals: inherited from parent material due to weathering in the catchment, the products of which enter the fluvial network and are deposited on floodplains (often referred to as detrital); modified *in situ* through weathering and other diagenetic processes; and neogenesis or neof ormation, sometimes referred to as authigenesis, where minerals precipitate from a solution containing the necessary components (Chamley, 1989; Gal *et al.*, 1974; Velde, 1985). Neof ormed clays and clays formed by weathering *in situ* are more likely to reflect equilibrium conditions in their current environment than detrital minerals, which have been transported from an area probably influenced by different environmental conditions (Velde, 1985). However, the formation of metastable intermediates during diagenesis and/or neof ormation is common and indicates kinetic supremacy over thermodynamic considerations (Velde, 1985). These metastable intermediates are by definition not in equilibrium with environmental conditions. A good example is the precipitation of the kinetically favoured amorphous silica over relatively short timescales, while the expected precipitate of quartz, although being thermodynamically favoured, is absent (Stumm and Morgan, 1981; Velde, 1985). It has been shown that amorphous silica becomes more crystalline over time, eventually forming the highly crystalline quartz, taking  $10^9$  years at  $0^\circ\text{C}$  and  $10^6$  years at  $100^\circ\text{C}$  and 10 000 kPa (Langmuir, 1997; Mizutani, 1970). Metastable intermediates of clay mineral transformations may include vermiculite in highly alkaline environments, which favour transformation to smectite (Velde, 1985).

#### Possible detrital origin of clay minerals in the uMkhuze Wetland System

It is expected that clay minerals produced by weathering of the igneous strata of the Lebombo Mountains and by remobilisation of smectites deposited to the east of the Lebombo Mountains, are

deposited in the uMkhuze Wetland System in the form of secondary minerals (McCarthy and Hancox, 2000). The smectites are possibly a weathering product of the Uloa Formation calcarenites (Partridge and Maud, 1987). Clay mineral precursors such as the feldspars (orthoclase (potassium), microcline (potassium), the plagioclase series from albite (sodium) to anorthite (calcium) as well as micas (muscovite or biotite), may be added to the system through weathering of Pongola granites and sandstone of the Makatini Formation (Allen and Hajek, 1989; Schulze, 1989). Illite or clay-sized mica is probably inherited from the parent material of limestone present on the coastal plain, or is derived from coarser particles of muscovite, which is abundant in igneous rocks (Allen and Hajek, 1989).

### **Clay minerals as products of in situ weathering in the uMkhuze Wetland System**

Due to the subtropical setting of the uMkhuze Wetland System with high summer temperatures and generally high rainfall (although interspersed with severe droughts and floods due to El Niño-Southern Oscillation events), intense weathering of minerals is expected. However, the weathering process may be hindered within the wetland due to high water tables and relatively stagnant groundwater that prevents leaching of elements (Allen and Hajek, 1989; Watkeys *et al.*, 1993).

Weathering and pedogenic trajectories have been well-studied under both laboratory and field conditions, although research in the natural environment is complicated by many variables that fluctuate over time (see Agrawal and Ramamoorthy, 1970; Brown and Jackson, 1956; Buol, 1965; Chatterjee and Rathore, 1976; Ducloux *et al.*, 1995; Eberl and Hower, 1976; El-Attar and Jackson, 1973; Fitzpatrick and Le Roux, 1977; Gjems, 1970; Harder, 1974; Herbillon *et al.*, 1981; Ismail, 1970; Johnson *et al.*, 1962; Kantor and Schwertmann, 1974; Kittrick, 1971a; Kittrick, 1971b; Mees, 2001; Southard and Southard, 1985; Velde, 1985; Ware *et al.*, 2003; Weaver *et al.*, 1971; Wiewióra *et al.*, 1996). As a result, minerals that were once in equilibrium with the environmental conditions may persist until a certain pedogenic threshold is surpassed, when transformation to the stable form expected under the current conditions will occur (Chadwick and Chorover, 2001; Derbyshire, 1976). The rate of transformation is often strongly dependent on temperature, with deeply buried sediments under high temperatures and pressures experiencing more rapid diagenesis than surface soils (Velde, 1985). This study is concerned with surface sediments and soils and therefore it is more important to consider other factors affecting transformation mechanisms (weathering or neogenesis) and rates. Other possible factors include the type of transformation, such as from gel to crystalline material or from one phyllosilicate to another, and the sizes of mineral particles

undergoing transformations (Fanning *et al.*, 1989). Further factors governing transformations of precursor minerals as well as new mineral formation include the nature and activity of ions in solution, the availability of metal-complexing agents that may, for example, enhance the rate of clay cation removal, redox potential, pH and the degree of fluctuation between saturated and dry conditions (Fanning *et al.*, 1989). The pH, nature and activity of ions in solution and fluctuation of the water table will be considered.

### *Weathering of micas*

Illite (mica) is present across the study area, occurring in Totweni, Yengweni and floodplain samples, and is concentrated in surface sediments. The presence of illite in the Totweni Drainage Line (although at lower concentrations than elsewhere in the study area), suggests at least partly aeolian origin, particularly for the Totweni. A similar pattern of distribution was documented by Dymond *et al.* (1974) for certain Hawaiian soils. This ubiquitous mineral is found in many igneous, sedimentary and metamorphic rocks (Norrish and Pickering, 1983).

It is unlikely that mica formation occurs in the uMkhuze Wetland System as it requires high potassium concentrations and alkaline pH's in the soil solution, and generally occurs in arid regions (Mahjoory, 1975; Nettleton *et al.*, 1973). Potassium concentrations in the uMkhuze Wetland System are uniformly low.

During weathering, it seems that illite might be transformed to a transient unstable vermiculite or a more stable smectite intermediate before forming kaolinite (Allen and Hajek, 1989; Borchardt, 1989; Brown and Jackson, 1956; Fanning *et al.*, 1989; Franzmeier *et al.*, 1969; Gjems, 1970; Kittrick, 1973; Ross and Mortland, 1966). Other weathering sequences list chlorite as the first weathering product of mica (Velde, 1985). However, no chlorite or interstratified chlorite mineral was detected in the study area, which might reflect the absence of chlorite in parent materials (as chlorite in soils is predominantly detrital), chlorite instability, or the difficulty of detecting it in the presence of other clays (Barnhisel and Bertsch, 1989). The remainder of the weathering sequence after chlorite is similar to that suggested by Ware *et al.* (2003), and is described in the next section for the coastal dune systems of Maputaland.

### *Weathering of feldspars*

Feldspars are also precursors to clay minerals under surface conditions and are produced by weathering of catchment volcanics, shales or limestones (Huang, 1977). Feldspars are present throughout all regions of the study area suggesting an aeolian origin, as there was a large proportion of feldspars in the clay fraction.

X-ray diffraction analyses of bulk samples allowed an approximate estimate of feldspars in the samples by applying an empirical formula using the intensities of the plagioclase (3.14 – 3.19 Å) and orthoclase peaks (3.21 – 3.26 Å). Totweni samples contained 5 – 8 % feldspars, floodplain samples comprised 10 – 21 % feldspar, and southern Yengweni samples fell in the range 0 – 22 % feldspar. This distribution suggests feldspars are predominantly added to the system as detrital material. Furthermore, the general trend for potassium feldspar, noted in the analysis of the fine fraction, is of higher concentrations in the upper soil layers suggesting consistent input from the uMkhuze River to the southern Yengweni and floodplain. However, this trend is reversed when the bulk samples are considered, with a consistent increase in feldspar concentration with depth, which suggests that weathering of feldspars is the dominant process in the upper sediment layers. Weathering of feldspars at depth is hindered due to lower leaching intensities where free drainage of water is restricted due to the finer textured nature of sediments at depth, which would decrease water flow around the mineral. Under such conditions, high water tables might retard leaching entirely depending on the ionic strength of the groundwater. Sodium feldspar (albite) is less abundant and presents no clear trend.

Ware *et al.* (2003) suggested that clay layers found beneath the coastal dunes of KwaZulu-Natal can be solely attributed to in situ weathering of primary minerals, particularly feldspars. The following weathering sequence was proposed under the consistently moderate conditions of weathering to which the coastal dunes of northern KwaZulu-Natal are subjected:

Feldspar (an important component of the primary minerals) → illite + vermiculite → interstratified illite → illite + montmorillonite → halloysite (hydrated kaolinite) + interstratifications + kaolinite → kaolinite + iron oxides + aluminium oxides.

Each mineral mentioned in the weathering sequence above will be considered in terms of its location and distribution through the soil profile in the uMkhuze Wetland System, in order to assess the suitability of the weathering model described above in the present study area.

It is possible that feldspar weathering is an important source of illite, due to the surface accumulation of illite throughout the study area. The inverse relationship recorded suggested that this weathering sequence might be important. Therefore, a fluvial or aeolian origin is possibly indicated for both illite and the feldspars, with illite concentrations potentially augmented by feldspar weathering.

Possible weathering products of illite include both vermiculite and montmorillonite. Different pedogenic environments will preferentially produce the one at the expense of the other clay mineral (Borchardt, 1989). Vermiculite forms authigenically under conditions of very low alkali and alkali earth metal concentrations and slightly acidic pH's, and is more likely to be present in cool temperate environments with relatively high leaching intensities, although vermiculite is generally an unstable intermediate under any conditions (Borchardt *et al.*, 1968; Ismail, 1970; Kittrick, 1973; Sellwood and Price, 1993; Velde, 1985). The occurrence of mica-vermiculite interlayer minerals in the study area was probably the result of the partial replacement of the potassium in interlayers of mica, with calcium typical of vermiculite (Norrish and Pickering, 1983). Vermiculite and mica-vermiculite only overlapped in two samples of the floodplain transect C, where the vermiculite predominated while mica-vermiculite was present in trace amounts. Mica-vermiculite was present in greater concentrations in surface sediments, probably reflecting the greater weathering intensities, preserving mica-vermiculite while the more unstable discrete mineral was removed. Although there was evidence that vermiculite may be precipitated from solution under the correct conditions, this process is thought to be rare (Norrish and Pickering, 1983). It is more likely that vermiculite was better preserved at depth where leaching intensities are low.

Smectites, including montmorillonite, normally occur in warm temperate to arid regions, but may be present in tropical and subtropical areas under conditions of high calcium, magnesium and silicon activities, as well as moderate sodium activity, in a neutral pH to alkaline environment (Borchardt, 1989; Chatterjee and Rathore, 1976; Curtis, 1990; El-Attar and Jackson, 1973; Ismail, 1970; Sellwood and Price, 1993; Velde, 1985; Ware *et al.*, 2003). Such conditions are conducive to the transformation of micas to smectites. Therefore, any environment where leaching is restricted, such as where there are consistently high water tables or where there is slow drainage of water due to soils of low hydraulic conductivity, the formation and persistence of montmorillonite will be favoured particularly in the presence of high alkaline earth concentrations that are found in the southern Yengweni and floodplain regions of the uMkhuze Wetland System (Allen and Hajek, 1989; Chatterjee and Rathore, 1976; El-Attar and Jackson, 1973).

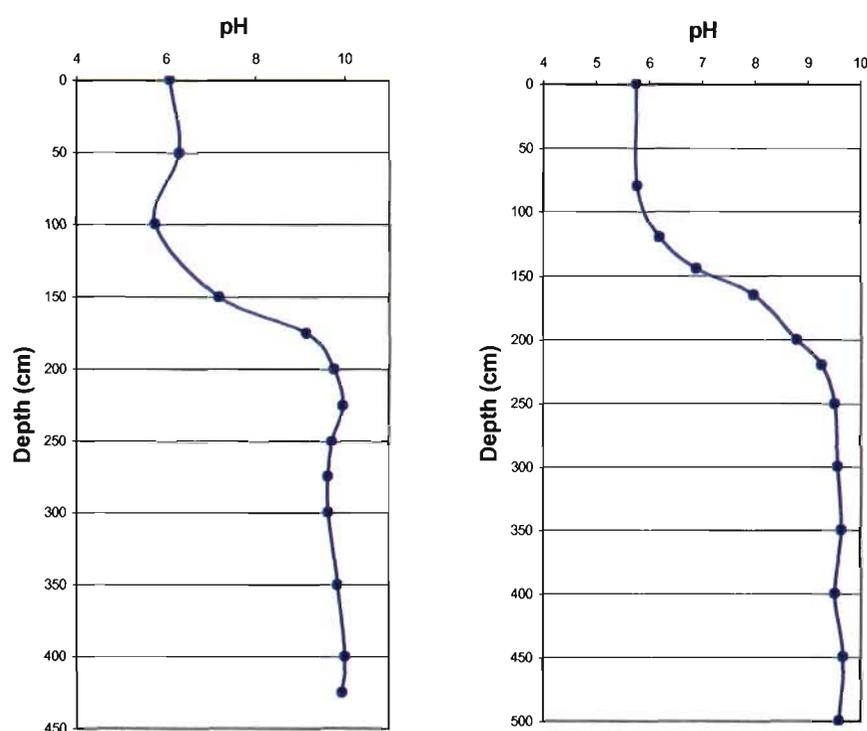
Weathering of illite via a vermiculite-smectite-kaolinite sequence did not seem to be a common process in the uMkhuze Wetland System due to the rarity of vermiculite. However, a vermiculite-montmorillonite interlayered mineral was abundant in the clay fraction in the Totweni and on the floodplain, predominantly in the surface layers. Therefore, although vermiculite probably does form in the weathering sequence, conditions do not favour the persistence of discrete vermiculite and it is transformed to montmorillonite, with the expected metastable intermediate of a mixed layer mineral (Borchardt, 1989; Velde, 1985). These processes of interlayer formation are common and are simply explained for the minerals mica, vermiculite and montmorillonite as these minerals differ primarily in the nature of their interlayer cations (Norrish and Pickering, 1983).

On the southern Yengweni no interlayered vermiculite-montmorillonite was detected, while montmorillonite was abundant in the clay fraction and increased with depth. This indicated that either, conditions on the southern Yengweni are distinctly different from those studied by Ware *et al.* (2003) or that an alternate set of processes is dominant in these two study areas, which were both on the coastal plain of northern KwaZulu-Natal.

There were only two samples where vermiculite-montmorillonite and montmorillonite occurred simultaneously, although the interlayer mineral was present in very low concentrations in both cases. The interlayer clay occurred preferentially in surface sediments, while montmorillonite occurred throughout the profile on the southern Yengweni, increasing in concentration with depth. Floodplain soils containing the mixed layer clay had discrete montmorillonite at depth under conditions of restricted drainage. Although it has been suggested that the absence of interlayer minerals indicates an intense weathering environment (Velde, 1985), the conditions of restricted drainage at many sites displaying discrete montmorillonite does not support this view in the uMkhuze Wetland System.

Conditions favouring the formation of montmorillonite over vermiculite at depth have been documented on the southern Yengweni. A previous study in the uMkhuze Wetland System returned slightly acidic pH's in southern Yengweni soils in the top 100 cm (pH 5-6), which increased rapidly to pH's of approximately 10 at about 2 m below land surface (Humphries, 2004; Figure 6.4.1). Soil and water chemistry data presented in Chapter 5 and in this chapter indicated that calcium, magnesium and sodium concentrations in the southern Yengweni reach factors between 12 and 362 times the background concentrations of the Totweni Drainage Line, often at depth. These conditions of high pH and elevated calcium, magnesium, sodium and silicon concentrations

sufficiently high to lead to amorphous silica saturation in a moderate leaching environment, favour montmorillonite formation (Borchardt, 1989; Chadwick and Chorover, 2001; Kittrick, 1969). Furthermore, an environment of alternate wetting and drying, as found on the southern Yengweni, also favours montmorillonite (Chadwick and Chorover, 2001). The exclusive occurrence of montmorillonite on the southern Yengweni suggests conditions and mechanisms that allow montmorillonite to form and persist at the base of the profiles around the water table.



**Figure 6.4.1** The variation of pH with depth for two sites on the southern Yengweni

Source: Humphries, 2004

No halloysite or interstratified kaolinite was detected, but kaolinite itself was ubiquitous. There was a tendency for kaolinite to be more concentrated in surface layers.

Gibbsite and goethite ( $\text{FeOOH}$ ) are seen as the end products in a mature weathered profile (Hsu, 1989). Both minerals occur on the floodplain, and goethite is also found in the southern Yengweni, predominantly in surface soil layers. Gibbsite is present in a few samples, mostly in surface samples. At pH's of 5-9, silica is more soluble than aluminium. This solubility differential governs the transformation of kaolinite to gibbsite ( $\text{Al}(\text{OH})_3$ ) under high leaching conditions (Leeder, 1999; Velde, 1985). This suggests that in general in the uMkhuze Wetland System, leaching is not sufficiently intense to produce large amounts of gibbsite from kaolinite and that silica activities are

sufficient to preserve kaolinite (Hsu, 1989). There is no obvious inverse relationship between kaolinite and gibbsite that would indicate an evolutionary sequence. Goethite is an earlier weathering product than gibbsite and is present in environments with high aluminium and low silica activities (Allen and Hajek, 1989). The presence of goethite at the soil surface probably reflects more intense leaching at the surface than at depth and more reducing conditions at depth than at the surface that maintain iron in the soluble Fe (II) form.

### **Neof ormation of clay minerals in the uMkhuze Wetland System**

The distribution of clay in the southern Yengweni does not comply with a purely clastic depositional or weathering model. Sediments in the southern Yengweni comprise reworked marine sediments (sand) mixed with clay, such that they can be described as a clayey sand. This is a groundwater recharge zone and there is very little clay present in the surface sediments. Furthermore, clay occurs at depth and increases in thickness away from the drainage line. This distribution pattern cannot be explained by deposition of clastic sediment, which would lead to increased clay content at surface and an increased thickness of clay-rich sediment towards the drainage line.

Many authors have reported neof ormation of smectites although there is some debate over origin in many systems, with some authors preferring a weathering or detrital explanation of smectite provenance (Chamley, 1989). Difficulties in tracing smectite formation mechanisms include the mineral's ubiquity, being a very common weathering product in soils; as well as its highly variable nature due to rapid response to its chemical environment (Borchardt, 1989; Velde, 1985). Therefore, aluminium, silicon and other cation activities in the surrounding pore or groundwater may simply reflect the presence of smectites rather than saturation of the mineral (Borchardt, 1989). However, neogenesis of smectites has been satisfactorily confirmed in a wide range of environments, with the only condition being the supply of the necessary components in sufficient concentrations (Fitzpatrick and Le Roux, 1977).

At a broader scale, Chamley (1989) noted that climatic and hydrological conditions are important in the concentration of solutes required for mineral saturation. Research on Lake Chad indicated that intense evaporation and fluctuating water tables favoured smectite neogenesis. Neof ormed smectites have been reported in Israel (Gal *et al.*, 1974), northern Spain (Armenteros *et al.*, 1995), northern Mexico (Borchardt, 1989), Lakes Tanganyika (Burundi, DRC, Tanzania and Zambia) and

Chad (Chad, Cameroon, Niger and Nigeria) (Chamley, 1989) as well as the Niger Delta (Mali) (Velde, 1985), and on the continental shelf of the Congo-Zaire River mouth (Wiewióra *et al.*, 1996).

Montmorillonite in the uMkhuze Wetland System accumulates at and above the water table, which indicates a neogenetic origin as weathering of precursor minerals such as micas and feldspars to form smectites results in concentration of clay minerals in surface horizons, while neogenetic smectites will form at the base of the profile (Borchardt, 1989; Buol, 1965). This region of the profile is where solutes will preferentially accumulate, particularly in association with the water table. Furthermore, there does seem to be a trend of smectite increase with increasing depth, with a concurrent trend of higher concentrations of montmorillonite-vermiculite interlayered clays at the surface. A weathering process is more likely to produce mixed-layer clays, while neogenesis produces a discrete clay mineral (Borchardt, 1989). This suggests a weathering origin for the interstratified minerals and neof ormation of the discrete montmorillonite on the southern Yengweni and possibly some areas of the floodplain.

Although accumulation at depth is an accurate description of smectites in the southern Yengweni, it is possible that illuviation (leaching of clay particles down the soil profile) of surface clay deposits through the fine to medium sand particles has resulted in the concentration of clays at the water table. If this process was active on the southern Yengweni, it must have occurred prior to the accumulation of calcite as both calcium and magnesium ions are powerful flocculants that would have prevented illuviation (Fitzpatrick and Le Roux, 1977; Muhs, 1984).

If alluvial sedimentation after flooding of the uMkhuze River was an important mechanism adding clay to the system, there should be evidence of deposition of clay at the soil surface, and along the pan edges between the maximum retention level and mean upper limit of flooding. Sampling in December 2000 took place a week after floodwaters began to subside. At the time of sampling, the floodplain was still flooded and lake levels were high, although they had dropped by about 1m based on the presence of flood debris along the banks of the lake. A hippo trail at the base of the lake defines the maximum retention level (MRL) of the Yengweni Lake and the water was flowing strongly out of the lake (Erickson and Förander, 2000). Observations thus suggest that lake levels drop rapidly following a flood, such that fine clay particles are not deposited on the lake margin above the MRL.

It is concluded that neof ormation is the source of the discrete montmorillonite discovered at depth in the southern Yengweni and possibly the floodplain margin.

### **6.5. Conclusion: Factors governing pedogenesis in the uMkhuze Wetland System**

Pedogenesis in the uMkhuze Wetland System is driven by two separate processes: weathering of minerals derived from the uMkhuze River catchment, which is most active in surface sediments and throughout the vadose zone, and chemical sedimentation at depth (3 – 6 m) in soil profiles, which occurs at similar depths to the current water table.

The two expected aluminosilicate end-members of these processes are kaolinite as the end result of weathering in humid climates, and montmorillonite, which is often associated with calcrete during chemical sedimentation. Surface and near-surface samples of both Fld B and C had high silicon and aluminium concentrations, with decreasing aluminium concentration as the silicon concentration increased. Possibly this trend reflects incongruent dissolution of the aluminosilicates in surface and subsurface samples to produce kaolinite (Figure 6.3.19). The inclusion of clay minerals in a factor analysis of soil chemical variables validates the above suggestion, with surface and near surface samples of the floodplain region plotting at similar Factor 2 scores as kaolinite (Figure 6.3.22; Appendix G).

The dilution of silicon and enrichment of aluminium in certain floodplain and southern Yengweni samples (indicated by 'a' in Figure 6.3.19) is primarily attributed to high calcium concentrations. The samples plotted in proximity to the montmorillonite point have the same characteristics of lower silicon concentrations and higher aluminium concentrations (Figure 6.3.22). The floodplain and southern Yengweni samples in close proximity to the montmorillonite sample were typically found at depth and were described in the field as having a 'clay-like' texture (Figure 6.3.22). It seems that high calcium concentrations often coincided with elevated montmorillonite concentrations.

In areas where chemical sedimentation is occurring, solute fractionation due primarily to mineral precipitation will influence further chemical evolution of the groundwater. Eugster and Hardie's (1978) model of geochemical evolution of closed-basin brines indicates calcite as the first fractionation step in all water chemistry groups (Eugster and Jones, 1979). The only silicates included in the model are the neoformed palygorskite and sepiolite that have high magnesium

concentrations. The latter minerals precipitate after calcite and dolomite precipitation has ceased (Eugster and Hardie, 1978; Eugster and Jones, 1979). In the uMkhuze Wetland System, using the southern Yengweni as an example, all transects have clay sediments that have modified the physical and chemical properties of the marine sands, while only some have calcrete formation. It seems that in the sandy sediments of uMkhuze Wetland System, silica and base cation concentrations attain appreciable concentrations allowing clay minerals such as montmorillonite to precipitate before calcite. It must be noted that the role of organic compounds particularly humic acids, has not been considered in this study. Research in the Okavango Delta has highlighted the accumulation of organic matter in the groundwater (Bauer-Gottwein *et al.*, 2007). Humic acids may play an important role in groundwater chemistry by complexing metal ions such that they remain in solution, thereby hindering a precipitation sequence (Bauer-Gottwein *et al.*, 2007).

The chemical composition of the soil in the study area is evidently strongly influenced by surface and groundwater chemistry, where base sediments are highly leached sands with only the alluvial depositions of the uMkhuze River as a sediment source. Furthermore, surface and groundwater chemistry cannot be considered in the absence of hydrological fluctuations and flow paths, which not only provide a reaction and transport medium, but also an additional source of solutes and sediments to the uMkhuze Wetland System. The integration of these factors in a model of chemical evolution in the uMkhuze Wetland System will be discussed in Chapter 7.

## CHAPTER 7

### CHEMICAL TRANSFORMATIONS IN THE uMKHUZE WETLANDS SYSTEM

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#### 7.1 Introduction

The datasets collected during this study cover a range of spatial and temporal scales, as well as media. Although the spatial scale is relatively limited within the uMkhuze Wetland System, the environments sampled display an unexpected degree of heterogeneity for two adjacent drainage lines with similar origins. The temporal scale of one seasonal cycle reveals monthly changes in water chemistry and yet incorporates timescales of decades to centuries of biogeochemical change within the soil. In an effort to integrate this large, diverse dataset, issues of scale will be addressed in order to formulate a spatio-temporal framework of chemical sedimentation and system evolution in the uMkhuze Wetland System. The implications of chemical sedimentation for wetland systems and for their management will also be briefly addressed.

#### 7.2 Scale

Studies of chemical transformations are plagued by issues of spatial and temporal scale. Chemical interactions could be considered over a range of spatial scales from the molecular level of solute interactions such as acid-base reactions, to an intermediate scale of a wetland hydrogeomorphic type in which minerals precipitate out of solution modifying sediment characteristics, to a landscape level at which the implications of chemical sedimentation in terms of geomorphological change are evident. Similarly for temporal scales, interactions between solutes may occur in fractions of seconds for reactions such as acid-base and redox, the concentration and precipitation of minerals will occur over months to decades, while dissolution and remobilization of refractory minerals such as quartz may require hundreds to thousands of years (Chadwick and Chorover, 2001; Jensen, 2003; Langmuir, 1997).

The intricacies of chemical processing and transformation in wetlands and its implications in terms of catchment-scale impacts, therefore necessitates a framework encompassing broad spatial scales and dramatic landscape modifications, to the fine scales and rapid processing typical of many chemical

interactions. The uMkhuze Wetland System on the wetland scale has been highlighted as a site of chemical retention in the order of tonnes of solutes retained per year (Barnes *et al.*, 2002). As presented in Chapters 4 to 6, investigations were conducted primarily at an intermediate spatiotemporal scale of a few hydrogeomorphic units over a number of seasons. Insights into stratigraphy, soil chemistry and mineralogy have allowed processes occurring over longer timescales to be considered, while chemical processing at a finer temporal scale could be predicted based on analysis of water chemistry data from each sampling event.

### 7.3 Hierarchy theory

Hierarchy theory is a concept with many applications, originally developed within general systems theory, mathematics and philosophy, and subsequently applied to control engineering, ecosystems as well as geomorphological systems among others (De Boer, 1992; O'Neill *et al.*, 1986; Wu and Loucks, 1995). This theory encourages the researcher to place their system in question into a broader landscape context while at the same time considering its constituent parts and processes. Wu and David (2002) advocate the integration of hierarchy theory, which emphasises differing spatiotemporal levels from coarse to fine, with patch dynamics that recognises spatial heterogeneity or 'patchiness' within a landscape. The resulting theory is hierarchical patch dynamics, with hierarchical levels encompassing holons or patches at each level.

Any landscape may therefore be viewed as a hierarchy of levels or functional units, within which patches exist that are sometimes referred to as holons, operating at different scales with each successive level encompassing the levels beneath it. In other words, lower levels integrate in form and process to produce successively coarser levels, in a nested hierarchy (De Boer, 1992; Koestler, 1976; Urban *et al.*, 1987; Wu and David, 2002). In this way the complexity of landscape components and interactions across a range of spatial and temporal scales may be reduced to fewer discrete units or holons (Wu and Loucks, 1995).

Both spatial and temporal scales may be addressed, and indeed are interlinked, in the application of hierarchy theory. Higher levels correspond to broader spatial scales, as well as longer timescales, since processes that operate at a coarse spatial scale often require long timescales (slow process rate), such as

erosion or deposition of a substantial landform (Wu and David, 2002). At such levels, time of reaction to changes in conditions is long, with a correspondingly long relaxation time until the system has equilibrated with the new conditions (O'Neill, 1989; Schumm and Lichty, 1965). Likewise lower levels comprise limited spatial dimensions and short timescales, and may be defined by short reaction and relaxation times (De Boer, 1992; O'Neill, 1989). As the lower levels integrate to coarse resolution holons, successive cycles of microscale (spatial and temporal) processes cumulatively cause change at the broad spatial scale over a long time period. Therefore, a mostly reasonable assumption on which hierarchy theory is based is that spatial and temporal scales expand and contract in synchrony. A further assumption is that spatiotemporal scales may be divided into distinct levels rather than being a continuum from fine with rapid processing, to coarse with slow rates of change (Gould, 1984; O'Neill, 1989). In addition, on the horizontal axis of a specific level, gradients in environmental resources and conditions are often steep, allowing differentiation into holons. This 'almost decomposability'<sup>1</sup> of an ecosystem allows application of a hierarchical framework to aid investigation without losing vital information (Wu and David, 2002). This theory is consequently well adapted to recognizing landscape heterogeneity, rather than assuming a homogeneous distribution of materials and energy.

Although the synchronous expansion and shrinkage of space and time windows is a useful concept, it must be noted that certain events fall outside the above framework. Events or agents might operate over very short timescales and yet produce major landscape changes similar to those produced by low energy, high frequency events (Brunsden and Thornes, 1979). For example, a flood of greater than 200 year return period, will act over days to weeks and yet remove and deposit vast amounts of sediment that would usually be associated with erosional processes over long time scales. In a similar way, anthropogenic catastrophic disturbances may have similar results, such as flattening of a gradient to accommodate a road.

When the spatiotemporal framework is collapsed in this manner by a catastrophic event, with changes within a limited timescale effecting change at a broad spatial scale, the concept of thresholds in factors responsible for change in a landscape, will be useful in interpreting these transformations.

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<sup>1</sup> If a system was completely decomposable, there would be no interaction between its components.

#### 7.4 Pedogenic thresholds: the process of chemical sedimentation

The concept of thresholds in the development of physical systems was extended to geomorphic thresholds by Schumm (1979), to describe periods of inertia followed by sudden changes in the development of landscapes. The application of the threshold concept to soil, as pedogenic thresholds, was explicitly presented by Muhs (1984). According to Muhs (1984) whose work extends ideas of Schumm (1979), a pedogenic threshold “is a limit of soil morphologic stability that is exceeded either by intrinsic change of the soil morphology, chemistry or mineralogy, or by a subtle but progressive change in one of the external soil-forming factors.” The external soil-forming factors include the climate and geomorphology of the region, as well as the parent material and any organisms within the soil profile. In the absence of change in the external soil-forming factors, changes in soil morphology, chemistry and mineralogy may be attributed to intrinsic factors acting within the soil profile, such as calcium carbonate attaining saturation in the groundwater.

The occurrence of a threshold point due to changes in external or intrinsic factors will largely depend on the ability of the soil to absorb the changes thus induced (Chadwick and Chorover, 2001). For example, *in situ* precipitation of the clay mineral smectite may occur without a noticeable change in soil properties, until the particles begin to aggregate and block pores in the parent material, resulting in horizontal flow of infiltrating water in place of vertical flow to the groundwater compartment. In this example, coarser sediment with large pore spaces has a greater intrinsic buffering capacity than fine silts or clays. Each threshold attained amplifies the effect of changes within the holon of interest to upper levels of the hierarchy, with the extent of the amplification dependent on the magnitude of change. The presence of such thresholds complicates the interpretation of soil profiles in wetland settings, and due care should therefore be taken in differentiating between the products of past chemical processing not yet in equilibrium with current conditions and the soil components undergoing active transformations.

## **7.5 A hierarchy of pedogenic thresholds for the uMkhuze Wetland System**

### **7.5.1 Environmental conditions governing pedogenesis**

The influence of the external factor of climate extends over spatial scales far broader than the uMkhuze Wetland System. Changes in climate and therefore the effects of climate change on pedogenesis occur over hundreds to thousands of years. These factors comply with the relationship between spatial and temporal scales laid out in hierarchy theory.

Geomorphological change in the uMkhuze Wetland System has been effected over hundreds to thousands of years. The current depositional phase within incised stream valleys of the coastal plain was initiated approximately 8 000 years ago at the end of the Last Glacial Maximum, with sea level stabilizing at the current level about 6 500 years ago (Ramsay, 1995; Watkeys *et al.*, 1993). The incised valleys of the uMkhuze River and its tributaries (the Muzi, Yengweni, Totweni and Mbazwane drainage lines) were back flooded to the base level dictated by sea level, and the system became a depositional and therefore aggradational environment. The aggradation of the uMkhuze River floodplain and the progressive damming of its tributaries from west to east, has increased uMkhuze River input to the tributary drainage lines, which have been converted from groundwater discharge zones to groundwater recharge zones. The higher solute inputs and longer residence times thus produced will continue to promote chemical sedimentation in the uMkhuze Wetland System. Therefore, a threshold influencing pedogenesis in the uMkhuze Wetland System is extrinsically-driven, and is defined by the floodplain elevation at which uMkhuze River water enters the Yengweni Drainage Line, providing more concentrated water and increasing residence time. This threshold, while important in the uMkhuze Wetland System, is not entirely necessary in a chemical sedimentation sequence as other factors might initiate and maintain concentration of waters. The addition of more concentrated inputs will simply enhance the ability of a wetland to sequester chemicals and increase their rate of sedimentation. The evolutionary pathway of groundwater chemistry and the accompanying precipitation sequence will depend on the chemical composition of the input waters as illustrated by Eugster and Jones's (1979) conceptual model (Figure 2.2.3).

Parent material is mostly invariable across the wetland system, being uniform reworked marine sand, with only the alluvial input of the uMkhuze River, mostly restricted to the floodplain, modifying the

base sediments of the wetland. Seasonal flooding of the uMkhuze River will add sediment to the wetland, in increments significant at a limited spatial scale but hardly noticeable within the study area in the absence of large-scale flooding events. Therefore, variations in parent material as the foundation of the wetland and starting material for chemical sedimentation should be viewed at a temporal scale of decades to centuries for the floodplain of the uMkhuze River (Ellery *et al.*, 2003), and longer (millennia) for the Totweni and Yengweni Drainage Lines due to limited uMkhuze River input to these systems.

Organisms affecting pedogenesis will include vegetation, burrowing organisms such as earthworms and termites, as well as fungi and bacteria. Vegetation rooted at or near the water table may have a direct influence on the concentration of solutes by withdrawing water through transpiration, accompanied by the selective uptake and exclusion of solutes (Bashkin, 2002; De Mars and Garritsen, 1997; Eugster and Hardie, 1978; Eugster and Jones, 1979; Jørgensen, 2002; Jørgensen, 1995; Logan *et al.*, 1999; Logan and Rudolph, 1997; McCarthy *et al.*, 1993; Salama *et al.*, 1993). The length of time required for compounds to saturate under the influence of this concentration process is dependent on the concentrations of the inputs to the groundwater, the ratio of rainfall as a diluting influence to evapotranspiration as a concentrating factor, as well as the density of vegetation and the rate of transpiration.

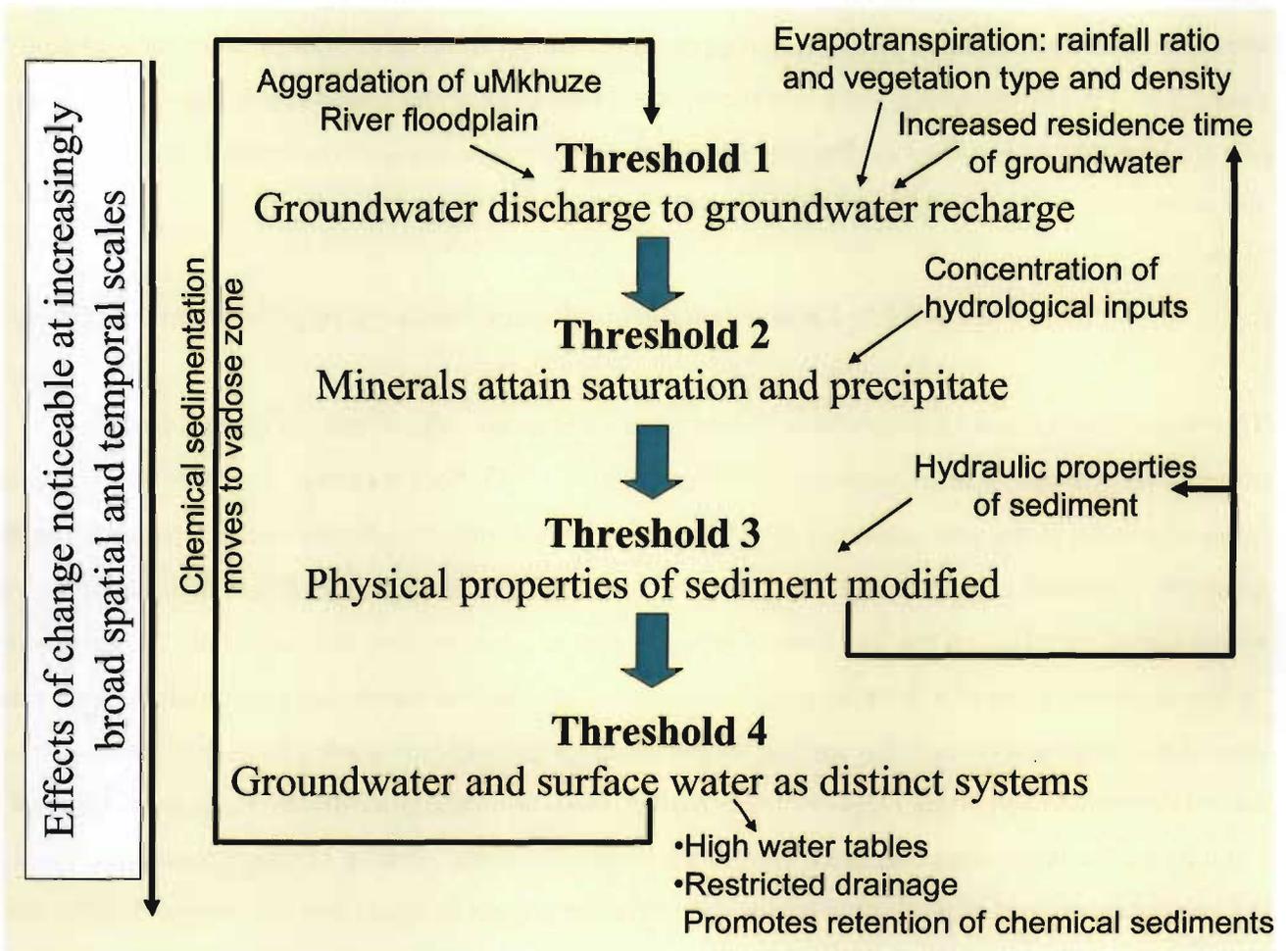
### **7.5.2 Intrinsic factors influencing pedogenesis: differentiating the Totweni and Yengweni Drainage Lines**

The most limited spatiotemporal context considered in this study is defined by an auger hole in space and represents a 'snapshot' in time. Although highly restricted in both space and time, the modifications on this microscale successively integrate upwards through the hierarchy of spatiotemporal scales that may cause change at the broadest landscape perspective. Increments of change at the lowest level must persist over longer time periods than the kinetics of the reverse reaction, which is also the timescale of interest for that holon. For example, calcium and carbonate concentrations might reach saturation for calcite, but high water flux in the system might dilute or remove ions before precipitation occurs. Therefore, within the spatial scale of interest this modification of calcium and carbonate ion concentrations will not cause change at higher hierarchical levels.

As modifications within this limited holon accumulate, the effect of these changes begins to be expressed at larger spatial scales with correspondingly longer timescales both in order for change to be detectable at the larger spatial scale and for a possible reversal of this change. The scales considered in this study extend to the level of drainage lines, and successive seasons of concentration of the groundwater up to hundreds if not a few thousand years.

#### **7.5.2.1 Threshold 1: Change from groundwater discharge to groundwater recharge**

Threshold 1 is an intrinsic threshold of hydrological conditions, which leads to change from groundwater discharge to groundwater recharge (Figure 7.5.1). Such a change increases the residence times of solutes in the groundwater possibly resulting in chemical transformations in areas such as the southern Yengweni and floodplain margins. The threshold is a consequence of floodplain aggradation, with a damming effect on the free flow of groundwater into pre-existing drainage lines. Superimposed on this is the presence of a floodplain with extremely variable flows over short- to medium-timescales (weeks and seasonally) such that surface waters recharge groundwater during high flows and surface water is maintained in lakes. Deep-rooted evergreen trees transpire groundwater from areas adjacent to tributary valley lakes. This leads to a more 'hydrologically closed' system of longer residence times for the groundwater, such that the products of concentration are not flushed from the system. In this way, the effects of change in a holon of limited spatiotemporal scale are propagated up the hierarchy to influence chemical interactions within the groundwater at a longer timescale.



**Figure 7.5.1** Conceptual model of chemical sedimentation in the uMkhuze Wetland System

Chemical sedimentation in the uMkhuze Wetland System is found in groundwater recharge areas, or where hydrological equilibrium occurs such that the groundwater is relatively stagnant. The velocities of flow of surface water into groundwater are thus reduced, allowing solute concentration to the point of mineral saturation. It is also possible that the density-driven downward flow of solutes described by Bauer-Gottwein *et al.* (2007) for the Okavango Delta could be removing solutes to the deep groundwater of the uMkhuze Wetland System. Simulations of groundwater subjected to a concentration process in this study showed that mineral precipitation hinders density-driven flow, but that in all scenarios considered density-driven flow was initiated at some point. The implication for the process of chemical sedimentation is that following initial saturation and precipitation of mineral phases in the shallow sediment of the system, density-driven flow may then supersede mineral

precipitation as the main mechanism of solute retention, resulting in stable solute concentrations in the shallow groundwater and highly saline deep groundwater.

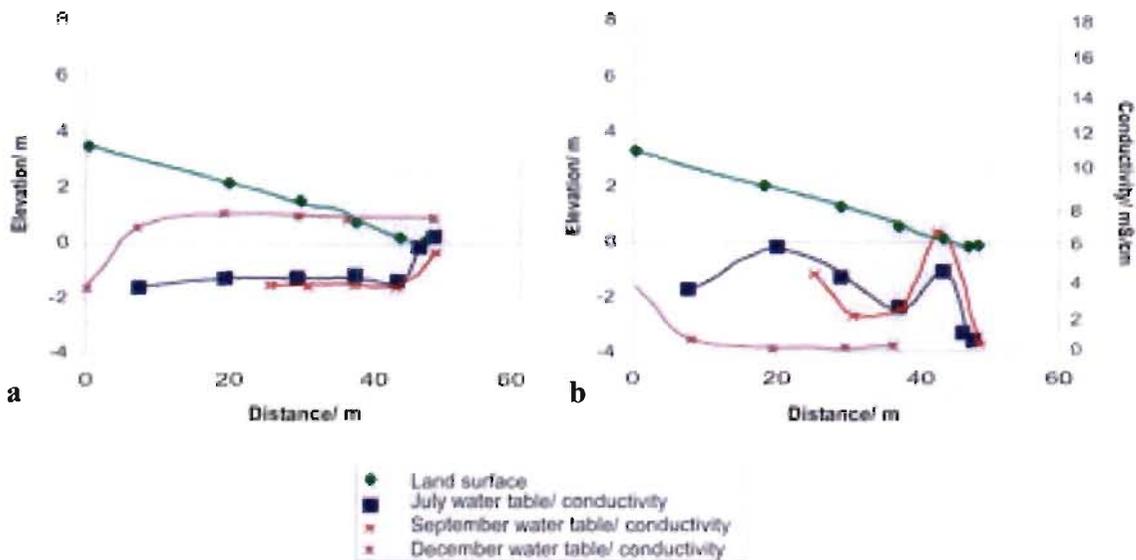
Studies on the groundwater and soil chemistry of islands in the Okavango Delta also identified chemical sedimentation in association with groundwater recharge situations (McCarthy *et al.*, 1993). This is contrary to solute concentrations documented in many wetlands, such as the prairie potholes of North Dakota, USA, due to their being founded on sediments that add solutes in increasing concentrations along groundwater flowpaths (Arndt and Richardson, 1989; Euliss *et al.*, 2004). In the case of sediment leaching adding solutes to groundwater, discharge wetlands are able to retain more solutes by evapotranspiration of surface waters, than recharge wetlands in the same setting. However, it is likely that under similar ratios of rainfall to evapotranspiration, groundwater recharge wetlands will sequester chemical sediments over long time periods.

#### **7.5.2.2 Threshold 2: Mineral saturation leading to solute precipitation**

A further intrinsic threshold to be reached pedogenically at this limited scale is saturation of minerals in solution, resulting in precipitation (Figure 7.5.1). The mechanism by which saturation is reached seems to be governed by two external factors, climate and vegetation.

##### **Mechanism of solute concentration**

The precipitation deficit in the uMkhuze Wetland System is around 500 mm per year, with rainfall of 800 – 1000 mm and evaporation of 1200 – 1600 mm per year. Therefore, in at least some months of the year evapotranspiration exceeds precipitation, which must cause concentration of solutes in the wetland. Concentration of solutes causing saturation in groundwater of both the southern Yengweni and floodplain, as well as a few Totweni samples, often occurs at three to four metres depth. At this depth solute concentration cannot be attributed to evaporation from the soil surface due to capillary rise from the water table. It seems that successive cycles of transpirational concentration by deep-rooted trees in all regions sampled cause concentration of groundwater solutes. Solutes in excess of plant requirements are selectively excluded, thereby allowing these solutes to concentrate in the groundwater. The mid-Yengweni transect, Yg E, illustrates this process (Figure 7.5.2).



**Figure 7.5.2** Water table elevations (a) and variations in electrical conductivity (b) for the southern Yengweni transect, Yg E, from July to December 2000

Both the July and September water tables have steep recharge gradients, indicating that water is removed faster than it is replenished. The water table in September is at a lower elevation than in July, due to September being the extension of the dry season. The electrical conductivity profiles for July and September both show two distinct conductivity peaks at distances of approximately 20 and 45 m along the transect, and do not simply reflect increasingly concentrated groundwater away from the water surface. A mechanism is acting at these positions at depths of 2 – 4 m below the land surface, causing solute concentration that persists over at least three months during the dry seasons, which intensifies during the winter months as the September maximum in the lower sampling point increased by approximately 2.5 mS/cm. These peaks in electrical conductivity coincide with two bands of *Acacia xanthophloea* (fever trees) that are found at distances of 20 and 45 m along the transect. The persistent elevated electrical conductivity at these two points on the transect suggests that these trees are the driver of the concentration of groundwater. The effects of evapotranspiration would intensify in the winter months in the absence of dilution by rainfall, as indicated by the Yg E profile.

### **Degree of flushing of concentration products**

Although, concentration of groundwater is evident in the Totweni and northern Yengweni, and a few samples do attain saturation of certain minerals, the degree of concentration is far less than that encountered in the southern Yengweni and floodplain regions. Both Chadwick and Chorover (2001) in terms of pedogenesis, and Sanford and Wood (1991) for the evolution of surface water bodies, note that water flux is of utmost importance in determining chemical transformations. High water fluxes, in terms of inflows and outflows, result in low residence times in a system and constrain chemical transformations to those that are sufficiently fast to occur given the low residence time. However, for this change to be registered within the holon of interest, those products must also be retained in the holon. Low water fluxes and associated long residence times, will allow a pedogenic trajectory to be more closely followed, if not to completion, then to a point determined by the diluting factor of any inputs. *This fundamental factor of water flux seems to differentiate the Totweni and northern Yengweni from the southern Yengweni and floodplain regions in the uMkhuze Wetland System.*

In the more 'hydrologically open' Totweni Drainage Line the high hydraulic conductivity of the sediment and the predominantly discharge conditions of the water table do not allow progressive concentration of solutes in the groundwater. Progressive concentration of solutes is not seen in spite of seasonal concentration of the groundwater by evapotranspiration. Minerals generally do not attain saturation in the groundwater due to the high water and solute fluxes, as recognised by Chadwick and Chorover (2001), Langmuir (1997) and Yechieli and Wood (2002).

In spite of the Totweni and Yengweni Drainage Lines occurring in the same climatic region on reworked marine sands with similar geomorphology, intrinsic factors within the southern Yengweni have also resulted in chemical sedimentation modifying wetland soils. In the southern Yengweni, it seems that seasonal concentration of the groundwater was not only more effective due to the higher initial starting concentrations of uMkhuze River water, but the concentration products were removed less efficiently than those of the Totweni. The Yengweni is more 'hydrologically closed' than the Totweni, due largely to the amount of aggradation on the uMkhuze River floodplain at this point. Given this, the input of uMkhuze River water to the Yengweni is far greater than to the Totweni (Figure 4.4.4). The more 'hydrologically closed' nature of the Yengweni is also currently evident in the

longer residence times of groundwater in the southern Yengweni. Groundwater on the southern Yengweni was removed such that discharge slopes on the groundwater were flattened, causing delayed removal of concentration products and leading to precipitation of minerals.

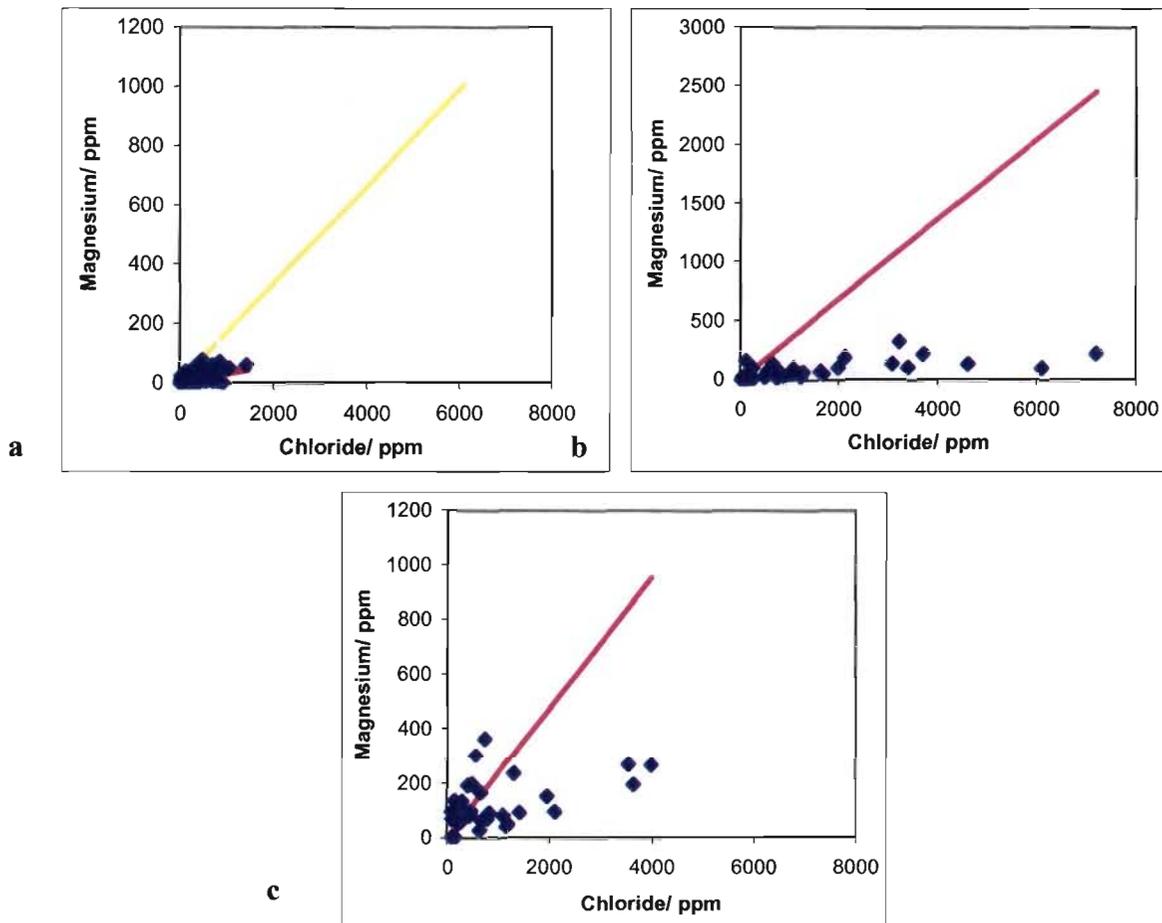
### **A precipitation sequence in the uMkhuze Wetland System**

For the southern Yengweni and floodplain regions, the combined influence of the low water flux, mineral saturation and reaction kinetics for each mineral, define the mineral assemblage precipitating from solution. The water flux is too high to allow saturation of evaporite minerals such as halite and trona, while quartz attains saturation in many areas, the sluggish reaction kinetics mean that this mineral is unlikely to precipitate in the uMkhuze Wetland System (Chadwick and Chorover, 2001).

It seems that a silicate mineral is the first product of chemical sedimentation, as silicon concentrations begin to decline at lower chloride concentrations than the other solutes considered, although a comparison between silicon and total alkalinity in the 2002 data set indicates simultaneous removal of silicon and neutralising of alkalinity (Section 5.3.3). The simultaneous neutralisation of alkalinity can be attributed to the hydrogen ions generated by the neoformation reactions. The formation of clay minerals first in the concentration sequence is at odds with the Eugster and Hardie (1978) model of closed-basin brine evolution, which predicts the initial precipitation of calcite and increasing amounts of magnesium with an intensifying concentration process. However, many silica compounds are relatively insoluble, and it may be expected that silica precipitation occurs first in a concentration sequence, provided sufficient silica is present in solution, as is the case for uMkhuze River water. Many authors have reported neoformation of clay minerals or the magnesian silicates palygorskite or sepiolite in a range of settings, including the continental shelf of the Congo-Zaire River mouth, closed basins in Israel, northern Mexico and Spain, as well as Lakes Chad, Tanganyika and the Ethiopian rift lakes (Armenteros *et al.*, 1995; Borchardt, 1989; Chamley, 1989; Ducloux *et al.*, 1995; Gac *et al.*, 1977; Gal *et al.*, 1974; Sebag *et al.*, 1999; Von Damm and Edmond, 1984; Wiewióra *et al.*, 1996; Yuretich and Cerling, 1983). Furthermore, calcrete and clay minerals are often found within the same deposit, with the clay component designated both detrital and neoformed. Wright and Tucker (1991) document the common co-occurrence of calcrete and smectite or illite in Australian soils, and Von Damm and Edmond (1984) detected rapid clay neoformation, with the simultaneous removal of

calcium as calcite, and magnesium as part of neoformed clays for closed-basin lakes of the Ethiopian Rift Valley. In Lake Chad, Gac *et al.* (1977) document the early removal of magnesium in neoformed silicates, probably montmorillonite, which controls magnesium concentration in the basin, and is followed by calcite precipitation.

In the uMkhuze Wetland System, magnesium concentrations in the groundwater are well correlated with magnesium concentrations in the soil chemistry, while the relationship between aqueous silicon and silica (quartz and other compounds) in the solid phase is complicated by the presence of quartz as the dominant mineral in the sediments of the coastal plain. As discussed in Chapter 6, montmorillonite at depth around the water table in the southern Yengweni and floodplain regions shows features consistent with neoformation, and would account for the solute removal documented for both silicon and magnesium in Section 5.4.3. The difference in magnesium concentrations between the analysed value and that expected if magnesium were to be conserved for the southern Yengweni, was the highest recorded. In a high chloride setting, this is unexpected due to the high solubility of magnesium chloride, which accounts for the good relationship between magnesium and chloride in uMkhuze waters (Figure 7.5.3 a – c).

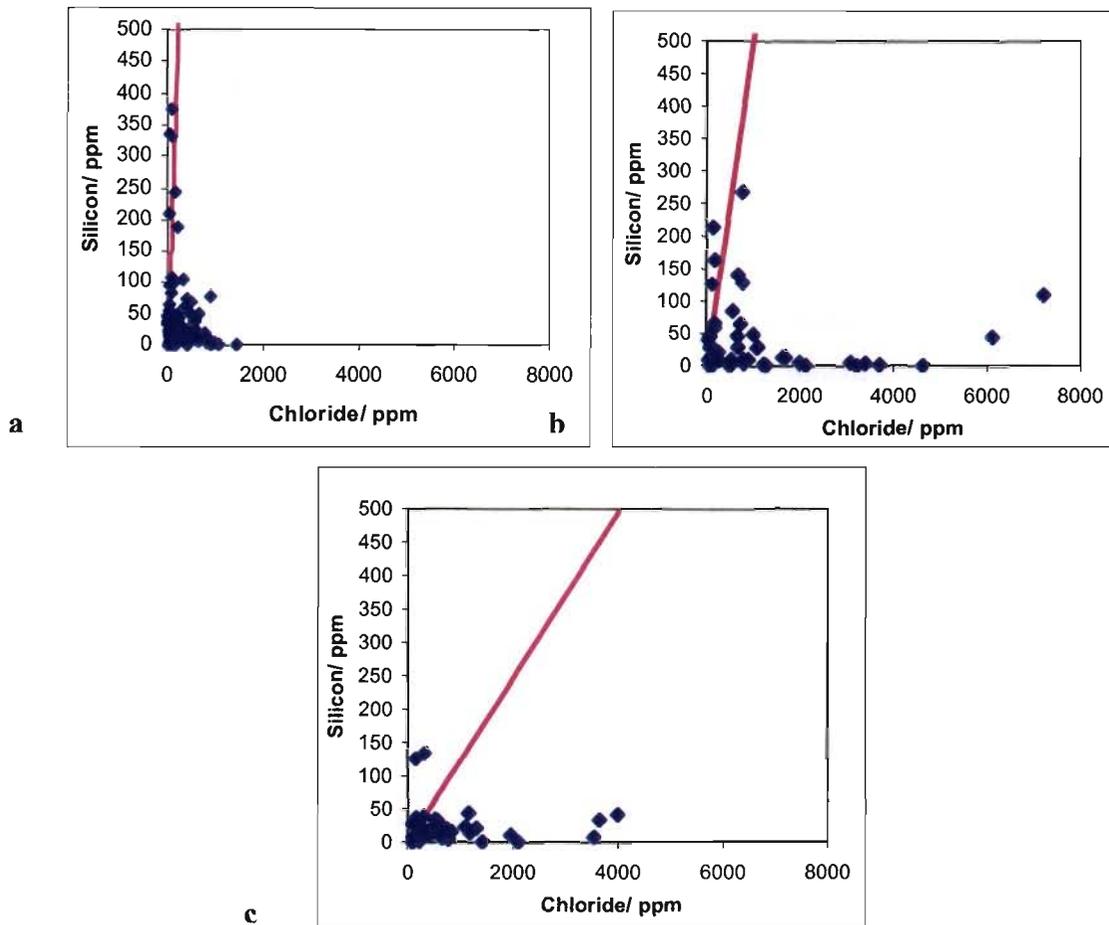


**Figure 7.5.3** The effect of a concentration process on magnesium concentrations, as compared to an ideal concentration process represented by the ideal concentration trendlines for (a) the Totweni and northern Yengweni (b) the southern Yengweni and (c) the floodplain regions  
 Note: The same data is presented in Figure 5.3.8, ideal concentration trendlines have been added here.

The ideal concentration trends for the Totweni (pink) and the northern Yengweni (yellow) in Figure 7.5.3 a, indicate that little magnesium removal is expected as the chloride concentrations encountered at these transects is very low. As expected for the neoformation of montmorillonite, magnesium is effectively removed from solution in both the southern Yengweni and floodplain margin. Studies on mineral sequences produced by a concentration process reported low magnesium contents of calcite precipitates (Gac *et al.*, 1977; Von Damm and Edmond, 1984; Yuretich and Cerling, 1983). This is at odds with Eugster and Hardie's (1978) suggestion that magnesium removal is accounted for by increasing magnesium co-precipitation in calcite. Calcite precipitates in the southern Yengweni were

also found to have low magnesium concentrations at about 1.5 weight % and those from the floodplain margin at a maximum of about 3 % (Humphries, 2007).

The behaviour of silicon is more complicated in that the southern Yengweni as well as the Totweni and northern Yengweni experience large-scale removal of silicon, which is surprising for the relatively low chloride concentrations of the Totweni and northern Yengweni (Figure 7.5.4 a – c). However, percolation through highly leached quartzitic sediments tends to produce high silicon concentrations in spite of the highly insoluble nature of quartz (Summerfield, 1983). It is possible that amorphous silica is precipitating on the Totweni and northern Yengweni, which was not detected by XRD analyses due to its more amorphous nature and the overwhelmingly high quartz contents, or the concentration products are simply flushed from the system. Opaline silica and amorphous clay minerals were detected by Humphries (2007) in the floodplain margin of the uMkhuze River, using transmission electron microscopy coupled to an energy dispersive X-ray spectrometer. However, it may be that the silicon concentration in the Totweni and northern Yengweni is better correlated with carbonic acid concentrations, and does not only reflect a concentration process, of which chloride is a tracer. The degree of solute precipitation predicted using chloride as a concentration tracer, may not be very useful for the Totweni and northern Yengweni groundwater due to the low pH conditions of these areas.



**Figure 7.5.4** The effect of a concentration process on silicon concentrations, as compared to an ideal concentration process represented by the ideal concentration trendlines for (a) the Totweni and northern Yengweni (b) the southern Yengweni and (c) the floodplain regions  
 Note: The same data is presented in Figure 5.3.5, ideal concentration trendlines have been added here.

Gal *et al.* (1974) report that calcite precipitates next, which is documented in the uMkhuze Wetland System with samples on the floodplain, southern Yengweni and lake samples at or approaching saturation, and calcite nodules and powdery precipitates found in these regions. Calcite may actually promote further clay mineral precipitation as calcite is a powerful flocculant for clay minerals (Doner and Lynn, 1977). Aqueous calcium concentrations are not well correlated with soil concentrations. This may either reflect the rapid reaction kinetics of calcite, which maintain calcium at a relatively low concentration, or that calcite precipitation is no longer occurring in certain areas (see Threshold 4).

Comparing water chemistry of the Totweni and northern Yengweni with the southern Yengweni and floodplain regions, it seems that pH might be a key factor controlling chemical sedimentation (initiation of a precipitation sequence), in addition to the hydrological considerations of longer residence times. Aqueous silicon concentrations in the Totweni and northern Yengweni reach values of 373 ppm, which is probably due to the high carbonic acid concentrations in groundwater. As such silicon concentrations in the uMkhuze Wetland System may exceed those of otherwise similar surface water, suggesting that silica compounds are more likely to attain saturation in groundwater. The high silicon concentrations recorded on the Totweni and northern Yengweni also indicate long residence times, allowing the solute to reach high concentrations. It is therefore strange that chemical sedimentation doesn't seem to be occurring in this region. Despite amorphous silica not being detected by XRD analyses, the lack of fine sediment in the sandy sediments of the margins of the Totweni and northern Yengweni suggests that if silica precipitation is occurring it is insufficient concentration to modify the physical properties of the soil observable in the field.

However, if high silicon concentrations are due to high carbonic acid concentrations in the groundwater of the Totweni and northern Yengweni, the southern Yengweni and floodplain groundwater should also attain such concentrations. The maxima recorded are 267 ppm for the southern Yengweni and 134 ppm for the floodplain, although the southern Yengweni samples mostly have concentrations less than 150 ppm silicon. Even though the Totweni and northern Yengweni region has higher silicon concentrations, the pH in these regions tends to be more acidic with an average value of 6.59, compared to 7.54 for the southern Yengweni and 7.55 for the floodplain. The Totweni and northern Yengweni regions have groundwater that is predominantly rainwater-derived and more acidic, than the uMkhuze River water at pH's of approximately 7.74, being comparatively rich in base cations. The lower pH values will retard the precipitation of both silicate minerals and calcite in the Totweni and northern Yengweni. The higher pH values in the southern Yengweni and floodplain groundwater, will then promote clay mineral neoformation and calcite precipitation, particularly at the higher solute concentrations (ionic strengths) as noted by Von Damm and Edmond (1984). It seems that bicarbonate ions dominate the anion chemistry of uMkhuze River water, as the groundwater is buffered at alkaline pH's in spite of precipitation of calcite and neoformation of clay minerals both of which increase acidity of the solution (Von Damm and Edmond, 1984; Yuretich and Cerling, 1983).

### **Factors affecting the rate at which Threshold 2 is attained**

The factors influencing the rate at which Threshold 2 is attained, or even if it is reached at all, are the same as those governing Threshold 1: the ratio of evapotranspiration to rainfall and by extension, the nature and density of vegetation governing the rate of transpiration, the rate of hydrological exchange ranging from 'open' to 'closed'; as well as the solute concentrations of hydrological inputs to the groundwater. All factors do not have to favour concentration of wetland waters for chemical sedimentation to occur. This is evident in the uMkhuze Wetland System where rainfall is higher than expected for a region of chemical sedimentation, and the reworked marine sands favour rapid flushing of any concentration products from the sediment of the drainage lines. If water in the system has low residence times, such as in the discharge transects of the Totweni Drainage Line, minerals may even attain saturation but the concentration products are flushed from the wetland sediment into the drainage line before precipitation occurs. In this way the Totweni may be maintained in an immature stage concerning chemical sedimentation. The rate of water cycling in the system through outflows to deeper groundwater or surface water also governs the degree to which the mineral precipitation sequence is accomplished. For example, at the Yengweni transects Yg B in the north and Yg D midway along the drainage line, high chloride, silicon and magnesium concentrations indicate that a magnesium-rich silicate is saturating. However, there is no indication of calcite saturation or precipitation, which is the next mineral expected in the concentration sequence. It seems that the aggregation of clay particles at these transects has not yet blocked sediment pores sufficiently, and still allows a degree of flushing of concentration products. The process of blocking sediment pores (Threshold 3) seems to allow further concentration of groundwater, leading to calcite precipitation in the uMkhuze Wetland System.

Precipitation of minerals at the finest scale suggested will start to effect change at higher hierarchical levels particularly once Threshold 3 is exceeded.

#### **7.5.2.3 Threshold 3: Changes in physical properties of sediment**

Precipitation of clay minerals will be of little consequence to the structure and functioning of the uMkhuze Wetland System until clay particles begin to block pore spaces of the fine to medium sands of the coastal plain (Figure 7.5.1). The rate of groundwater recharge will be reduced over time, as

solute precipitation progresses because the accumulation of fine material in soil pore spaces reduces hydraulic conductivity.

Significant modifications to the texture of the reworked marine sands were noted during sampling, particularly on the southern Yengweni. Steep recharge gradients were maintained in all southern Yengweni transects, probably largely due to the lower hydraulic conductivity of the soils due to calcite and smectite precipitates.

The spatiotemporal scale is now defined at the level of the recharge groundwater regions, at longer timescales probably of decades to centuries dependent on the rate of chemical sedimentation.

#### **7.5.2.4 Threshold 4: Separation of groundwater and surface water bodies**

Once Threshold 3 is obtained, Threshold 4 can be seen as the end point of chemical sedimentation associated with transpirational water loss from groundwater in the study area (Figure 7.5.1). The sediment pores are almost completely blocked by clay mineral neoformation, and no further, or very little, transpirative concentration of the groundwater may take place. In this way the process of chemical sedimentation is self-terminating, and the groundwater chemistry simply reflects the nature of the chemical sediments with which it is in contact and any inflows not blocked by the chemical sediments.

The southern Yengweni transects Yg E and F, may be approaching this state as chloride concentrations are relatively low compared to calcium, magnesium and silicon concentrations; while the maximum chloride concentrations of the other southern Yengweni transects, Yg D and G, are between 5 and 6 times greater than those at Yg E and F. Furthermore, the water table in December for Yg E as presented in Figure 7.5.2 a, shows a raised water table for most of the transect to approximately 2.5 m higher than was measured in July and September. The upper transect point in December seems to reflect the dry season level. It seems that the clay material in soils at Yg E allowed little infiltration of floodwaters to the water table below, as the transect was sampled about two weeks after a major flood event. However, the conductivity maxima associated with fever trees at Yg E, indicate that some degree of concentration is still occurring.

#### **7.5.2.5 Chemical sedimentation: a combination of extrinsic and intrinsic factors**

Although the extrinsic factors influencing chemical transformations in the uMkhuze Wetland System have broad spatial scales of influence, it is the localized intrinsic factors that have successively differentiated adjacent drainage lines. Chemical sedimentation is effectively immobilizing solutes in the sediments of one system, while the other drainage line largely reflects the conditions at the time of wetland formation. Microscale transformations driven by plants, in groundwater volumes and chemical composition, incrementally accumulate over hundreds to thousands of years to produce fundamental differences in sediment chemical and physical properties (Figure 7.5.1). A number of thresholds are successively attained that lead to modifications of sediment properties. The first is the initiation of groundwater recharge conditions initiated by aggradation of the uMkhuze River floodplain, which increases the residence time of groundwater in the wetland (Figure 7.5.1). This allows a concentration process to bring certain minerals to saturation, after which they precipitate as chemical sediments within the wetland. On sufficient accumulation of chemical sediments, the physical properties of the substrate are modified such that water flowpaths are modified within the wetland. Over time, the physical properties of the sediment may be transformed to such an extent that the surface water and groundwater of the wetland become increasingly separated. At this point, the process of chemical sedimentation may begin afresh in the upper soil profile at the boundary of the chemical sediments. These transformations have far-reaching effects on vegetation distribution, hydrological flows and geomorphology at the broad spatial scale of the wetland system as a whole.

### **7.6 Chemical sedimentation in wetland systems**

Although wetlands are defined by an abundance of water just below or at the soil surface, they share some characteristics with arid and semi-arid terrestrial systems in terms of chemical sedimentation. Due to low hydrological inputs in arid and semi-arid regions, sediment leaching rates are low and base cations build up in a zone of accumulation within the profile, the depth of which is related to the amount of water infiltrating the soil profile. With consistent evapotranspiration of vadose waters, the accumulation of solutes leads to mineral saturation and precipitation in this zone. The nature of the minerals depends on the solute inputs to the zone, and their relative contributions to the soil solution.

Wetland sediments experience similarly low leaching rates, due to the high water tables in these systems that restrict the region of leaching to the vadose zone. Consequently, base cations may accumulate, predominantly as solutes within the groundwater. As groundwater flow patterns in wetlands often favour water retention, these solutes may also be available as constituents of chemical sediments. The nature of solutes accumulating and their concentrations are dependent on the chemical composition of the overlying sediment, and of any hydrological inputs.

Wetlands are also predisposed to further chemical processing by progressive concentration. High water tables mean that wetland plants are often rooted in or just above the water table, which allows progressive concentration of solutes by transpiration. Again the restricted drainage often encountered in wetlands will allow successive cycles of concentration to act on shallow groundwater. Minerals saturate progressively based on concentrations in groundwater and their respective saturation limits, resulting in precipitation of solutes.

Retention of chemicals by the above-mentioned process is less limited by the capacity of the system to accommodate chemical sediments than other retention mechanisms. For example, a cation-exchange mechanism will be limited by the availability of exchange sites, and furthermore, will probably only constitute a short-term sink. Adsorption reactions, although a generally more persistent sink than cation-exchange, are also reliant on adsorption sites. Retention by chemical sedimentation is largely independent of sediment type, as well as chemical composition of the groundwater, as this factor simply governs the nature of the chemical sediments. Even in the absence of sufficient base cations such as occurs in highly leached settings, amorphous silica will preferentially precipitate as documented in the Okavango and Cape coastal regions (Botha, 2000; McCarthy *et al.*, 1993; Summerfield, 1983).

With chemical sedimentation driven by evapotranspiration, it is expected that tropical and subtropical wetlands with a rainfall deficit in at least some months of the year will be active sites of chemical sedimentation. This extrinsic factor of rainfall deficit, is seen as fundamental to the evolution of soils (Chadwick and Chorover, 2001). The Okavango Delta, Botswana, and the uMkhuze Wetland System, fulfill these conditions. Usually pedogenesis is influenced both by *in situ* transformation of the minerals present through weathering and formation of secondary minerals, and by the addition of

solutes leached from the sediment. However, in the quartz-dominated environment of the uMkhuze Wetland System and the Okavango Delta, it is not weathering and formation of secondary minerals that dictates the pedogenic trajectory but neoformation.

Concentration of shallow groundwater driven by transpiration by vegetation rooted at or in the water table is widely recognized, from arid and semi-arid systems in Western Australia (Salama *et al.*, 1993), to the tropical semi-humid climate of the Pantanal of Mato Grosso (Barbiéro *et al.*, 2002), and the temperate regions of the Vecht River floodplain of the central Netherlands (De Mars and Garritsen, 1997), La Plata region of Argentina (Logan *et al.*, 1999; Logan and Rudolph, 1997), North Wales (Batty *et al.*, 2006) as well as the Island of Læsø in Denmark (Jørgensen, 2002). It is surprising that concentration up to mineral saturation is documented in temperate regions such as a marsh 50 km from Buenos Aires, Argentina, where rainfall exceeds evapotranspiration by a large degree (Logan *et al.*, 1999). In this case, conditions of restricted recharge created by the combination of a topographic-focussing of recharge in depressions, and low hydraulic conductivity sediments, have allowed groundwater to concentrate to the point where minerals must be precipitating out of solution (Logan *et al.*, 1999; Logan and Rudolph, 1997). In systems in areas of high rainfall, restricted drainage due to confining clay layers, with low recharge and therefore limited flushing of concentration products must be present to allow for the concentration sequence normally associated with a regional precipitation deficit (Jørgensen, 1995; Logan *et al.*, 1999). Few studies link water chemistry observations to soil chemistry, although many include saturation indices for carbonate and silicate minerals. Particularly interesting is the calculated saturation of magnesium-rich silicates followed by calcite in the Pantanal wetland in Brazil, in spite of its semi-humid setting (Barbiéro *et al.*, 2002).

Therefore, it seems that not only is chemical sedimentation largely independent of sediment and water chemistry characteristics, but that chemical sedimentation may be active in temperate and humid regions, where precipitation deficits are uncommon.

### **7.7 Implications of chemical sedimentation for wetland structure and function**

A rough mass balance of the non-limiting solutes calcium, chloride, iron, magnesium, potassium, silicon and sodium in the uMkhuze Wetland System indicated a retention of 16 100 kg per year across 440 km<sup>2</sup> of wetland, at a rate of 36.5 kg/km<sup>2</sup>/a (Barnes *et al.*, 2002). The vast Okavango Delta at 15

000 km<sup>2</sup> in extent, accumulates 360 000 tonnes of solutes per year, translating to a rate of 24 000 kg/km<sup>2</sup>/a<sup>1</sup> (Ellery *et al.*, 2004; McCarthy and Ellery, 1998). Since clastic sedimentation in the Okavango Delta only amounts to 210 000 kg per year this system is dominated by chemical sedimentation (McCarthy and Ellery, 1998). This extensive accumulation of chemical sediments in wetland systems cannot be insignificant in terms of their impact on wetland structure and function.

The implications of chemical sedimentation may be addressed by considering both on-site effects on the wetland system itself and off-site effects for the catchment of the wetland.

### **7.7.1 On-site consequences of chemical sedimentation**

The consequences of chemical sedimentation are not only limited to on-site effects on a local scale of transformations in water chemistry, the physical and chemical nature of sediments, and the distribution of vegetation; but also to effects at the wetland scale due to modifications in geomorphology and therefore hydrology of a wetland.

#### **7.7.1.1 Local consequences of chemical sedimentation**

Chemical sedimentation affects the chemical composition of wetland waters as described by the Eugster-Hardie model of chemical divides in the evolution of water bodies under a concentration process. The resulting precipitates modify both the chemical and physical characteristics of wetland sediments, which not only affects further chemical processing, but it may disturb or even interrupt hydrological flow paths due to a decrease in hydraulic conductivity of sediments.

Increasing salinisation of groundwater and sediments will result in a change in vegetation distribution as the deep-rooted initiators of chemical sedimentation, adapted to freshwater with relatively low solute concentrations, will be poisoned. The initial vegetation is replaced by species better adapted to saline soils as documented in the Okavango Delta (Ellery *et al.*, 1993a) and noted in the uMkhuze Wetland System by the transformation from sandveld vegetation characterized by grassland, scattered palms and broadleaved evergreen trees to sparse microphyllous deciduous savanna dominated by fever trees (*Acacia xanthophloea*) in regions of chemical sedimentation. Fever trees are known to concentrate

excess solutes in their lower branches, that then senesce. Initial comparative analyses of lower and upper branches of fever trees in the southern Yengweni, revealed a marked increase in calcium, sodium and magnesium in the lower branches, which appear to be actively senesced from the tree. It is hypothesized that the active and rapid shedding of lower branches by this species is an adaptation to dispose of waste products that are taken up in quantities that are not required by the plant.

Due to the retention and concentration of solutes in the groundwater, the surface water of wetlands influenced by processes documented in the uMkhuze Wetland System and the Okavango Delta remains remarkably fresh in spite of being situated in regions where evaporation exceeds rainfall in many months of the year.

#### **7.7.1.2 Geomorphological implications of chemical sedimentation**

Due to the effect of wetland basin physiography on hydrology, wetlands are sensitive to physiographic change. There are three forms of sedimentation in wetlands that influence the slope of wetlands, these being clastic, chemical and organic. Clastic sedimentation is well documented in wetland systems, and is expected due to the wetland characteristics of low slope, large areas of shallow inundation and high roughness of the wetland surface (Ellery *et al.*, 2004; McCarthy *et al.*, 1997; McCarthy *et al.*, 1986; Mitsch and Gosselink, 1993). Clastic sediments are generally deposited at the head as the wetland characteristics mentioned above cause reduction in velocity of inflowing waters and therefore a reduction in their capacity to transport sediment. The deposition of sediment decreases slope in the upstream direction and oversteepens the slope in the downstream direction in respect of the focal point or region of deposition. Continued sediment deposition will create an instability of slope that may well initiate erosion in the wetland (Ellery *et al.*, 2004).

Chemical sedimentation is also likely to affect wetland slope. The precipitation of chemical sediments is unlikely to occur in wetland headwaters where discharge is still relatively high, residence times are low and clastic sedimentation is dominant. Therefore the potential for concentration of solutes to the point of saturation is limited in the proximal reaches. It is the distal reaches of a wetland system that are the more likely location for chemical sedimentation, where water may have been concentrated across the wetland system in either a surface water or groundwater setting, discharge is diffuse, and

residence times are long. The distal reaches of the Okavango Delta are found to be accumulating solutes, and probably account for much of the chemical sediment retained there every year (McCarthy *et al.*, 1997; McCarthy and Ellery, 1998). Chemical sedimentation in the distal reaches affects slope such that there is a decrease in slope in an upstream direction and an increase in the downstream direction. Chemical sedimentation may thus be an important mechanism maintaining uniform slopes within wetland systems as clastic sedimentation and chemical sedimentation interact to sustain a uniform longitudinal slope, thereby protecting wetlands from catastrophic erosion (Ellery *et al.*, 2004).

Chemical sedimentation in the uMkhuze Wetland System occurs where hydrological flows are hindered, resulting in long residence times in the groundwater, and often in association with stagnant surface water, such as the Yengweni Lake. Preliminary sampling at the Muzi Lake, also once a dammed tributary of the uMkhuze River, suggests that chemical sedimentation is present along its entire length. Further work in the uMkhuze Wetland System has also identified chemical sedimentation as an important process in the distal reaches of the uMkhuze River floodplain, with chemical sediments concentrated on the floodplain downstream of the current study site (Humphries, 2007). The pattern of sedimentation is similar to that discovered at the floodplain margin at transects Fld B and C in the study area. Based on current understanding of hydrological and associated sediment fluxes, clastic sedimentation seems to have had a profound influence on the geomorphology of the uMkhuze Wetland System, aggrading from east to west and progressively damming the uMkhuze River tributaries. The increased uMkhuze River inflows probably initiated chemical sedimentation in the Muzi and Yengweni Drainage Lines due to their more closed nature and the higher solute load entering the former tributary streams.

Organic sedimentation is expected in flooded areas where geomorphological accommodation space exists (Ellery *et al.*, 2004). Depressions in the uMkhuze Wetland System where peat is accumulating include the Totweni Drainage Line and the Manzibomvu Streams where flooding is sufficiently prolonged for organic sediments to accumulate. Accommodation space is present in the tributary drainage lines because clastic sedimentation along the uMkhuze Floodplain axis has dammed the drainage line, causing backflooding and the accumulation of peat.

## **7.7.2 Off-site consequences of chemical sedimentation**

### **7.7.2.1 Water quality enhancement in wetland systems**

The sequestration of solutes in wetland sediment allows wetland surface waters to remain remarkably fresh. A striking example of this effect is the Okavango Delta where 96 % of the inflowing water is lost to evapotranspiration, with a further 2 % recharging local groundwater and only 2 % leaving as surface water outflow (McCarthy and Ellery, 1995; Wilson and Dinçer, 1976). In spite of this water balance that should result in highly saline surface waters, solute concentrations only increase by a factor of approximately 2 across 15 000 km<sup>2</sup> of swamp system (McCarthy and Metcalfe, 1990). The elevated solute concentrations of surface water that are expected due to the high atmospheric demand of the region, are instead found in the groundwater and the sediment, where solutes are sequestered in chemical sediments. As a result, relatively fresh water is available for the town of Maun just downstream of the Delta, as well as other downstream users.

The uMkhuze Wetland System supplies 56 % of the mean annual runoff to the World Heritage and Ramsar-accredited Lake St Lucia. The Lake naturally undergoes large variations in salinity governed by climatic cycles of drought and flooding, and occasional mouth closure. The role of the uMkhuze Wetland System, which supplies over 50 % of the freshwater supply to the Lake, is therefore of importance in sustaining the Lake St Lucia system (Stormanns and Breen, 1987).

### **7.7.2.2 Protecting the water quality enhancement function in wetland systems: catchment considerations**

The water quality enhancement of waters within wetlands is linked to wetland hydrology and geomorphology such that any modifications to the hydrology of wetland systems may alter their ability to maintain water quality of wetland waters through chemical sedimentation. Increasing hydrological inputs may increase discharge across a wetland system, allowing insufficient time for processing of wetland waters through concentration thereby limiting chemical sedimentation. On the other extreme, increasing water loss to the atmosphere by increasing evaporation relative to transpiration, such as constructing dams upstream of wetlands, will result in the concentration sequence running to completion resulting in extensive salinisation of the system. Problems that can arise as a consequence

of human impacts on biogeochemical processes in wetlands are well illustrated by the Mesopotamian Wetland of Iraq, which was a vast freshwater swamp in the central parts of the country. The wetland was largely drained or starved of water through dams by the regime of Saddam Hussein with a loss of pristine wetland area of 7 600 km<sup>2</sup> between 1970 and 2000, and even further loss of wetland to less than 7 % of their original extent by 2003 (Anonymous, 2003; Partow *et al.*, 2006). Salinisation of the system has occurred, seriously affecting local livelihoods, particularly those of the Marsh Arabs who historically relied solely on the wetland's resources. After the overthrow of the regime in 2003, the local community destroyed damming and drainage infrastructure, reflooding large sections of the marsh (up to 50 % of the formerly drained area; Partow *et al.*, 2006). Attempts to rehabilitate the wetland are underway.

#### **7.8 Conclusion: The usefulness of hierarchical patch dynamics-threshold theory in contextualising chemical sedimentation in wetland systems**

Hierarchy theory applied to landscapes cannot be strictly defined, as the structure of the hierarchy is dependent on the specific landscape and the purpose of examination. As such, the hierarchical division of the landscape is the result of individual perception and is governed by the researcher's motives. Therefore the hierarchical division of the landscape may be structured according to different criteria (O'Neill, 1989; Urban *et al.*, 1987; Wu and David, 2002). However, as chemical sedimentation is neither restricted to substrates of a certain type, nor to water of a specific chemical composition, nor to a limited climatic range, hierarchical patch dynamics incorporating an understanding of thresholds is useful in contextualising chemical sedimentation in wetlands. Chemical sedimentation may require hundreds of years to manifest in a wetland, with the rate dependent on the concentration of hydrological inputs and the water flux within the system as governed by the ratio of evaporation to precipitation, as well as within-wetland factors relating to residence time. Hierarchical patch dynamics allows the entire process of chemical sedimentation to be considered within a single framework, recognizing the fine scales and rapid reaction rates at the initiation of chemical sedimentation, to the accumulated effects of modifications to holons of lower levels of the landscape. It is at this scale that the implications of chemical sedimentation are seen to fundamentally affect wetland structure and function, a view that is not possible when the focus is limited to hydrological and water chemistry variations over a single seasonal cycle, and their relationship to soil chemistry in a moment in time.

Attaining pedogenic thresholds during chemical sedimentation may not have the dramatic and catastrophic effects as do geomorphic exceedances that trigger channel-switching in floodplains or landslides in imposing landforms. Nevertheless, pedogenic thresholds explain the sluggish response of some wetland systems to intrinsic and extrinsic drivers of pedogenesis. For example, a wetland on fine to medium sands similar to the uMkhuze Wetland System will take longer to attain Threshold 3 (modification of physical properties of the sediment) than will a wetland situated predominantly on silty alluvial deposits. The amount of clay required to block pores in the latter system will be far less than required in a sandy system. Once the buffering capacity of the system is exhausted, change in the holon of interest will influence successive levels of the hierarchy. Here the important concept for each wetland is not the rate of change, but the attainment of a certain threshold. The time taken to attain the thresholds described in the process of chemical sedimentation may be long in a wetland with very dilute inputs and high hydraulic conductivity sediments. However, high atmospheric demand within its region and concentration of water incrementally season by season may lead to chemical sedimentation on the scale noted for such a system, the Okavango Delta.

Each successive threshold attained, magnifies the effects of chemical sedimentation up the spatiotemporal hierarchy, from the scale of solutes interacting at fine temporal scales, to the scale of clay particles precipitating and then aggregating at a scale of a single hydrological type such as in a situation of groundwater recharge or where there is hydrological equilibrium. The changes at this point, on integration over long timescales, start to affect landscape biogeochemical processing, by altering hydrological flowpaths and even affecting topography.

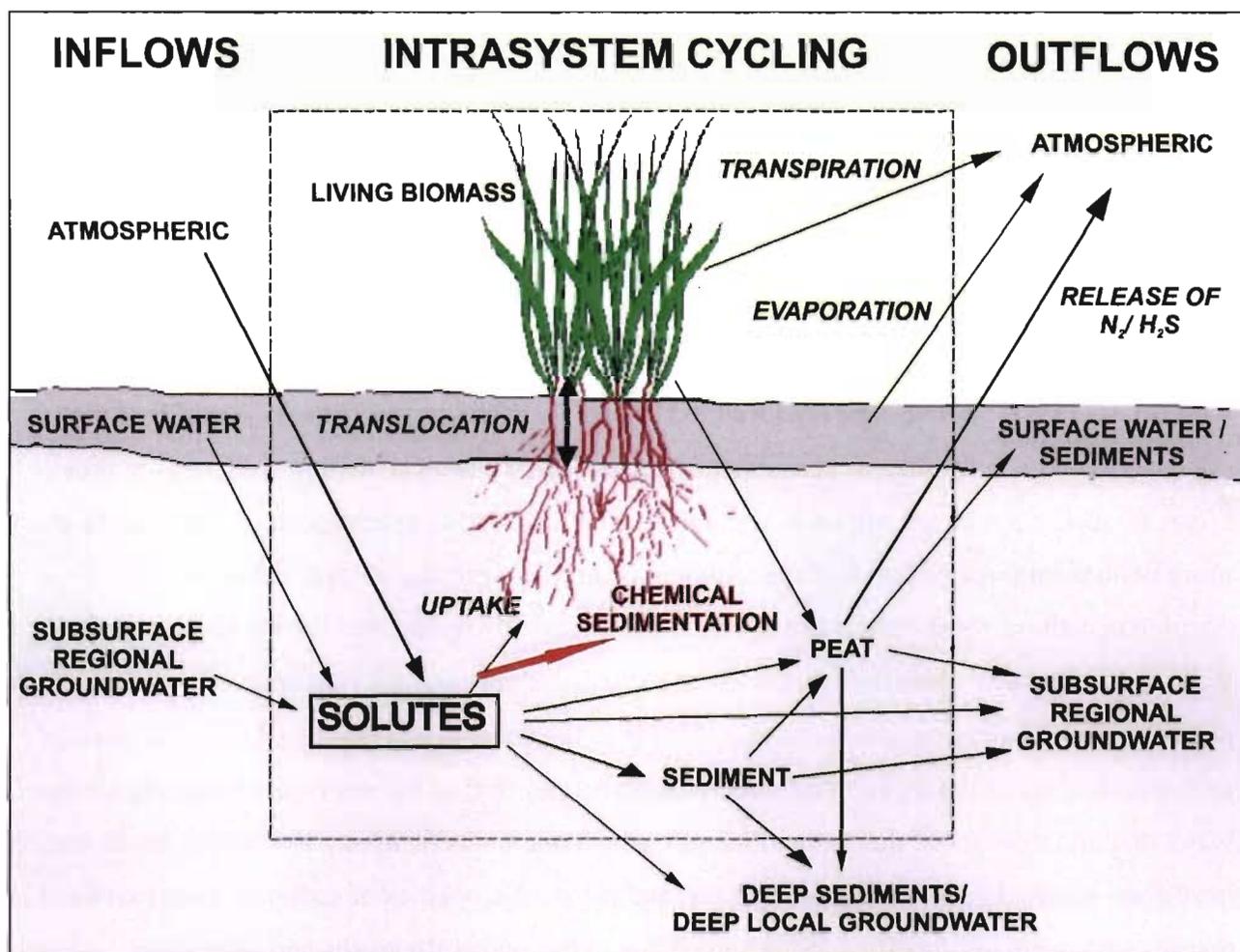
## CHAPTER 8

### CONCLUSION

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#### 8.1. Chemical cycling in wetland systems

Chemical cycling in wetland systems is traditionally conceptualised as involving inputs from atmospheric deposition, surface water and regional groundwater inflows, with outputs associated with degassing to the atmosphere, as well as surface water and groundwater flowing from the system. Common sinks seen as accounting for retention of chemicals within wetlands are the biomass, absorption or adsorption to wetland sediment as well as peat deposits, which might also be more permanent through burial of the sediment layers sequestering solutes. However, as documented above for the uMkhuze Wetland System and by researchers for the Okavango Delta, a further sink has been identified: that of chemical sediments within the root zone of wetland margin and floodplain vegetation, and in close proximity to the water table (Figure 8.1). The location of this sink in upper sediment layers allows for efficient removal of solutes from recharging surface water and groundwater of the wetland margin, which maintains relatively low solute concentrations in surface waters. Furthermore, the chemical and physical properties of sediment on the wetland margin are potentially modified to the degree that hydrological flowpaths and vegetation distribution will be changed over time with progressive chemical sedimentation. The shallow depth of chemical retention may also allow remobilization of the chemicals sequestered depending particularly on the position of the water table within the profile and the nature of the precipitates. These factors further highlight wetlands as dynamic systems with natural changes to wetland structure and function over years to decades. Through this study and work in the Okavango Delta, wetlands are shown to be capable of effectively removing and retaining the non-limiting solutes calcium, iron, magnesium, potassium (sometimes limiting), silicon and to some degree sodium. The mostly more enduring nature of the compounds thus formed, and their greater potential toxicity at high concentrations, suggest that non-limiting solutes have greater potential to modify ecosystem structure and function.



**Figure 8.1** A conceptual model of potential solute inputs to, sites of chemical retention and solute outputs from a wetland system, highlighting chemical sequestration in the root zone

Modified after: Mitsch and Gosselink, 2000

In the light of increasing global temperatures and the intensification of drought cycles and extreme weather events, such as cyclones, affecting southern Africa, it is expected that chemical sedimentation of this nature will intensify in the region. Higher atmospheric water demand will increase transpiration rates leading to more effective concentration of solutes in the groundwater, with lower rainfall resulting in less dilution of the groundwater. Extreme rainfall events will flood the system and have the potential to dilute groundwater substantially in areas of low hydraulic conductivity. However, in areas of established chemical sedimentation, the hydraulic conductivity of the sediment is low and therefore dilution effects will be limited. Surface water flow to wetland systems will also be under increasing pressure from higher atmospheric water demand as well as any efforts in the catchment to protect water supply for certain areas such as damming. As the process of chemical sedimentation is driven by transpiration, if water tables fall below the rooting

depth of the wetland vegetation, there will be no further concentration of groundwater by this mechanism.

## 8.2. Recommendations for further research

Chemical sedimentation on the scale documented in both the Okavango Delta, Botswana and the uMkhuze Wetland System, South Africa, has not been recognised in wetland systems elsewhere, with traditional perspectives limiting such accumulations to terrestrial arid and semi-arid settings. The discovery of chemical sedimentation in the uMkhuze Wetland Systems has indicated that such a process is not limited to semi-arid wetland areas, but may also occur in more humid subtropical regions, and it may also occur in temperate systems under conditions of restricted drainage. The ability of wetlands to enhance the water quality of inflowing waters, previously documented for the plant macronutrients nitrogen, phosphorus and on rare occasions potassium, may be applied to a wider range of solutes. Chemical sedimentation in the Okavango Delta, Botswana, indicates that non-limiting solutes account for 84 % of the total load of chemical sediments deposited in the system. Therefore, it seems that the focus on wetlands as sinks and transformers of nutrients, particularly nitrogen and phosphorus, while useful, is only the tip of an iceberg. Non-limiting and non-nutrient solutes therefore, have a great potential to modify wetland structure and function. Further research in this area is required if wetlands are to be fully characterised in terms of water quality enhancement of inflowing waters:

- Considering that chemical sedimentation is occurring in both the uMkhuze Wetland in a humid subtropical climate and the Okavango Delta in a semi-arid region, and possibly even wetlands in temperate zones as mentioned in Section 7.6, chemical sedimentation as a mechanism of solute retention should be more widely investigated in wetland systems;
- In this way the model of chemical sedimentation in wetland systems could be improved such that greater predictive capability concerning wetland evolution would be possible, thus informing management;

Within the uMkhuze Wetland System, further studies that would enhance our understanding of chemical sedimentation include

- Geomorphological studies on the origin and evolution of the Muzi, Yengweni and Totweni systems, with the aim to model further system evolution in terms of chemical sedimentation;

- To study the Muzi Drainage Line in a similar way to the Yengweni and Totweni systems, to investigate the theory that Muzi represents a drainage line in an advanced stage of chemical sedimentation (see Section 7.7.1.2);
- Studying the regional water table on the coastal plain to get a sense of wetland-wide and larger slopes on the water table and direction of flow in order to track evolution of the regional groundwater;
- The contribution of uMkhuze River water, the greatest potential solute input, to the wetland and its role in enhancing chemical sedimentation;
- Salinity mapping of the groundwater at regional scale possible by electromagnetic survey would give insight into the functioning of the coastal plain as a whole and highlight potential areas of chemical sedimentation;
- Further in-depth analyses of groundwater chemistry,
- Thermodynamic modeling of the groundwater system with the goal of modeling the trajectory of groundwater evolution from initiation (prior to the present) to possible endpoints (modeling different scenarios) and the length of time required to reach the present water and sediment chemistry;
- Monitoring of water chemistry over longer timescales to allow better estimates and modeling of the evolution of groundwater and sediment chemistry;
- The investigation of the possibility of density-driven flow of solutes is necessary to understand the nature and longevity of solute retention in the uMkhuze Wetland System (see Bauer-Gottwein *et al.*, 2007);
- Further in-depth analyses of the nature of the chemical sediments including clay mineralogy, nature and chemical composition of the calcrete (which could also be dated and feed into estimations of time concerning chemical sedimentation), and other minerals and amorphous precipitates present;
- Study of the vegetation distribution both in response to chemical sediments and the role vegetation plays in initiating and maintaining chemical sedimentation;
- The contribution of vegetation to solute sequestration in the plant tissues and the cycling of these solutes within the system.

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**Appendix A: List of Permanent Stakes  
uMkhuze Wetland System**

Table 1: Totweni Stakes

<b>Site</b>	<b>Description</b>	<b>GPS</b>
Totw A	North Totweni	27° 36.569' S 32° 28.403' E
Totw B		27° 37.161' S 32° 28.234' E
Totw C		27° 37.904' S 32° 28.169' E
Totw D		27° 38.344' S 32° 28.040' E
Totw E	South Totweni	27° 39.040' S 32° 28.181' E

Table 2: Yengweni Stakes

<b>Site</b>	<b>Description</b>	<b>GPS</b>
Yg A	North Yengweni	27° 37.086' S 32° 26.038' E
Yg B		27° 37.903' S 32° 25.942' E
Yg C		27° 38.135' S 32° 25.960' E
Yg D		27° 38.412' S 32° 25.930' E
Yg E		27° 38.740' S 32° 25.905' E
Yg F		27° 39.342' S 32° 25.762' E
Yg G	South Yengweni	27° 39.521' S 32° 25.644' E

Table 3: Floodplain Stakes

<b>Site</b>	<b>Description</b>	<b>GPS</b>
Fld A	South of Totweni, just north of oxbow	27° 39.209' S 32° 28.071' E
Fld B	Inbetween Totweni and Yengweni drainage lines	27° 39.482' S 32° 26.524' E
Fld C	South of Yengweni	27° 39.491' S 32° 26.142' E

## Appendix B: Raw Water Chemistry Data

Sample	pH	Conductivity mS/cm	Chloride ppm	Sodium ppm	Potassium ppm	Silicon ppm	Iron ppm	Magnesium ppm	Calcium ppm	Total Alkalinity ppm	Sulphate ppm	Nitrate ppm	Phosphate ppm	Fluoride ppm
<b>Fld A Mpanza 07</b>	7.72	1.039	174	140.2	10.85	14.1	0.22	38.4	40.4					
<b>Fld A Mpanza 09</b>	7.49	1.214	221	153.3	6.59	1.483	0	58.25	72.18					
<b>Fld A Mpanza 12</b>	6.80	4.46	1171	568.9	14.51	15.3	0	195	198					
<b>Fld A Oxbow 07</b>	7.62	1.238	266	157.1	2.91	14.2	0	47	36.5					
<b>Fld A Oxbow 09</b>	6.92	1.31	304	173.7	22.89	1.832	0	39.77	47.26					
<b>Fld A Oxbow 12</b>	6.87	0.515	57	55.81	11	7.088	0	17.18	17.54					
<b>Fld A1 07</b>	7.97	3.76	1089	710.1	3.46	22.2	0.25	78.7	29.1					
<b>Fld A1 09</b>	7.28	1.46	216.5	144.1	3.83	1.754	0	88.89	90.24					
<b>Fld A1 12</b>	7.37	4.27		725.7	1.6	3.151	0	90	125.9					
<b>Fld A11 07</b>	8.29	1.66		254.3	3.07	10.7	0	46	34.8					
<b>Fld A12 07</b>	7.91	6.53		970.3	2.98	23.4	0	333	34.9					
<b>Fld A13 07</b>	8.00	4.68	1299	767.3	2.62	20.7	0	232	12					
<b>Fld A2 07</b>	7.93	5.08	658	99.32	2.54	22.5	0.11	163	48.1					
<b>Fld A2 09</b>	7.36	1.553	260	195.7	3.44	6.681	0	73.05	47.31					
<b>Fld A2 12</b>	7.44	5.53	1948	993.2	3.81	10.23	0	148.6	6.911					
<b>Fld A3 07</b>	7.88	3.15	827	527	3.72	15.4	0.1	88.6	79					
<b>Fld A3 09</b>	7.21	5.21	1410	736.2	2.21	0	0	90.18	39.3					
<b>Fld A3 12</b>	6.84	0.704	86	92.69	9.57	0	0	0	0					
<b>Fld A4 07</b>	7.28	2.57	658	373.1	5.13	6.28	0	60.1	49					
<b>Fld A4 09</b>	7.07	4.68		778	2.05	1.751	0	148.1	111.5					
<b>Fld A5 09</b>	6.52	2.93	770	402	2.53	4.35	0	66.93	64.41					
<b>Fld A6 (OSP) 09</b>	6.41	2.21	594											
<b>Fld A7 07</b>	8.07	1.232	223	137	7.58	15.5	0	51.8	38.1					
<b>Fld ASP 07</b>	7.89	1.374	266	181.4	1.88	14.7	0	58.2	31.3					
<b>Fld B1 07</b>	7.88	11.28	3623	2302	5.42	32.8	0.29	191	20					
<b>Fld B1 09</b>	7.57	15.86	3526	3489	4.74	7.18	0	264.4	11.34					
<b>Fld B2 07</b>	8.07	4.61	1148	1228	1.8	43	0.26	39.6	10.1					
<b>Fld B2 09</b>	7.86	7.93	2095	2182	2.66	0	0	93.55	9.991					
<b>Fld B3 09</b>	8.10	3.97	629	1089	2.29	6.801	0	26.19	0					
<b>Fld B4 07</b>	7.77	2.72	294	295.5	1.68	38.4	0.23	131	118					
<b>Fld B4 09</b>	7.00	3.01	407	273.7	2.84	8.475	0	188.5	210.6					
<b>Fld B5 07</b>	7.49	3.92	556	351.1	4.01	32.4	0.18	300	253					
<b>Fld B Lake 07</b>	7.87	0.903	122	105.7	6.64	12.2	0.18	54.9	34.5					

Sample	pH	Conductivity mS/cm	Chloride ppm	Sodium ppm	Potassium ppm	Silicon ppm	Iron ppm	Magnesium ppm	Calcium ppm	Total Alkalinity ppm	Nitrate ppm	Sulphate ppm	Phosphate ppm	Fluoride ppm
Fld B Lake 09	9.09	1.22	208	133.1	8.45	1.317	0	67.78	50.98					
Fld C Hippo Channel 07/02	7.44	1.02	76.8	154.3	5.892	60.55	0.065	28.15	429	185.6	171.404	24.324		0.136
Fld C Hippo pool 07	7.91	0.967	158	93.38	6.63	17.4	0.21	61	40.7					
Fld C Hippo Pool 12	7.09	0.495	72	40.97	4.43	5.364	0	13.98	13.07					
Fld C0 07	7.88	13.45	3969	2859	8.02	40.5	0.25	262	12.3					
Fld C1 07	8.20	1.793	148	207.3	1.93	36.2	0.2	133	20.7					
Fld C1 09	7.52	3.95	735	396.5	3.45	19.45	0	362	41.95					
Fld C1 12	7.39	6.93	1181	1276	2.57	13.36	0	47.69	0					
Fld C10 07	7.50	1.213	103	128.2	3.04	30.5	0.25	64.6	47.5					
Fld C2 07	8.10	2.96	464	532.8	1.42	18.7	0.23	95.1	17.5					
Fld C2 07/02	7.73	2.43	148.61	711.3	6.808	126	0.162	0	122	1113.6	102.323			1.449
Fld C2 09	7.61	1.598	90	124	3.65	7.591	0	92.86	55.39					
Fld C3 07/02	7.05	2.37	312.3	412	4.027	134	0	93.2	1100	336.8	641.662			0.188
Fld C3 09	7.88	2.76	441	553.1	5.24	13.97	0	83.8	21.84					
Fld C4 09	7.47	2.01	304	327.3	2.29	15.15	0	100.6	32.79					
Fld C5 07	7.02	2.45	423	375.3	2.99	18.7	0.28	77.1	56.5					
Fld C6 07	7.84	3.26	508	273.6	1.98	33.7	0.22	190	167					
Fld C7 07	6.85	2.94	485	243.7	3.58	18.6	0.18	194	131					
Fld C9 07	6.77	1.793	308	170.6	13.98	18.8	0.24	83.2	68.6					
Fld CSP 07	7.84	1.28	86	97.27	1.78	26.4	0.25	64.7	60.1					
Totw A1 04	5.84	0.235		39.24	3.11	12.03	1.29	0.258	1.918					
Totw A1 07	5.87	0.533	222	94.54	8.15	3.571	0	12.9	24.61					
Totw A1 07/02	5.98	0.447	70.71	98.93	5.747	373	8.55	0	101	#				
Totw A1 12	5.28	0.52	114	65.49	2.7	1.318	0	0	0					
Totw A1(h2) 09	6.09	0.607	146	92.7	3	9.386	0	10.39	13.05					
Totw A2 04	5.60	0.187		46.06	5.35	152.6	26.61	4.523	2.724					
Totw A2 07	6.41	0.584	152											
Totw A2 07/02	5.25	0.517	98.36	106.1	7.462	82.3	0.246	0	160	#				
Totw A2 12	5.32	0.322	72	22.16	4.81	0	0	4.211	2.251					
Totw A2(h3) 09	6.13	0.489	108	69.77	4.06	5.671	0	8.74	10.18					
Totw A3 04	5.58	0.938		235.1	4.43	17.1	0.43	33.5	37.2					
Totw A3 07	5.30	0.359	58	58.58	3.91	96.32	16.16	2.622	1.846					
Totw A3 07/02	5.98	0.558	70.71	104.3	7.476	106	0	0	336					
Totw A3 12	5.11	0.277	59	31.09	2.02	20.47	1.929	1.485	0	36.8	175.96			
Totw A3(h4) 09	6.43	0.343	61	39.82	2.61	0.93	0	3.25	0					

Sample	pH	Conductivity mS/cm	Chloride ppm	Sodium ppm	Potassium ppm	Silicon ppm	Iron ppm	Magnesium ppm	Calcium ppm	Total Alkalinity ppm	Sulphate ppm	Nitrate ppm	Phosphate ppm	Fluoride ppm
Totw A4 07	5.53	0.259	44	38.76	4.93	209.3	36.55	8.002	3.75					
Totw A4 12	6.04	0.503	151	75.3	4.29	27.6	1.595	5.789	0.334					
Totw A4 HOLE5 09			153	172.3	5.17	26.68	2.415	3.443	8.916					
Totw A4(h6) 09	6.42	0.238	40	30.85	16.56	334.2	63.12	12.2	5.153					
Totw A5 07	3.73	0.519	104	86.89	6.43	3.864	0	26.61	69.1					
Totw A5(h7) 09	6.79	0.551	98	66.6	2.06	4.446	0	9.319	1.216					
Totw A Lake 07	6.91	0.779	109	83.8	14.35	6.7	0	26.07	48.39					
Totw A Lake 09	7.34	1.628	137.5	130.3	22.51	12.77	5.76	22.51	56.79					
Totw A Lake 12	6.39			106.8	4.47	3.738	0	7.183	6.547					
Totw B1 04	4.78	1.95		376.6	11.79	20.6	0.44	27.7	29.6					
Totw B1 09	6.48	3.54	846	592	16.36	4.106	0	71.56	92.65					
Totw B1 12	5.97	3.32	987	543.9	12.01	3.678	0	49.8	69.25					
Totw B2 04	7.71	2.66	695	475.43	15.08	15.83	0.13	58.47	61.13					
Totw B2 09	6.95	1.461	309	217.2	15.73	5.395	0	51.52	85.4					
Totw B2 12	6.68	2.71	668	491.6	14.85	5.289	0	54.19	80.19					
Totw B3 04	7.84	3.21		462.2	33.48	12.5	0.44	84.4	98.1					
Totw B3 09	6.85	2.29	477.5	282	19.95	6.816	0	76.36	218					
Totw B3 12	6.67	2.42	1053	317	17.51	0.291	0	49.45	83.19					
Totw B4 09	7.20	2.92	758	482.3	19.53	19.24	0	54.52	120					
Totw B4 12	7.00	2.54	522	358.5	20.46	17.62	0	52.28	92.74					
Totw B Lake 09	7.54	3.72	932	590.6	19.98	0	0	73.2	149.1					
Totw C1 04	7.34	0.572	117			99.2	32.2	6.53	3.78					
Totw C1 07	7.88	2.41	569	561.1	8.81	37.01	11.37	12.07	14.28					
Totw C1 07/02	7.04	1.875	400.1	539.5	9.425	72.6	0.675	0	144	#				
Totw C1 09	7.14	2.36	600	426.8	8.38	6.137	1.689	13.73	12.39					
Totw C1 12	6.89	1.021	153	150.8	16.87	241.2	111	13.8	3.571					
Totw C2 04	6.55	0.579		98.03	7.12	51.43	21.2	0.043	0					
Totw C2 07	7.50	1.902	559	400.1	10.14	38.46	17.69	10.06	9.627					
Totw C2 07/02	6.94	2.27	556.5	699.8	16.12	25.6	0.069	5.71	162	#				
Totw C2 09	6.91	2.6	814	442.8	11.59	2.195	0.23	21.22	12.64					
Totw C2 12	6.74	1.117	267	135	5.92	29.8	10.55	3.853	0.465					
Totw C3 04	6.57	0.375		87.21	8.37	126.1	33.95	0.843	0					
Totw C3 07	7.14	0.978	265	209.6	5.71	41.67	12.33	0	1.187					
Totw C3 07/02	7.00	2.96	913.2	795	17.63	76.5	1.08	0	103	310.4	246	37.356		
Totw C3 09	6.52	2.19	526	417.1	13.29	10.59	0.417	14.15	14.51					

Sample	pH	Conductivity mS/cm	Chloride ppm	Sodium ppm	Potassium ppm	Silicon ppm	Iron ppm	Magnesium ppm	Calcium ppm	Total Alkalinity ppm	Sulphate ppm	Nitrate ppm	Phosphate ppm	Fluoride ppm
Totw C3-12	6.47	0.926	229	167.6	8.38	42.38	14.63	0.958	0					
Totw C4 07	6.80	0.702	163	116.9	5.13	43.44	15.22	1.327	0					
Totw C4 09	7.01	0.955	207	183.9	4.59	49.15	15.84	0	0					
Totw C4 12	5.54	0.653	135	80.26	3.58	25.51	8.517	0.743	0					
Totw C Lake 04		0.744												
Totw C Lake 07	7.90	0.983	175	156.8	9.85	4.737	0	19.35	7.407					
Totw C Lake 07/02	7.17	1.012	116.02	192.5	18.55	149	0.125	9.02	444	304.8	3.014			0.076
Totw C Lake 09	6.22	1.02	216	185.01	7.26	0	0	0	0					
Totw C Lake 12	7.00	0.751	157	92.53	10	1.165	3.585	13.93	19.91					
Totw D1 04	5.24	0.146		28.35	2.94	21.8	2.96	0.9	0					
Totw D1 07	5.73	0.209	21	26.97	4.55	33.28	11.83	0	2.771					
Totw D1 09	6.41	0.116	14	17.63	3.08	33.07	9.06	4.464	0					
Totw D1 12	5.23	0.175	33	19.66	5.19	38.2	3.507	3.622	0					
Totw D2 04	7.01	0.307		63.07	3.4	19.3	4.76	0.06	0					
Totw D2 07	5.94	0.134	20	20.69	1.97	34.52	8.251	1.477	11.55					
Totw D2 09	6.10	0.18	41	32.36	2.67	19.78	3.855	3.941	7.382					
Totw D2 12	4.95	0.144	27	19.1	2.05	4.597	0.648	0	0					
Totw D3 04	7.97	0.453	36	119.7	6.87	44.6	15.2	1.5	0					
Totw D3 07	6.27	0.195	30	34.86	3.44	40.29	15.45	0	10.24					
Totw D3 09	6.36	0.161	34	31.62	1.72	13.29	4.664	0	0					
Totw D3 12	5.40	0.19		24.5	2.86	2.395	0.452	0	0					
Totw D4 07	7.32	0.432	15	95.1	3.81	37.44	11.34	0.472	0					
Totw D4 09	6.91	0.296	19	50.09	2.37	0	3.443	8.791	1.527					
Totw D4 12	6.24	0.418	75	79.72	2.91	11.89	8.183	0	0					
Totw D Lake 04	7.56	0.878		174	13.85	6.72	0.44	31.6	26.5					
Totw D Lake 07	7.13	1.185	173	178.5	11.58	0	0	14.4	13.45					
Totw D Lake 09	7.80	1.242	284	64.61	12.43	0.91	0	30.91	51.35					
Totw D Lake 12	7.33	0.875	199	125	11.65	0.385	0	25.94	26.36					
Totw E1 04	7.43	0.203	38	47.94	3.41	30.4	9.71	4.91	0					
Totw E1 07	6.50	0.768	109	143.6	6.51	24.43	17.68	5.23	14.63					
Totw E1 07/02	6.85	2.21	656.5	473	17.88	47.9	0.073	11	339	292				
Totw E1 09	6.82	0.662	161	89.22	3.83	11.86	6.599	2.841	0					
Totw E1 12	6.53	0.32	45	38.07	7.48	53.91	32.56	2.421	0					
Totw E2 04	7.08	3.13	716	728.6	6.17	7.904	3.511	5.407	27.96					
Totw E2 07	7.20	0.963	217	192.1	12.93	188.2	145.1	9.538	20.14					

Sample	pH	Conductivity mS/cm	Chloride ppm	Sodium ppm	Potassium ppm	Silicon ppm	Iron ppm	Magnesium ppm	Calcium ppm	Total Alkalinity ppm #	Nitrate ppm	Sulphate ppm	Phosphate ppm	Fluoride ppm
Totw E2 07/02	5.87	1.56	471.9	331.8	20.06	67.4	0.882	7.48	258					
Totw E2 09	6.90	1.819	531	376.3	3.47	15.2	5.574	7.193	0					
Totw E2 12	6.73	0.212	17.5	30.29	6.15	45.37	23.93	1.107	2.295					
Totw E3 04		6.02		621	5.76	56.97	26.33	9.023	20.93					
Totw E3 07	7.60		452	463.1	7.2	52.59	25.88	5.135	4.219					
Totw E3 07/02	6.67	1.545	400.1	366	16.28	25.8	0.067	5.39	168	190.4	74.862			0.184
Totw E3 09	8.16	2.97	814	377.7	5.33	13.41	5.89	5.489	0					
Totw E3 12	7.19	1.679	383	199.2	5.47	11.7	3.465	2.869	0					
Totw E4 07	7.37	4.68	1413	933	4.69	0	0	59.28	70.11					
Totw E4 09	6.77	3.71	886	647.3	5.21	1.383	0	39.33	36.02					
Totw E4 12	6.91	2.04	609	405	2.1	5.745	1.505	7.861	2.542					
Totw E Lake 07	7.17	1.147	227	148.4	12.47	0	0	32.87	16.94					
Totw E Lake 07/02	7.63	1.397	206.7	246.7	23.87	31.1	0.072	22.3	365	332.8	4.016	2.747		0.211
Totw E Lake 09	7.35	1.17	279	158.7	32.2	0	0	38.23	31.93					
Totw E Lake 12	6.84	0.502	89	54.65	8.52	6.736	0	10.16	8.169					
Rainwater in tank 05	7.14			4.98	1.71	11.2	0.5	0.33	2.2					
Samango Crossing 07	7.63	0.312	61.5			15.4	0.48	5.51	9.58					
uMkhuze 07/02	7.29	10.33	65.1	182.2	5.797	56.5	0.065	25	423	160	172.23			0.195
uMkhuze River 05			77			7.53	0	0.14	4.44					
uMkhuze River 06/03	7.66	1.074	98.85	294.5	7.37	3.19	0.16	2.89	17.9	184				
uMkhuze River 07	7.90	1.354	279	182.6	4.78	22.8	0.42	68.9	16.9					
uMkhuze River 08	7.67	1.456	235	209.3	5.34	22.4	0.21	75.9	38.9					
uMkhuze River 09	8.35	1.456	331	214.4	6.32	19.31	0.22	72.99	31.7					
uMkhuze River 12	7.23	0.612	109	70.51	5.97	13.37	0.21	28.54	23.16					
uMkhuze River upstream1	127.77	0.412	9.876092294			13.6	0.39	18.6	21.8					
uMkhuze River upstream2	127.72	0.1238	10.30843903	10.14	1.65	12.5	0.6	6.46	1.25					
uMkhuze River upstream3	127.53	0.0459	5.658276556	20.14	2.2	14.1	0.4	1.88	0					
uMkhuze River upstream4	127.13	1.618	7	51.7	9.39	19.5	0.21	127	207					
uMkhuze River upstream5	127.33	0.1767	6	15.31	3.06	8.66	0.53	7.49	3.37					
W10 05	8.06	0.925	81	111.8	4.15	26.4	0.43	49.2	29.3					
Yengweni Lake Remnant	4.60	12.55	1671.3	1679.5	61.05	1.61	0.166	33.8	460	14.4				
Yengweni Sediment 07/02	7.00	0.89	116.02	165.1	17.01	21.8	0.069	7.61	214	133.6				
Yg A1 07	6.45	0.742	215	128.9	11.2	15	0	10.5	4.6					
Yg A1 09	6.70	0.808	194	103.5	7.49	12.92	3.114	29.31	3.536					
Yg A2 07	6.99	0.867	279	122.3	12.62	11.6	0.06	19.3	6.2					

Sample	pH	Conductivity mS/cm	Chloride ppm	Sodium ppm	Potassium ppm	Silicon ppm	Iron ppm	Magnesium ppm	Calcium ppm	Total Alkalinity ppm	Sulphate ppm	Nitrate ppm	Phosphate ppm	Fluoride ppm
Yg A2 09	6.59	0.887	234	112.8	9.61	9.698	1.076	11.42	0					
Yg A3 07	5.46	0.894	244	125.9	10.18	15.4	0	11.1	4.51					
Yg A3 09	6.46	1.149	267	119.1	16.55	13.99	2.767	25.99	8.744					
Yg A4 07	5.04	1.061	224	154.9	6.84	17.2	0	34.8	16.6					
Yg A4 09	5.18	0.967	130	244.9	2.86	14.48	0	37.98	34.36					
Yg ASP 07	6.69	0.734	145	83.03	6.42	8.83	0	32.4	4.91					
Yg B1 07	7.39	11.36		2453	18.98	25.12	0	172.3	74.39					
Yg B1 09	6.65	12.34	4163.5	2019	21.18	1.387	0	234.3	136.5					
Yg B2 07	5.29	1.578	562	318.7	9.2	17.8	0	13.8	5.08					
Yg B2 09	5.77	1.479	600	287.6	12.26	8.415	0	17.4	13.22					
Yg B3 07	7.09	1.64	413	244	5.19	11	0	45.1	16.8					
Yg B3 09	6.64	1.788	404	296.2	14.28	0	0.128	35.66	23.93					
Yg B4 07	7.54	0.89	235	172.8	5.46	14.7	2.23	24	2.15					
Yg B4 09	6.54	1.988	415	310.3	10.21	6.675	0	25.56	3.959					
Yg B5 07	5.77	1.201	175	211.8	11.68	16.8	0	19.7	5.4					
Yg B6 07	6.44	2.37	538	336.5	8.4	14.6	0	39.8	16.7					
Yg B Lake 07	7.56	1.919	665	333.1	9.93	9.76	0	51.9	19.2					
Yg B Lake Oil 07	6.96		613	384.9	11.19	20.1	0	60.6	22.7					
Yg BSP 07	7.11	0.607	144	88.33	3.24	13.7	0.37	15.2	2.4					
Yg C1 07	7.23	0.262	21	31.22	4.77	17.31	7.82	5.024	63.7					
Yg C1 09	7.01	0.711	147	82.91	6.53	0	0	0	0					
Yg C1 12	5.28	0.28	59	44.45	9.41	63.94	22.99	2.52	0					
Yg C2 07	6.78	0.304	34	40.61	3.8	25.7	5.2	13.1	3.56					
Yg C2 07/02	4.23	1.266	312.3	274.3	20.12	103	0.082	9.29	132	#				
Yg C2 09	6.75	0.417	63	59.63	2.83	8.193	3.083	4.262	13.36					
Yg C2 12	6.78	0.472	75	57.09	6.07	0	0	11.66	3.583					
Yg C3 07	6.94	0.235	42	31.55	2.38	17	1.91	4.56	0.69					
Yg C3 07/02	6.08	1.672	368.4	351.05	9.592	62.7	1.07	0	57.6	#				
Yg C3 09	6.46	0.406	64	67.7	15.41	330.6	93.46	16.96	2.642					
Yg C3 12	5.63	0.324	63.5	55.59	5.94	9.24	1.675	2.736	0					
Yg C4 07	7.30	0.355	35	27.21	8.65	16.9	0.52	25.8	6.08					
Yg C4 09	6.79	0.28	40	47.25	8.5	41.16	11.89	6.837	0					
Yg C4 12	5.92	0.385	65	40.81	5.34	2.004	0	9.315	10.63					
Yg C5 07	7.36	0.559	63	70.03	10.5	13.5	1.34	8.37	3.55					
Yg C5 09	6.64	0.32	39	32.03	4.7	17.43	3.906	11.41	2.475					

Sample	pH	Conductivity mS/cm	Chloride ppm	Sodium ppm	Potassium ppm	Silicon ppm	Iron ppm	Magnesium ppm	Calcium ppm	Total Alkalinity ppm	Sulphate ppm	Nitrate ppm	Phosphate ppm	Fluoride ppm
Yg C5 12	5.83	0.422	34	25.89	8.82	5.554	0.866	5.582	0					
Yg C Lake 07	7.48	0.483	68	55.98	9.21	9.64	0	20.6	15.1					
Yg C Lake 07/02	7.05	0.912	98.4	187.5	17.05	20	0.065	3.72	227	130.4	96.221			0.442
Yg C Lake 09	7.50	0.526	66	57.39	9.82	3.274	0	23.14	14.75					
Yg C Lake 12	7.41	0.444	62	45.36	8.7	0	0	14.42	10.88					
Yg CSP 07	6.30	0.236	37	33.58	4.83	44.63	14.9	5.06	0					
Yg D Lake 07/02	7.14	0.891	161.39	153.4	17.24	24.7	0.067	4.9	251	108	95.566	5.063	12.332	0.064
Yg D1 07	8.38	16.4	107	3779	3.7	15.1	0	158	19.2					
Yg D1 07/02	7.96	12.5	6094.6	3870	5.646	43.4	0.072	93.8	203	1968	561	165	0	1.2
Yg D1 09	7.83	15.34	4613	2783	3.89	0.123	0	132.3	18.11					
Yg D1 12	4.67	0.687	130	120.4	5.36	3.294	0	13.27	0.479					
Yg D2 07	5.77	0.496	117	131.7	1.45	13.8	0	1.92	0					
Yg D2 07/02	7.55	1.18	116.02	304	1.796	125	0.5	0	56.4	328.8	117.355			0.229
Yg D2 09	7.63	9.84	3388	2130	1.21	3.942	0	102.4	34.94					
Yg D2 12	5.58	0.364	78	65.98	3.67	26.59	10.63	2.274	0					
Yg D3 07/02	6.55	0.622	70.71	81.65	9.17	45.2	0.072	7.49	237	92.8	136.54	18.959	10.309	2.02
Yg D3 09	7.76	5.99	1226	921.1	1.2	0	0	23.02	5.489					
Yg D3 12	2.64	2.52	43	36.09	6.16	9.64	5.134	22.92	26.14					
Yg D4 09	7.68	5.14	886	1207	2.04	8.882	0	25.63	9.601					
Yg D4 12	5.53	0.177	19	25.64	4.33	39.82	14.83	0	0					
Yg D5 09	7.40	3.22	781	562.8	1.88									
Yg D6 07	7.41	1.177	173	287.8	8.3	64.82	23.02	13.29	3.724					
Yg D6 09	7.07	1.144	108	118	7.89	0	0	39.22	40.96					
Yg D7 07		1.334	60	57.7										
Yg D7 09	6.99	0.713	60		4.54	0	0	18.17	13.51					
Yg D8 07	7.62	1.015		136.8	8.89	11.4	0	39.1	21.6					
Yg D Lake 07	7.56	0.436		63.34	12.59	63.9	0	22.6	34.2					
Yg D Lake 09	8.83	0.505	79	55.14	8.69	0	0	18.1	11.65					
Yg D Lake 12	7.33	0.418	45	45.62	7.84	0	0	14.16	10.41					
Yg DSP 07	6.53	0.472	760	99.01	12.05	267.1	92.27	17.37	0					
Yg E Lake 07/02	7.23	0.884	136.8	149.2	16.52	22.3	0.065	5.26	251	134.4	81.518	7.278		0.698
Yg E1 07	8.17	3.63	559			83.5	0	76	10.9					
Yg E1 12	7.80	4.01	516	815.7	1.47	9.24	0	25.51	7.109					
Yg E2 09	7.51	4.72	780	874	3.78	9.335	0	69.02	29.01					
Yg E2 12	6.88	0.813	172	135.5	8.09	57.82	20.15	1.964	0					

Sample	pH	Conductivity mS/cm	Chloride ppm	Sodium ppm	Potassium ppm	Silicon ppm	Iron ppm	Magnesium ppm	Calcium ppm	Total Alkalinity ppm	Sulphate ppm	Nitrate ppm	Phosphate ppm	Fluoride ppm
Yg E2 07	8.54	4.59		1352	4.7	41.9	0	13.7	2.71					
Yg E2 07/02	7.36	1.739	136.8	349.8	2.804	213	0.064	26.3	486	728.8	34.171	48.193		0.074
Yg E3 07	8.14	2.35	79	658.2	11.24	29.4	0	11.1	5.98					
Yg E3 07/02	8.15	2.58	175.3	739.1	3.653	163	0.23	0	52.9	1267.2	67.787			0.596
Yg E3 09	8.08	2.3	156	608.3	1.59	19.11	0	7.417	8.142					
Yg E3 12	6.12	0.38	86	46.54	2.24	5.714	0	0	0					
Yg E3A 07	8.38	4.78	726			63.3	0.38	19.8	4.55					
Yg E4 07	6.94	1.003		160.3	9.36	15.4	0	41	22.6					
Yg E4 09	7.93	2.64	265	660.9	3.6	8.032	0	10.57	1.856					
Yg E4 12	5.64	0.283	62	29.46	1.88	0	0	1.896	0					
Yg E5 09	7.74	7.26	1226	1936	2.33	0.674	0	60.23	2.667					
Yg E Lake 07	7.55	0.444	65			11.4	0	21	15.7					
Yg E Lake 09	8.37	0.672	73	60.3	10.68	0	0	23.23	18.01					
Yg E Lake 12	7.27	0.39	57	47.13	7.69	5.676	0	15.46	11.02					
Yg E Lake Oil 09	7.59		57	51.59	7.47	0	0	19.38	18.03					
Yg ESP 07	7.96	6.06	658	1420	1.55	44.9	0.23	131.5	12.3					
Yg F1 07	8.01	4.17	1001.498334	1043	3.15	47.5	0.25	47.5	15.7					
Yg F2 07	7.62	1.94	244.8926696	228.4	1.89	20.6	0.23	100	61.3					
Yg F2 09	8.74	4.21	1214	909.5	4.34	2.558	0	55.33	21					
Yg F3 09	7.53	2.81	487	628.4	4.02	0	0	20.52	7.317					
Yg F4 09	7.64	3.15	531	686.8	2.29	8.259	0	53.28	21.31					
Yg F Lake 07	7.81	0.312	72	56.45	6.81	24.6	0.22	23	19.8					
Yg F Lake 09	8.74	0.614	88	47.46	6.83	0	0	16.39	18					
Yg G1 07/02	8.06	3.72	774.3	1181	1.341	126.5	0.067	36.6	288.5	1065.6	156.98			0.11
Yg G1 09	7.49	7.34	2115	2181	2.32	0	0	185.2	3.322					
Yg G1 12	7.37	8.47	3074	1651	2.17	4.668	0	136.1	23.22					
Yg G2 07	8.40	4.99	665	1213	2.17	28.3	0.31	53	9.7					
Yg G2 07/02	7.84	3.33	656.5	820.4	4.443	140	0.069	48.9	246					
Yg G2 09	7.50	11.59	1981	1577	6.4	4.337	0	97.42	10.63					0.021
Yg G2 12	7.49	4.64	1680	1048	2.02	11.38	0	44.99	6.202					
Yg G3 09	7.55	13.79	792	1348	2.76	3.721	0	66.28	12.7					
Yg G3 07	8.41	8.89	1073	2332	3.46	27.4	0.27	93.5	8.03					
Yg G3 07/02	7.99	13.49	7188.4	7780	3.338	108	0.068	218	548	1560				
Yg G4 09	7.74	5.08	3213	2797	3.4	0	0	323.7	21.39					
Yg G5 09	7.75	6.83	3694	2548	3.96	1.685	0	216.5	23.94					

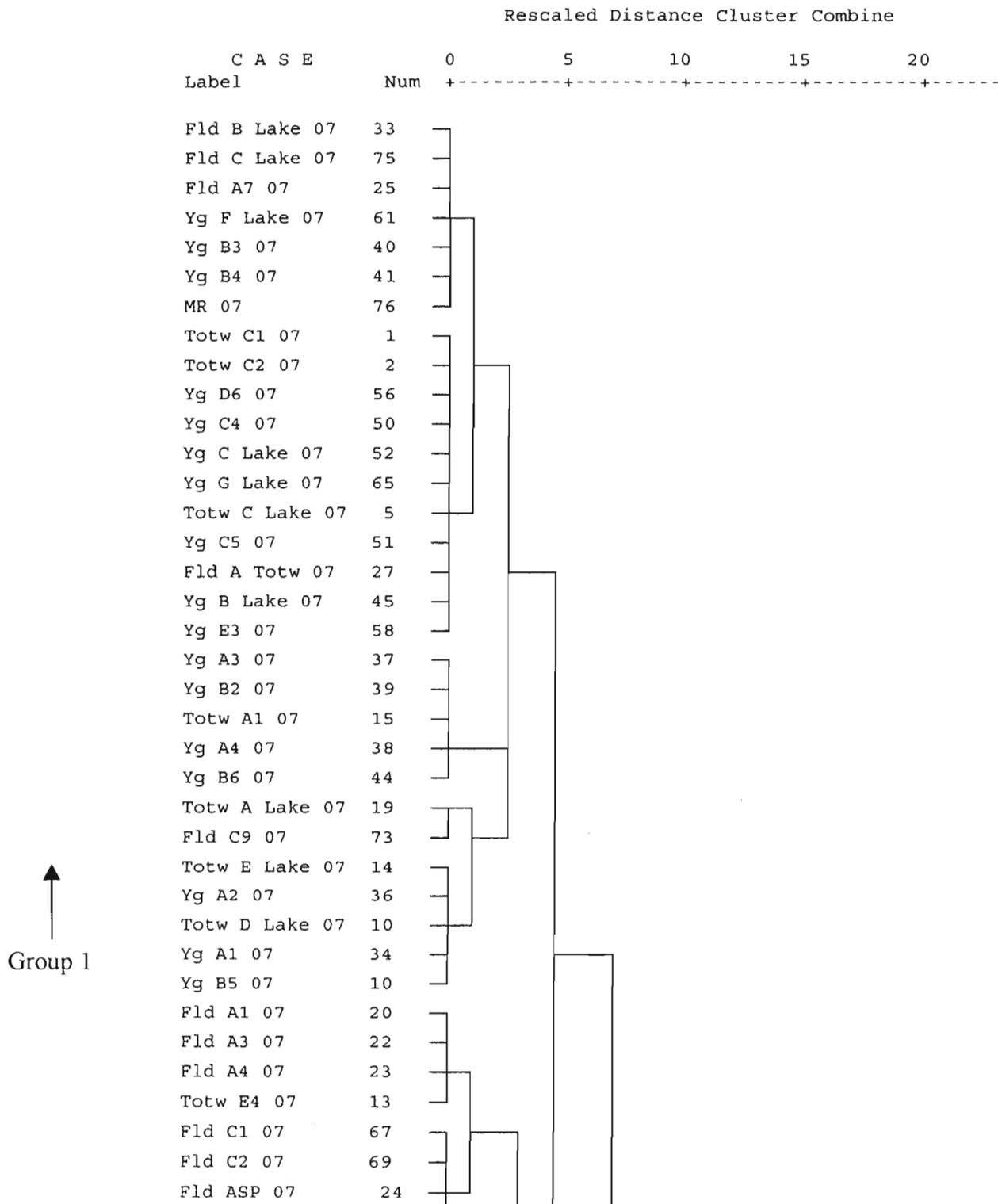
Sample	pH	Conductivity mS/cm	Chloride ppm	Sodium ppm	Potassium ppm	Silicon ppm	Iron ppm	Magnesium ppm	Calcium ppm	Total Alkalinity ppm	Sulphate ppm	Nitrate ppm	Phosphate ppm	Fluoride ppm
Yg G6 09	7.98	10.49	1621	1934	3.79	12.15	0	67.98	33.42					
Yg G Lake 07	7.54	0.493	72	54.55	8.17	25.6	0.26	21.3	12.1					
Yg G Lake 09	8.58	0.609	65.5	209.2	9.18	0	0	15.66	15.24					
Yg G Lake 12	7.10	0.441	59	44.14	8.78	7.263	1.005	13.42	16.92					
Yg GSP 07	8.45	6.94	1084	1831	2.33	28.2	0.31	71.6	8.98					
<b>Number of analyses</b>	278	276	259	272	272	278	278	278	278	24	19	8	3	17
<b>Minimum</b>	2.64	0.0459	5.66	4.98	1.2	0	0	0	0	14.4	3.014	2.747	0	0.021
<b>Maximum</b>	9.09	16.4	7188.4	7780	61.05	373	145.1	362	1100	1968	641.662	165	12.332	2.02

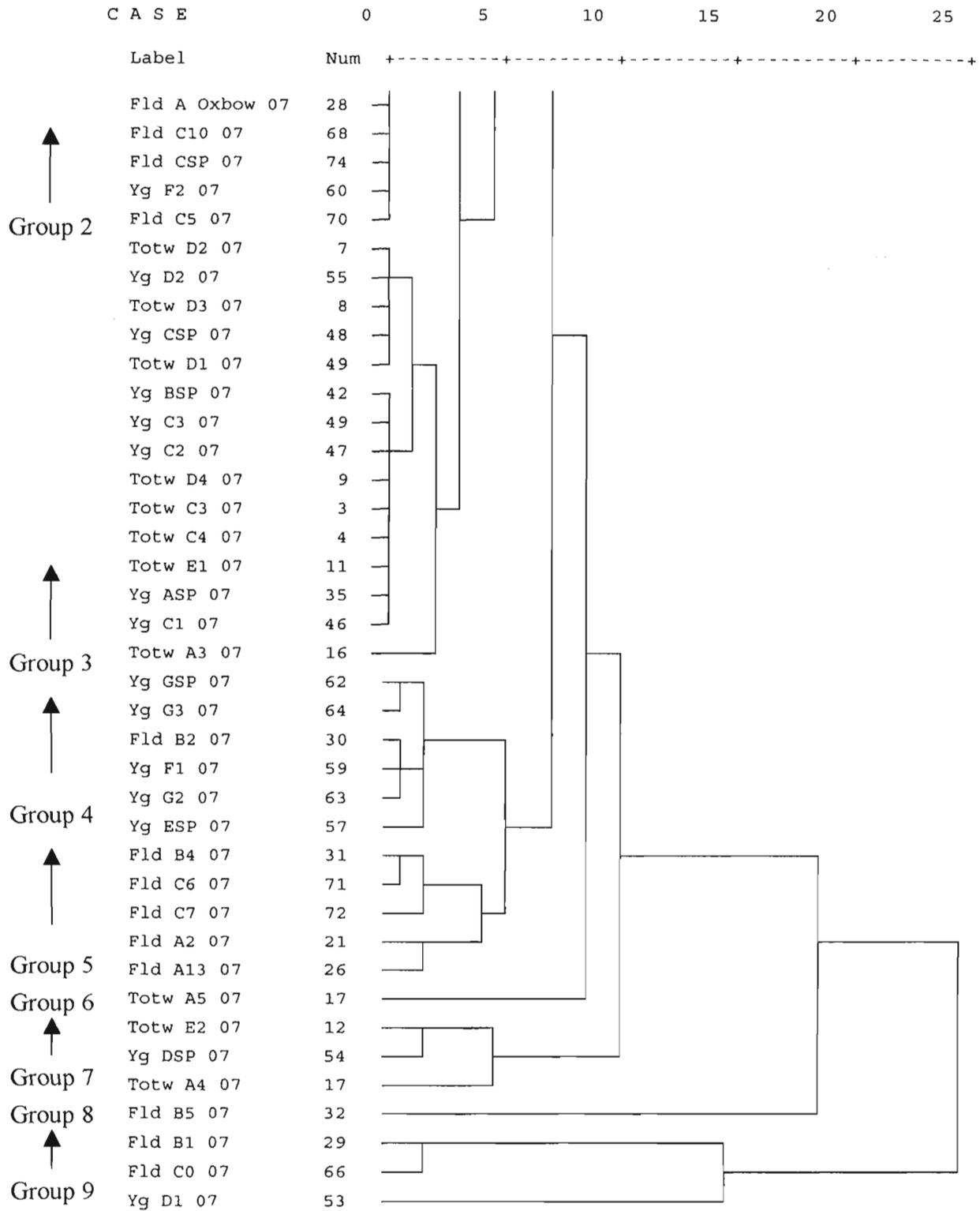
Note all replicates averaged  
 # = not suitable for analysis  
 04/05 = April/ May 2000  
 07/08 = July/August 2000  
 09 = September 2000  
 12 = December 2000  
 07/02 = July 2002  
 06/03 = June 2003

### Appendix C: Dendrograms derived from hierarchical cluster analysis of water chemistry data

July 2000

Excluding iron, data standardized 0 - 1.

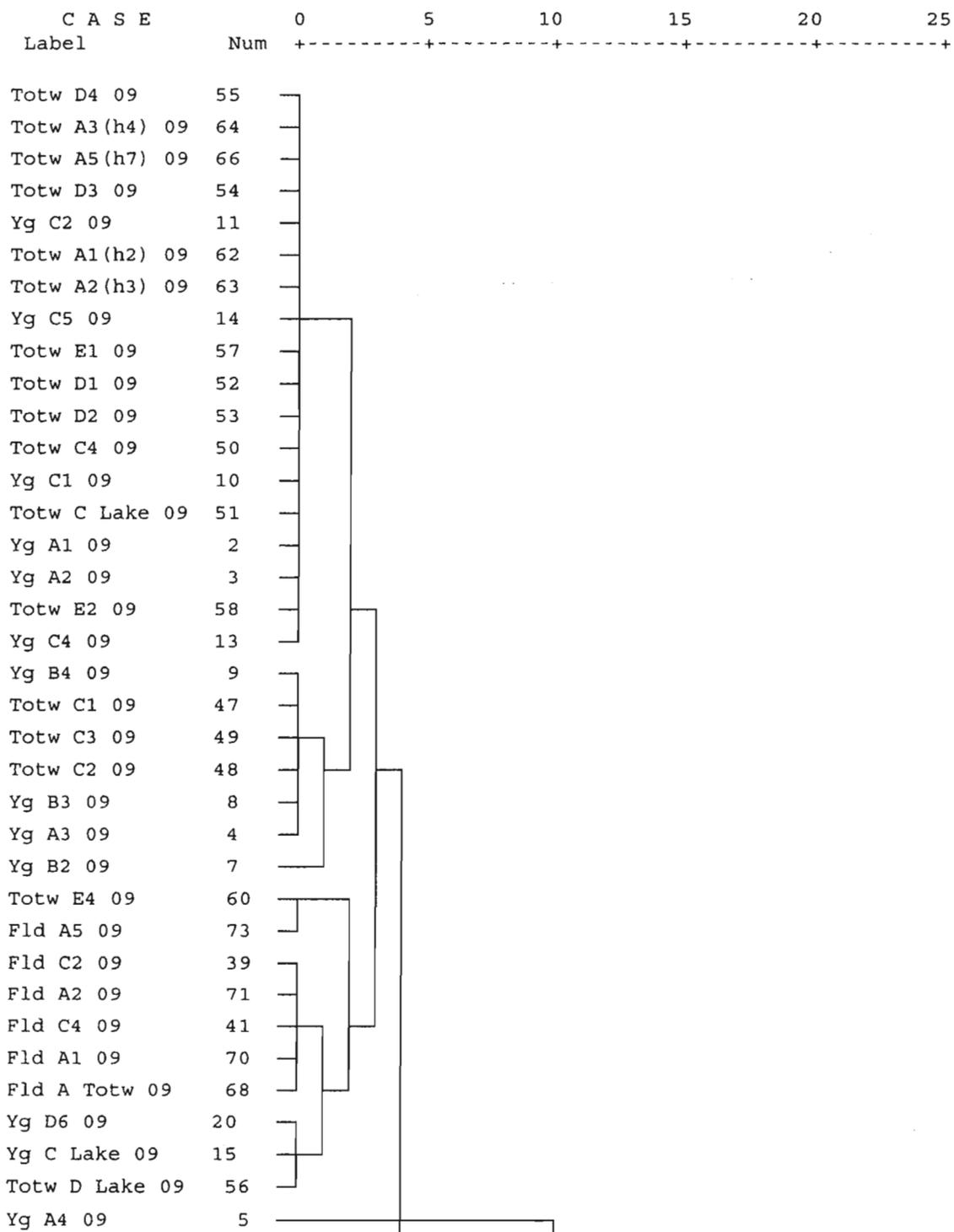




September 2000

Excluding iron, data standardized 0 - 1

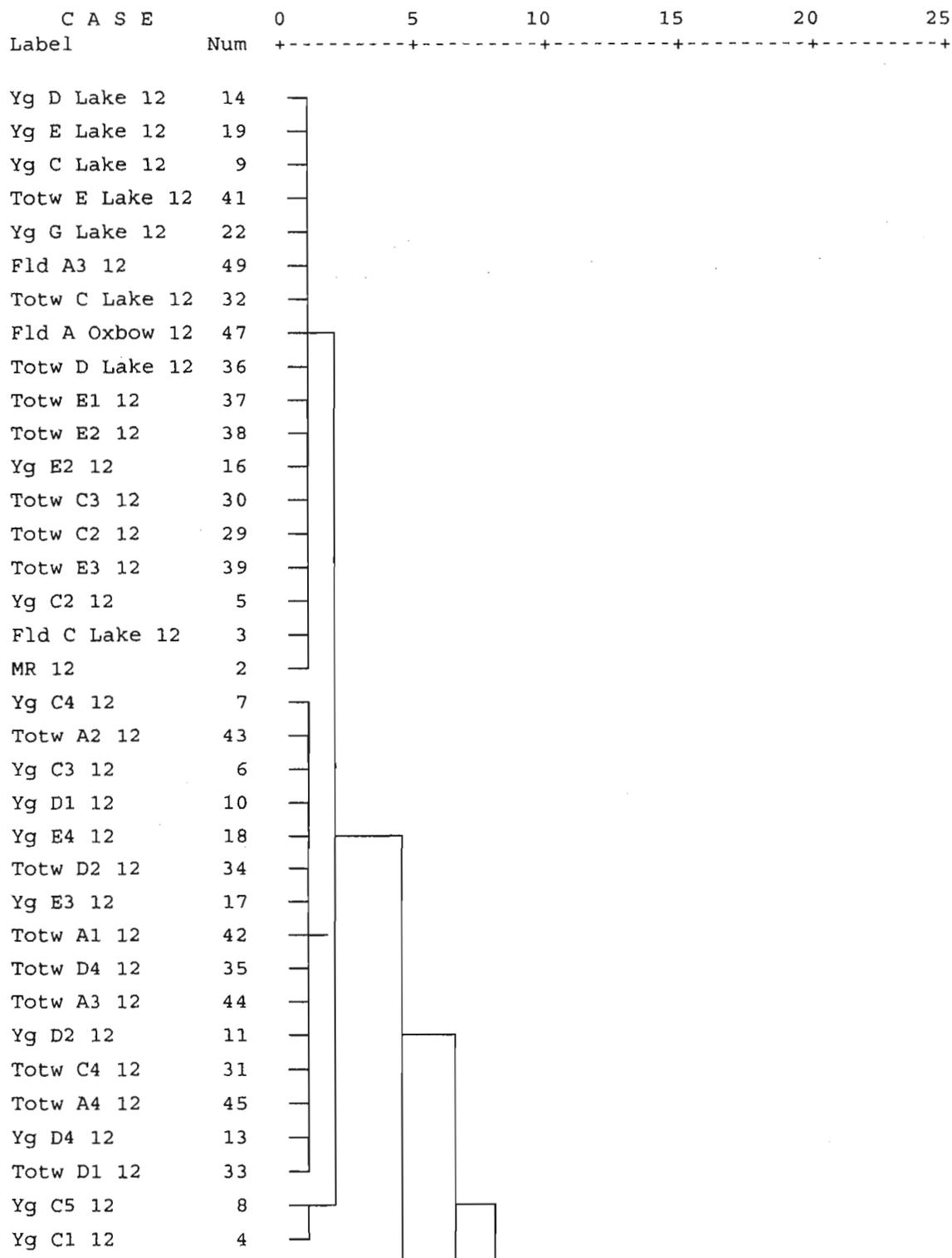
Rescaled Distance Cluster Combine

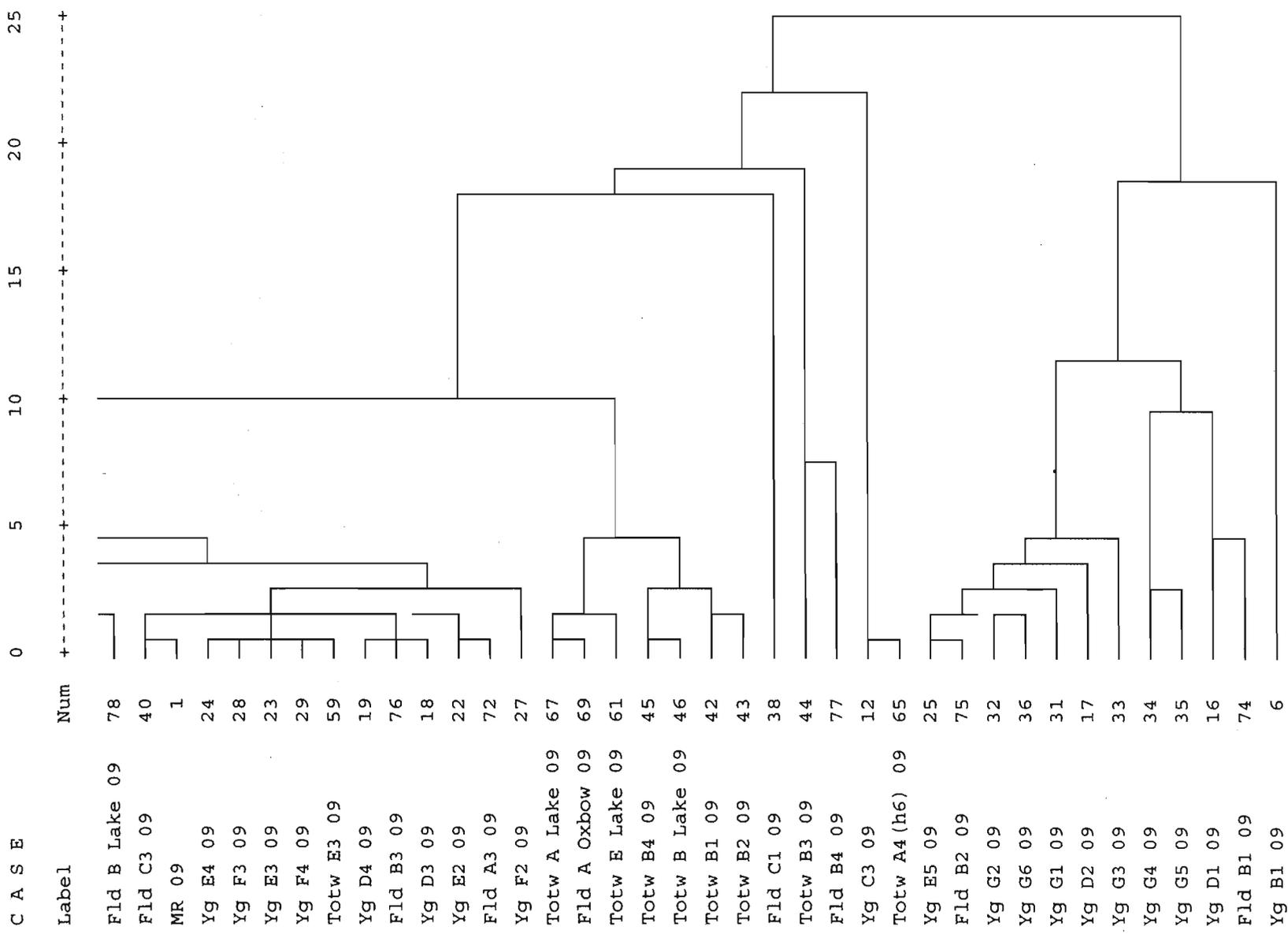


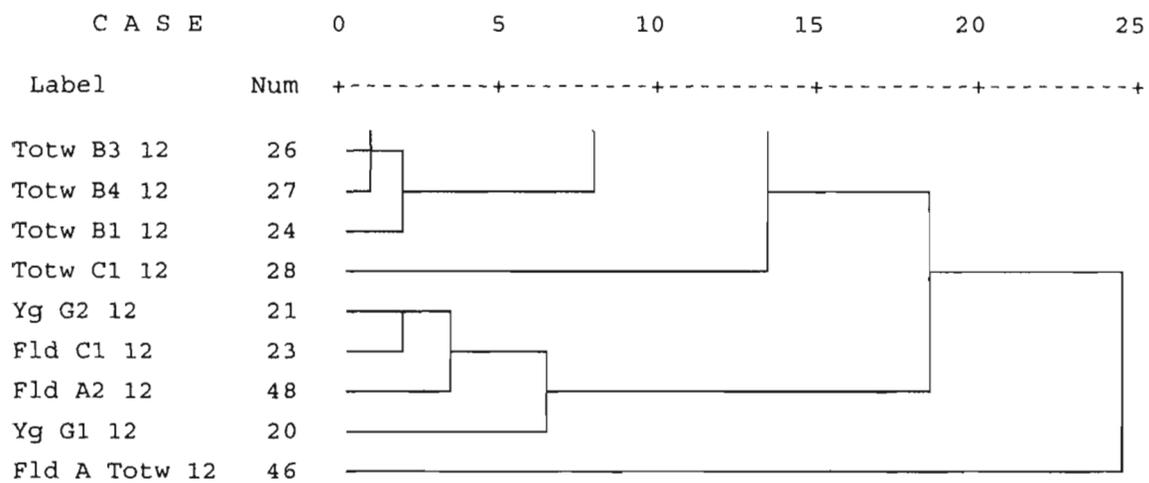
December 2000

Excluding iron, data standardized 0 - 1

Rescaled Distance Cluster Combine







## Appendix D: Factor analysis

### Factor Loadings

	<b>Factor</b>		
	<b>1</b>	<b>2</b>	<b>3</b>
<b>pH</b>	0.498021	-0.06234	-0.04692
<b>Conductivity</b>	0.912061	0.088744	-0.06719
<b>Chloride</b>	0.888989	0.164232	-0.03608
<b>Sodium</b>	0.911703	0.169794	-0.07147
<b>Potassium</b>	-0.22172	0.347071	0.586472
<b>Silicon</b>	-0.17673	0.883117	-0.14886
<b>Iron</b>	-0.28263	0.746701	-0.47421
<b>Magnesium</b>	0.778889	0.016138	0.01104
<b>Calcium</b>	0.195293	0.413749	0.732152

### Factor Scores for Each Sample

<b>Sample</b>	<b>Factor 1</b>	<b>Factor 2</b>	<b>Factor 3</b>
<b>FldA Oxbow 07</b>	-0.09585	-0.60442	-0.33368
<b>FldA Oxbow 09</b>	-0.4255	0.09341	1.69283
<b>FldA Oxbow 12</b>	-0.56389	-0.42623	0.40729
<b>FldA Totweni 07</b>	-0.25051	-0.30911	0.44422
<b>FldA Totweni 09</b>	-0.10472	-0.50872	0.25921
<b>FldA Totweni 12</b>	0.89369	0.44416	1.61766
<b>FldA1 07</b>	0.65932	-0.33092	-0.47674
<b>FldA1 09</b>	0.03058	-0.55687	0.10651
<b>FldA13 07</b>	1.36907	-0.35445	-0.64937
<b>FldA2 07</b>	0.77951	-0.40746	-0.40437
<b>FldA2 09</b>	0.00086	-0.60952	-0.19728
<b>FldA2 12</b>	1.2941	-0.30304	-0.5823
<b>FldA3 07</b>	0.53025	-0.33797	-0.11104
<b>FldA3 09</b>	0.84203	-0.48402	-0.48384
<b>FldA3 12</b>	-0.5799	-0.5768	0.18021
<b>FldA4 07</b>	0.17156	-0.46498	-0.06989
<b>FldA5 09</b>	0.18904	-0.49725	-0.20521
<b>FldA7 07</b>	-0.08346	-0.43498	0.10257
<b>FldASP 07</b>	0.01305	-0.65341	-0.47705
<b>FldB Lake 07</b>	-0.15611	-0.5163	0.01702
<b>FldB Lake 09</b>	0.1328	-0.55041	0.25062
<b>FldB1 07</b>	2.82322	0.4266	-0.69465
<b>FldB1 09</b>	3.80222	0.36392	-0.88841
<b>FldB2 07</b>	0.77606	-0.16177	-0.86067
<b>FldB2 09</b>	1.80192	-0.26342	-0.81861
<b>FldB3 09</b>	0.52041	-0.60269	-0.74011
<b>FldB4 07</b>	0.43474	-0.18708	-0.09033
<b>FldB4 09</b>	0.63123	-0.18522	0.65492
<b>FldB5 07</b>	1.23043	0.22182	0.91051
<b>FldC Lake 07</b>	-0.11884	-0.45016	0.03534
<b>FldC Lake 07/02</b>	-0.14755	0.77424	2.06198
<b>FldC Lake 12</b>	-0.46742	-0.7119	-0.2511
<b>FldC0 07</b>	3.48731	0.73218	-0.59106
<b>FldC1 07</b>	0.31447	-0.46535	-0.59716
<b>FldC1 09</b>	1.43834	-0.34682	-0.29604

<b>Sample</b>	<b>Factor 1</b>	<b>Factor 2</b>	<b>Factor 3</b>
FldC1 12	0.93552	-0.36864	-0.78346
FldC10 07	-0.11847	-0.42593	-0.28896
FldC2 07	0.46932	-0.56879	-0.6817
FldC2 07/02	-0.11217	0.86609	0.17381
FldC2 09	0.0465	-0.60768	-0.13167
FldC3 07/02	0.56521	2.94217	5.4577
FldC3 09	0.34135	-0.46232	-0.2636
FldC4 09	0.20673	-0.57505	-0.43004
FldC5 07	0.13635	-0.41635	-0.2454
FldC6 07	0.77744	-0.08171	0.21587
FldC7 07	0.57561	-0.21518	0.25733
FldC9 07	-0.15384	-0.00967	0.9182
FldCSP 07	-0.04998	-0.50399	-0.34211
TotwA1 07	-0.63419	-0.49245	0.21789
TotwA1 07/02	-1.03083	3.33484	-0.69595
TotwA1 12	-0.75562	-0.7672	-0.40601
TotwA1(h2) 09	-0.57467	-0.67304	-0.36238
TotwA2 07/02	-0.80615	0.5429	0.74703
TotwA2 12	-0.79847	-0.70863	-0.18109
TotwA2(h3) 09	-0.61221	-0.68495	-0.26502
TotwA3 07	-0.95791	0.63401	-0.92921
TotwA3 07/02	-0.63399	1.10839	1.65588
TotwA3 12	-0.84197	-0.5627	-0.55105
TotwA3(h4) 09	-0.60382	-0.83087	-0.45704
TotwA4 07	-1.14193	2.31421	-1.63541
TotwA4 12	-0.65814	-0.43424	-0.39175
TotwA4(h6) 09	-1.38372	4.6608	-1.55372
TotwA5 07	-0.90589	-0.38641	0.40477
TotwA5(h7) 09	-0.48734	-0.81826	-0.53349
TotwALake 07	-0.50491	-0.22373	0.89277
TotwALake 09	-0.48487	0.32864	1.51347
TotwB Lake+A116 09	0.37712	0.31882	1.87099
TotwB1 09	0.18258	0.12998	1.25038
TotwB1 12	0.07066	-0.06783	0.72624
TotwB2 04	0.16077	0.03446	0.89315
TotwB2 09	-0.25157	-0.05425	1.20841
TotwB2 12	0.01231	0.00231	1.05092
TotwB3 09	-0.02873	0.44994	2.33632
TotwB3 12	-0.00799	0.0748	1.3398
TotwB4 09	0.08334	0.39004	1.65949
TotwB4 12	-0.11212	0.3137	1.632
TotwC Lake 07	-0.28498	-0.52234	0.18014
TotwC Lake 07/02	-0.45946	2.15293	3.14734
TotwC Lake 09	-0.55712	-0.61028	-0.03056
TotwC Lake 12	-0.49737	-0.40296	0.22786
TotwC1 07	-0.03356	0.19219	-0.32924
TotwC1 07/02	-0.22468	0.5379	0.70846
TotwC1 09	-0.09683	-0.37842	-0.00845
TotwC1 12	-1.33477	5.13437	-2.61982
TotwC2 07	-0.24668	0.40853	-0.35952
TotwC2 07/02	-0.11712	0.41058	1.55914
TotwC2 09	-0.04923	-0.29622	0.34622
TotwC2 12	-0.52329	-0.09969	-0.52794

Sample	Factor 1	Factor 2	Factor 3
TotwC3 07	-0.48194	0.0473	-0.64068
TotwC3 07/02	-0.04384	0.91422	1.18677
TotwC3 09	-0.28165	-0.16703	0.52973
TotwC3 12	-0.65261	0.23424	-0.41918
TotwC4 07	-0.6191	0.1076	-0.75224
TotwC4 09	-0.53965	0.16746	-0.85484
TotwC4 12	-0.768	-0.26842	-0.62027
TotwD Lake 07	-0.41015	-0.45348	0.41883
TotwD Lake 09	-0.24228	-0.35698	0.68786
TotwD Lake 12	-0.36916	-0.43479	0.49928
TotwD1 07	-0.86048	-0.09203	-0.61014
TotwD1 09	-0.72285	-0.26274	-0.71948
TotwD1 12	-0.89688	-0.23848	-0.33347
TotwD2 07	-0.77989	-0.26951	-0.72321
TotwD2 09	-0.70755	-0.51724	-0.53761
TotwD2 12	-0.87439	-0.75024	-0.46489
TotwD3 04	-0.51498	0.12121	-0.63118
TotwD3 07	-0.78247	0.03012	-0.81107
TotwD3 09	-0.67615	-0.62077	-0.68717
TotwD4 07	-0.5709	-0.1513	-0.77319
TotwD4 09	-0.53564	-0.7716	-0.5788
TotwD4 12	-0.67738	-0.47169	-0.66739
TotwE Lake 07	-0.34488	-0.40972	0.52588
TotwE Lake 09	-0.50366	0.37308	2.48647
TotwE Lake 12	-0.56164	-0.5409	0.11782
TotwE Lake07/02	-0.25914	1.06148	3.46353
TotwE1 04	-0.54664	-0.29035	-0.74854
TotwE1 07	-0.65547	0.0891	-0.54473
TotwE1 07/02	-0.11677	1.05543	2.68925
TotwE1 09	-0.53463	-0.48963	-0.57112
TotwE1 12	-0.87099	0.76362	-0.98039
TotwE2 04	-0.1598	-0.34664	-0.17074
TotwE2 07	-1.34801	5.46073	-3.69325
TotwE2 07/02	-0.51531	1.16595	2.44601
TotwE2 09	-0.21354	-0.41023	-0.64567
TotwE2 12	-0.79524	0.38177	-0.85215
TotwE3 07/02	-0.3668	0.37325	1.6641
TotwE3 09	0.12442	-0.34942	-0.55951
TotwE3 12	-0.3013	-0.47762	-0.38292
TotwE4 07	0.75978	-0.3198	-0.09025
TotwE4 09	0.25987	-0.44376	-0.15435
TotwE4 12	-0.11419	-0.64607	-0.64173
uMkhuze River 05	-0.14236	-0.49051	-0.29985
uMkhuze River 07	0.00507	-0.48241	-0.31046
uMkhuze River 07/02	0.61108	0.88451	1.85541
uMkhuze River 08	0.00582	-0.41316	-0.11789
uMkhuze River 09	0.11445	-0.43755	-0.09171
uMkhuze River 12	-0.38646	-0.5432	-0.08152
YGA1 07	-0.5837	-0.32604	0.33702
YGA1 09	-0.457	*0.41357	-0.10752
YGA2 07	-0.45706	-0.31171	0.4618
YGA2 09	-0.53088	-0.42007	0.13527
YGA3 07	-0.70179	-0.31674	0.27835

<b>Sample</b>	<b>Factor 1</b>	<b>Factor 2</b>	<b>Factor 3</b>
YgA3 09	-0.5556	-0.0333	0.79455
YgA4 07	-0.61976	-0.37609	0.04029
YgA4 09	-0.53366	-0.52086	-0.2414
YgASP 07	-0.44029	-0.58521	-0.10466
YgB1 09	2.8372	1.05973	1.59512
YgB2 07	-0.50516	-0.25524	0.15173
YgB2 09	-0.45012	-0.23145	0.49492
YgB3 07	-0.11662	-0.53745	-0.21481
YgB3 09	-0.28656	-0.25416	0.72942
YgB4 07	-0.28177	-0.52139	-0.33664
YgB4 09	-0.28124	-0.38255	0.21288
YgB5 07	-0.60753	-0.24676	0.40092
YgB6 07	-0.15204	-0.31987	0.08571
YgBLake 07	0.04518	-0.34031	0.21459
YgBSP 07	-0.41723	-0.67537	-0.46352
YgC Lake 07	-0.44055	-0.49806	0.19003
YgC Lake 07/02	-0.47987	0.39445	2.10224
YgC Lake 09	-0.42629	-0.53632	0.26033
YgC Lake 12	-0.46876	-0.61957	0.14459
YgC1 07	-0.54476	-0.27552	-0.16931
YgC1 09	-0.50436	-0.69395	-0.1194
YgC1 12	-1.04258	0.71722	-0.51251
YgC2 07	-0.58704	-0.41133	-0.53222
YgC2 07/02	-0.93646	1.25478	1.76675
YgC2 09	-0.55678	-0.64704	-0.47657
YgC2 12	-0.53814	-0.70743	-0.12228
YgC3 07	-0.55953	-0.65565	-0.58319
YgC3 07/02	-0.49355	0.28427	0.31358
YgC3 09	-1.46771	5.43224	-2.47664
YgC3 12	-0.77928	-0.54445	-0.16835
YgC4 07	-0.48535	-0.45566	0.06911
YgC4 09	-0.71178	0.09412	-0.31803
YgC4 12	-0.68308	-0.67172	-0.11628
YgC5 07	-0.52445	-0.39398	0.20485
YgC5 09	-0.61135	-0.48973	-0.39217
YgC5 12	-0.77389	-0.50531	0.13015
YgCSP 07	-0.77738	0.08818	-0.73317
YgD Lake 07/02	-0.45245	0.49659	2.24115
YgD Lake 09	-0.22509	-0.66998	0.08313
YgD Lake 12	-0.4787	-0.65229	0.06427
YgD1 07	2.77722	0.06434	-0.93352
YgD1 07/02	3.82235	1.36638	0.09312
YgD1 09	3.41263	0.26432	-0.91946
YgD1 12	-0.79859	-0.60882	-0.13254
YgD2 07	-0.65103	-0.7063	-0.58161
YgD2 07/02	-0.35619	0.46841	-0.61702
YgD2 09	2.31414	-0.05909	-0.89046
YgD2 12	-0.81335	-0.20951	-0.66298
YgD3 07/02	-0.53379	0.35772	1.38157
YgD3 09	0.75582	-0.60982	-0.82828
YgD3 12	-0.99873	-0.2258	0.00348
YgD4 09	0.66438	-0.49485	-0.73637
YgD4 12	-0.91489	0.04702	-0.73191

<b>Sample</b>	<b>Factor 1</b>	<b>Factor 2</b>	<b>Factor 3</b>
YgD6 07	-0.48147	0.66596	-0.73273
YgD6 09	-0.3135	-0.54349	0.23487
YgDSP 07	-1.15097	4.73041	-2.65865
YgE Lake 07/02	-0.43502	0.43958	2.17545
YgE Lake 09	-0.28326	-0.5589	0.32698
YgE Lake 12	-0.48511	-0.5988	0.0426
YgE1 12	0.37	-0.62753	-0.74743
YgE2 09	0.61376	-0.42783	-0.41076
YgE2 12	-0.66028	0.4974	-0.64102
YgE2 07/02	-0.10549	2.28418	1.69366
YgE3 07	-0.0701	-0.1728	0.1728
YgE3 07/02	-0.05088	0.94688	-0.63173
YgE3 09	0.03219	-0.63091	-0.70867
YgE3 12	-0.65105	-0.78334	-0.49274
YgE4 09	0.0785	-0.64438	-0.53222
YgE4 12	-0.72813	-0.83865	-0.4879
YgE5 09	1.2977	-0.41533	-0.8324
YgESP 07	1.1428	-0.13286	-0.8827
YgF Lake 07	-0.37919	-0.44492	-0.0659
YgF Lake 09	-0.21085	-0.722	-0.05706
YgF1 07	0.64325	-0.09694	-0.6794
YgF2 07	0.18708	-0.49595	-0.32299
YgF2 09	0.83277	-0.49944	-0.45005
YgF3 09	0.12154	-0.65477	-0.43094
YgF4 09	0.33407	-0.59351	-0.54964
YgG Lake 07	-0.43278	-0.3857	0.02574
YgG Lake 09	-0.22225	-0.61504	0.14762
YgG Lake 12	-0.53107	-0.4944	0.1561
YgG1 07/02	0.63874	1.15116	0.49896
YgG1 09	2.02968	-0.26999	-0.84724
YgG1 12	2.02706	-0.13855	-0.77653
YgG2 07	0.7817	-0.34365	-0.79608
YgG2 07/02	0.40164	1.25605	0.57437
YgG2 09	1.8007	-0.08638	-0.47149
YgG2 12	0.82077	-0.41524	-0.75681
YgG3 09	1.53694	-0.34472	-0.79846
YgG3 07	1.70394	-0.05865	-0.84617
YgG3 07/02	6.01504	3.25473	1.32374
YgG4 09	2.85702	-0.03064	-0.67201
YgG5 09	2.66523	0.04394	-0.65592
YgG6 09	1.72672	-0.09766	-0.63157
YgGSP 07	1.32499	-0.18845	-0.88208
Totw C1 07	-0.07292	0.43424	-0.60032
Totw C2 07	-0.33536	0.59891	-0.59362
Totw C3 07	-0.53664	0.21051	-0.38795
Totw C4 07	-0.68296	0.21288	-0.25323
Totw D1 07	-0.94398	-0.08235	-0.19874
Totw D2 07	-0.7955	-0.295	0.0702
Totw D3 07	-0.81981	-0.00327	0.06261
Totw D4 07	-0.60182	-0.05067	-0.21951
Totw E1 07	-0.71883	0.05092	-0.18264
Totw E2 07	-1.56091	4.88186	2.01624
Totw E4 07	0.9609	-0.20008	0.00482

Sample	Factor 1	Factor 2	Factor 3
Totw A1 07	-0.71812	-0.52876	-0.41052
Totw A3 07	-1.07677	0.69308	0.27147
Totw A4 07	-1.33607	2.36731	1.24161
Totw A5 07	-0.94693	-0.81111	0.49589
Yg A1 07	-0.75007	-0.18598	-0.86747
Yg ASP 07	-0.50878	-0.48438	-0.47488
Yg A2 07	-0.62763	-0.15601	-0.92106
Yg A3 07	-0.87415	-0.20199	-0.80627
Yg A4 07	-0.71979	-0.36431	-0.29552
Yg B2 07	-0.63957	-0.05124	-0.86583
Yg B3 07	-0.1105	-0.41285	-0.28709
Yg B4 07	-0.30838	-0.34698	-0.50262
Yg BSP 07	-0.42044	-0.54111	-0.37734
Yg B5 07	-0.79998	-0.11992	-0.86346
Yg B6 07	-0.21662	-0.14935	-0.56962
Yg C1 07	-0.47987	-0.59986	0.59654
Yg C2 07	-0.62205	-0.3423	-0.21776
Yg CSP 07	-0.8603	0.13165	-0.13424
Yg C3 07	-0.56334	-0.55314	-0.31216
Yg C4 07	-0.59141	-0.3653	-0.51369
Yg C5 07	-0.66314	-0.26553	-0.79719
Fid A1 07	0.79171	-0.0281	-0.13524
Fid A2 07	0.92361	-0.38477	0.89155
Fid A3 07	0.72265	-0.45494	0.77168
Fid A4 07	0.26046	-0.46772	0.12994
Fid ASP 07	0.11647	-0.6447	0.28297
Fid A7 07	-0.07766	-0.46596	0.04895
Fid A13 07	1.50598	0.04732	0.33785
Fid B1 07	3.09417	1.59778	-1.10961
Fid B2 07	0.91852	0.40596	-0.64011
Fid B4 07	0.67893	-0.69188	2.06807
Fid B5 07	1.67234	-1.15933	4.74912
Fid C0 07	3.73082	2.12146	-1.3276
Fid C1 07	0.3902	-0.39924	0.63649
Fid C10 07	-0.04089	-0.55824	0.66116
Fid C2 07	0.58677	-0.35753	0.08009
Fid C5 07	0.25168	-0.52033	0.59394
Fid C6 07	1.11553	-0.88301	3.03361
Fid C7 07	0.80154	-0.85235	2.33978
Fid C9 07	-0.25029	-0.24655	0.28471
Fid CSP 07	0.08332	-0.71738	0.91479
Yg D1 07	2.97442	0.97211	-1.46577
Yg DSP 07	-1.43943	4.72317	1.65781
Yg D2 07	-0.66117	-0.59825	-0.377
Yg D6 07	-0.58745	0.78217	-0.18475
Yg ESP 07	1.27321	0.35143	-0.14847
Yg E3 07	-0.18523	0.11973	-1.00748
Yg F1 07	0.75045	0.37517	-0.44992
Yg F2 07	0.33189	-0.68601	0.9694
Yg GSP 07	1.49522	0.49749	-0.93426
Yg G2 07	0.90951	0.13946	-0.62158
Yg G3 07	1.86936	0.73865	-1.17735
uMkhuze River	0.02463	-0.37279	-0.00274

<b>Sample</b>	<b>Factor 1</b>	<b>Factor 2</b>	<b>Factor 3</b>
Totw C Lake 07	-0.3753	-0.36682	-0.78758
Totw D Lake 07	-0.54065	-0.35389	-0.86466
Totw E Lake 07	-0.48361	-0.33455	-0.76415
Totw A Lake 07	-0.64718	-0.38314	-0.31758
Fld A Mpanza 07	-0.31545	-0.37016	-0.16802
Fld B Lake 07	-0.1488	-0.57009	0.09216
Fld C Hippo pool 07	-0.10126	-0.53317	0.24945
Fld A Oxbow 07	-0.01151	-0.63765	0.25747
Yg B Lake 07	-0.00558	-0.14852	-0.59811
Yg C Lake 07	-0.53002	-0.44775	-0.51036
Yg F Lake 07	-0.41493	-0.40782	-0.1784
Yg G Lake 07	-0.51524	-0.29911	-0.38689

Appendix E: XRF Soil chemistry data

Sample	Depth m	Silica SiO <sub>2</sub>	Alumina Al <sub>2</sub> O <sub>3</sub>	Iron Fe <sub>2</sub> O <sub>3</sub>	Manganese MnO	Magnesium MgO	Calcium CaO	Sodium Na <sub>2</sub> O	Potassium K <sub>2</sub> O	Titanium TiO <sub>2</sub>	Phosphorus P <sub>2</sub> O <sub>5</sub>	Chromium Cr <sub>2</sub> O <sub>3</sub>	Nickel NiO
Fld A Mpanza	0	61.26	21.6	10.04	0.0593	1.55	0.92	0.82	2.37	1.1315	0.23	0.0205	0.0129
Fld A Oxbow	0	64.33	18.84	9.9	0.092	1.27	0.82	1.05	2.24	1.3024	0.18	0.0176	0.0107
Fld A1.1	0	70.26	14.89	7.79	0.0841	1.24	1.3	1.21	2.11	0.9444	0.17	0.0146	0.0095
Fld A1.2	0.4	70.03	15.19	8.31	0.1048	1.13	1.07	1	2.02	1.2707	0.09	0.0262	0.0074
Fld A1.4	0.9	82.32	7.96	4.41	0.082	0.79	0.85	1.14	1.52	0.8728	0.06	0.0019	0.0011
Fld A1.6	2	80.39	8.7	5.1	0.1429	0.77	1.03	1.14	1.62	1.0471	0.05	0.0137	0.0038
Fld A2.1	0	64.37	18.09	9.95	0.1747	1.53	1.29	1.03	2.25	1.0447	0.28	0.0253	0.0078
Fld A2.3	0.7	82.48	7.95	4.42	0.0559	0.77	0.88	1.01	1.57	0.8504	0.06	0.0228	0.0025
Fld A2.5	1.5	80.06	9.01	5.09	0.1074	0.83	1.04	1.26	1.68	1.0852	0.06	0.0072	0.0056
Fld A3.1	0	60.58	20.57	11.46	0.1583	1.53	1.07	0.94	2.3	1.005	0.29	0.0108	0.0066
Fld A3.3	0.9	80.11	9.34	5.1	0.0481	0.75	0.82	1.02	1.59	0.8812	0.07	0.0125	0.0033
Fld A3.4	1.7	80.29	9.1	4.75	0.0514	0.8	0.97	1.19	1.68	0.9765	0.06	0.01	0.0028
Fld A4.1	0	61.3	21.84	9.87	0.0765	1.49	0.86	0.82	2.47	1.1121	0.21	0.0172	0.0104
Fld A4.3	0.9	71.65	14.63	7.22	0.0503	1.1	0.97	1.14	1.94	1.2049	0.1	0.0194	0.0116
Fld A4.4	1.7	79.44	9.55	5.51	0.0429	0.82	0.96	1.05	1.68	0.9892	0.08	0.0162	0.0014
Fld A7.1	0	69.46	14.75	8.46	0.1197	1.18	1.07	1	2.08	1.298	0.14	0.0217	0.0052
Fld A7.3	0.7	78.05	10.27	5.72	0.096	0.85	0.9	0.97	1.69	1.0646	0.07	0.0187	0.0028
Fld A7.5	1.6	83.02	7.72	4.17	0.0597	0.85	0.87	0.97	1.55	0.8438	0.06	0.0208	0.0062
Fld A7.5	2	82.51	7.92	4.46	0.0482	0.8	0.86	0.88	1.52	0.9507	0.05	0.0115	0.002
Fld ASP.1	0	77.41	10.63	5.55	0.0769	0.9	1.1	1.18	2.06	1.1822	0.11	0.0189	0.0046
Fld ASP.3	0.7	83.44	7.93	4.21	0.0596	0.7	0.7	0.92	1.49	0.6518	0.05	0.0105	0.001
Fld ASP.5	2	83	7.74	4.35	0.0569	0.77	0.9	0.93	1.47	0.9374	0.05	0.0175	0.0007
Fld B Lake	0	56.04	24.01	13.47	0.08	1.57	0.68	0.48	2.43	1.0646	0.18	0.0126	0.0169
Fld B1.1	0	73.6	12.58	7.46	0.1642	0.88	0.93	0.99	1.97	1.399	0.13	0.0214	0.009
Fld B1.3	1	74.44	13.3	7.46	0.135	0.64	0.42	0.69	1.58	1.3322	0.05	0.0221	0.0087
Fld B1.5	1.7	54.6	10.15	6.24	0.2431	1.67	23.96	0.95	1.28	1.0941	0.04	0.0211	0.0067
Fld B1.7	2.6	69.02	14.12	8.52	0.3484	1.48	1.41	2.01	1.85	1.3206	0.06	0.0187	0.0115
Fld B1.8	3.1	67.38	13.48	8.21	0.3497	1.46	4.09	1.99	1.68	1.2584	0.08	0.0236	0.0121
Fld B1.9	3.7	71.09	13.49	7.93	0.2382	1.3	1.23	1.53	1.82	1.3377	0.06	0.0281	0.0125
Fld B1.10	4	66.13	15.9	9.64	0.3113	1.59	1.58	1.64	1.83	1.3107	0.07	0.0398	0.0099
Fld B1.11	4.5	65.39	14.44	8.93	0.3668	1.63	4.36	1.7	1.85	1.3054	0.06	0.0367	0.0101
Fld B2.1	0	73.21	13.13	7.49	0.1318	0.81	0.76	1	1.86	1.3526	0.11	0.0229	0.0063
Fld B2.3	1.2	74.43	12.85	7.28	0.1825	0.87	0.4	0.96	1.61	1.3997	0.04	0.0309	0.0138

Sample	Depth m	Silica SiO <sub>2</sub>	Alumina Al <sub>2</sub> O <sub>3</sub>	Iron Fe <sub>2</sub> O <sub>3</sub>	Manganese MnO	Magnesium MgO	Calcium CaO	Sodium Na <sub>2</sub> O	Potassium K <sub>2</sub> O	Titanium TiO <sub>2</sub>	Phosphorus P <sub>2</sub> O <sub>5</sub>	Chromium Cr <sub>2</sub> O <sub>3</sub>	Nickel NiO
Fld B2.4	1.4	70.04	12.02	6.87	0.1743	1.12	5.73	1.17	1.62	1.325	0.04	0.0261	0.0056
Fld B2.6	2.7	67.3	15.12	9.17	0.198	1.59	1.57	1.75	1.91	1.3081	0.06	0.0268	0.0124
Fld B2.9	4.5	61.5	15.04	8.93	0.198	1.62	7.6	1.79	1.73	1.271	0.07	0.0331	0.012
Fld B3.1	0	73.47	12.8	7.67	0.1587	0.92	0.79	1.07	1.7	1.3712	0.07	0.0157	0.0083
Fld B3.3	1.1	76.21	11.42	6.81	0.1265	0.68	0.56	1.01	1.63	1.4325	0.05	0.0308	0.0048
Fld B4.1	0	58.44	23.86	11.08	0.0745	1.54	0.68	0.73	2.31	1.0979	0.15	0.0409	0.0095
Fld B4.2	0.3	68	15.64	9.79	0.1375	1.19	1	1.08	1.76	1.3221	0.12	0.023	0.0106
Fld B4.4	1.5	72.59	12.36	7.71	0.2487	1.19	2	1.12	1.45	1.2876	0.05	0.0257	0.0077
Fld B4.6	1.9	69.68	10.72	6.68	0.3099	1.27	7.87	0.84	1.41	1.2275	0.05	0.0186	0.0093
Fld B4.7	2.1	73.01	11.19	6.9	0.2709	1.11	4.13	0.78	1.48	1.2582	0.05	0.0264	0.0071
Fld B4.8	2.3	69.27	10.33	6.13	0.2077	1.27	9.21	0.94	1.4	1.1709	0.04	0.0221	0.0121
Fld B5.1	0	56.07	24.1	13.1	0.0908	1.68	0.65	0.77	2.35	1.0418	0.19	0.0369	0.0129
Fld B5.1G		58.01	23.56	11.83	0.0741	1.66	0.64	0.63	2.3	1.1245	0.18	0.0405	0.0106
Fld B5.3	0.7	55.3	23.32	14.86	0.0905	1.68	0.77	0.56	2.16	1.1147	0.15	0.0432	0.014
Fld B5.5	1.4	62.01	19.61	11.07	0.1372	1.64	1.02	1.01	2.08	1.1869	0.2	0.033	0.0129
Fld B5.6	1.6	63.42	17.43	11.63	0.2504	1.57	1.19	1.19	1.92	1.282	0.14	0.0264	0.0118
Fld B5.7	1.7	69.5	14.62	9.24	0.1235	1.37	1.14	1	1.75	1.1111	0.17	0.0189	0.0103
Fld C0.1	0	79.32	9.79	5.56	0.14	0.48	0.52	0.85	1.86	1.546	0.1	0.0277	0.0091
Fld C 0.3	0.9	76.35	11.85	6.69	0.1512	0.59	0.5	0.79	1.73	1.4228	0.05	0.0255	0.0092
Fld C 0.5	1.9	74.54	11.86	6.83	0.1948	0.87	0.86	1.74	1.76	1.4373	0.04	0.0308	0.0093
Fld C 0.8	2.6	75.73	11.18	6.32	0.1744	0.93	1.11	1.53	1.78	1.3376	0.04	0.0315	0.0089
Fld C 0.11	3.7	78.28	9.36	5.45	0.1151	1	1.25	1.44	1.81	1.3373	0.04	0.0189	0.0069
Fld C 0.14	5	70.07	13.64	7.83	0.1658	1.4	1.77	1.9	1.93	1.4325	0.06	0.0354	0.0111
Fld C 1.1	0	75.98	11.58	6.59	0.1505	0.72	0.7	0.94	1.91	1.4616	0.1	0.0194	0.0077
Fld C 1.5	0.7	69.72	12.11	6.84	0.1873	1.15	5.35	1.5	1.73	1.4002	0.05	0.0235	0.0068
Fld C 1.7	1.7	74.51	11.46	6.52	0.1557	1.09	1.32	1.62	1.87	1.392	0.04	0.0199	0.0064
Fld C 1.11	2.8	73.57	12.25	7.03	0.1432	1.35	1.19	1.22	1.9	1.2296	0.05	0.0237	0.0084
Fld C 1.13	4	71.12	13.3	7.82	0.1536	1.57	1.37	1.47	1.89	1.3882	0.05	0.0291	0.009
Fld C 2.1	0	57.43	24.57	10.7	0.0507	1.51	0.63	0.56	2.63	1.134	0.14	0.0315	0.0123
Fld C 2.3	0.7	70.74	13.74	8.32	0.1802	1.14	1.05	1.2	1.92	1.4584	0.08	0.0339	0.0111
Fld C 2.6	2	73.74	12.61	7.34	0.1566	0.94	0.76	1.07	1.73	1.4084	0.03	0.0317	0.0074
Fld C 2.9	3.1	69.38	13.92	7.98	0.1308	1.47	2.01	1.82	1.8	1.4835	0.07	0.0195	0.017
Fld C 2.12	3.9	67.37	15.29	9.16	0.1535	1.81	1.37	1.57	1.9	1.321	0.07	0.0315	0.0084
Fld C 5.1	0	57.98	23.11	11.56	0.1093	1.63	0.8	0.62	2.48	1.1412	0.17	0.04	0.0137
Fld C 5.3	0.9	58.45	22.98	11.62	0.0828	1.57	0.72	0.65	2.38	1.2151	0.14	0.0308	0.0158

Sample	Depth m	Silica SiO <sub>2</sub>	Alumina Al <sub>2</sub> O <sub>3</sub>	Iron Fe <sub>2</sub> O <sub>3</sub>	Manganese MnO	Magnesium MgO	Calcium CaO	Sodium Na <sub>2</sub> O	Potassium K <sub>2</sub> O	Titanium TiO <sub>2</sub>	Phosphorus P <sub>2</sub> O <sub>5</sub>	Chromium Cr <sub>2</sub> O <sub>3</sub>	Nickel NiO
Fld C 5.5	2	65.46	16.73	9.85	0.1381	1.49	1.31	1.4	2.03	1.4034	0.13	0.0433	0.0119
Fld C 6.1	0	59.46	22.71	10.49	0.0683	1.53	0.78	0.62	2.52	1.1605	0.16	0.0385	0.0138
Fld C 6.3	0.9	61.6	19.64	11.37	0.1902	1.61	1.14	0.94	2.17	1.3146	0.15	0.0325	0.0161
Fld C 6.7	1.9	66.56	15.82	9.82	0.1691	1.6	1.56	1.16	1.89	1.3826	0.16	0.0263	0.0121
Fld C 7.1	0	63.42	19.94	9.59	0.0591	1.42	0.84	1.01	2.36	1.2142	0.14	0.0243	0.0132
Fld C 7.2	0.8	57.95	23.92	11.32	0.0826	1.6	0.78	0.55	2.46	1.1588	0.17	0.0319	0.0153
Fld C 7.4	1.5	62.37	19.09	11.27	0.2125	1.55	1.12	0.83	2.19	1.2883	0.2	0.0306	0.014
Fld C 7.6	2.4	70.02	14.21	8.5	0.1883	1.42	1.33	1.13	1.97	1.2227	0.15	0.031	0.0099
Fld C 9.1	0	58.93	22.9	11.08	0.078	1.52	0.8	0.54	2.53	1.1117	0.22	0.0436	0.0112
Fld C 9.3	0.9	68.08	15.01	9.61	0.1376	1.28	1.27	1.27	2.09	1.376	0.15	0.0199	0.0091
Fld C 9.5	1.5	71.73	12.94	7.81	0.1521	1.22	1.44	1.33	1.98	1.3373	0.11	0.0319	0.0102
Fld C 10.1	0	63.03	19.06	10.49	0.1077	1.55	1.26	0.8	2.44	1.1875	0.29	0.0453	0.0131
Fld C 10.3	0.9	75	11.43	6.6	0.1108	1.14	1.48	1.24	1.86	1.2616	0.11	0.022	0.0085
Fld C 10.5	1.5	82.73	7.24	4.05	0.067	0.84	0.97	0.95	1.56	0.7911	0.07	0.0209	0.0053
Fld C SP.1	0	59.34	23.33	10.68	0.0619	1.52	0.72	0.57	2.52	1.1349	0.14	0.0354	0.0127
Fld C SP.5	1	73.92	12.22	7.21	0.1912	0.93	0.92	1.1	1.81	1.4676	0.05	0.0312	0.0091
Fld C SP.8	1.8	76.09	10.56	6.19	0.1261	1.03	1.74	1.32	1.78	1.3312	0.04	0.0206	0.009
Fld C SP.11	2.8	75.4	10.72	6.03	0.1109	1.11	2.17	1.36	1.75	1.116	0.05	0.0243	0.0055
Fld C SP.13	3.7	71.08	13.11	7.65	0.1241	1.42	2.11	1.3	1.82	1.4497	0.05	0.0318	0.0102
Totw A1 292	0	96.6	1.65	0.22	0.0114	0	0.09	0.22	0.88	0.1889	0.02	0	0.0002
Totw A1 296	1	96.56	1.82	0.24	0.0001	0.01	0.06	0.24	0.97	0.2486	0.01	0.0054	0
Totw A1 300	2	97.04	1.55	0.2	0.0023	0.03	0.04	0.17	0.85	0.2194	0.01	0.0022	0.0028
Totw A1 305	3	96.6	1.78	0.27	0.0022	0.01	0.04	0.22	0.8	0.2678	0.01	0.0042	0
Totw A1 308	3.5	96.27	1.96	0.29	0.003	0.03	0.05	0.18	0.89	0.2842	0.01	0.0055	0
Totw A2 309	0	96.02	2.13	0.31	0.0017	0.02	0.07	0.34	0.94	0.2103	0.02	0	0.0004
Totw A2 313	0.9	96.26	1.87	0.28	0.0052	0.02	0.05	0.25	1	0.3247	0.01	0	0
Totw A2 316	1.4	95.31	2.01	0.31	0.0045	0.03	0.06	0.24	1.01	0.3447	0.01	0.0098	0
Totw A3 317	0	92.02	4.81	1.16	0.0059	0.18	0.23	0.16	0.95	0.2941	0.05	0.0125	0
Totw A3 319	0.5	95.26	2.62	0.49	0.0018	0.04	0.08	0.27	0.99	0.3258	0.01	0	0.0004
Totw A3 322	1.1	95.54	2.14	0.39	0.0028	0.02	0.07	0.29	1.04	0.3918	0.01	0.0059	0
Totw B1 14	0	94.99	2.65	0.62	0.0023	0.12	0.25	0.35	0.85	0.2391	0.04	0	0
Totw B1 18	1.1	96.17	2.22	0.35	0.0004	0.05	0.12	0.19	0.83	0.2225	0.01	0	0
Totw B1 22	2	94.16	3.41	0.79	0	0.14	0.17	0.29	0.81	0.2394	0.02	0	0.0003
Totw B1 26	2.66	96.01	2.27	0.54	0	0.1	0.12	0.22	0.64	0.2456	0.02	0.0014	0.0039
Totw B2 7	0	94.29	3.11	0.75	0.0019	0.14	0.22	0.39	0.9	0.2012	0.02	0.0027	0

Sample	Depth m	Silica SiO <sub>2</sub>	Alumina Al <sub>2</sub> O <sub>3</sub>	Iron Fe <sub>2</sub> O <sub>3</sub>	Manganese MnO	Magnesium MgO	Calcium CaO	Sodium Na <sub>2</sub> O	Potassium K <sub>2</sub> O	Titanium TiO <sub>2</sub>	Phosphorus P <sub>2</sub> O <sub>5</sub>	Chromium Cr <sub>2</sub> O <sub>3</sub>	Nickel NiO
Totw B2 9	0.5	93	4.25	1.09	0.0008	0.19	0.22	0.41	0.84	0.2175	0.01	0	0
Totw B2 11	0.9	92.44	4.53	1.18	0.0012	0.2	0.23	0.2	0.85	0.2316	0.02	0	0
Totw B2 13	1.3	95.08	2.83	0.58	0.0001	0.1	0.18	0.31	0.85	0.1864	0.02	0	0
Totw B3 1	0	93.36	3.66	1.32	0.0019	0.15	0.2	0.29	0.84	0.2267	0.04	0	0
Totw B3 4	1.7	94.4	2.96	0.63	0.0002	0.12	0.2	0.28	0.85	0.2254	0.01	0	0.0013
Totw B3 6	1.1	94.33	3.29	0.69	0	0.13	0.22	0.28	0.87	0.1944	0.01	0.0001	0
Totw C1 52	0	96.55	1.67	0.35	0.0175	0.01	0.14	0.12	0.81	0.2033	0.02	0.0024	0
Totw C1 55	0.9	97.25	1.42	0.33	0.0035	0.01	0.05	0.08	0.75	0.2429	0.01	0	0
Totw C1 60	1.9	97.07	1.46	0.32	0.0014	0.04	0.04	0.12	0.78	0.2644	0.01	0.0078	0
Totw C1 63	2.32	97.02	1.39	0.25	0.0034	0.01	0.04	0.19	0.75	0.2405	0.01	0	0
Totw C2 46	0	95.66	2.14	0.65	0.0181	0.07	0.2	0.15	0.83	0.2225	0.03	0.0016	0.0006
Totw C2 48	0.8	97.08	1.51	0.29	0.0013	0.02	0.03	0.14	0.76	0.2402	0.01	0.0025	0.0006
Totw C2 49	1.3	97.08	1.44	0.26	0.0025	0.04	0.04	0.12	0.77	0.2357	0.01	0.005	0
Totw C3 50	0	96.04	2.12	0.54	0.0065	0.07	0.06	0.22	0.77	0.2664	0.02	0.0032	0.002
Totw C3 51	0.5	96.62	1.44	0.27	0.0005	0.02	0.04	0.12	0.73	0.2444	0.01	0.0067	0
Totw D1 220	0	95.94	1.8	0.41	0.0159	0.07	0.08	0.1	0.82	0.1772	0.02	0	0
Totw D1 223	0.8	97.01	1.64	0.28	0	0.03	0.04	0.12	0.81	0.2134	0.01	0.01	0
Totw D1 226	1.4	96.56	1.44	0.16	0.0027	0.03	0.03	0.08	0.81	0.1608	0.01	0	0
Totw D2 229	0	95.39	2.09	0.62	0.0096	0.08	0.07	0.03	0.8	0.2103	0.03	0	0
Totw D2 230	0.5	96.57	1.98	0.4	0.0047	0.04	0.03	0.1	0.8	0.2213	0.01	0.0068	0
Totw D2 231	0.7	96.58	1.58	0.26	0.004	0.04	0.03	0.01	0.76	0.1998	0.01	0	0
Totw D3 227	0	94.48	2.67	0.81	0.0052	0.09	0.07	0.12	0.8	0.2657	0.03	0	0
Totw D3 228	0.5	96.43	2.02	0.37	0.0009	0.05	0.03	0.11	0.77	0.2165	0.02	0.0061	0
Totw D4	0	83.85	9.61	3.27	0.0045	0.6	0.7	0.4	1.05	0.4523	0.13	0	0
Totw E1 250	0	91.99	3.65	1.56	0.0427	0.2	0.24	0.28	1.16	0.3846	0.04	0.0023	0.0005
Totw E1 251	0.4	95.11	2.5	0.84	0.0281	0.1	0.1	0.23	1.03	0.3175	0.02	0.0047	0.0012
Totw E1 253	0.9	95.25	1.96	0.52	0.0143	0.06	0.07	0.26	1.02	0.3057	0.01	0	0
Totw E2 254	0	91.29	3.95	1.75	0.0444	0.24	0.3	0.34	1.17	0.4196	0.05	0.0018	0
Totw E2 255	0.4	94.25	2.76	1.1	0.0343	0.13	0.13	0.2	1.06	0.3369	0.02	0.0178	0
Totw E2 257	0.9	93.87	2.2	0.72	0.0048	0.06	0.08	0.22	1.02	0.2777	0.01	0	0
Totw E3 258	0	87.07	6.01	3.11	0.1037	0.5	0.63	0.47	1.36	0.5425	0.07	0.009	0.0048
Totw E3 260	0.7	91.01	3.59	3.24	0.0157	0.16	0.13	0.45	1.11	0.3745	0.04	0.0003	0.0019
Totw E3 270	1	94.82	2.24	0.78	0.0078	0.1	0.09	0.23	0.99	0.367	0.02	0	0
Totw E4	0	73.34	13.63	7.2	0.0596	1.01	0.71	0.89	1.87	0.9077	0.16	0.0061	0.0157
Yg A1.1	0	97.44	1.3	0.28	0	0.03	0.09	0.15	0.41	0.2522	0.02	0.0009	0

Sample	Depth m	Silica SiO <sub>2</sub>	Alumina Al <sub>2</sub> O <sub>3</sub>	Iron Fe <sub>2</sub> O <sub>3</sub>	Manganese MnO	Magnesium MgO	Calcium CaO	Sodium Na <sub>2</sub> O	Potassium K <sub>2</sub> O	Titanium TiO <sub>2</sub>	Phosphorus P <sub>2</sub> O <sub>5</sub>	Chromium Cr <sub>2</sub> O <sub>3</sub>	Nickel NiO
Yg A1.2	0.4	97.93	1.18	0.16	0	0.03	0.08	0.19	0.44	0.1723	0.02	0	0.0009
Yg A1.4	1.8	97.69	1.24	0.2	0.0002	0.05	0.07	0.19	0.46	0.2816	0.01	0	0
Yg A1.5	2.4	97.54	1.02	0.27	0.0006	0.04	0.06	0.1	0.39	0.3468	0.01	0.0063	0.0045
Yg A2.1	0	97.56	1.24	0.32	0.0006	0.05	0.12	0.14	0.39	0.2334	0.03	0	0
Yg A2.2	0.3	98.05	1.02	0.25	0	0.06	0.1	0.14	0.33	0.248	0.02	0.0016	0.0007
Yg A2.4	1.4	98.04	1.07	0.14	0	0.03	0.08	0.1	0.44	0.197	0.01	0	0
Yg A3.1	0	96.72	1.87	0.55	0.0027	0.1	0.1	0.15	0.39	0.2266	0.04	0	0
Yg A3.3	0.7	98.07	1.2	0.15	0.0002	0.04	0.06	0.1	0.4	0.1393	0.01	0.0051	0
Yg A3.4	0.9	97.59	1.22	0.19	0.0008	0.05	0.08	0.18	0.46	0.2656	0.01	0	0
Yg A4.1	0	95.21	2.61	1	0.0005	0.09	0.13	0.25	0.46	0.2121	0.07	0	0
Yg A4.3	0.6	92.09	5.45	1.34	0.0012	0.17	0.1	0.19	0.5	0.2735	0.03	0	0.0013
Yg A4.4	1	97.72	1.2	0.17	0.0008	0.02	0.08	0.23	0.44	0.2366	0.01	0	0.0003
Yg ASP.1	0	97.66	1.17	0.25	0.002	0.05	0.07	0.22	0.39	0.2709	0.02	0	0
Yg ASP.4	1.5	97.76	1.12	0.17	0.0003	0.04	0.08	0.11	0.44	0.2294	0.01	0	0.0015
Yg B Lak <sup>o</sup> 0-2	0	74.5	14.71	6.49	0.0291	1.06	0.54	0.57	1.35	0.6218	0.3	0.0203	0.0059
Yg B1.1	0	96.35	2.02	0.61	0.001	0.08	0.1	0.13	0.51	0.2476	0.03	0	0
Yg B1.2	0.4	96.48	1.56	0.32	0.0008	0.04	0.06	0.19	0.54	0.2616	0.02	0	0
Yg B1.4	1.1	89.4	6.96	1.98	0.0043	0.27	0.12	0.17	0.65	0.4136	0.02	0.0144	0
Yg B1.6	2.4	92.42	4.65	1.38	0.005	0.21	0.1	0.22	0.56	0.4574	0.02	0.0125	0.0015
Yg B1.9	3.4	91.13	5.27	1.61	0.0086	0.25	0.09	0.39	0.64	0.4445	0.02	0.008	0.0036
Yg B1.11	4.8	92.44	4.58	1.57	0.0106	0.2	0.09	0.23	0.52	0.4631	0.02	0.0053	0.0011
Yg B2.1	0	85.09	8.01	4.35	0.0132	0.5	0.35	0.41	0.72	0.511	0.07	0.0092	0.0031
Yg B2.3	1	90.3	6.59	1.55	0.0006	0.26	0.08	0.23	0.58	0.4162	0.02	0.0091	0
Yg B2.3	2.2	93.13	3.78	1.56	0.0019	0.15	0.07	0.19	0.46	0.4267	0.02	0.0094	0.0016
Yg B2.6	3	94	3.7	1.16	0.0013	0.17	0.1	0.2	0.42	0.4925	0.01	0	0.0026
Yg B3.1	0	89.46	6.39	2.16	0.0028	0.28	0.16	0.35	0.62	0.4504	0.06	0.0067	0
Yg B3.2	0.3	96.01	2.38	0.54	0.0001	0.07	0.09	0.25	0.53	0.3171	0.02	0	0
Yg B4.1	0	95.24	2.75	0.78	0.001	0.12	0.14	0.17	0.51	0.2667	0.03	0	0.0023
Yg B5.1	0	95.15	2.32	1.14	0.0019	0.16	0.19	0.25	0.46	0.3036	0.04	0	0
Yg B5.4	0.7	97.17	1.15	0.25	0	0.06	0.09	0.18	0.44	0.3713	0.01	0.0005	0
Yg B6.1	0	88.2	7.21	2.25	0.0079	0.42	0.3	0.42	0.73	0.4675	0.07	0.0089	0.0007
Yg B6.2	0.2	96.07	2.13	0.51	0.0001	0.09	0.14	0.23	0.52	0.3119	0.02	0	0
Yg BSP.1	0	96.8	1.69	0.55	0.0018	0.07	0.12	0.11	0.53	0.2721	0.02	0	0
Yg BSP.2	0.2	97.16	1.44	0.33	0.0003	0.07	0.1	0.23	0.49	0.2548	0.01	0	0
Yg BSP.4	0.8	97.67	1.23	0.17	0	0.05	0.09	0.28	0.49	0.2004	0.01	0	0

Sample	Depth m	Silica SiO <sub>2</sub>	Alumina Al <sub>2</sub> O <sub>3</sub>	Iron Fe <sub>2</sub> O <sub>3</sub>	Manganese MnO	Magnesium MgO	Calcium CaO	Sodium Na <sub>2</sub> O	Potassium K <sub>2</sub> O	Titanium TiO <sub>2</sub>	Phosphorus P <sub>2</sub> O <sub>5</sub>	Chromium Cr <sub>2</sub> O <sub>3</sub>	Nickel NiO
Yg C Lake	0	77.4	13.18	5.27	0.0144	0.79	0.32	0.44	1.49	0.7054	0.12	0.0087	0.0035
Yg C1.1	0	96.33	1.75	0.58	0.0129	0.09	0.16	0.2	0.5	0.3705	0.03	0	0
Yg C1.3	0.8	96.77	1.26	0.38	0.0022	0.07	0.11	0.26	0.47	0.4381	0.01	0	0.0008
Yg C1.5	1.8	96.92	1.27	0.47	0.0028	0.09	0.11	0.12	0.46	0.5286	0.01	0.0016	0
Yg C2.1	0	96.37	1.74	0.55	0.0102	0.1	0.14	0.22	0.52	0.3576	0.03	0.0029	0.0009
Yg C2.3	0.8	97.25	1.28	0.31	0.0015	0.05	0.1	0.18	0.5	0.3888	0.01	0.0008	0.0003
Yg C2.4	1.2	97.02	1.3	0.32	0.0006	0.06	0.09	0.19	0.52	0.4146	0.01	0.0022	0.0009
Yg C3.1	0	92.71	3.65	1.43	0.0078	0.23	0.17	0.32	0.74	0.387	0.04	0.0021	0.004
Yg C3.3	0.6	96.85	1.56	0.33	0.0036	0.06	0.09	0.22	0.59	0.37	0.02	0	0.0017
Yg C3.4	1	97.03	1.42	0.26	0.003	0.06	0.11	0.26	0.57	0.3495	0.01	0	0
Yg C4.1	0	94.02	3.18	1.02	0.0006	0.18	0.17	0.33	0.7	0.4198	0.04	0.0086	0.0045
Yg C4.2	0.2	96.08	2.21	0.49	0.0032	0.1	0.13	0.26	0.61	0.3371	0.02	0	0.001
Yg C4.3	0.5	97.01	1.57	0.29	0.0013	0.08	0.1	0.26	0.6	0.3115	0.01	0.012	0
Yg C5.1	0	92.71	4.29	1.21	0.0013	0.19	0.19	0.29	0.73	0.4413	0.05	0.0115	0.0013
Yg C5.3	0.4	96.02	1.78	0.36	0.0009	0.08	0.1	0.25	0.6	0.3593	0.02	0.0002	0.0011
Yg CSP.1	0	96.08	2.08	0.66	0.0002	0.11	0.13	0.16	0.59	0.3476	0.02	0.0004	0
Yg CSP.3	0.7	97.03	1.48	0.32	0.0004	0.06	0.1	0.21	0.56	0.3827	0.02	0.0035	0.0002
Yg CSP.4	0.9	97	1.39	0.25	0.0012	0.05	0.11	0.29	0.56	0.356	0.01	0	0
Yg D Lake	0	92.98	3.97	1.41	0.0017	0.24	0.17	0.28	0.72	0.3421	0.06	0.0018	0.0014
Yg D1.1	0	94.49	2.25	1.08	0.0401	0.17	0.15	0.17	0.73	0.4546	0.03	0	0
Yg D1.5	1	95.61	1.79	0.75	0.0137	0.05	0.05	0.04	0.71	0.4609	0.02	0	0
Yg D1.12	2	93.09	3.09	1.5	0.0141	0.19	0.06	0.16	0.71	0.52	0.01	0.0031	0
Yg D1.14	3	92.2	3.41	1.7	0.0129	0.22	0.06	0.29	0.71	0.5722	0.01	0.0047	0.0008
Yg D1.16	3.7	90.73	4.43	2.2	0.0234	0.32	0.1	0.32	0.73	0.569	0.01	0.0124	0.0018
Yg D2.1	0	92.38	3.6	1.83	0.0187	0.22	0.17	0.16	0.83	0.4518	0.04	0	0
Yg D2.5	1	93.75	2.87	1.3	0.005	0.11	0.06	0	0.72	0.4508	0.01	0	0
Yg D2.8	2	93.26	3.19	1.44	0.0082	0.17	0.06	0.14	0.73	0.4571	0.01	0.01	0
Yg D6.1	0	93.59	2.82	1.36	0.0069	0.17	0.13	0.17	0.75	0.4228	0.02	0.0054	0
Yg D6.4	0.8	94.38	2.56	0.99	0.006	0.13	0.08	0.11	0.72	0.4177	0.01	0.0047	0
Yg D6.9	1.6	92.42	4.21	1.79	0.0086	0.26	0.07	0.25	0.75	0.4317	0.01	0	0
Yg D7.1	0	92.06	3.74	2.37	0.0516	0.29	0.2	0.17	0.85	0.4046	0.02	0.004	0.0015
Yg D7.3	0.5	95	1.58	0.59	0.0048	0.09	1.79	0.04	0.68	0.3236	0.01	0	0
Yg D8.1	0	88.75	5.76	3.14	0.0451	0.39	0.24	0.22	1.02	0.4839	0.03	0.0105	0.0018
Yg D8.3	0.5	94.12	2.53	1.59	0.0203	0.15	0.12	0.15	0.7	0.3404	0.01	0.0051	0.0002
Yg DSP.1	0	95.01	2.32	0.99	0.0104	0.13	0.11	0.17	0.74	0.4218	0.02	0.0107	0.0009

Sample	Depth m	Silica SiO <sub>2</sub>	Alumina Al <sub>2</sub> O <sub>3</sub>	Iron Fe <sub>2</sub> O <sub>3</sub>	Manganese MnO	Magnesium MgO	Calcium CaO	Sodium Na <sub>2</sub> O	Potassium K <sub>2</sub> O	Titanium TiO <sub>2</sub>	Phosphorus P <sub>2</sub> O <sub>5</sub>	Chromium Cr <sub>2</sub> O <sub>3</sub>	Nickel NiO
Yg DSP.3	0.7	95.21	2.08	0.85	0.0071	0.09	0.05	0.16	0.71	0.4678	0.01	0.0119	0
Yg E Lake	0	78.94	12.26	4.97	0.0163	0.72	0.28	0.49	1.43	0.6917	0.07	0	0.0012
Yg E1.1	0	92.91	3.1	1.48	0.0576	0.2	0.39	0.24	0.79	0.4834	0.05	0.0027	0.0004
Yg E1.4	1	94.22	2.69	1.19	0.0423	0.15	0.15	0.14	0.72	0.4438	0.01	0.0056	0.0008
Yg E1.6	2	90.38	4.81	2.45	0.0305	0.26	0.17	0.32	0.79	0.5439	0.02	0.0049	0.0021
Yg E1.9	2.9	84.64	5.86	2.85	0.0655	0.61	3.53	0.57	0.78	0.5258	0.01	0.0174	0.0047
Yg E1.11	3.8	89.57	4.93	2.18	0.0355	0.52	1.25	0.36	0.72	0.4325	0.01	0.0076	0.0014
Yg E1.14	5.3	84.66	4.29	1.76	0.068	0.5	6.75	0.33	0.82	0.4163	0.01	0.0126	0
Yg E2.1	0	93.75	2.84	1.26	0.0382	0.12	0.17	0.23	0.8	0.4257	0.03	0.0056	0
Yg E2.4	1	95.58	1.98	0.79	0.0163	0.08	0.12	0.3	0.74	0.424	0.01	0.0109	0.0012
Yg E2.6	1.8	92.34	3.61	1.79	0.024	0.19	0.1	0.28	0.77	0.501	0.02	0.0064	0
Yg E2.8	2.8	86.71	6.82	3.77	0.0479	0.46	0.13	0.64	0.93	0.5679	0.01	0.0224	0.0024
Yg E2.10	4.8	75.68	5.28	2.63	0.0535	0.64	13.88	0.34	0.72	0.4564	0.01	0.0064	0.0012
Yg E3.1	0	93.57	3.2	1.28	0.0145	0.16	0.16	0.42	0.7	0.4664	0.03	0.0038	0.0122
Yg E3.4	0.8	92.94	3.3	1.66	0.0187	0.17	0.1	0.2	0.82	0.5033	0.02	0.0042	0
Yg E3.8	1.8	86.53	7.09	3.67	0.0518	0.46	0.1	0.56	0.98	0.5634	0.01	0.019	0.003
Yg E3.10	2.7	82.57	7.97	4.42	0.0777	0.67	2.22	0.5	0.89	0.5656	0.02	0.0172	0.0055
Yg E3.12	3.5	81.33	5.78	3.05	0.0497	0.61	7.57	0.31	0.79	0.4789	0.01	0.0106	0.0012
Yg E3A.2	0.2	93.36	3.11	1.61	0.0142	0.17	0.15	0.24	0.83	0.502	0.02	0.0023	0.0011
Yg E3A.5	0.9	87.18	6.91	3.45	0.0281	0.4	0.15	0.32	0.91	0.5511	0.02	0.0092	0.0011
Yg E3A.8	1.9	85.07	7.96	4.11	0.03	0.48	0.2	0.66	1.02	0.5596	0.02	0.0108	0.005
Yg E3A.11	2.8	62.39	7.07	5.57	0.1251	0.84	21.33	0.49	0.77	0.539	0.02	0.0175	0.0081
Yg E3A.12	4	62.6	5.63	4	0.1061	0.78	24.77	0.29	0.64	0.4739	0.02	0.0243	0.0026
Yg E5.1	0	89.17	5.96	2.52	0.0155	0.34	0.26	0.26	1.04	0.5556	0.04	0.023	0.0026
Yg E5.3	0.6	91.94	3.44	1.89	0.0169	0.17	0.15	0.39	0.78	0.4776	0.01	0.0156	0.0011
Yg E5.4	0.9	92.34	3.85	1.96	0.0156	0.2	0.14	0.09	0.81	0.4994	0.02	0.0115	0
Yg ESP.1	0	94.09	2.45	1.02	0.0463	0.12	0.17	0.21	0.75	0.4446	0.03	0.0047	0.0006
Yg ESP.3	0.8	94.94	1.92	0.72	0.0311	0.07	0.12	0.29	0.73	0.4104	0.01	0	0.0004
Yg ESP.6	1.9	90.2	5.04	2.51	0.0321	0.29	0.13	0.59	0.84	0.5309	0.01	0.0109	0.0013
Yg ESP.9	3	81.1	5.25	2.55	0.0647	0.6	8.52	0.47	0.77	0.5044	0.01	0.0198	0
Yg ESP.11	4.1	85.45	4.45	1.98	0.044	0.55	5.5	0.16	0.72	0.4143	0.01	0.0145	0
Yg F Lake	0	85.58	7.37	4.23	0.0452	0.48	0.37	0.32	0.85	0.7187	0.04	0.0162	0.0066
Yg F1.1	0	86.04	6.97	4.16	0.0661	0.5	0.48	0.31	0.81	0.7487	0.07	0.0053	0.0039
Yg F1.4	0.7	73.03	9.89	5.91	0.0611	1.41	6.88	0.96	1.06	1.0067	0.03	0.0221	0.0084
Yg F1.6	1.1	70.08	11.17	7.13	0.0878	1.52	6.38	1.26	1.22	1.1326	0.03	0.0247	0.0077

Sample	Depth m	Silica SiO <sub>2</sub>	Alumina Al <sub>2</sub> O <sub>3</sub>	Iron Fe <sub>2</sub> O <sub>3</sub>	Manganese MnO	Magnesium MgO	Calcium CaO	Sodium Na <sub>2</sub> O	Potassium K <sub>2</sub> O	Titanium TiO <sub>2</sub>	Phosphorus P <sub>2</sub> O <sub>5</sub>	Chromium Cr <sub>2</sub> O <sub>3</sub>	Nickel NiO
Yg F1.8	2.2	65.54	16.14	12.21	0.0616	1.7	0.32	1.37	1.48	1.1739	0.05	0.0301	0.0129
Yg F1.9	3	63.06	16.71	13.79	0.0589	1.88	0.26	1.51	1.44	1.241	0.05	0.0222	0.0164
Yg F1.11	4.5	63.47	17.55	12.28	0.0945	1.79	0.39	1.35	1.74	1.3239	0.04	0.0315	0.0215
Yg F1.14	5.3	88.07	6.31	3.14	0.0222	0.54	0.23	0.38	0.91	0.6801	0.02	0.0053	0.0056
Yg F2.1	0	82.44	8.78	5.43	0.0857	0.68	0.64	0.3	0.88	0.8056	0.05	0.0113	0.0059
Yg F2.3	0.7	69.26	8.16	5.3	0.1352	1.21	13.86	0.45	0.72	0.7247	0.03	0.01	0.0043
Yg FSP.1	0	80.59	9.71	5.6	0.1001	0.65	0.76	0.43	1.12	0.9399	0.11	0.0173	0.0086
Yg FSP.3	0.6	82.76	8.31	4.96	0.0843	0.69	1.38	0.47	0.75	0.7612	0.03	0.02	0.0043
Yg G Lake	0	74.35	12.52	8.05	0.1139	0.87	0.72	0.87	1.42	1.0562	0.1	0.0235	0.0061
Yg G1.1	0	81.71	9.03	5.21	0.1137	0.6	0.59	0.45	1.11	0.8726	0.1	0.0114	0.006
Yg G1.2	0.6	84.7	7.67	4.28	0.0869	0.48	0.43	0.35	0.92	0.7783	0.04	0.0018	0.0058
Yg G1.4	2	74.98	10.69	5.99	0.0776	1.18	3.97	0.85	1.01	0.9446	0.02	0.0126	0.0064
Yg G1.6	3.4	82.67	9.67	3.94	0.0374	0.78	0.41	0.61	1.03	0.8342	0.02	0.0211	0.0006
Yg G2.1	0	73	13.12	7.82	0.1432	0.99	0.85	0.89	1.52	1.1726	0.1	0.0144	0.0094
Yg G2.3	0.8	83.09	9.02	4.97	0.0549	0.51	0.2	0.25	0.9	0.8237	0.03	0.0121	0.0047
Yg G2.5	1.9	69.51	11.42	6.86	0.1398	1.51	7.15	1.03	1.11	1.066	0.03	0.0166	0.009
Yg G2.6	2.9	65.23	17.74	9.53	0.1401	1.84	1.09	1.5	1.61	1.3928	0.04	0.0283	0.0145
Yg G2.7	3.9	78.44	12.11	4.76	0.0507	0.95	0.42	0.79	1.34	1.055	0.02	0.0186	0.0053
Yg G3.1	0	67.76	16.1	9.5	0.1821	1.25	1.11	0.79	1.85	1.2961	0.12	0.0292	0.015
Yg G3.2	0.4	76.7	11.4	7.07	0.1111	0.92	0.79	0.53	1.25	1.1032	0.05	0.0205	0.0095
Yg G3.4	1	79.61	10.27	5.73	0.1499	0.73	1.2	0.6	0.96	0.9331	0.03	0.0146	0.007
Yg G4.1	0	65.2	17.4	10.09	0.1496	1.34	1.01	0.96	1.96	1.2935	0.14	0.0224	0.0149
Yg G4.2	0.4	71.99	13.6	8.53	0.1795	1.21	1	0.75	1.39	1.245	0.06	0.0243	0.0116
Yg G5.1	0	72.52	13.05	8.65	0.1411	1.02	0.85	0.75	1.51	1.1656	0.09	0.0231	0.01
Yg G5.3	0.4	77.14	11.47	6.5	0.1274	0.81	1.29	0.67	0.97	1.0803	0.03	0.0231	0.0078
Yg G5.4	0.9	66.51	11.88	7.04	0.1197	1.55	9.77	0.84	1.11	1.1631	0.03	0.015	0.0097
Yg GSP.1	0	74.23	12.2	7.24	0.1457	0.91	0.85	0.92	1.48	1.143	0.09	0.0271	0.0065
Yg GSP.3	0.8	83.53	8.37	4.73	0.0878	0.58	0.29	0.59	0.93	0.884	0.02	0.0197	0.0067
Yg GSP.6	1.9	70.68	12.03	7.2	0.174	1.47	4.53	1.25	1.12	1.1094	0.02	0.0266	0.0084
Yg GSP.7	2.8	66.31	16.41	9.54	0.19	1.86	0.52	1.71	1.52	1.327	0.04	0.0294	0.0138
Yg GSP.9	4	84.57	8.04	3.69	0.0487	0.61	0.28	0.53	0.97	0.7888	0.02	0.0177	0.0073

**Appendix F: XRD of bulk samples, peak intensities at specific d-spacings**

Sample	Depth M	Quartz Line			Clay Line 4.45	Plagioclase feldspar 3.14 - 3.19	Orthoclase feldspar 3.21 - 3.26	Extra Feldspar peak	Calcite 3.05
		4.26	3.33	1.81					
Fld C1.1	0	1550	5286	749	315	595	335		151
Fld C1.13	3.6	1140	5853	747	356	433	628		0
Fld C1.5	0.7	1183	6983	517	343	318	277	270	367
Fld C10.1	0	1062	4442	512	547	479	322		0
Fld C10.3	0.9	2316	7985	1130	316	677	344	317	0
Fld C2.1	0	640	1752	344	532	304	290		193
Fld C2.12	3.9	1315	4203	617	441	423	692		0
Fld C5.1	0	874	2956	343	666	355	296		0
Fld C5.3	0.85	748	2933	350	620	325	285		0
Fld C5.5	2.55	1077	3570	1277	492	603	478		0
Fld C7.1	0	868	3390	680	547	558	303		0
Fld C7.4	1.45	1049	4806	522	532	547	324		0
Fld C7.6	2.4	1352	4014	659	363	563	306		0
Fld C9.3	0.9	1522	5888	730	429	3504	435		0
Fld C9.5	1.5	1173	6479	639	357	279	612	276	0
Fld CSP.1	0	722	2843	319	735	300	362	242	0
Fld CSP.13	3.7	1230	4028	751	369	506	495	303	154
Totw C2 46	0	3164	15502	2052	0	96	210		0
Totw C2 48	0.8	3798	15591	2075	0	0	214		0
Totw C3 50	0	3179	16164	2141	113	107	304		102
Totw E1 253	0.9	2822	13269	1759	67	129	253		0
Totw E2 255	0.4	2785	12526	1597	118	155	288		0
Totw E3 258	0	1992	11359	1075	235	212	267		0
Yg D1 07/02	5.6	2131	10256	1346	280	323	234		0
Yg E1.13	4.5	1838	10084	1472	194	241	1125		194
Yg E1.3	0.45	2751	16242	1722	101	144	194		0
Yg E1.8	1.45	2381	9548	1742	309	329	166	250	166
Yg E2.1	0	3372	14986	1563	116	207	205		0
Yg E2.9	3.75	2255	12459	1273	295	163	249		0
Yg E3.11	3	1298	5250	720	263	0	0		1548
Yg E3.6	1.3	2908	14084	1803	288	212	223		0
Yg E3A.1	0	3098	15934	2019	174	172	460		0

Sample	Depth m	Quartz 4.26	LineClay 3.33	LinePlagioclase 1.81	feldspar 4.45	Orthoclase 3.14 - 3.19	Extra Feldspar peak 3.21 - 3.26	Calcite 3.05
Yg E3A.10	2.4	2215	8874	1057	343	194	239	1118
Yg E3A.6	1.4	3701	10662	1256	291	174	305	0
Yg ESP.1	0	3849	17149	1998	95	165	209	0
Yg ESP.10	3.5	2875	10708	1771	208	169	173	940
Yg ESP.3	0.8	3681	16286	1859	0	166	235	157
Std 1		3235	15037	2078	0	0	0	0
Std 2		3072	14788	2097	0	0	0	0

**Appendix G: Factor analysis of transformed XRF oxide data, including clay minerals**

<b>Sample</b>	<b>Factor 1</b>	<b>Factor 2</b>
Totw B1 14	-0.90333	-0.07108
Totw B1 18	-1.0035	-0.13731
Totw B1 22	-0.8776	-0.14237
Totw B1 26	-0.99385	-0.09009
Totw B2 7	-0.85511	-0.09386
Totw B2 9	-0.77756	-0.12487
Totw B2 11	-0.80801	-0.24784
Totw B2 13	-0.9158	-0.10619
Totw B3 1	-0.82492	-0.17234
Totw B3 4	-0.90359	-0.129
Totw B3 6	-0.88605	-0.14319
Totw A1 292	-1.00453	-0.06946
Totw A1 296	-1.00725	-0.13767
Totw A1 300	-1.05278	-0.14009
Totw A1 305	-1.02894	-0.10704
Totw A1 308	-1.01694	-0.16019
Totw A2 309	-0.96107	-0.09091
Totw A2 313	-0.96929	-0.10803
Totw A2 316	-0.97206	-0.16441
Totw A3 317	-0.77394	-0.25872
Totw A3 319	-0.93606	-0.16399
Totw A3 322	-0.95268	-0.14762
Totw C1 52	-1.00318	-0.05773
Totw C1 55	-1.0878	-0.15321
Totw C1 60	-1.06807	-0.15057
Totw C1 63	-1.0608	-0.09638
Totw C2 46	-0.94156	-0.07262
Totw C2 48	-1.06735	-0.13337
Totw C2 49	-1.07291	-0.14544
Totw C3 50	-0.96813	-0.08674
Totw C3 51	-1.07088	-0.13259
Totw D1 220	-0.98571	-0.10421
Totw D1 223	-1.06214	-0.16029
Totw D1 226	-1.07789	-0.17538
Totw D2 229	-0.99985	-0.19625
Totw D2 230	-1.04396	-0.18693
Totw D2 231	-1.09058	-0.20713
Totw D3 227	-0.93348	-0.17731
Totw D3 228	-1.0412	-0.1766
Totw D4	-0.284	-0.41504
Totw E1 250	-0.66391	-0.11431
Totw E1 251	-0.84856	-0.09028
Totw E1 253	-0.9286	-0.12593
Totw E2 254	-0.61144	-0.09809
Totw E2 255	-0.81447	-0.13181
Totw E2 257	-0.9224	-0.20264
Totw E3 258	-0.18332	0.06451
Totw E3 260	-0.57585	-0.1657
Totw E3 270	-0.90551	-0.15488
Totw E4	0.59853	-0.49447
Yg A1.1	-1.10712	-0.01702

Sample	Factor 1	Factor 2
Yg A1.2	-1.11189	0.00223
Yg A1.4	-1.10041	-0.01327
Yg A1.5	-1.13216	-0.0378
Yg ASP.1	-1.09805	0.0209
Yg ASP.4	-1.13021	-0.04027
Yg A2.1	-1.1103	-0.01365
Yg A2.2	-1.13335	0.00572
Yg A2.4	-1.14144	-0.03996
Yg A3.1	-1.05849	-0.05105
Yg A3.3	-1.14063	-0.03966
Yg A3.4	-1.10229	-0.0157
Yg A4.1	-0.95642	-0.04946
Yg A4.3	-0.80796	-0.21415
Yg A4.4	-1.09806	0.02326
Yg B1.1	-1.04121	-0.09623
Yg B1.2	-1.05912	-0.05149
Yg B1.4	-0.66634	-0.35216
Yg B1.6	-0.79399	-0.16076
Yg B1.9	-0.68701	-0.13418
Yg B1.11	-0.78884	-0.14916
Yg B2.1	-0.31882	-0.32413
Yg B2.3	-0.70727	-0.28251
Yg B2.5	-0.86948	-0.16346
Yg B2.6	-0.905	-0.12732
Yg B3.1	-0.62867	-0.23492
Yg B3.2	-0.99689	-0.04884
Yg B4.1	-0.97702	-0.10467
Yg BSP.1	-1.06535	-0.09272
Yg BSP.2	-1.06304	-0.00978
Yg BSP.4	-1.07523	0.03058
Yg B5.1	-0.94776	-0.0477
Yg B5.4	-1.09504	-0.0118
Yg B6.1	-0.50903	-0.21609
Yg B6.2	-1.00965	-0.04164
Yg B Lake 0-2	0.37453	-0.6935
Yg C1.1	-1.00729	0.00226
Yg C1.3	-1.05334	0.01508
Yg C1.5	-1.08598	-0.061
Yg C2.1	-1.00216	0.00208
Yg C2.3	-1.08456	-0.02855
Yg C2.4	-1.07448	-0.03472
Yg CSP.1	-1.01329	-0.10592
Yg CSP.3	-1.06011	-0.03773
Yg CSP.4	-1.04597	0.01226
Yg C3.1	-0.77926	-0.11901
Yg C3.3	-1.04918	-0.0459
Yg C3.4	-1.05084	-0.00894
Yg C4.1	-0.8656	-0.10262
Yg C4.2	-0.99149	-0.05591
Yg C4.3	-1.03979	-0.02845
Yg C5.1	-0.80762	-0.16995
Yg C5.3	-1.01662	-0.04512
Yg C Lake	0.1163	-0.7789

<b>Sample</b>	<b>Factor 1</b>	<b>Factor 2</b>
Yg D1.1	-0.84479	-0.00788
Yg D1.5	-1.01494	-0.16047
Yg D1.12	-0.84987	-0.19461
Yg D1.14	-0.77848	-0.15247
Yg D1.16	-0.65349	-0.16322
Yg DSP.1	-0.93018	-0.12956
Yg DSP.3	-0.95906	-0.11982
Yg D2.1	-0.76556	-0.19495
Yg D2.5	-0.92687	-0.24783
Yg D2.8	-0.85827	-0.20619
Yg D6.1	-0.8674	-0.16677
Yg D6.4A	-0.93117	-0.17054
Yg D6.9	-0.75556	-0.21381
Yg D7.1	-0.6451	-0.10393
Yg D7.3	-0.99877	0.19117
Yg D8.1	-0.45093	-0.22718
Yg D8.3	-0.86132	-0.11875
Yg D Lake	-0.80964	-0.184
Yg E1.1	-0.69348	0.09813
Yg E1.4	-0.83245	-0.03293
Yg E1.6	-0.59923	-0.13011
Yg E1.9	-0.17691	0.76846
Yg E1.11	-0.51498	0.13531
Yg E1.14	-0.2726	1.44602
Yg E2.1	-0.78865	-0.00517
Yg ESP.1	-0.80482	0.0578
Yg ESP.3	-0.88432	0.04982
Yg ESP.6	-0.5091	-0.02867
Yg ESP.9	-0.08261	1.79606
Yg ESP.11	-0.418	0.96881
Yg E2.4	-0.90783	0.00816
Yg E2.6	-0.74595	-0.12568
Yg E2.8	-0.24763	-0.08298
Yg E2.10	0.0838	2.85361
Yg E3.1	-0.79973	-0.02431
Yg E3.4	-0.79	-0.16104
Yg E3.8	-0.2589	-0.14881
Yg E3.10	-0.00894	0.32707
Yg E3.12	-0.12978	1.42679
Yg E3A.2	-0.81579	-0.16428
Yg E3A.5	-0.40719	-0.29658
Yg E3A.8	-0.19881	-0.21418
Yg E3A.11	0.94003	4.6531
Yg E3A.12	0.77875	5.36563
Yg E5.1	-0.54692	-0.30272
Yg E5.3	-0.7107	-0.05653
Yg E5.4	-0.77361	-0.23913
Yg E Lake	0.07079	-0.65065
Yg F1.1	-0.24941	-0.08983
Yg F1.4	0.56258	1.1755
Yg F1.6	0.87461	1.19077
Yg F1.8	1.21489	-0.63191
Yg F1.9	1.4052	-0.67525

<b>Sample</b>	<b>Factor 1</b>	<b>Factor 2</b>
Yg F1.11	1.39408	-0.64142
Yg F1.14	-0.44631	-0.28866
Yg F2.1	0.00278	-0.13801
Yg F2.3	0.71236	2.96316
Yg FSP.1	0.14824	-0.09902
Yg FSP.3	-0.01281	0.1334
Yg F Lake	-0.27171	-0.21114
Yg G1.1	0.10762	-0.03757
Yg G1.2	-0.13684	-0.05207
Yg G1.4	0.4764	0.60211
Yg G1.6	-0.06963	-0.26904
Yg GSP.1	0.71839	0.08166
Yg GSP.3	-0.00283	-0.02107
Yg GSP.6	1.01838	1.11465
Yg GSP.7	1.48854	0.14886
Yg GSP.9	-0.18633	-0.18719
Yg G2.1	0.77711	-0.04971
Yg G2.3	-0.15836	-0.3818
Yg G2.5	0.9416	1.47587
Yg G2.6	1.3937	-0.09524
Yg G2.7	0.23139	-0.35991
Yg G3.1	1.17037	-0.17778
Yg G3.2	0.42931	-0.19884
Yg G3.4	0.35321	0.29034
Yg G4.1	1.27271	-0.34561
Yg G4.2	0.91715	0.02213
Yg G5.1	0.7921	-0.15144
Yg G5.3	0.45224	0.1795
Yg G5.4	0.98544	1.83796
Yg G Lake	0.64904	-0.14432
Fld C0.1	0.41601	0.06004
Fld C0.3	0.59137	-0.02642
Fld C0.5	1.01077	0.62473
Fld C0.8	0.85766	0.51218
Fld C0.11	0.59036	0.35832
Fld C0.14	1.27803	0.5734
Fld C1.1	0.65863	0.0289
Fld C1.5	1.17135	1.41669
Fld C1.7	0.92684	0.48828
Fld C1.11	0.86878	0.06917
Fld C1.13	1.09648	0.17141
Fld CSP.1	1.32656	-1.36277
Fld CSP.5	0.89713	0.25916
Fld CSP.8	0.70469	0.38271
Fld CSP.11	0.69223	0.40647
Fld CSP.13	0.96378	0.18658
Fld C2.1	1.37609	-1.49674
Fld C2.3	1.09032	0.13703
Fld C2.6	0.83031	0.09063
Fld C2.9	1.19243	0.4281
Fld C2.12	1.33902	0.05902
Fld C5.1	1.52788	-1.15641
Fld C5.3	1.4397	-1.23761

Sample	Factor 1	Factor 2
Fld C5.5	1.35727	-0.11715
Fld C6.1	1.3351	-1.26204
Fld C6.3	1.60427	-0.39274
Fld C6.7	1.3235	-0.02011
Fld C7.1	1.19495	-0.90471
Fld C7.2	1.44605	-1.32128
Fld C7.4	1.58324	-0.34433
Fld C7.6	1.17207	0.10986
Fld C9.1	1.38309	-1.2846
Fld C9.3	1.19953	-0.10022
Fld C9.5	1.01139	0.1773
Fld C10.1	1.31599	-0.77196
Fld C10.3	0.71486	0.11812
Fld C10.5	0.09063	0.06085
<b>Fld A Mpanza</b>		
Fld A4.1	1.27004	-1.08223
Fld A4.3	1.31568	-1.02937
Fld A4.4	0.72083	-0.42078
Fld A3.1	0.25357	-0.1604
Fld A3.3	1.58469	-0.57918
Fld A3.4	0.21129	-0.10645
Fld ASP.1	0.24458	-0.00209
Fld ASP.3	0.49491	-0.05648
Fld ASP.5	0.04892	-0.02796
Fld A1.1	0.07085	0.01102
Fld A1.2	0.90799	-0.29531
Fld A1.4	0.9141	-0.35147
Fld A1.6	0.19844	0.16099
Fld A2.1	0.43933	0.37224
Fld A2.3	1.41836	-0.30123
Fld A2.5	0.11872	0.01137
Fld A7.1	0.42678	0.27674
Fld A7.3	0.9756	-0.29171
Fld A7.5	0.4303	-0.0122
Fld A7.6	0.08617	-0.00679
<b>Fld A Oxbow</b>		
Fld B1.1	0.06031	-0.09373
Fld B1.3	1.21663	-0.68014
Fld B1.5	0.83705	0.03264
Fld B1.7	0.64574	-0.17773
Fld B1.8	1.76987	5.4713
Fld B1.9	1.78686	1.24465
Fld B1.10	1.82071	1.89651
Fld B1.11	1.29534	0.60238
Fld B2.1	1.76933	0.8176
Fld B2.3	1.93081	1.75091
Fld B2.4	0.77191	-0.0947
Fld B2.6	0.81383	0.08001
Fld B2.9	1.02837	1.28819
Fld B3.1	1.48151	0.44588
Fld B3.3	1.705	1.82744
Fld B4.1	0.85344	0.09277
Fld B4.2	0.5996	0.03384
	1.42458	-1.22795
	1.13268	-0.17425

<b>Sample</b>	<b>Factor 1</b>	<b>Factor 2</b>
Fld B4.4	1.1155	0.7667
Fld B4.6	1.27585	2.222
Fld B4.7	1.03613	1.21124
Fld B4.8	1.06647	2.19356
Fld B5.1	1.65088	-1.25236
Fld B5.1G	1.44681	-1.32794
Fld B5.3	1.66299	-1.32066
Fld B5.5	1.47444	-0.55635
Fld B5.6	1.70196	0.12309
Fld B5.7	1.00367	-0.24996
Fld B Lake	1.56548	-1.44256
Montmorillonite	0.48912	0.14938
Kaolinite	0.74988	-1.21924
Vermiculite	4.46561	-5.39201
Microcline	1.39183	-5.05585
Plagioclase	1.55906	4.64343
Beidellite	1.46595	1.03725
Illite	1.18132	-3.28645

