# A GEOCHEMICAL INVESTIGATION OF THE LAKE SIBAYA SYSTEM, NORTHERN ZULULAND

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# GLOSSARY OF TERMS

**Authigenesis:** Defining a mineral formed in place (Emiliani, 1987).

**Benthos:** The assemblage of organisms associated with the solid-liquid interface in aquatic systems. (Wetzel, 1983).

**Congruent dissolution:** Dissolution of a binary mineral salt as a whole, to give equimolal quantities of either ion. (*cf.* incongruent dissolution). (Krauskopf, 1967).

**Endorheic system:** A closed inwardly draining lake system lacking outflow. (*cf.* exorheic lake) (Davies and Day, 1998).

**Epilimnion:** An upper lake water stratum of more or less uniformly warm, circulating, and fairly turbulent water characteristic of summer stratification. The surface waters of lakes of sufficient depth are generally heated more rapidly than the heat is distributed by mixing. As the surface waters are warmed and become less dense, the relative thermal resistance of mixing increases markedly. A difference of only a few degrees is then sufficient to prevent circulation, and to thermally divide the water column into an epilimnion, which essentially floats upon a cold and relatively undisturbed region, the hypolimnion (*cf.* hypolimnion) (Wetzel, 1983).

**Eutrophication:** An increase in plant nutrients that results in increased plant production. Excessive inputs commonly exceed the capacity of the ecosystem to be balanced. (Wetzel, 1983).

**Exorheic lake:** A lake system containing an outlet to the sea (Wetzel, 1983).

**Gyttja (yît'-ja):** A fine sapropelic sediment (mud) containing the remains of all particulate organic matter, inorganic precipitations and minerogenic matter. In a fresh state, gyttja is very soft and hydrous, with a dark greenish-grey to black colour. The organic carbon content of gyttja is less than 50%. Hansen (1959) distinguished between gyttja and dy (or tyrfopel), on the basis that the latter is brown in colour and contains a carbon content greater than 50 per cent. Both terms are of Scandinavian origin, introduced in the mid 19th century by von Post (Hansen, 1959) to describe the general character of organic sediments. (Wetzel, 1983).

**Hypolimnion**: The lowest water stratum in lakes of sufficient depth. The stratum is generally cold and relatively undisturbed, the temperature in this region changing little throughout the period of summer stratification. The final water temperature during the spring turnover (cf. epilimnion) determines the initial temperature of the hypolimnion. (Wetzel, 1983).

**Incongruent dissolution:** Preferential dissolution of the more soluble ion in a binary mineral salt, to yield different molal quantities of the individual ions. (Krauskopf, 1967).

**Macrophyte (aquatic):** The macroscopic forms of aquatic vegetation, encompassing macroalgae, the few species of mosses and ferns adapted to the aquatic habitat, as well as true angiosperms. Macrophytes may be either attached to the substratum (in which case they may be emergent, floating-leaved or submersed) or freely floating. (Wetzel, 1983).

**Meromictic lake:** A lake which does not undergo complete circulation, the primary water mass not mixing with a lower portion. (Wetzel, 1983).

**Metamict:** Defining a mineral whose crystal structure has suffered damage because of radionuclides present in trace amounts in the crystal lattice. (Emiliani, 1987).

**Neoformation (of minerals):** The precipitation of silica, alumina, iron, and the various base cations that are dissolved by primary mineral weathering to form new low-temperature minerals. The particular secondary minerals formed are controlled by the leaching intensity of the local soil environment, and by the extent to which the environment is confining, allowing the more soluble weathering products (silica, base cations) to accumulate. Neoformation is distinguished from weathering processes (alteration) in which part of the parent mineral structure is inherited by the weathering product. (McBride, 1994).

**Non-specific adsorption (oxides):** Electrostatic (coulombic) bonding of counter ions balancing surface charge. In a multicomponent system, ions of equal charge would be adsorbed according to their activity in solution. A certain degree of specificity may be introduced by ionic size or steric hindrances. (Schwertmann and Taylor, 1989).

**Oligotrophic lake:** A lake characterised by low nutrient inputs and low organic production. Nauman (1919) introduced the general concept of oligotrophy, which he based on phytoplanktonic populations. Oligotrophic lakes contained a few planktonic algae, and were common in regions dominated by primary rocks. (Wetzel, 1983).

**Pelagial water:** The free open water in a lake, separable from the bottom of the lake basin and the littoral zone. (Wetzel, 1983).

**Primary mineral:** A mineral that is formed at the same time as the rock in which it is contained, and that retains its original form and composition. (McBride, 1994).

**Regic (sand):** A recent (usually aeolian) deposit, which, except for a possible darkening of the topsoil by organic matter, shows little or no further evidence of pedogenesis. Such deposits are usually coarse-textured and of loose, friable or soft texture (Dixon and Weed, 1989).

**Seston:** A collective term for all particulate material present in the free water. Seston includes both bioseston (plankton and nekton) and abioseston or tripton (nonliving particulate material). (Wetzel, 1983).

**Specific adsorption (oxides):** Stronger surface bonding of anions and cations at a mineral surface than non-specific bonding. This is because the adsorbate is able to penetrate the coordination shell and, by ligand exchange, becomes covalently bound directly to the structural cation via O and OH groups. Also termed chemisorption or ligand exchange. (Schwertmann and Taylor, 1989).

# ABSTRACT

Lake Sibaya (27°15′–27°25′S; 32°32′-32°44′E) is situated in the northern region of the Zululand coastal plain, and is remarkable in that it embodies a near-pristine freshwater coastal lake preserving clear residual signs of its former estuarine origin. Despite the fact that the lake constitutes perhaps the most intensively studied of all freshwater bodies in South Africa, little is known of its geochemical character. The objective of this study was therefore to conduct an investigation of the waters and sediments of the lake system, which might then provide a chemical baseline against which the future environmental quality of the system could be gauged, and in terms of which the current functioning of the ecosystem can be better understood.

In line with this rationale, water and sediment samples were collected from each of fourteen sampling sites located along three transects running, variously, S-N, SW-NE and W-E across peripheral arms of the lake. Waters in direct contact with the sediments were thoroughly agitated with the sediments and thereafter decanted for analysis. Since the lake is purported to be fed almost exclusively by groundwater flow, water samples were collected from three groundwater wells located north-west of the lake. The Department of Water Affairs (DWAF) databases for groundwater chemistry, and for lake level and chemistry over the period 1980 to 1998, were used to supplement this data, and to provide an indication of any medium-term parameter changes. A water sample was also collected from the non-perennial Mseleni River, although the river is known to contribute minimally to the lake volume. The majority of laboratory analyses were conducted within the Department of Geological Sciences at the University of Cape Town, adhering to standard analytical methods wherever possible.

The water column was found to be thoroughly mixed by wind action, with narrow pH (8.0 to 8.3) and EC (543 to 566 µS/cm) ranges being recorded. Bicarbonate alkalinity (≈ 130 mg $HCO_3^-$/l) appeared to effectively buffer the solution pH. The groundwaters appeared to be equally well buffered, through alkalinity generated via the dissolution of carbonate minerals, primary aluminosilicates and $CO_2$ (produced by metabolic activity) in the aquifer sands. Bicarbonate constituted the dominant ion in the groundwaters.

Two distinct types of sediments were identified within the collected samples. The minority (2 of 14) of the sediments represented accumulations of fine sapropelic mud (gyttja) containing in excess of 20% organic carbon. Such accumulations comprised decomposing littoral matter incorporated into the sediment during high lake levels, and subsequently deposited in tranquil regions of the lake bed by water currents and sediment slumping. The elevated alkalinity (319 to 557 mg $HCO_3^-$/l) of the sediment-contacted waters presumably derives from the raised levels of soluble organic acids associated with this gyttja. The remaining sediments are predominantly fine-grained (0.25 to 0.106 mm), siliceous sands overlain only by a fine layer of gyttja, and consequently organic-poor (≤4%). These sediments derive mainly from Quaternary coastal dune sediments, which have been reworked and sorted by wind-generated currents and waves, acting at various lake levels. Their meagre carbon content arises from low levels of primary productivity, the decomposition of particulate organic matter within the water column, and subsequent methanogenesis within the anaerobic sediments. The dissolved organic matter (DOM) thus released, complex readily with metal cations (in the ascending order of affinity Mg < Zn < Ca < Cu) and/or are rapidly recycled through the food chain. None of the trace elements investigated appeared to associate with organic carbon in the sediments, suggesting that many of the reactive ligands had been lost during decomposition.

The minimal clay fraction (≤ 6% combined silt and clay) of these sandy sediments was dominated by quartz and kaolinite, with a subdominant mica and 2:1 layer silicate (probably smectite) component. The low reactivity of these sands translated into a low CEC. This is borne out by the relatively weak association between the content of clay and each of Sr, Zr, Nb, Cr, V and Y, not all of which are necessarily causally correlated with the reactivity of the clay. As could be expected under the intensive leaching regime of the Zululand coastal plain, the alkali metals have been predominantly removed from the aquifer sands of the lake catchment. The comparatively high levels of Ca in these sands (Pooley, 1996), and in the lake sediments, may relate to the occurrence of the Ca titanosilicate mineral, sphene, which would likely constitute a mechanism of slow Ca release upon weathering. This aspect requires confirmation. Total and labile concentrations of calcium were generally suboptimal, but probably not sufficiently so, as to incur a major limitation on the distribution and abundance of various algae, molluscs or crustaceans.

Atmospheric control over major ion composition would appear to outweigh that exerted by the local geology. Evidence to suggest that the lake waters are evaporated above their feeder groundwaters comes by way of climatic data, isotopic fractionation, the disparity in EC (60 to 70% difference) between these respective waters, and the inverse relationship observed between TDS and lake level. The rate at which the lake water is concentrated up by evaporation appears to be limited, judging from the low ionic strength. Exposures of diatomaceous marl, near the lake, provide an historical precedent for evaporative concentration of the lake water, albeit at lower lake levels during the Last Glacial Maximum.

Calculations using the MINTEQA2 chemical model predicted the incipient precipitation of calcite from the lake waters. The absence of detectable carbonate in the sediments suggests that reaction kinetics are not favourable to calcite crystallisation. Forward modelling of additional evaporative concentration, using the PHREEQC chemical model, suggests that additional evaporation of these waters to approximately one hundred times present concentration would see the precipitation of both magnesite and gypsum. The composition of the residual water would then likely tend towards a Na-Cl dominated brine, with relatively minor contributions of Mg and $SO_4$. It is unlikely, however, that the lake waters will be evaporated to such an extent in the foreseeable future. The pelagial waters of Lake Sibaya are presently dominated by Na and Cl (both ≈ 4.0 $mmol_c/l$), with relatively high contributions of $HCO_3^-$ (≈2.3 $mmol_c/l$), Ca (≈2.0 $mmol_c/l$) and Mg (≈1.3 $mmol_c/l$). The PHREEQC model differs from the conceptual Hardie-Eugster model of evaporative concentration, in that it does not necessarily require the precipitation of supersaturated minerals to proceed independently of each other.

The solubility equilibria established between the solid and aqueous phases of the lake system will undoubtedly exert a degree of control over the bioavailability of nutrient elements. MINTEQA2 calculates the pelagial and sediment-associated waters to be in near-equilibrium (SI ≈ 0.1) with respect to quartz (although slow reaction kinetics are likely to prevent its contemporary crystallisation) suggesting that the latter water samples have a composition approaching that of interstitial waters. The limit to dissolved silica is rather set by the solubility of amorphous silica (SI ≈ -0.9), which, in turn, is presumably governed by the dissolution of diatom frustules upon senescence. Levels of Si are uniformly sufficient (≈5 to 45 mg $SiO_2/l$) throughout the lake body to favour the dominance of diatoms above the non-siliceous algae. The large disparity noted between the diversity and number of diatoms within the various sediments is rather proposed to arise through the attenuation of light within the water column.

# CHAPTER 1: INTRODUCTION

The only significant natural true lakes in South Africa are its coastal water bodies. Southern Africa possesses two major groupings of coastal lakes which date back to the Pleistocene era. A closely contiguous group of lakes occurs in the Wilderness area (south-eastern Cape), whereas a northern series of lakes are dispersed over the sandy coastal plain of northern KwaZulu-Natal and southern Mozambique. Lakes of the northern series are widely spread from Durban in the south to Lagoa Poelela in the north. Lake Sibaya occurs as one of the lakes in the northern series, and constitutes the largest natural freshwater lake in the country. It is isolated from the Indian Ocean by means of a narrow range of forested sand dunes, which attain altitudes of up to 165m. Recent geohydrological studies (Meyer and Godfrey, 1995; Meyer *et al.*, 1993) have indicated that Lake Sibaya is fed almost exclusively by the shallow groundwater aquifer of the Zululand coastal plain.

Considerable research has been conducted on various aspects of the lake and its environs over the past three decades. Despite the plethora of information that has emanated from these studies, no comprehensive investigation of the aqueous and sedimentary chemistry of the lake and its associated waters has ever been conducted. As a virtually endorheic water body, Lake Sibaya is particularly susceptible to pollution introduced into the diffuse catchment. Geochemical characterisation of the system in its present state would provide an indication of baseline conditions against which future water quality could be assessed.

Micronutrient levels have been demonstrated (Pooley, 1996) to occur at suboptimal levels in soils and crops of the Mseleni region adjacent to Sibaya. Similar deficiencies may well occur in the lake system, with possible significant repercussions in terms of ecological functioning. The advent and advancement of analytical techniques such as inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence spectrometry (XRFS) have allowed for accurate detection of minute concentrations of trace elements in solutions and solids. Applying these analytical techniques to water and sediment samples from the Lake Sibaya system would, therefore, enable a comprehensive investigation of the geochemical dynamics in the lake system to be made, to a level of detail previously considered impossible. This represents a crucial milestone in terms of understanding the character and functioning of the Lake Sibaya system.

In line with this goal the following primary study objective has been identified:

- ***To establish the geochemical character of the waters and sediments of the Lake Sibaya system. Such a characterisation would provide a chemical baseline against which the future environmental quality of the system may be gauged.***

Further objectives have been identified which will serve to explore the derivation and potential biotic implications of Lake Sibaya chemistry, namely:

- ***To identify the processes which are most likely to influence the major ion composition of the Lake Sibaya waters.***

- ***To investigate the degree of geochemical similarity between the waters of Lake Sibaya and groundwaters of the Zululand coastal plain aquifer. The literature indicates that the lake is fed almost solely by shallow groundwaters.***

- ***To establish whether the waters and/or sediments of the Lake Sibaya system are deficient with respect to macro- and/or micronutrients considered essential for biological functioning.***

# CHAPTER 2: THE LAKE SIBAYA SYSTEM AND FACTORS AFFECTING ITS CHEMICAL COMPOSITION – A REVIEW

## 2.1 INTRODUCTION

Lake Sibaya (27°15′ – 27°25′S; 32°32′ - 32°44′E) is situated on the seaward margin of the low-lying coastal plain in eastern Zululand (refer to Figure 2.1). This permanent freshwater lake is isolated from the Indian Ocean by a narrow range of forested sand dunes, which attain altitudes of up to 165 m. Lake Sibaya is the largest natural freshwater lake in the country, with an average volume of 700 x $10^6$ $m^3$ and a mean depth of 10.9m. The total catchment area is estimated at 530 $km^2$, of which roughly 60-70 $km^2$ comprises the lake surface itself. The lake is situated on state land and falls under the local jurisdiction of the KwaZulu-Natal Government. The water surface was proclaimed, in 1994, as a Nature Reserve in terms of the KwaZulu Nature Conservation Act, and is managed by the KwaZulu Bureau of Natural Resources. Lake Sibaya was awarded RAMSAR status as 'a wetland of international importance, especially as a waterfowl habitat' on 28 June 1991.

The surrounding land is predominantly rural, and is jointly administered by three different chiefs, namely: Zikhali, Nxumalo and Tembe. The amaThonga who inhabit the vicinity of Lake Sibaya differ linguistically and culturally from the other African people of southeast Africa. The population within a 5km radius of the shoreline of Lake Sibaya is estimated at 1451 people (631 huts), at an average population density of 3.12 persons/$km^2$ (ILEC Webpage). The majority of local inhabitants rely on subsistence agriculture (following a shifting cultivation method). The region is heavily grazed by livestock, and natural resources (fish, reeds, sedges and wild fruits) are used in everyday routine. Domestic water use from the lake is estimated at 63 100 $m^3$/year (ILEC Webpage). Large plantations (predominantly *Pinus* and cashew) were established to the north (near Mazengwenya) and south (near Mbazwana) of the lake. The combined extent of the former plantations is approximately 70 $km^2$ (ILEC Webpage). Pulp mills constitute the only form of secondary industry located within the catchment area of the lake.

The lake and its catchment are at present largely unspoilt. The remote situation of Lake Sibaya, in an area proclaimed for rural development since 1936, has limited the extent to which the lake has been utilised on an intensive basis. The rapidly expanding population of Zululand, and the initiation of the Spatial Development Initiative (SDI), linking the Northern Zululand region to Mozambique, both physically and economically, may soon alter this situation.

Numerous studies were conducted in the region during the 1960's and 1970's, following the establishment of a Research Station at the lake. This research was focussed primarily on ecological and, more particularly, limnological aspects. The station was abandoned in 1976 following intense flooding. In recent years there has been a renewed interest in the geohydrological and sedimentary aspects of the Zululand coastal plain. This chapter presents an account of the findings of these and subsequent studies. The author speculates as to which factors are likely to exert a significant effect over the geochemical nature of the lake, drawing on appropriate case studies from the literature where necessary. For further details of scientific studies conducted in the region, the reader is referred to Allanson (1979) and to Bruton and Cooper (1980).

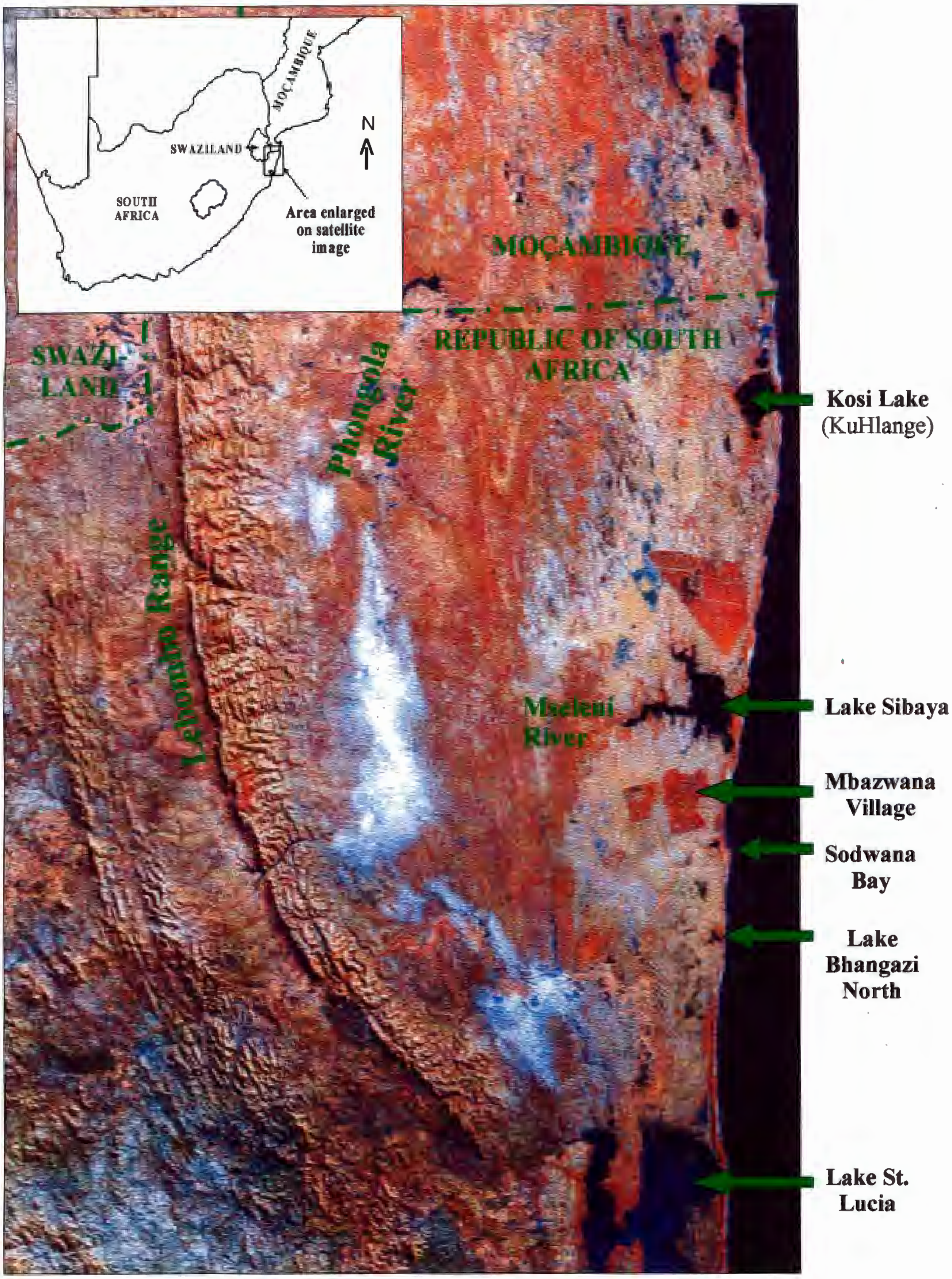

**Figure 2.1:** The location of Lake Sibaya within the Republic of South Africa
Scale 1:1000 000

## 2.2 STRATIGRAPHY: SEDIMENTS AND SOILS

### 2.2.1 The evolutionary history of Lake Sibaya

Hill (1975) recognised that the coastal lakes of southern Africa could be categorised, (on the basis of their geomorphological origin) into one of three types, namely drowned valley lakes, inundation lakes, or deflation basins. Coastal lakes of the Zululand coastal plain fall within the former category. Several of these lakes (e.g. Sibaya and Mzingazi) are presently fresh, but possess relict estuarine/marine components disclosing their estuarine origins (Fowles and Archibald, 1987). The following general model was presented by Wright (1991) to describe the evolution of the coastal plain.

Rifting associated with the break-up of Gondwanaland formed a shallow sea by the late Cretaceous, with the beach raised approximately 130 m above present levels. Steep gradient rivers, carved eastward of the Lebombo Mountains, formed large fluvial outwash pans, which were subsequently worked into beaches by wave action. Erosion of the mountains caused the rivers to decrease their gradient thereby creating coastal lagoons by the Neogene (Mio-Pleiocene). Beach sediments were reworked by the prevailing winds into a large coastal dune cordon. Raised sea levels (+5m above present levels) during the Last Interglacial (± 125 000 BP) had three main effects. The Lebombo Mountains and the Neogene dune cordon were eroded down. A new dune cordon was subsequently formed along the late Pleistocene shoreline. Finally the rivers were forced to migrate northward, thereby forming the palaeo-Pongolo system, due to decreasing river gradients and the formation of a barrier dune complex.

Rejuvenation of rivers, associated with a sudden sea-level drop to 130 m below present levels approximately 18 000 BP, led to their incision into the unconsolidated sediments of the coastal plain (Hill, 1975). Over the period 15 000 to 18 000 BP the Pongolo River (which flowed into Lake Sibaya) deposited fluvial sediments directly onto the continental slope, by exploiting the route of least resistance along the axes of White Sands- and Wright- Canyons (Ramsay, 1991). Subsequent sea level rises during periods of interglaciation [labelled the Flandrian Transgression (Mörner, 1970)] culminated in the flooding of these river valleys and the reactivation of old inland dunes, thereby redistributing sand over the coastal plain. Unconsolidated sediments were transported by longshore- and onshore- drift, creating sandbars across the outlet of the Lake Sibaya estuary. Behind this dune cordon estuarine conditions prevailed, in which lacustrine and fluvial sediments were subsequently deposited. The range in present depths of individual lakes in the region can be attributed to the different siltation rates of the influent river systems. Radiocarbon dating conducted on the bottom sediments of Lake St. Lucia indicated that the sediments were laid down during the last 4 000 years (Meyer, 1991), as may well be the case for the Lake Sibaya estuarine system. Fluvial flow via the Pongolo River was insufficient to prevent the encroachment of sandbars, with the result that the river was eventually dammed behind the dune barrier. The youngest dune cordon was thereafter heightened, through both the reworking of shelf sediment in an onshore direction and the northward drift of delta deposits further south along the shelf (Ramsay, 1991). Sea level stabilised to its present level 7 000 – 6 000 years BP (Mörner, 1970; Tankard, 1976).

### 2.2.2 Sedimentology and bathymetry of Lake Sibaya

The bathymetry of Lake Sibaya is presented in Figure 2.2, reproduced by kind permission of W.R. Miller of the Council for Geoscience in Durban. As mentioned previously, the bathymetry of Lake Sibaya is representative of an erosion surface created during the Last Glacial Maximum, and subsequently isolated from the Indian Ocean through the development of a coastal dune barrier 5000 years BP (Miller, 1998). The lake is bedded on predominantly fine-grained aeolian sands of Pleistocene to Recent age. Fluvial sedimentation of the lake has been minimal, owing to the dominance of ground water recharge over surface runoff (Pitman and Hutchinson, 1975). Rather, sedimentation has been restricted to the redistribution and sorting of sand sized sediments in the shallower areas around the lake margin (Miller, 1996). These processes are governed by oscillating water levels (generated in response to rainfall) and the action of water currents and waves (generated through wind action).

Erosion of the coastal dune cordon adjacent to the east bank of Lake Sibaya during high lake levels increases the contribution of aeolian sediment to the lake sediment. These lake sediments are transported as sub-aqueous dunes which migrate in a downwind direction, to form large-scale bedforms, which prograde outwards from lake margins (Miller, 1998). Wave-cut terraces are developed during lake level still-stands, and are characterised by moderately to well sorted sediments with a fine to medium sand grain-size. This suggests that the actions of waves and currents in these shallow waters rework the sediment, removing the finer sand fraction to deeper water. Miller (1998b) noticed an inverse relationship between grain-size and water depth.

Seismic profiling and the analysis of sediment cores collected from Lake Sibaya (Miller, 1996) indicated a sequence of fine grained loose aeolian sands of late Pleistocene vintage resting unconformably on sediments of the Port Durnford Formation. Within depressions in the former sequence are preserved isolated lenses of freshwater diatomite. Radiocarbon dating placed a minimum age of younger than 25 500 BP and a maximum age of > 43 500 BP on the diatomite. A thin palaeosol separates the diatomite from the older aeolian sediments (Miller, 1996).

Breaching of the coastal dune barrier, and the deep incision of the valley now underlying Lake Sibaya, was concordant with the last glacial maximum (± 18 000 BP) when sea level was at -180m (Miller *et al.*, 1997). Subsequent rebuilding of the coastal barrier began to occur during the Flandrian Transgression, through deposition of a series of marine washovers. With the recovery of sea level to its present elevation and the re-establishment of the coastal barrier circa 7 000 BP, sediments began accumulating, initially within a marine lagoon, and subsequently within a coastal lake environment as exists today. Cores analysed by Miller (1996) revealed a thin veneer of fine sapropelic lacustrine muds (gyttja) overlying marine lagoonal sediments.

Miller (1996) identified five sediment types in and around Lake Sibaya, namely: gyttja (organic muds), ground-water ferricrete, diatomite, red consolidated dune sand, and quartz sand.

Gyttja deposits are found within the deeper, sheltered areas of the lake, where current velocities are sufficiently tranquil to facilitate this material dropping out of suspension (Figure 2.3). The gyttja exposures are apparently preserved at depths exceeding 22 m in the main basin. Reduced wind fetch and complex bathymetry retard the current velocities to such an extent in the southern basin; and in the northern-, western-, and south-western arms, that gyttja accumulates at depths of –10m and greater. A total surface area of 11.6 km$^2$ of the lake (16%) is underlain by such gyttja.

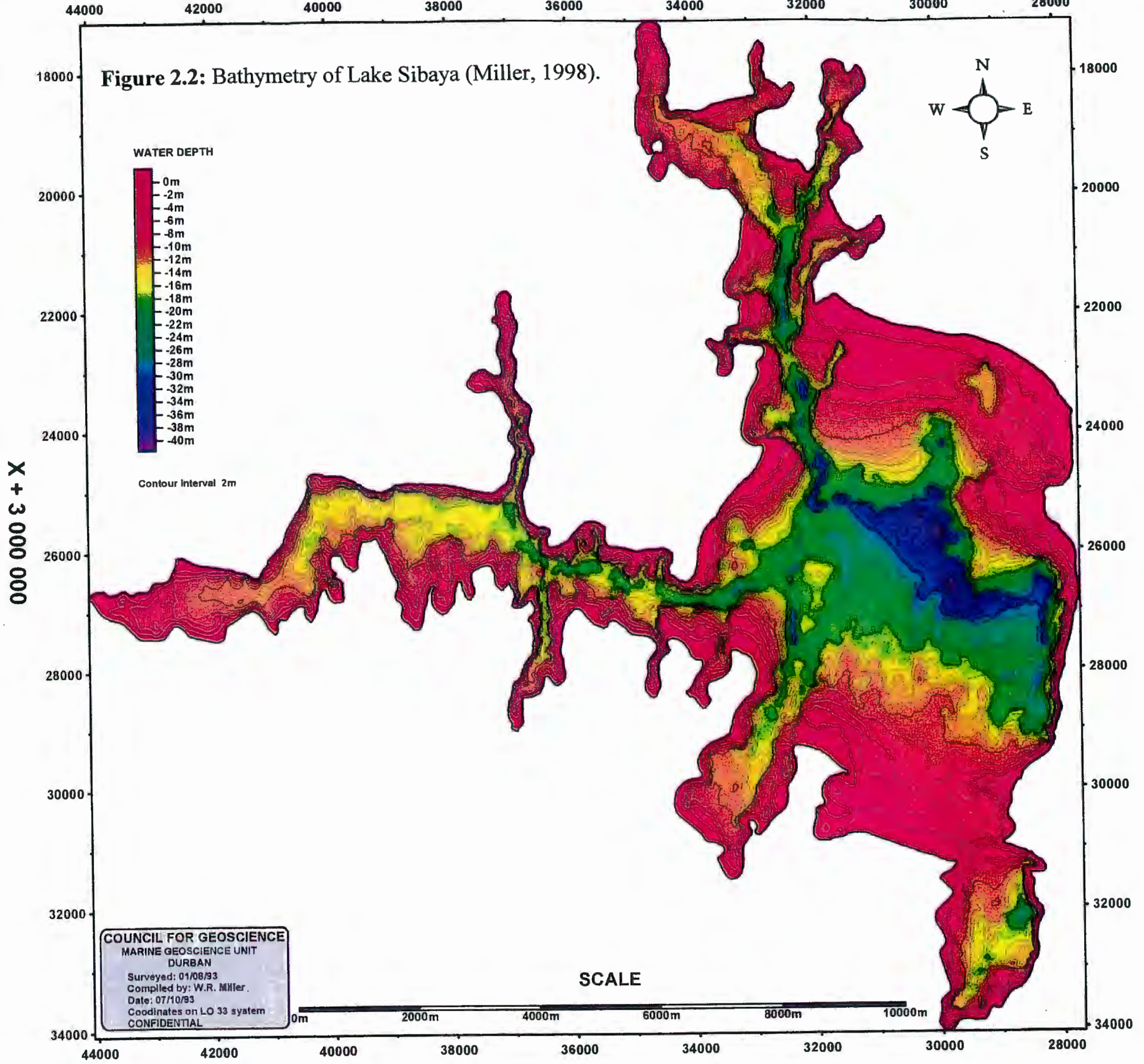

**Figure 2.2:** Bathymetry of Lake Sibaya (Miller, 1998).

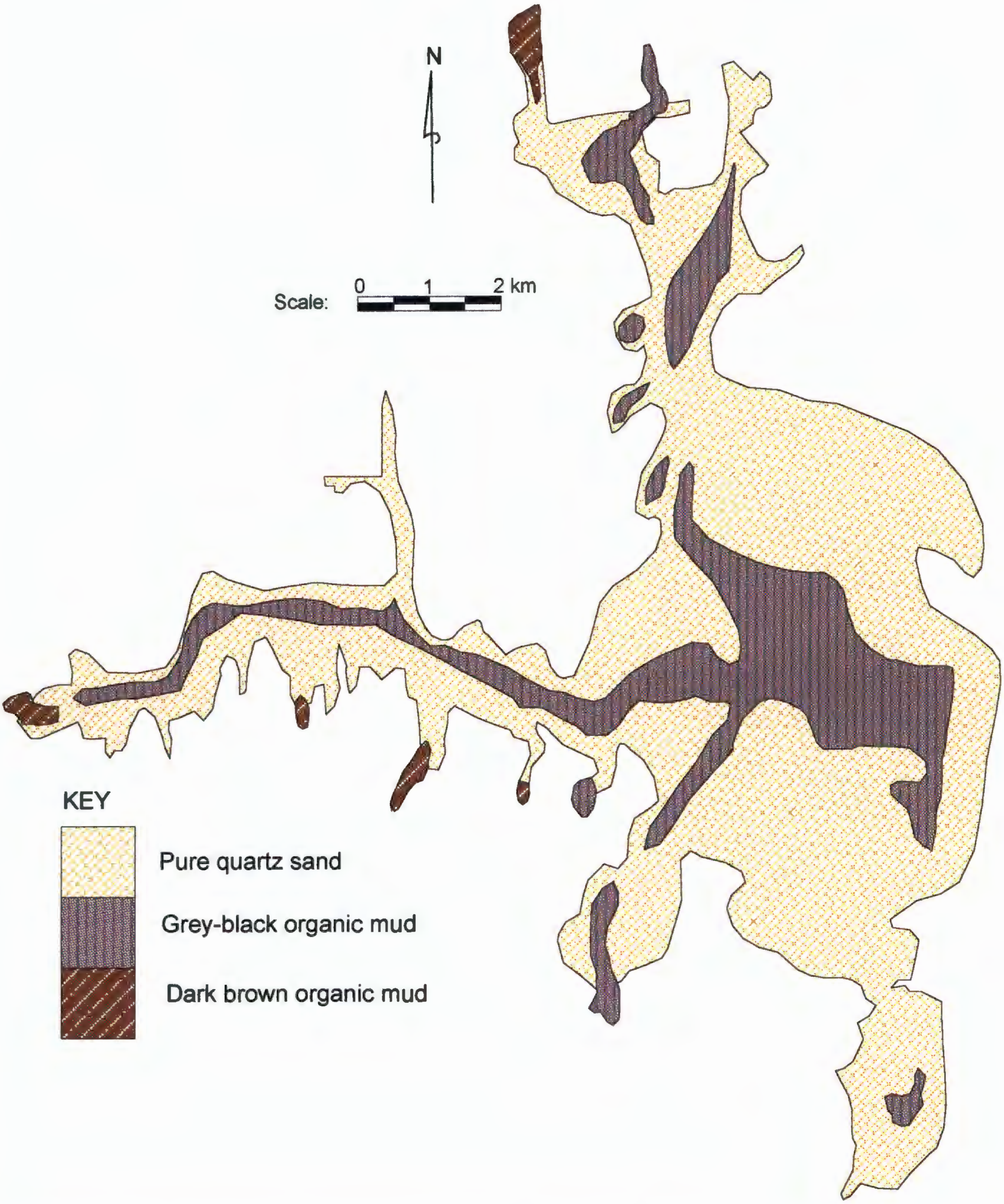

Figure 2.3: The distribution of sediment types in Lake Sibaya (after Miller, 1998).

Gyttja is a dark grey to black organic-rich sapropelic mud, consisting of the breakdown products of fringing vegetation that is destroyed during periods of high lake levels. Miller (1996) claims that the high methane content of such deposits results in their characteristic dome shape on the lake floor. Average sand (>63 µm) and organic carbon contents of 22% and 27%, respectively, were reported by Miller (1998).

Outcrops of ground-water ferricrete occurring intermittently around the periphery of Lake Sibaya, and below its water level, constitute the only lithified material exposed in the immediate vicinity (Miller, 1998). Ferricrete nodules of 20 mm to 2 000mm diameter consist of sub-angular to rounded nodules coated with ferric oxides. The mineral composition of such ferricretes is typically in the order of 66% quartz, 17 % feldspar, 12 % heavy minerals and 5% lithic fragments (Miller, 1998). The high feldspar content of these nodules may relate to occlusion by the ferric oxide coating, preventing further weathering of the feldspar (*pers. comm.* Willis, Prof. J.P, Department of Geological Sciences, University of Cape Town).

Anderson (1904) identified intermittent diatomite exposures, 10 to 15 metres in thickness, along the incised valley sides of the Mseleni River and in the low cliffs along the western margin of the lake itself. Eroded remnants of diatomite deposits are also located beneath Lake Sibaya, where they overlie the drowned dune topography of the Kosi Bay Formation (Miller, 1996). The diatomites represent late Pleistocene lacustrine siliceous deposits, comprising of microscopic diatom cell walls (frustules) that accumulated under variable climatic conditions between ± 45 000 BP and ± 20 000 BP (Miller *et al.*, 1997). The diatomite exposures were shown to be punctuated with horizons rich in freshwater molluscs and black horizons rich in organic material (Miller, 1996).

Two diatomite exposures (both being borrow-pits for road construction) are located in the immediate vicinity of the Msleni River water sample collection point (refer to Figure 3.1). Their diatom content is relatively low, their composition generally consisting of a grey calcareous, shelly marl, including a number of organic palaeosol horizons and a probable microbialitic, silcrete horizon (Maud *et al.*, 1993). The high percentage of lime is accounted for by the presence of large quantities of fossil land shells and Ostracoda in the deposit. The friable marl has a CaO content of approximately 40% (Anderson, 1904). An organic clay horizon located in the clay band of one of the exposures produced C$^{14}$ dates of 32 100 ± 580 BP ($\delta$ $^{13}$O=-0.1‰) (*pers. comm.* Dr. R. Maud, Drennan Maud and Associates). The calcareous marl of the second borrow pit yielded a slightly older C$^{14}$ date of 36 400 ± 460 years BP ($\delta$ $^{13}$O=+5.6‰) (*pers. comm.* Dr. R. Maud). Organic matter in the lowermost horizon of a larger diatomite excavation, approximately 5km southwest of the Mbazwana settlement, yielded a C$^{14}$ age of 24 800 ± 350 years BP (Maud *et al.*, 1993). The diatomite deposits are underlain and overlain by aeolian sands of the KwaMbonambi Formation (Formation name pending).

Maud *et al.* (1993) propose that the benthic and the few epiphytic forms of diatoms present in the various horizons clearly reflect a progressive shallowing of the lake with time, the diatoms present in the uppermost horizon indicating a very shallow water environment. These findings are consistent with the general trend of wetter conditions over southern Africa during Isotope Stage 3 (± 40 000 –25 000 years BP), the age of the basal portion of the diatomite sequence at Mbazwana placing this occurrence near the end of this Isotope Stage. Likewise, the shallowing of the lake corresponds with the onset of widespread drier conditions of Isotope Stage 2 (the Last Glacial Maximum).

Red consolidated "Berea type" ancient dune sediments occur as an isolated exposure in the northern arm of Lake Sibaya. These sediments are distinguishable from the younger dune sands by virtue of their red-brown colour, their semi-consolidated nature and their finer grain size (Miller, 1998). The relatively high mud fraction of such sediments (10 – 15% of the total sediment) is dominated by quartz grains, kaolinite and an amorphous aluminium-iron hydroxide (Dunlevey, 1997). The mineralogy of the bulk sediment is primarily siliceous (75 – 90% quartz), the remaining mass comprising of heavy minerals (2-20%) and feldspar (<3%) (Dunlevey, 1997).

Wright (1991) and Miller (1996) determined that the sand grains lying at the sediment-water interface below Lake Sibaya derive from different generations of aeolian dunes. The lake floor sediments were reworked and sorted by wind-generated currents and waves, acting at various lake levels. The sediments of a large area in the south of the main basin, and almost the entire southern basin, display great similarity with aeolian sediment, suggesting a more recent input of aeolian sediment into this area of the lake. The sediments typically comprise fine to medium grained, moderately to well sorted sand with near symmetrical grain size distributions. The mud content of such sediment is typically less than 2%, but can reach levels as high as 20%. The mineralogy of the sand fraction is dominated by quartz (± 99%), with minor amounts of feldspar, heavy minerals, organic matter ($\bar{x} < 1\%$, maximum = 8%) and shell fragments. The heavy mineral concentrations are highest along the eastern shores of the main basin, adjacent to the coastal dune cordon. A total of 62.4 $km^2$ (84%) of the lake surface area is underlain by this clean quartz sand, varying in colour from white to light olive (Miller, 1998).

The surface sediments of Lake Sibaya were shown (Miller, 1998) to be, for the large part, well sorted, fine grained sands with a coarse skewed grain-size distribution. Approximately 64% of surface sediments are classified as being well sorted ($\phi$ = 0.35 to 0.5), 27% as being moderately well sorted ($\phi$ = 0.51 to 0.7), 7% as being very well sorted ($\phi < 0.35$) and 2% as being moderately sorted ($\phi$ = 0.71 to 1.00). The coarse skewed grain-size distribution of the bed sediments distinguishes them from modern aeolian sediments peripheral to the lake. Miller (1998) suggests that this indicates winnowing of the sediments that were associated with a channel lag deposit formed on the lake site during the Last Glacial Maximum. Furthermore, the very slow sedimentation rate in Lake Sibaya would contribute to the predominance of coarse skewed grain-size distributions on the lake floor.

### 2.2.3 Soils of the Zululand coastal plain

The Zululand Coastal Plain is composed predominantly of Quaternary sediments. The sands, clayey limestones and diatomites of the Port Durnford Beds were deposited under marine shallow-water, terrestrial and fresh-water lacustrine conditions, following erosion of the underlying Tertiary sediments (Hobday, 1979; Maud, 1980). This formation extends from eastwards of the Pongola River to the coastline and does not appear to exceed approximately 50 metres depth (Hobday, 1979). Reworking of the surface of this formation in later Pleistocene and Recent time by wind-action has produced a linear north-south trending dune cordon of grey Fernwood form sands overlying either the coastal sandy limestone or the Port Durnford Beds. In the northern section of the coastal plain, six palaeo dune cordons age progressively away from the coast (Meyer and Godfrey, 1995). The most pronounced and youngest of these is the present dune cordon stretching from Port Durnford in the south to the Mozambique border in the north, skirting the eastern shore of Lake Sibaya in the process. This very young, relatively high coastal dune ridge along the shoreline is stabilised only by its vegetation (Hobday, 1979).

These Quaternary sands are characteristically acidic and of low water-holding capacity (Maud, 1980; Pooley, 1996). Grey sands of the Fernwood form are characterised by a poorly developed orthic A horizon overlying a deep E horizon. These soils were shown by Pooley (1996) to be moderately acidic ($pH_{H2O} \approx 5.8$) and highly weathered, rendering them inherently infertile. Low effective cation exchange capacity (<2 $cmol_c/kg$) of these soils is associated with low clay content (< 4%, of which most is kaolinitic) and minimal (<1.5%) organic carbon (Pooley, 1996). Pooley (1996) described the concentration of calcium within Fernwood soils of the Mseleni region (250 mg/kg) as being suboptimal for crops. He further classified several plant nutrients as being deficient in these soils, including P (1.9 mg/kg), Zn (0.4 mg/kg), Cu (0.4 mg/kg), B (0.4 mg/kg) and Mn (4.5 mg/kg). In response to these low nutrient levels, the local Tonga-Zulu rural population practices shifting slash-and-burn cultivation methods, in an attempt to temporarily boost nutrient levels required for satisfactory crop yields. The water table in the eastern region of the coastal plain is perched on the surface of the more clayey and impermeable Port Durnford Beds, with the result that interdune areas are waterlogged. By contrast, rapid drainage through the deep sands of the relatively drier (≈ 700 mm) western regions of the coastal plain, proves deleterious to agricultural practices.

## 2.3 GROUNDWATER

The Zululand Coastal Plain is probably the largest primary aquifer in South Africa (Meyer, 1991), but has, due to the generally high rainfall in the region, received little attention in terms of water supply. The extensive overburden of aeolian sands renders the application of conventional field mapping techniques ineffective. Geophysical techniques (resistivity, electromagnetic and gravity) are, therefore, often employed to determine the thickness to the top of the Cretaceous, and to identify drilling targets. A brief account of the current state of knowledge regarding the hydrogeology of the Zululand coastal plain follows. The relative abundance of recent studies reflects the renewed interest in the groundwater of this region as an exploitable resource by the local inhabitants. The geometric mean blown borehole yield (i.e. the average immediate "blown test" borehole yield) for the Zululand coastal plain region falls within the maximum category (>3 l/sec) for the country (Seymour and Seward, 1996).

### 2.3.1 Geohydrology

The absence of major surface water drainage features and the shallow groundwater table on the flat coastal plain of Zululand, result in an intimate relationship between the surface water bodies (inland lakes) and the groundwater (Meyer and Godfrey, 1995). The flow of groundwater on the northern coastal plain is generally in the direction of the larger inland lakes, with a groundwater divide separating flow towards the coast and towards the Pongolo River (Meyer and Godfrey, 1995). Lake Sibaya, in particular, appears to obtain its water supply almost entirely from groundwater (Meyer and Godfrey, 1995), since no major rivers feed into it (Figure 2.4).

The unconsolidated to semi-consolidated fine sands which overlie rocks of Tertiary and Cretaceous age are not expected to be of value as either aquifers or storage layers. The combined thickness of the sedimentary sequence above the Cretaceous varies from zero metre (where the Cretaceous outcrops in the west near the Pongolo River), to approximately 80 m along the coast (Meyer, 1991). The water table is elevated within the coastal dunes, this phenomenon apparently being controlled by the less permeable, underlying Pleistocene sediments which act as an aquitard (Hattingh, 1991). The latter sediments effectively reduce subsurface flow to the underlying Miocene sediments. The east-west discontinuity of the Miocene sediments, as well as the age of the groundwater determined from these sediments, negate the concept that the Miocene sediments constitute the major conduit for subsurface flow from the coastal plains towards the sea. The regic dunes on the coast contain relatively small quantities of clay or silt, with the result that the permeability of the dunes is considered higher than the average Pleistocene horizon (Hattingh, 1991).

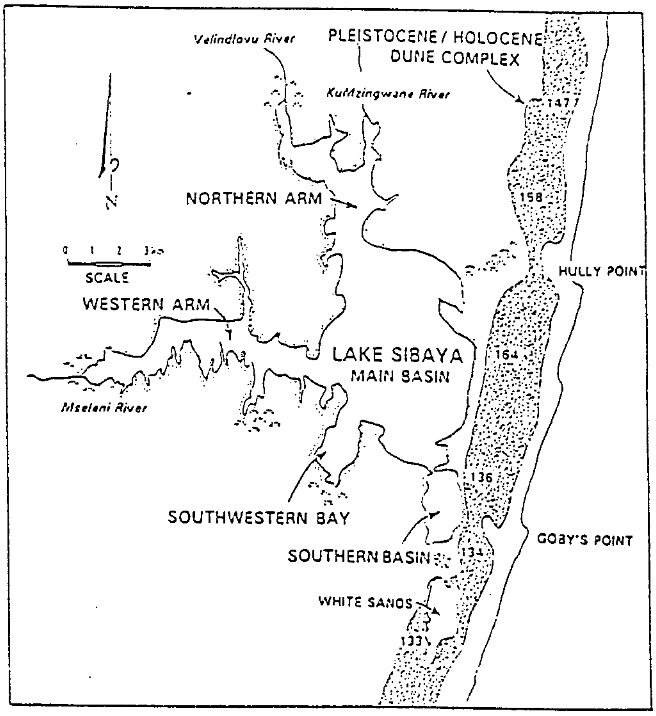

**Figure 2.4:** The morphology of the Lake Sibaya system (after Miller, 1998).

The inland flow direction of subsurface water from these dunes is directed towards the lakes scattered throughout the coastal fringe of the plain. Simulation of piezometric contour surfaces for the region (using a ground water simulation model developed by the Institute for Groundwater Studies, UOFS) confirmed a general flow pattern directed both towards the sea and Lake Sibaya (Meyer, *et al.*, 1995). The coastal dune barrier complex at Lake Sibaya was shown not to support a ground water mound, and thereby also to act as a hydrogeological barrier which affords strong protection against saline water intrusion.

Recharge to the coastal aquifer was calculated utilising the relationship between the chloride content of rainwater and that of groundwater. This produced a figure ranging between 5% and 18% of mean annual rainfall at the coast and at a distance of 50km inland, respectively (Meyer and Godfrey, 1995). The generally shallow aquifer in the Holocene age sands surrounding Lake Sibaya is frequently exploited as a source of water by the local population. Extraction from the aquifer was shown, however, to be negligible in terms of the total volume of groundwater storage (Meyer and Godfrey, 1995). Hand-dug wells of approximately one-meter diameter and seldom more than 5m depth are dispersed throughout the area. These are usually equipped with either hand pumps or windmills, but are also often used as open wells. Waters from three such open wells in the vicinity of Lake Sibaya were sampled for chemical analysis in this study.

Isotope determinations of water sampled at springs on the coastline opposite Lake Sibaya revealed that the spring water originates in the lake, and therefore that it is in direct hydraulic connection with the lake (Talma, 1992). Geophysical measurements in this region indicate that the coastal dune barrier does not everywhere sustain a groundwater divide. These results confirm the presence of a broad (approximately 20 km wide) channel eroded into the Cretaceous formations, to a depth of 120 m below mean sea level, and believed to be filled with approximately 120-140 m of younger Holocene sediments (Meyer, 1995). Meyer *et al.* (1995) calculated the magnitude of the outflow towards the sea to be between 5,5 x $10^6$ and 22 x $10^6$ $m^3$/y, based on an average permeability of 4 m/d (Meyer and Godfrey, 1995). This volume is small (<2.5%) in comparison with that of the lake, namely approximately 981 x $10^6$ $m^3$ (Ramsay, 1991).

### 2.3.2 Groundwater chemistry

Meyer *et al.* (1995) report that, in general, shallow groundwater from the Zululand Coastal Plain is of good quality for domestic use. Chemical analysis of 706 groundwater samples by various institutions showed a pH range of 6 to 9, and electrical conductivity readings generally less than 100mS/m (Meyer and Godfrey, 1995). No clear correlation was found to exist between groundwater pH and geological formation (Meyer and Godfrey, 1995). Electrical conductivity, by comparison, appeared to be lowest (<50mS/m) in the eastern parts of the coastal plain, and generally highest when associated with the older Uloa, Cretaceous and Lebombo geological formations (Meyer and Godfrey, 1995).

The Cretaceous is considered to be the effective base of a sequence of permeable aquifers in this environment and demonstrates a definite briny component dominated by chloride, sodium and sulphate (Meyer, 1991; Hattingh, 1991). The hydrogeochemistry of the overlying Miocene sediments is typically characterised by high calcium and bicarbonate, and low sulphate values (Hattingh, 1991). At the interface between Miocene- and the overlying Pleistocene- sediments, there is a decrease in the calcium and bicarbonate content, but relatively little disparity with regards to sodium and chloride concentrations (Hattingh, 1991). Analysis of water samples from the Pleistocene sediments verified the consistent trend of decreasing calcium and bicarbonate content and stability of sodium and chloride values.

Meyer and Godfrey (1995) constructed a 'fingerprint' table (a summary of which is presented in Table 2.1) from which to classify unknown, unpolluted groundwater samples on the basis of highly probable origin from a specific lithological unit. Chemical concentration ratios of various elements in collected groundwater samples can be related either directly to those obtained for specific lithological units, or can be interpreted in terms of being a mixture of waters from different lithological units. In some unresolved instances, additional information – such as borehole depth, screen position and geological borehole descriptions – may be required to determine whether the sample is a mixture of waters from two strata, or whether confusion arises due to a lack of resolution (Meyer and Godfrey, 1995).

**Table 2.1:** Selected chemical concentration (mmol/l) ratios for fingerprinting the origin of ground water samples from the Zululand coastal plain (after Meyer et al., 1995).

| Stratigraphic position | Ca/TDS | Mg/TDS | Na/TDS |
|---|---|---|---|
| Pleistocene (Upper Port Durnford Fmn) | 1.02 – 15.24 | 2.23 – 4.33 | 15.51 – 26.21 |
| Lignite (Port Durnford Fmn) | 4.20 – 10.12 | 0 – 8.56 | 12.03 – 16.87 |
| Pleistocene (Lower Port Durnford Fmn) | 16.13 – 24.99 | 2.36 – 2.96 | 7.62 – 9.08 |
| Miocene sandstone (Uloa Fmn) | 1.56 – 7.80 | 2.63 – 4.21 | 19.93 – 23.87 |
| Miocene calcarenite (Uloa Fmn) | 11.96 – 20.14 | 2.27 – 4.31 | 9.82 – 18.86 |
| Mudstone (St. Lucia Fmn) | 4.55 – 26.19 | 0.61 – 2.15 | 19.39 – 35.93 |

## 2.4 CLIMATE AND LIMNOLOGY

### 2.4.1 Weather systems

The coastal peneplain of northern KwaZulu Natal is subtropical and windswept, the climate of this region being dominated by the southern sub-tropical high-pressure belt (Hunter, 1988). Seasonal air temperatures are moderated by the maritime influence, fluctuating between a mean temperature of 11.5° C in July to 28.7° C in January. Dyer (1976) reported a mean annual air temperature of 21.6° C for the period 1972-1976. The region under scrutiny experiences, on average, 2 748 hours of bright sunshine per year (ILEC Webpage). Tropical cyclones, though relatively rare, (approximately one each year affects the Zululand coast) are responsible for short duration, heavy rainfalls generally exceeding 400mm (Hunter, 1988). These weather systems develop north-east of Madagascar between November and April.

### 2.4.2 Rainfall and evaporation

The most striking feature of the climate of the Zululand coastal plain is the variation in rainfall across the area in an east to west direction. Mean annual precipitation to the east of Lake Sibaya over the past three decades approximates 1200 mm, whereas that associated with the western extent of the catchment approximates 800 mm (ILEC Webpage). A mean annual precipitation of 1030 mm falls upon the lake surface itself, compared with an annual evaporation figure of 1420 mm/a (Pitmann and Hutchinson, 1975). Relative humidity ranges at the Lake Sibaya Research Station in 1973 were recorded as 56-88% in winter and 60-83% in summer.

Tyson (1978) identified a quasi-20-year oscillation in rainfall, most notable in summer rainfall regions of southern Africa. Allanson (1979) and Hill (1979) note the marked influence of direct precipitation on water levels in Lake Sibaya, claiming that this is to be expected within an endorheic basin. The extent to which seepage loss from Lake Sibaya to the Indian Ocean was apparently underestimated by both authors is discussed later, with respect to hydrology. The water level of, and rainfall over, Lake Sibaya mirror quite reasonably the conclusions of Tyson. Allanson therefore proposes that "although evaporation is high, the steady inexorable rise in lake level reflects the importance of flow from underground aquifers within its catchment, the state of charge of which is reflected by the overall rain pattern and cycling." Dyer (1979) noticed remarkable temporal similarity between rainfall levels and the desiccation versus inundation phases of Lake Chilwa (Malawi), claiming that both Lake Sibaya and Lake Chilwa act as sensitive indicators of climatological change in the Eastern subcontinent.

### 2.4.3 Wind and waves

Winds blow predominantly from the south and north over the coastal plain, in response to cyclonic or anticyclonic activity in the atmosphere. North to north-easterly winds dominate in summer months, while the winter winds show a rough balance in frequency between southerly and northerly winds (Allanson, 1979). These winds also blow for substantial periods of time. The amplitude and length of waves set up by wind acting on the water surface of Lake Sibaya will depend upon the strength, duration and fetch of the wind. Wind speeds over the coastal plain are generally strong, with the mode shifting between 4.5 and 8.5 m/s (Ramsay, 1991). Allanson (1979) recognised two primary wave-mixed areas in the lake: those associated with the eastern and western terraces, and those associated with the more extensive gentle slopes of the northern and southern shores. The former areas experience wave movement to 2-3 m and can be adequately defined by a mean fetch of 3.7 km; whilst the latter areas are subject to wave induced circulation to between 5-10 m, defined by a fetch of 6.1 km. Mixing of the water column by wave action is, therefore, limited largely to the steep east and west terraces and the more gently sloping north and south shores.

The dominance of onshore winds may be instrumental in terms of imbuing Lake Sibaya water with a marine signature. Analyses conducted by Pierre and quoted by Clarke (1924) indicate the main salt in rainwater to be sodium chloride, with some enrichment of calcium and sulphate relative to seawater. Owing to surface tension, the minute droplets of water that constitute clouds cannot form unless nuclei are present in the supersaturated air from which cloud formation may be expected. Very finely divided sea salt particles derived from sea spray, and nitrogen compounds (either ammonia or $HNO_2$) are believed to be the most important kind of nucleus around which cloud droplets form over the ocean in unpolluted air (Woodcock, 1953; Simpson, 1941). Due to the presence of magnesium chloride, salt particles are hygroscopic and enter into solution at a relative humidity of approximately 70 percent. Accordingly, chloride forms a practically constant constituent of rain, the mean content of which is estimated to lie between 0.3 mg/l and 3.0 mg/l (Riffenburg, 1925). The chloride contribution for any given station certainly depends greatly on the distance from the ocean and the prevalent direction of rain-bearing winds. Drischel (1940) expects that a chloride concentration in precipitation of between 4-9 mg/l be expected within a distance of 2-50 km from the coast. This is the belt in which the majority of the Lake Sibaya waterbody and its catchment is located. Hutchinson (1975) notes that the range in chloride concentration suggested by Drischel may, however, constitute an exaggeration. Mean expected iodine concentration values in rainfall of 1 to 2 µg/l, and bromine contents of approximately 30 µg/l were provided by Selivanov (1946).

Numerous studies have indicated that an $SO_4^{2-}$ : $Cl^-$ ratio greater than that exhibited by seawater is the most salient feature of the chemistry of atmospheric water droplets. Sugawara (1948) proposes that the excess of sulphate in rainwater arises due to the fact that salts crystallising out when sea spray evaporates tend to produce two kinds of solid particles dispersed in the atmosphere. As a droplet of seawater evaporates, calcium sulphate will first be precipitated as gypsum (Sugawara, 1948). Sodium and magnesium will later crystallise out. The calcium sulphate particles, not being hygroscopic, will form a stable aerosol, while the chlorides will act as condensation nuclei. Over a sea surface, more of the chloride than sulphate will be rapidly returned to the ocean, with the result that the air circulating over the continents will become enriched in sulphate relative to the proportion of the two ions in sea water. This enrichment will ultimately be exhibited in the rain that washes out the suspended particles in the air (Hutchinson, 1975).

Calcium enrichment in rainwater is likely the result of calcareous dust. The compatibility of the Sr:Ca ratio in precipitation samples with that of terrestrial calcareous rocks (rather than the much higher value given by sea water) suggests that the majority of calcium in atmospheric precipitation is of terrigenous origin (Odum, 1971). In contrast, much of the magnesium content of rain can be attributed to sea spray (Hutchinson, 1975).

Tropical rains - typical of the Zululand coastal plain - contain mean nitrate and ammonia concentrations of 0.31 mg $N{\cdot}NH_3$ /l and 0.27 mg $N{\cdot}NO_3$/l, respectively (Hutchinson, 1975). Such nitrate figures normally include nitrite, which may vary from 1 or 2 percent up to about 40 percent of the total (Hutchinson, 1975).

### 2.4.4 Water currents

The influence of southerly winds was shown by Allanson (1979) to produce a surface flow pattern down to 1m towards the north-west of Lake Sibaya. A return flow was generally noticed within the main basin at a depth greater than 5-10 m, although this was complicated by lake morphometry in some localities, noticeably in the region of one of the sampling transects (WM) chosen for this study (*cf.* Figure 3.1). Northerly winds introduce a surface downwind drift confined to within a metre of the Lake Sibaya water surface. Thereafter the reverse current occupies the depth of the basin. The inflection point was shown to lie between 10-15m below surface. The return flow occurs within the depth of frictional resistance, as defined by:

$$D = \frac{3.67\sqrt{W^3}}{\sqrt{\phi}}$$

where W = wind speed (m/s), $\phi$ = latitude (Hutchinson, 1957). A depth of frictional resistance of 52m was determined by this method, which is, in fact, greater than the maximum depth of the lake (approximately 43m). The reason for this lies in the comparative average shallowness of the lake ($\bar{Z}$ = 13 m) and the windiness of the region in which it exists (Allanson, 1979).

Current monitoring studies conducted by Allanson in January 1970, quoted in Allanson (1979), revealed there to be a complex arrangement of moving water strata within the water column. Since mixing by wave action was shown to be minimal, the work of the wind is largely translated into mixing the water column down to its maximum depth of 40-45 m.

### 2.4.5 Thermal stability of the water column

Allanson (1979) and Allanson and van Wyk (1969) noted that no obvious thermocline exists throughout the Lake Sibaya water column in summer. Any stratification that is set up during summer months is temporary, with homothermal conditions generally being re-established under the stress of wind and evaporative heat loss.

Richardson's number, which expresses the relation between the work of the wind which promotes turbulence ($\partial u/\partial z$) and the density differential ($\partial \rho/\partial z$) which suppresses it, is described by:

$$R_i = \frac{g(\frac{\partial \rho}{\partial z})}{\rho(\frac{\partial u}{\partial z})^2}$$

where g = the gravity constant, ρ = density, u = current velocity and z = depth (In: Allanson, 1979). Increases in velocity will, therefore, exert a substantial effect upon the magnitude of the ratio, with turbulent motion dominating when $R_i$ is less than 0.25 (Hutchinson, 1957). Very rapid distribution of heat energy is, therefore, to be expected throughout the depth of the lake.

Allanson (1979) calculates that there will be a net transfer of heat from the lake to the atmosphere, with sensible heat loss and evaporative heat loss comprising approximately 30% and over 50% of the total, respectively. By his own admission, the accuracy of these findings is questionable.

### 2.4.6 Dissolved gases

Allanson and van Wyk (1969) observed no significant departure from saturation of the lake water column with oxygen during the cool season months of 1967 (July) and 1970 (March). By contrast, considerable reductions in dissolved oxygen concentration were noted (Allanson and van Wyk, 1969; Hart, 1979) in waters deeper than 15 metres over the summer month of January in 1967, 1968 and 1977. This suggests that photosynthetic activity extends to such a depth, after which rapid utilisation of oxygen occurs. The rate of oxygen depletion is related in the literature to a general progressive fining of Lake Sibaya sediments with depth, (Boltt, 1969; Miller, 1998) with a resultant increase in their oxygen demand; as well as to the vertical distribution of surficial material (tripton) and its associated microflora (Allanson, 1979). Furthermore, active respiration by deeply circulating phytoplankton located below their compensation depth would serve to deplete dissolved oxygen within the deeper lake waters. Benthic and pelagic biota, therefore, exercise a considerable role in terms of influencing oxygen concentration within the water column.

Variation in the $CO_2$ concentration throughout the water column is mediated by the high buffering capacity of the lake water.

## 2.5 GEOCHEMICAL PROCESSES

### 2.5.1 Adsorption and ion exchange

For the most part, sediments represent complex mixtures of a considerable number of compounds that, from a physico-chemical point of view, are unrelated. It is possible to distinguish between four major types of end member, namely:

- Weathering residues of rocks
- Minerals formed at low temperatures in the presence of water
- Mobile phases (gases, water)
- Organic constituents

These materials are capable of chemical sorption and may induce a change in the concentration of a chemical in the solid phase, through the process of mass transfer between solution and solid (Appelo and Postma, 1994). Three subdivisions of sorption processes exist, namely adsorption (involving the adhesion of a chemical to the surface of a solid); absorption (the uptake of the chemical into the solid) and exchange (involving the replacement of one chemical for another at the solid surface). Ion exchange models explicitly account for all ions competing for the exchange sites, whereas sorption models consider the effects of one solute in isolation.

The adsorptive capacity of a sediment is generally determined by the solid fractions of clay minerals, organic matter (% C) and oxide-hydroxides. An empirical formula relating CEC to percentage clay and organic matter is offered by Breeuwsma *et al.*, (1986) as:

CEC (meq/100g) = 0.7 * (% clay) + 3.5 * (%C)

According to the above formula, a cation exchange capacity of approximately 8 meq/100g is to be expected of the terrestrial Fernwood Formation soils analysed by Pooley (1996). Pooley measured a considerably lower effective cation exchange capacity (<2 meq/100g) associated with these sediments. The overestimation provided by the application of this formula in this instance possibly relates, in part, to the dominance of kaolinite within the clay mineral fraction (which, in turn, comprises <4%) of these Recent wind-redistributed Quaternary sediments. Cation exchange capacity is limited to approximately 3-5 meq/100g (Appelo and Postma, 1994) within the kaolinite mineral structure, by virtue of the fact that the outer oxygens of the octahedra of one layer share protons with those of the tetrahedra from the next layer, thereby limiting effective surface charge. The cation exchange capacity (CEC) of various common soil constituents is presented in Table 2.2.

**Table 2.2**: Cation exchange capacities of common soil and sediment materials. (After Appelo and Postma, 1994).

| MATERIAL | CEC (meq/100g) |
|---|---|
| Kaolinite | 3-5 |
| Halloysite | 5-10 |
| Montmorillonite | 80-120 |
| Vermiculite | 100-200 |
| Glauconite | 5-40 |
| Illite | 20-50 |
| Chlorite | 10-40 |
| Allophane | ≤ 100 |
| Goethite and Hematite | ≤ 100 |
| Organic matter (C) (at pH =8) | 150 –400 |

Approximate ion-exchange coefficients for various monovalent, divalent and trivalent cations, (using $Na^+$ as the reference cation) are listed in Table 2.3 (after Appelo and Postma, 1994). A range of exchange coefficients is presented in instances where substantial data exist for different soils or minerals, and for various water compositions. The activity coefficients of these exchangeable ions were calculated according to the Gaines-Thomas convention, which is based on an assumption of constant CEC of a sediment neutralised by cations with different charges

(Bolt, 1982). The activities of heterovalent exchangeable cations (e.g. the exchange of $Ca^{2+}$ for $Na^+$) can therefore be calculated as equivalent fractions, with respect to a fixed CEC.

At the molecular level, the attraction or repulsion of ions by a charged surface is described through the use of the Guoy-Chapman theory of the diffuse double layer. Cations and anions are assumed to act as point charges capable of mobility within an electric field (McBride, 1994). Diffusion acts to dissipate concentration effects, which would otherwise arise due to the attraction and repulsion of cations and anions, respectively, by a negatively charged surface. The resultant gradient of concentrations establishes the phenomenon of a diffuse double layer surrounding the charged surfaces in a solution. Accordingly, the electric potential will not change abruptly at the solid-solution interface, but will rather decay exponentially with increasing distance from the interface. Electric potential will therefore also show faster decay as the concentration in the bulk solution increases (Appelo and Postma, 1994). The relative deficit of anions (co-ions) towards the surface of a negatively charged surface will result in part of the charge of the solid being balanced. A higher anion deficit will result in less cations being adsorbed, with the result that CEC is expected to decrease with increasing ionic strength of solution. The waters of the Lake Sibaya system are of relatively low salinity and are not expected to limit the effective cation exchange capacity of the solid phase to any marked extent.

**Table 2.3:** Exchange coefficients calculated using equivalent fractions for exchangeable cations (Gaines-Thomas convention). Coefficients are expressed with respect to $Na^+$, according to the heterovalent exchange formula shown. (After Appelo and Postma, 1994). *I* refers to the ion of concern; $\beta_I$ to the equivalent fraction for such ion; and X to the exchanger site.

Equation:

$$Na^+ + \frac{1}{i} I - X_i \leftrightarrow Na - X + \frac{1}{i} I^{i+} \quad with\ K_{Na/I} = \frac{[Na - X][I^{i+}]^{1/i}}{[I - Xi]1i[Na^+]} = \frac{\beta_{Na}[I^{i+}]^{1/i}}{\beta_I^{1/i}[Na^+]}$$

| **Ion $I^+$** | **$K_{Na/I}$** | **Ion $I^{2+}$** | **$K_{Na/I}$** | **Ion $I^{3+}$** | **$K_{Na/I}$** |
|---|---|---|---|---|---|
| Li | 1.2 (0.95-1.2) | Mg | 0.5 (0.4-0.6) | Al | 0.6 (0.5-0.9) |
| K | 0.20 (0.15-0.25) | Ca | 0.4 (0.3-0.6) | Fe | uncertainty |
| NH4 | 0.25 (0.2-0.3) | Sr | 0.35 (0.3-0.6) | | |
| Rb | 0.10 | Ba | 0.35 (0.2-0.5) | | |
| Cs | 0.08 | Mn | 0.55 | | |
| | | Fe | 0.6 | | |
| | | Co | 0.6 | | |
| | | Ni | 0.5 | | |
| | | Cu | 0.5 | | |
| | | Zn | 0.4 (0.3-0.6) | | |
| | | Cd | 0.4 (0.3-0.6) | | |
| | | Pb | 0.3 | | |

### *2.5.1.1 Primary minerals*

The proportion of primary mineral particles in a sediment or aquifer will affect the permeability and, therefore, the rate of throughflow of water, gases and heat. These factors will, in turn, affect rates of weathering, solute removal and sorption processes (Appelo and Postma, 1994). Primary mineral particles are generally characterised by low surface areas and low chemical reactivities.

Direct chemical adsorption by these minerals is, therefore, for the most part, insignificant. Primary minerals may, however, act as substrates for coating by oxyhydroxides and organic materials which, in turn, may influence metal-ion sorption in natural systems. Coston *et al.* (1992) showed, for example, that approximately 90% of Zn sorbed by composite sands of a shallow, unconfined aquifer in Falmouth, Massachusetts, was by surface reactive sites on the medium to coarse quartz fraction (which constituted approximately 95% of sand content). Surface analytical techniques demonstrated that quartz and feldspar grains of this aquifer were stained with composite (3-5) monolayers of Fe, Al and other elements often associated with weathering. Sorbtion onto pure phases of oxyhydroxides is highly pH dependent, the transition from zero to nearly 100% sorbtion usually occurring over a range of less than one pH unit. The broad pH edges (>2 pH units) measured on the Falmouth sand suggest that Zn was sorbed onto multiple oxide surfaces, rather than one type of surface site.

#### *2.5.1.2 Secondary Minerals*

The affinity of nutrient cations for the surfaces and interlayer positions of various clay minerals has been the subject of exhaustive coverage in the literature, and treatises on this subject can be found in any standard soil chemistry textbook (Dixon and Weed, 1989; Sposito, 1984; McBride, 1994). Readers unacquainted with the theory underlying this subject are referred to such texts for detailed information. A brief overview of the theory deemed particularly relevant to the purpose of this study is presented below.

Clay minerals can possess a deficit of positive charge, arising through substitutions of cations within the interlayer sheets of the crystal structure. Smaller metal ions such as Si or Al occupy the centres of tetrahedral co-ordination units, whereas larger metal ions such as Mg, Fe and Mn occupy the central position in octahedra. Adsorption by minerals with fixed sites is independent of pH, fixed charge arising as a result of substitutions of one element for another within the mineral structure. In clays, the permanent negative charge is compensated for by the presence of interlayer cations.

Clay minerals of the kaolinite group are relatively simply constituted. Layers of tetrahedra, (indicated as T) of approximately 3Å, alternate with those of octahedra (indicated as O) of approximately 4Å, to give a regular repetition of the TO structure every 7Å. The outer oxygens of the octahedra of one layer share protons with those of the tetrahedra from the next layer. Cation exchange capacity is therefore restricted within the clay minerals of the kaolinite group.

Requirements for the formation of kaolinite clays are merely unlimited access to Al and Si in a chemical-structural arrangement that permits crystallisation to a simple hydrous aluminium silicate. However, to satisfy this modest "demand", a series of chemical weathering reactions effective in removing the bases from the clay-forming system is required, since constituents other than Al, Si and the active hydrogen ion interfere quite significantly in the structural framework of these clays. These requirements are largely realised within the coastal belt of Zululand. The region is characterised by a dominance of rainfall over evaporation, (Hutchinson, 1975) and permeable acid catchment sands which constitute an excess of $H^+$ ions (Pooley, 1996). The only weathering products of primary minerals to be conserved in this type of environment are alumina and Fe oxides or hydroxides. As a result, the trend is towards desilication of the initial weathering products and complete loss of base cations.

Feldspars comprise the most abundant rock-forming minerals in the earth's crust. The weathering series of K-feldspar will be examined here as an example of the alteration and neoformation pathways that may have been instrumental in producing the secondary minerals which are likely to occur within the extended Lake Sibaya system. Feldspar weathering is believed, (McBride, 1994), to proceed according to the following steps:

1. $H^+$ ions cause the hydrolysis of surface Si-O-Al or Si-O-Si bonds, breaking open the "silicate cage" and increasing the accessibility of the alkali metal ion.
2. The structural charge is balanced by the proton, thereby releasing the metal ion into solution.
3. A "metal-leached" residual layer of no more than 15 to 25Å is created at the feldspar surface.
4. Weathering reaches a steady state in which the leached layer dissolves at a rate equal to that of $H^+$ replacement of alkali metals.

Steps 1 to 3 constitute incongruent dissolution, whereby the alkali and alkali earth metal ($Na^+$, $Ca^{2+}$, $K^+$) portion of the feldspar mineral is dissolved selectively, leaving a residue enriched in refractory silica and alumina. Step 4 accounts for the later (and considerably kinetically slower) stage of congruent dissolution, in which the elements are released into solution in proportion to their mole fractions in the structure.

In acidic soil environments that are open to $CO_2$ and other acidifying agents of weathering, K feldspar dissolution replaces strong acids ($H^+$) with less strongly acidic forms ($Al^{3+}$ and monosilicic acid). The latter component constitutes a very weak acid, which is easily leached through the soil in undissociated form. The Al component is usually conserved as a solid phase in the soil, $Al^{3+}$ reacting with dissolved silica to precipitate as kaolinite (or non-crystalline allophane and imogolite), in accordance with the following equation:

$$\underset{K-feldspar}{2KAlSi_3O_8} + 2H^+ + 9H_2O \rightarrow \underset{Kaolinite}{Al_2Si_2O_5(OH)_4} + 2K^+ + 4H_4SiO_4$$

A high rainfall climate, such as that experienced along the Zululand coastal plain, generally represents an intense leaching environment. If the leaching is very intense or prolonged, desilication results in oxides of Fe and Al, which then constitute the only important secondary minerals remaining in the soil or sediment. The present rainfall regime of the Zululand coastal belt (approximately 700-1000 mm/yr) would appear to favour the retention of kaolinite/halloysite, at levels approaching 60% of the total clay mineral composition (Figure 2.5). Dissolution of the kaolinite structure to produce gibbsite, under more intense leaching conditions, is represented through the following equation:

$$0.5\underset{Kaolinite}{Al_2Si_2O_5(OH)_4} + 2.5H_2O \rightarrow \underset{Gibbsite}{Al(OH)_3} + H_4SiO_4$$

Within environments akin to those experienced at the study site at present, K-feldspar may also undergo alteration to form the secondary mineral muscovite, such:

$$\underset{K-feldspar}{3KAlSi_3O_8} + 2H^+ + 12H_2O = \underset{Muscovite}{KAl_3Si_3O_{10}(OH)_2} + 2K^+ + 6H_4SiO_4$$

In the mica mineral structure, the octahedra are sandwiched between two layers of tetrahedra. Interlayer cations maintain cohesion between the 10Å thick 2:1 layer framework. Mica-type minerals display exceedingly greater propensity to undergo charge imbalance than other clay minerals (Sposito, 1984). Consequently, micas lose their structural $K^+$ relatively rapidly, by a process of cation exchange with $H^+$ or metal ions in the weathering solution. The secondary mineral formed directly is a vermiculite, which inherits the 2:1 layer structure of the mica parent. The expected weathering sequence of muscovite – a commonly occurring mica species – in a leaching environment is as follows (McBride, 1994):

$$\mathit{mus}\,\mathrm{cov}\,\mathit{ite} \xrightarrow[-K]{} \mathit{illite} \xrightarrow[-K]{} \mathit{vermiculite}(\mathit{dioctahedral}) \rightarrow \mathit{smectite}$$

The chemical composition of the clay minerals of the montmorillonite group is more complicated than that of the kaolinite group, requiring magnesium, iron and probably calcium to build up the montmorillonite structure (Degens, 1965). The Al:Si ratio is appreciably lower than for kaolinite. It is inferred that the environment favourable for a montmorillonite formation is generally the opposite of that in which kaolinite formation takes place. Certain bases that are required for formation can only be retained and kept labile in the clay-forming system if intensive leaching is prevented. The water circulation must be comparatively low, the pH must be high (alkaline conditions) and the redox potential has to maintain iron in an accessible form. Clearly these conditions are more characteristic of a semi-arid climate than that encountered on the Zululand coastal plain. The expected scarcity of montmorillonite clay members within Lake Sibaya sediments holds significant consequence in terms of restricted cation exchange capacity. Smectites expand to 18Å as the Mg interlayer cations become increasingly hydrated. These cations are then free to move into solution, to be exchanged for other ions. Smectites have been shown to possess an interlayer charge in the range of 0.6 to 0.3 (Appelo and Postma, 1994).

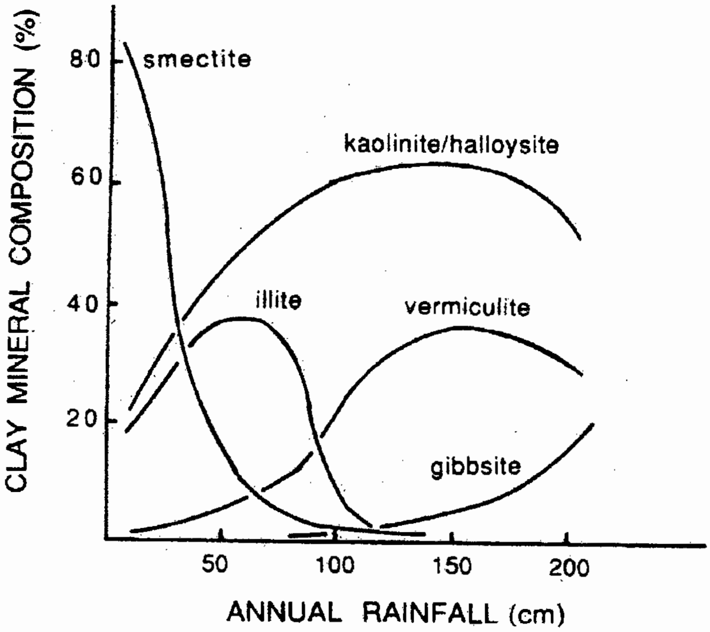

**Figure 2.5:** Clay mineral composition of residual soils weathered from igneous rock under different moisture regimes (after McBride, 1994: p225).

The general tendency associated with weathering of the mica structure, therefore, is toward decreasing particle size, decreasing layer charge, and increasing expandability in water. Weathering conditions also tend to favour the conversion of trioctahedral layer silicate clays (with octahedral sites dominated by $Mg^{2+}$ and $Fe^{2+}$) to dioctahedral layer silicates (with dominantly $Al^{3+}$ and $Fe^{3+}$ in octahedral sites). The formation of smectites from vermiculites involves slow kinetics, the structural alteration process requiring perhaps centuries or millennia (McBride, 1994). Neoformation of smectite may occur in alkaline environments formed as a result of restricted drainage and/or evaporative salt accumulation of alkaline and alkaline earth ions (Na, K, Ca, Mg) within Na-rich saline water. Neoformation processes involve the precipitation of new low-temperature minerals following the dissolution of silica, alumina, iron and the various base cations by primary mineral weathering.

Apart from their capacity to undergo interlayer exchange of cations, clay minerals also possess variable charge, due to protonation of surface oxygens, and deprotonation of hydroxyls. Surface sites with variable charge are often amphoteric (Stumm and Morgan, 1981) and, in the presence of competing solutes, will be protonated, neutral or deprotonated, depending on the pH and the relative acidity of the functional groups.

The process of gradual protonation of surface oxygen, (indicated by ≡SO below) occurring either as a part of the solid structure, or as an adsorbed water molecule, is summarised below:

$$\equiv SO^{-} + 2H^{+} \quad \leftrightarrow \quad \equiv SOH + H^{+} \quad \leftrightarrow \quad \equiv SOH_2^{+}$$

Specific adsorption of ions may likewise transmit a surface charge, such:

$$Pb^{2+} + \equiv SOH \leftrightarrow \equiv SOPb^{+} + H^{+}$$

Solution pH is a primary determinant of surface charge. The magnitude of the exchange capacity of a mineral depends on the difference between the pH of the solution and the pH at which the charge of the mineral is zero, namely the point of zero charge (or PZC). Anion exchange will result under conditions of solution pH falling below the point of zero charge (PZC) of a mineral, whereas the mineral will demonstrate cation exchange where pH is greater than the PZC. Both cations and anions may be adsorbed in small, equal quantities at the PZC of the mineral.

The $pH_{PZC}$ of various clay minerals, and soil oxides and hydroxides common in soil and sediment are presented in Table 2.4. The $pH_{PZC}$ values of kaolinite and montmorillonite fall below both the pH range (6.5 to 8.5) typical of natural groundwater (Appello and Postma, 1994), and that determined for waters of Lake Sibaya (Allanson, 1979). These minerals are therefore expected to behave as cation exchangers only.

The following exchange affinity series were identified in early clay exchange experiments conducted by Jenny (1932) using diluted alkaline and alkaline earth solutions: Li < Na < K < Rb < Cs and Mg < Ca < Sr < Ba. The Al- or Fe- oxides and calcite may serve a role as anion exchangers within the extended Lake Sibaya system, should these occur within the sediments of the Zululand coastal aquifer and the Lake Sibaya bed. Decreasing affinity for anion sorption follows the general sequence (Appelo and Postma, 1994): $PO_4^{3-} > F^{-} > SO_4^{2-} > HCO_3^{-} > Cl^{-}$. Substantial evidence exists (Nkedi-Kizza *et al.*, 1982; Griffioen, 1992) to suggest that no adsorption of $Cl^{-}$ occurs within aquifer sands or non-aggregated soils at pH > 6.

**Table 2.4:** Point of zero charge $pH_{PZC}$ of clay minerals and soil oxides and hydroxides (After Appelo and Postma, 1994).

| Solid phase | $pH_{PZC}$ |
|---|---|
| Birnessite ($\delta$-$MnO_2$) | 2.2 |
| Montmorillonite | 2.5 |
| Quartz ($SiO_2$) | 2.9 |
| Kaolinite | 4.6 |
| $\alpha$-$Al(OH)_3$ | 5.0 |
| Rutile ($TiO_2$) | 5.8 |
| Goethite ($\alpha$-FeOOH) | 7.3 |
| Hydroxyapatite $Ca_5OH(PO_4)_3$ | 7.6 |
| $\gamma$-$Al_2O_3$ | 8.5 |
| Hematite ($\alpha$-$Fe_2O_3$) | 8.5 |
| $Fe(OH)_3$ | 8.5 |
| Corundum ($\alpha$ -$Al_2O_3$) | 9.1 |
| Calcite ($CaCO_3$) | 9.5 |

### *2.5.1.3 Adsorption and complexation by organic matter*

Adsorption and chelation of major and trace elements by dissolved- (DOC < 0.45μm) and colloidal- (5g/mol < DOC < 0.45μm) organic matter influences their speciation (and hence their availability, toxicity and transport) in surface, lake and interstitial waters. Organic colloids may also alter mineral sorbent properties by coating (Davis and Kent, 1990). Besides the total concentrations of the major and trace elements in soluble and particulate phases of organic carbon, therefore, it is also important to investigate details of their speciation. In this manner it becomes possible to gauge their biological availability and ultimate fate in aquatic systems.

Eyrolle *et al.* (1996) made use of ultrafiltration, differential pulse anodic stripping voltametry (DPASV) and atomic absorption spectrometry to determine the distribution of major and trace elements, and their association with different size fractions of DOC (< 0.45μm) in three small tropical catchments in Brazil. Typical ranges for DOC in such tropical climates range from 2 – 15 mg C/l (Thurman, 1985: cited in Davis and Kent, 1990). The ratio of dissolved to particulate organic carbon (DOC/POC) for tropical waters averages 0.5 (Richet *et al.*, 1980: cited in Davis and Kent, 1990).

DOC within the Brazilian catchments was concentrated primarily within the low (<20 g/mol) molecular weight fractions of the tropical Brazilian waters. This fraction probably comprises fulvic acids and/or low molecular weight organic (amino or hydroxy) acids. The higher molecular weight fractions (humic acids and/or recently decomposed living organisms or algae) were found to display higher site densities. This fact can be explained in terms of both the nature of the reactive group, and the particle size effect on electrostatic interactions. De Wit *et al.* (1993) showed that the carboxylic functional groups of humic acids have considerably greater affinity for Cu (II) complexation than those of fulvic acids. Furthermore, humic acids contain a greater number of functional groups (e.g. phenolic groups) which were demonstrated by Benedetti *et al.* (1995) to bind Cu (II) within purified peat at high pH (6 – 8) and low metal loading. Increasing the size of colloidal organic matter also serves to increase electrostatic interactions (De Wit et al., 1993) and will thus favour the binding of metal ions to the organic molecules.

Eyrolle *et al.* (1996) further showed that major elements occurred as free ions within the tropical catchments. Over 50% of total Fe was found within that fraction with particles < 5 g/mol. This fraction is representative either of the dissolved state, or of particles of small size (Eyrolle *et al.*, 1996). The low molecular weight fraction of DOC was therefore shown to control the speciation of major and trace metals.

### 2.5.1.4 Oxides and hydroxides

Olivines, pyroxenes and amphiboles are characteristically rich in reduced iron ($Fe^{2+}$). Where these minerals occurred within aerated soil environments of the Zululand coastal plain, they would have weathered rapidly, as the $Fe^{2+}$ became oxidised to $Fe^{3+}$. The limited resistance to weathering in these minerals is a function of the lack of Si-O-Si bonding, especially in island silicates such as olivine (McBride, 1994). $H^+$-promoted dissolution of a structural metal ion from a mineral surface requires the breaking, and subsequent reformation, of a metal-oxygen bond. Large metal cations (e.g. $Ca^{2+}$) which are octahedrally co-ordinated within the structures of these minerals generally have faster ligand exchange rates than small cations of the same charge (e.g. $Mg^{2+}$). Consequently, the island silicate $Ca_2SiO_4$ has a dissolution rate at least six orders of magnitude faster than the rate of dissolution of more resistant silicates such as feldspar (Casey and Westrich, 1992).

The overall oxidation reaction of ferromagnesian minerals can be expressed through the general equation:

$$\{Fe^{2+}, 0.5Mg^{2+}\}silicate + H^+ + 0.25O_2 \rightarrow \{Fe^{3+}\}silicate + 0.5Mg^{2+} + 0.5H_2O$$

As indicated by the reaction, weathering of the ferromagnesian minerals through oxidation occurs most readily at low pH. The introduction of dissolved oxygen causes rapid oxidation of $Fe^{2+}$ and precipitation of ferric hydroxides and oxides if the solution pH is much higher than 6 (McBride, 1994). The accumulation of iron oxides in soils that have been subjected to leaching and desilication over many thousands of years is generally marked by an intense red colour in the case of hematite ($Fe_2O_3$), and a yellow-brown colour in the case of goethite (FeOOH). Autocatalytic $Fe^{3+}$- mediated surface oxidation is possible, however, and generally occurs at a faster rate than oxidation by $O_2$ (McBride, 1994).

Fluctuating water tables appear to have been relatively common within the recent history of the shallow aquifers of the Zululand coastal plain. During wet periods, any iron oxides present in the soil would have undergone reduction, with organic matter (directly or indirectly) supplying the electrons:

$$Fe(OH)_3 \xrightarrow[CO_2]{e^-} Fe(HCO_3)_2$$

The $Fe^{2+}$ ions would probably occupy a significant fraction of exchange sites on the soil colloids (clay and humus):

$$Fe(HCO_3)_2 + Ca^{2+} - colloid \quad = \quad Fe^{2+} - colloid + Ca(HCO_3)_2$$

Because $Ca(HCO_3)_2$ is a soluble salt that can be leached from the soil, exchangeable $Fe^{2+}$ may accumulate within the soil as base cations are lost. If reducing conditions prevail in solution, soluble $Fe^{2+}$ should be stable only if the pH is below approximately 8 (Stumm and Morgan, 1981). Above this pH, solid $FeCO_3$ would constitute the predominant form of iron. The overall process of soil acidification by alternating iron reduction and oxidation is termed ferrolysis. It appears unlikely that ferrolysis will occur within the Lake Sibaya catchment region, since drainage through the permeable sands is presumably sufficient to allow bicarbonate to leach through the soil profile.

Microbes catalyse the reduction of $O_2$ to $H_2O$ via enzyme systems. In the process the oxidative power of $O_2$ may - in alkaline aerated solutions - be converted into the form of Mn (+3 or +4) oxides. The oxidation of Mn is autocatalytic, oxidation accelerating with the precipitation of Mn oxides in response to the increased surface available for selective adsorption of Mn (McBride, 1994). Except for $NO_3^-$ which tends to be kinetically inert, $O_2$ is the only sufficiently strong and common oxidant in soils to be capable of oxidising $Mn^{2+}$ (McBride, 1994).

Iron-, manganese-, and aluminium- oxides and hydroxides are not inclined to develop a structural charge through isomorphous substitution, (unlike layer silicate clays) and therefore possess low cation exchange capacities, despite the fact that they possess extensive surface area (Sposito, 1984). Nevertheless tropical and subtropical soils and sediments - which are characterised by significant proportions of these oxides - typically possess a high capacity to chemisorb metal ions, as well as organic and inorganic ions (Mengel and Kirkby, 1978). If present in reasonable quantities, these oxides and hydroxides may, therefore, exert a vital role in terms of sorbing nutrients within the sediments of Lake Sibaya and the Zululand coastal aquifer. Exposure of ground-water ferricrete was found (Miller, 1996) to occur around the periphery of Lake Sibaya and to outcrop in places below lake level. The ferricrete consists of sub-angular to rounded nodules coated by ferrous oxides, and has been previously described in this review with regard to the sedimentology of Lake Sibaya. The potential sorptive capacity of these sediments is particularly important, given the fact that intensive leaching of subtropical soils commonly removes those structural components required for secondary mineral formation (layer silicate clays). Pooley (1996) showed the layer silicate content of the Recent sediments of the Zululand coastal plain to be minimal, and typically of relatively inert kaolinite mineralogy. Similarly, the quartz fraction typically occupies ± 99% of the bulk of quartzitic sands dominant within Lake Sibaya, with organic carbon content generally in the order of 1% (Miller, 1996). The potential implications of the dissolution of metal oxides associated with the onset of reducing conditions in the sediments of Lake Sibaya are discussed at a later stage in this review in this review.

Lind and Anderson (1992) identified a greater affinity of Cu, Ni, Zn and Pb for Fe in amorphous iron oxides, than for Mn in manganese oxide crusts developed in the streambed of aerated, trace-metal rich, near-neutral water of Pinal Creek, Arizona. The high Cu-Fe affinity, in particular, was hypothesised to occur as a result of the many possible Cu-Fe oxides and the greater adsorption capacity of goethite relative to $\delta$-$MnO_2$ (Lind and Anderson, 1992). Similarly, concentrations of Cu, Zn and Cd were higher in cemented crusts than in non-cemented sediments.

They further showed that trace-rich manganese oxide precipitates and coatings can form not only from the aerated, near-neutral streamwater, but also by oxidation, both of exchangeable Mn, and of Mn in carbonate minerals. Junta *et al.* (1992) confirmed earlier observations that oxidation of $Mn^{2+}$ in solution occurs more rapidly in the presence of a solid phase. Under such conditions, manganese was shown to precipitate as islands, which originally began near uneven fracture surfaces of minerals and subsequently spread over flat surfaces. The amount of precipitation of manganese due to oxidation showed strong positive correlation with the solution pH (Junta *et al.*, 1992).

### 2.5.2 Dissolution-precipitation processes

Mineral precipitation and dissolution proceed through a chain of processes. These include the transport of solutes from bulk solution to the mineral surface, adsorption at the surface, chemical reactions at the surface, desorption of product solutes from the surface, and finally the transport of product solutes back into the bulk solution. These processes must occur simultaneously, but some may proceed at a faster rate than others (Berner, 1980).

The growth and dissolution of sparingly soluble minerals is generally controlled by surface processes which act only at those sites on the mineral surface (e.g. irregularities) which are energetically favourable. Ions or atoms which are least surrounded by other crystal units will have lower binding energies and will therefore be favourably dissolved. By contrast, crystal growth will take place preferentially at those sites where bonds in several directions can be established. Etch patterns on mineral surfaces – observed by scanning electron microscopy (SEM) – may act as indicators of surface reaction dissolution control (Berner, 1978). Transport processes – as opposed to those occurring at the surface - are expected to exert the primary control over the dissolution of soluble minerals (Appelo and Postma, 1994).

The fate of trace elements in sedimentary basins is dependent upon their speciation during deposition, and upon subsequent reactions during diagenesis. As described previously, trace metals within the polymictic, oxygenated water column of Lake Sibaya could hypothetically be associated with reactive particles such as amorphous to crystalline oxides of Fe and Mn, organic coatings on suspended particles, and biological material. With the increase in reducing conditions expected at the aqueous-sediment boundary and below, however, both dissolution of metal oxides and anaerobic degradation of organic matter may occur (Lind and Anderson, 1992; McBride, 1994). Support for this hypothesis comes by way of Webster (1992), who showed redox conditions to be the prime control over Fe and Mn solubilities in the waters of Lake Vanda, Antarctica. Both metals formed insoluble oxide phases (Fe: ferrihydrite and goethite; Mn: manganite) in the oxic lake waters, yet underwent reduction to the mobile divalent ions with the onset of anoxic conditions at greater depth. Trace metals (Ni and Zn) adsorbed onto the surface of Mn oxides were, therefore, also indirectly affected by redox conditions.

As the concentration of an ion in solution is increased, precipitation of a new solid phase will not occur until the solubility product of that phase has been exceeded. For many of the more abundant elements found in sediments and soils (e.g. Al, Fe, Si, Mn, Ca and Mg) precipitation of mineral forms is common, and can control the solubility of these elements. For most of the trace elements, however, precipitation is less likely than chemisorption because of their low concentrations in the substrate. This assumption would appear to be valid in the case of the Lake Sibaya system, given the low levels of trace elements to be expected within the rainfall (Hutchinson, 1975) and the coastal sands of the Lake Sibaya catchment (Pooley, 1976, Meyer, 1991). Solubility products of some of the least soluble minerals, which are therefore most likely to precipitate in the chemical environment of the lake sediments are presented in Table 2.5 (after McBride, 1994). This table shows, for example, that $Cd^{2+}$ or $Pb^{2+}$ solubility is most likely to be limited by carbonate or sulphide precipitation, depending on the redox potential of the sediments.

Note that the speciation of the dissolved metal should be considered - in addition to the solubility product - when assessing the mobility and bioavailability of elements in sediments or soils.

**Table 2.5:** Solubility products of metal carbonates, oxides and sulphides (after McBride, 1994).

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Carbonates:** $K_{sp} = (M^{2+})(CO_3^{2-})$ | | | | | | | |
| | Pb | Cd | Fe | Mn | Zn | Ca | |
| $K_{sp}$ | 13.1 | 11.7 | 10.7 | 10.4 | 10.2 | 8.4 | |
| **Oxides and Hydroxides:** $(K_{sp} = (M^{n+})(OH^-)^n$ | | | | | | | |
| | $Fe^{3+}$ | $Al^{3+}$ | $Cu^{2+}$ | $Zn^{2=}$ | $Fe^{2+}$ | $Mn^{2=}$ | $Mg^{2+}$ |
| $K_{sp}$ | 39.0 | 31.2 | 20.3 | 16.9 | 15.3 | 12.8 | 11.2 |
| **Sulphides:** $K_{sp} = (M^{2+})(S^{2-})$ | | | | | | | |
| | Cu | Pb | Cd | Zn | Fe | Mn | |
| $K_{sp}$ | 36.1 | 27.5 | 27.0 | 24.7 | 18.1 | 13.5 | |

At moderate to low concentrations, trace metal solubility is usually much lower than that expected from the solubility product of likely precipitates. The most likely explanation appears to be that the trace ion in question achieves a lower solubility by co-precipitating into another component to form a mixed solid phase (McBride, 1994). Selective scavenging of one metal over another as the solid precipitates, results in the preferred ion being occluded in the centre of the growing crystallites, while the less preferred ion concentrates in the outer layers. The occluded metal may become essentially inaccessible to desorption, with the result that the effective solubility product may be orders of magnitude less than that of the pure solid.

Jacobs *et al.* (1985) suggested that trace metals are not in equilibrium with pure metal sulphides during low temperature diagenesis, but instead are involved in co-precipitation reactions, possibly with Fe sulphides. Domagalski and Eugster (1992) conducted a series of selective sediment extractions to determine the phase chemistry of selected trace metals within the waters and Recent sediments of alkaline ($Na-CO_3-Cl-SO_4$) lake systems in western United States. They demonstrated that metals in alkaline sediments are not present in stable phases during early diagenesis. Mobilisation of metals to produce an ore-forming fluid is, therefore, possible under the right set of conditions. Pyrite formation, for example, was prevented during the early stages of diagenesis in alkaline lakes, due to supersaturation of the brines with respect to FeS. Metastable iron monosulphide was shown to persist within the upper metre of Mono Lake (Nevada) and Walker Lake (California) sediments, because of high pH conditions associated with alkaline buffering and high sulphide concentrations. Formation of sedimentary pyrite in subsequent stages of diagenesis would, by necessity, require the dissolution of Fe monosulphide. The dissolution of FeS could be achieved through either oxidation, or a decrease in the concentration of sulphide or pore water pH.

Equations for the dissolution of minerals are usually written as dissociation reactions. In reality, total concentrations of ions in aqueous solution have to be corrected for the effect of electrostatic shielding, through the use of an activity coefficient relating activities to molal concentrations. The activity of ions in solution is further reduced by the presence of ion pairs or aqueous complexes. The necessary corrections are covered extensively in the literature (e.g. Appelo and Postma, 1994: p49-54) and will not be discussed here. The MINTEQA2 computer program used in this study to model mineral saturation and element speciation adopts the Davies equation as the default means of estimating activity coefficients. A comparison of the individual geochemical modelling software packages, and the assumptions that they make with regard to the correction of activity, is presented in Nordstrom *et al.* (1979).

### 2.5.3 Oxidation-reduction reactions

The importance of pH as a "master variable" controlling chemical reactions in soils, sediments and waters has been well documented. However, soils subjected to fluctuations in water content fall under the influence of another master variable: the reduction-oxidation (redox) potential. Under conditions of water saturation, the lack of molecular oxygen can result in a series of redox reactions that changes the soil/sediment pH. In such an environment, the redox state of the substrate exerts control over the pH.

Reduction and oxidation processes exert an important control over the stability and distribution of redox species and mineral phases such as $O_2$, $Fe^{2+}$, $H_2S$ and $CH_4$ under natural conditions in groundwater, lake and soil/sediment systems. Many metals, for example, possess more than one potentially stable positive oxidation state, each of which may have dramatically different chemical properties that, in turn, will affect their biogeochemical forms and significance. Redox reactions can lead to orders of magnitude changes in the concentration of metals in various phases, and hence in their mode and rate of transport. It is evident that the presence or absence of an oxidised microzone at the sediment-water interface effects an immense influence over the amount and nature of the substances leaving the solid substrate and passing into the water column. When materials produced at a low redox potential are precipitated at a higher redox potential (e.g. ferrous iron precipitated as ferric hydroxide; phosphate precipitated as ferric phosphate) it will become impossible for such substances to pass into the free water across the oxidative microzone, due to their propensity to precipitate. Mortimer (1942) suggests that the adsorptive material in oxidised mud may well consist of a ferrilignoprotein complex. Reduction of the iron abolishes the adsorptive capacity and liberates bases and some anions into both the free water and the interstitial water.

Redox conditions in lakes are determined by the balance between (i) the decomposition of organic matter (normally from photosynthesis in the lake) and (ii) the supply of oxygen by circulation or vertical mixing of the water (Drever, 1997). Allanson (1979) showed that there was no significant departure from complete saturation of the water column with $O_2$ during winter months (refer to Table 2.6). In summer, however, quite marked decreases in dissolved oxygen concentration could occur in deeper waters (≥15m). Solar radiation, by the process of photosynthesis, provides the energy to create simultaneously within the cells of photosynthetic organisms (cyanobacteria, algae and plants), both molecular oxygen (positive Eh) and pockets of strongly reducing conditions (negative Eh). In this manner, a state of extreme disequilibrium is established at the subcellular level (Butcher *et al., 1992*). The localised reducing conditions convert $CO_2$ to reduced organic compounds possessing high-energy C-H (as well as P, N and S) bonds. Non-photosynthetic organisms then use the raised oxidation state of $O_2$ to oxidise the energy-rich organics, returning the system to "equilibrium" (McBride, 1994). The reduced forms of carbon in the organic matter of water-saturated soils therefore provide the energy (and the electrons) that drive chemical reduction. Electron transfer reactions are often slow, with the result that reaction kinetics also play a significant role. Bacterial catalysis may, in some instances, mediate reactions (e.g. the reduction of sulphate in both aquifers and marine sediment by organic matter) which would otherwise progress at insignificant rates (Butcher, *et al.* 1992).

**Table 2.6**: Dissolved oxygen concentration and percentage saturation in Lake Sibaya (adapted from Allanson and Van Wyk, 1969).

| | January 1967 | | | July 1967 | | |
|---|---|---|---|---|---|---|
| **Depth (m)** | **T (°C)** | **Diss. $O_2$ (mg/l)** | **% sat.** | **T (°C)** | **Diss. $O_2$ (mg/l)** | **% sat.** |
| 0 | 25.7 | 7.6 | 95 | 19.2 | 8.9 | 100 |
| 5 | 26.0 | 7.8 | 98 | 19.2 | 8.9 | 100 |
| 10 | 26.0 | 8.0 | 100 | 19.0 | 8.7 | 97 |
| 15 | 26.2 | 8.1 | 102 | 19.0 | 8.5 | 95 |
| 20 | 26.3 | 8.1 | 102 | 19.0 | 8.4 | 94 |
| 25 | | | | 19.0 | 8.4 | 94 |
| 30 | 25.6 | 6.9 | 85 | 18.9 | 8.4 | 94 |
| 35 | 27.7 | 6.6 | 82 | 18.9 | 8.4 | 94 |

## 2.6 BIOLOGICAL FACTORS

Extensive ecological investigations have been conducted in the Lake Sibaya region in recent years (Bayer, 1938; Allanson, 1979; Bruton and Cooper, 1980). A brief account of the biological diversity within Lake Sibaya and its immediate surrounds is presented below. Emphasis is here placed upon those organisms which inhabit the lake, and which are, therefore, most likely to influence, and be influenced by, geochemical processes acting within the lake. The reader is referred to the above-mentioned texts and to the Ramsar Webpage for further details of these studies.

The origin of the elevated levels of dissolved chloride within Lake Sibaya is proposed (Allanson, 1979) to be largely a response to cyclical salt from the sea, and from fossil sources within the Tertiary sands of its catchment. This latter source of chloride seems unlikely, given the high degree of leaching that could be expected from these porous, generally inert sands. A $Na^+$:$Cl^-$ molar charge ratio of 1.003 in Lake Sibaya water, based on measurements conducted by Allanson and van Wyk (1969: p231), confirms the marine influence on these waters. These latter dissolved species are conservative and do not alter their comparative molar charge ratio (1:1) as a result of processes such as evaporation (Drever, 1988). The importance of the raised $Cl^-$ levels, relative to neighbouring freshwater lakes, is reflected in the astounding number of estuarine faunal relict species which appear in the lake. The fact that none of these taxa is represented in the typically freshwater of southern Africa implies – Hart (1979) argues – on the one hand a boundary limit beyond which they are incapable of crossing so as to invade the truly freshwaters; and on the other a remarkable degree of ionic tolerance.

Photosynthesis in Lake Sibaya is dominated by diatom algae (Hart, 1979). Diatom production proceeds more or less continuously in oligotrophic lakes such as Lake Sibaya (Allanson, 1979). Diatoms assimilate large quantities of silicon in the synthesis of their frustules (skeletons), these frustules often settling to the sediments upon senescence. In deep lakes many of the diatom frustules undergo partial dissolution before reaching the sediments. The dissolution of suspended silica can be accelerated by consumption and fragmentation of diatom frustules by zooplankton (Ferrante and Parker, 1978: cited in Wetzel, 1983). Nevertheless, this biochemical condensation of dissolved silica and sedimentation greatly exceeds inputs to the sediments from abiogenic sources (Tissenow, 1966: cited in Wetzel, 1983).

Silicates are predicted to comprise the bulk mineralogy of the Recent wind-redistributed Quaternary sands upon which Lake Sibaya is bedded. The only crystalline modification of $SiO_2$ that can form in low temperature and pressure environments is α-quartz (Degens, 1965). Amorphous silica refers to substances of relatively pure $SiO_2$ but of extremely small size, and arranged in a crystallographic disordered state, as evidenced by the lack of a characteristic X-ray diffraction pattern.

The waters in contact with Lake Sibaya sediments are likely to be enriched in amorphous silica at concentrations far in excess of those of water entering the lake (Harriss, 1967). The dissolved silica of interstitial water is not in equilibrium with amorphous silica, but rather with chemically bound or adsorbed silica. Silica concentration of the interstitial water is controlled by dissolution of ferroaluminium silicate (McCall and Tevesz, 1982). This complex is formed in the sediments by the reaction of silica from diatoms with aluminium and ferric oxyhydroxides, or through the hydrolysis of clay minerals (Nriagu, 1978). These reactions decrease the solubility of silicates in sediments, especially in interstitial waters at pH values above 7 (Ohle, 1964). The solubility of silica is increased by humic compounds, however, and through the formation of iron and aluminium silicate humic complexes. Liberation of silica to the overlying water in relatively isolated lake systems is governed by these equilibria, which are stable only in the presence of the solid phase of adsorbed silica.

Surface waters, groundwaters and interstitial waters generally have silica values below 100 mg/l. Since amorphous silica dissolves in water and forms a true solution ($H_4SiO_4$) of concentrations up to 140 mg/l at room temperatures, amorphous silica in natural waters is generally in the molecularly dispersed state (Krauskopf, 1956). The rate of silica dissolution is influenced by temperature, and by the difference in silica concentrations between the sediments and the overlying water. By contrast, quartz at ordinary temperatures is soluble in near neutral solutions to the extent of only about 6-10 mg/l (McCall and Tevesz, 1982). Owing to the extremely slow kinetics of quartz dissolution, therefore, amorphous silica can be carried in solution at concentrations far in excess of the solubility of the crystalline $SiO_2$ varieties. Equilibrium is not attained because of the slow diffusion kinetics, which generally act over weeks (Harriss, 1967). The difference between silica of interstitial water and in the overlying water is further influenced by currents, bioturbation due to benthic organisms, and gas bubbles escaping from the sediments.

As described previously, substantial evidence exists from the investigation of current patterns and the thermal regime of the water column to suggest that Lake Sibaya is in almost complete circulation. This phenomenon is due largely to the prevalence of substantial current movements initiated by wind stress. Allanson and Hart (1975) forward the suggestion that the low productivity associated with the phytoplankton assemblage can be explained in terms of the lack of a hypolimnion during the summer months. Thorough mixing of the water column, therefore, prevents the occurrence of nutrient pulses, which would otherwise serve to boost biomass levels and production rates, in accordance with the concentration of immediate nutrients. It therefore appears as if increased production within the lake will only occur if the external inputs of nutrients are increased.

Bowen (1976, 1978) emphasised the limit to productivity exerted by the overall low protein levels associated with available food resources within the lake, particularly within its pelagic regions. Of the eighteen fish species that occur in the lake and its feeder streams, only one species, the Mozambique tilapia, *Oreochromis mossambicus*, (then known as *Sarotherodon mossambicus*) relies predominantly on the benthic diatom community for its diet. The low numbers of primary consumers within the lake is a reflection of the low primary productivity level of Lake Sibaya. The low standing crop of phytoplankton (< 5µg chlorophyll/litre; Allanson and Hart, 1975), was shown by Bowen to be sufficient only to maintain good growth and condition in that sector of the *O. mossambicus* population (the juveniles) which can feed in the well-lit, warm, shallow (< 1m) parts of the terrace. Both juveniles and adults feed on a mixture of detritus, bacteria and diatoms that occur as a flocculent layer on sandy substrata, as well as on phytoplankton in suspension. Adult individuals of this species never develop the rounded, deep-bodied shape characteristic of adults from other populations, (e.g. the Pongolo River) but instead show marasmus, indicative of malnutrition. Bowen linked the poor growth and condition of this fish species with the low nitrogen levels within the waters and sediments of Lake Sibaya. He indicated that the decreased availability of dissolved organic matter (DOM) - on which bacteria are largely dependent for nutrition - at increasing depths, may explain the distribution of bacteria implied by the distribution of protein found in benthic floc samples. The ratio of digestible protein to digestible energy in the diet of *O. mossambicus* exceeded 20:1 at depths greater than 1.2 m (Bowen, 1976), resulting in retarded growth and poor condition. Russell-Hunter (1970) proposed that such relationships between diet and growth were commonplace.

The aquatic vegetation of Lake Sibaya consists of submerged macrophytes (*Ceratophyllum demersum, Myriophyllum spicatum,* etc); semi-emergent plants (*Potamogeton schweinfurthii* and *Nymphaea capensis*) and free-floating aquatics (*Pistia statiotes*). Marginal vegetation consists predominantly of sedges (*Scirpus littoralis, Cladium mariscus, Phynchospora spp, Typha latifolius* and *Phragmites mauritianus).* Drainage lines leading into the lake are vegetated either by remnant swamp forest or hydrophilous grasses and sedges.

Because of strong currents active in Lake Sibaya, the role of macrophytes in the reduction of water turbulence, and the resulting trapping of external matter introduced into the lake is negligible (Howard-Williams, 1979). Macrophytes also constitute a minuscule nutrient reservoir in Lake Sibaya. *Cyperus papyrus* swamps located at the surface inlets may remove nutrients from surface inflows to some extent. However, the overall significance of such a process is likely to be negligible in the greater scale, owing to the dominance of groundwater flows to the lake. Macrophytes or their detritus are believed (Howard-Williams, 1979) to be unimportant as a food source for the two most abundant fish species (*Clarias gariepinus, Oreochromis mossambicus*) but may provide nesting sites and shelter. In the case of Lake Sibaya, Howard-Williams endorses the statement made by Shelford (1918) that, were macrophytes to be replaced with inert structures of the same surface area, the effect on the ecology of the lake as a whole would hardly be noticed.

Vegetation fringing Lake Sibaya, (including the dune canopy proximal to the lake on the eastern shores) constitutes an important input of organic material into the deeper and sheltered regions of the lake. This vegetation is destroyed during periods of high lake levels, is subsequently decomposed, and is finally incorporated into black organic-rich mud (gyttja). The incorporation of gyttja into the sediments has been described elsewhere, with regard to Lake Sibaya sedimentology.

Freshwater sediments are inhabited by a variety of macroinvertebrates (operationally defined as those animals retained by a 500 µm mesh sieve), principally arthropods (insects and crustaceans), annelids (oligochaetes and leeches) and molluscs (bivalves and gastropods). Zooplankton in Lake Sibaya is dominated by copepods and cladocerans (Crustacea), one species of copepod being endemic to Lake Sibaya. Zoobenthos in the lake is similarly dominated by crustaceans (particularly burrowing amphipods and taniads) and by molluscs (15 aquatic species). All of these organisms interact in some way with their substratum. The nature of this interaction is determined by the manner in which each particular organism obtains its food (trophic type); the mobility of the organism; and where, in relation to the sediment-water interface, life cycle activities are enacted (McCall and Tevesz, 1982). The feeding biology of benthic invertebrates which scrape sand grains and gyttja on the Lake Sibaya bed is poorly understood (Hart, 1979).

The importance of any organism or group of organisms in modifying sedimentary physical and/or chemical properties is further dependent upon individual size, population density and activity rates - which are typically temperature-dependent (McCall and Tevesz, 1982). Zooplankton, zoobenthos and littoral fauna were all shown by Hart (1979) to exhibit generally low standing stocks within the Lake Sibaya system. Likewise, levels of production were shown to be low. The smaller infaunal organisms numerically dominate the zoobenthos overall, the three species of amphipod and one of tanaid comprising over 90% of the community by number, and contributing substantially to the total biomass of the benthos (Hart, 1979). It would appear, therefore, as if the influence of the macrobenthos upon the geochemical nature of the Lake Sibaya system is relatively minor in the context of other freshwater lake systems.

Eight species of reptiles are recorded to be directly associated with Sibaya - including a species of water monitor (*Varanus niloticus*), six snake species and the Nile crocodile (*Crocodylus niloticus*). A total of 279 bird species had been recorded for the Lake Sibaya region, 62 of which are closely associated with the lake through their breeding, feeding or roosting habits. Six mammal species are associated regularly with the lake, including four rodent species, the reedbuck (*Redunca arundinum*) and the hippopotamus (*Hippopotamus amphibius*). A total of 154 hippopotami were counted in the lake in July 1988, with a 13% infant composition. Since hippopotami graze on land and usually defecate in the water, there is a net transfer of nutrients to the lake, with no major return pathways. Using a population figure of 150-200, the dissolved and suspended nutrients released into the lake system per day from dung are estimated (based on a similar study of Lake George by Viner, 1975) as 100kg carbon, 55kg nitrogen, 2kg phosphorous, 1,5kg iron, 6kg silica, 9kg sodium, 8kg potassium, 4kg calcium and 3kg magnesium.

## 2.7 CONCLUSIONS

A review of the literature relating to the Lake Sibaya system highlights the fact that there is a distinct paucity of information that is pertinent to the geochemistry of the system.

Solute concentration levels reported in the freshwaters of Lake Sibaya would appear to be related, primarily, to the influx of marine cyclical salts; to mineral dissolution within the aquifer sands; as well as to dissolution-precipitation, adsorption-ion exchange and redox processes within the lake itself. Evaporation is reported to exceed precipitation over the surface of Lake Sibaya leading to a possible increase in concentration of solutes. Lake Sibaya water is presently fresh, but substantial evidence exists to conclude that the lake represents a former estuary, formed within the drowned former (Pongolo?) river valley that was incised during the Last Glacial Maximum.

The wet and dry deposition of marine cyclical salts by onshore winds imparts to the lake waters a distinct marine signature, as evidenced by the approximate 1:1 ratio obtained for the conservative species $Na^+$ and $Cl^-$.

The literature notes the importance of groundwater influx in maintaining the Lake Sibaya water level in the general absence of significant surface water inflow. Given the intensive leaching conditions of the Zululand coastal plain, the aquifer sands are understandably reported as being of low reactivity and low nutrient status, being heavily dominated by residual quartz of low reactivity. The literature predicts that kaolinite would constitute approximately 60% of the total mineral composition of these sands, based on the regime of high rainfall and permeable acid sands. The $pH_{PZC}$ of kaolinite falls below the pH recorded for the waters of the extended Lake Sibaya system, with the result that the mineral is expected to act as a cation exchanger only. Low organic carbon content was also reported in these soils. What few base cations exist in these soils could conceivably be expected to leach into the groundwater and, subsequently, the lake waters.

Redox conditions in lake systems are determined by the balance between the decomposition of organic matter (normally due to photosynthesis) and the supply of oxygen by circulation and vertical mixing of the water column. The persistently strong winds and the large wind fetch are credited, in the literature, with ensuring that the water column of the lake remains well mixed to all depths. Oxidising conditions are therefore expected within the water column, although the decrease in the $O_2$ saturation of waters $\geq$15m during summer months was interpreted in terms of the cessation of photosynthesis, and the increased oxygen demand by finer sediments and respiring phytoplankton at greater depth. Fe and Mn oxyhydroxides may well be expected to influence the speciation and phase chemistry, and hence the availability of metal cations within the Lake Sibaya system. Potentially significant in this regard is the release of cations from the sediments through the dissolution of these oxides and hydroxides under reducing conditions, and the presence of an oxidative microzone at the sediment-water interface. Anaerobic degradation of organic matter may similarly effect the release of trace elements under reducing conditions in the sediments. This is significant, given the fact that organic-rich (± 27% organic carbon) muds (gyttja) comprise approximately 16% of the surface area of the Lake Sibaya bed. Organic matter (in the dissolved, colloidal or solid form) may significantly influence the speciation, transport and availability of major and trace elements, through adsorption and chelation processes.

Diatom algae dominate within the waters of Lake Sibaya, and may significantly influence Si saturation, through the release of molecularly dispersed Si from dissolving diatom frustules. Indeed, Si in solution arises primarily through amorphous silica, rather than from the dissolution of crystalline $SiO_2$ from clay minerals and quartz (the latter exhibiting particularly slow dissolution kinetics). Si (as $H_4SiO_4$) may react with Al and Fe oxyhydroxides to form ferro aluminium silicate in the sediments. Subsequent dissolution of these compounds may re-release Si to the overlying waters. Similarly, the solubility of Si may also be increased through the formation of humic compounds, and Fe and Al silicate humic complexes.

This chapter has presented the theory against which many of the results from the analysis of the Lake Sibaya water and sediment samples will be interpreted in the following chapters of this report.

# CHAPTER 3: THE AQUEOUS CHEMISTRY OF LAKE SIBAYA

## 3.1 INTRODUCTION

Lake Sibaya constitutes perhaps the most intensively studied of all South African freshwater bodies (*pers. comm.* Dr. M. Bruton, Two Oceans Aquarium, Cape Town). Despite this fact, little is known of the geochemical character of the lake system, or of the dynamic geochemical processes operational at the sediment-water interface. The prime objective of this chapter is therefore to investigate the chemical character of the waters of the Lake Sibaya system, as gleaned from the analysis of water samples collected for this study and from existing databases. The means by which water samples were collected, chemically analysed, and incorporated within the MINTEQA2 geochemical speciation model are described. The results of the analyses are thereafter discussed, with respect to the chemical composition, and the predicted speciation and mineral solubilities within the waters of the greater Lake Sibaya system.

## 3.2 SAMPLING

A total of twenty-six water samples were collected, on 3rd August 1998, from fourteen sampling sites located throughout Lake Sibaya. Each site was chosen to coincide with one of three transects running, variously: S-N (transect SA); SW-NE (transect WM); and W-E (transect WA). Water samples were also collected from each of three groundwater wells located in the vicinity of the lake (see Plate 1). A further water sample was gathered from the Mseleni River, prior to inflow into Lake Sibaya. Figure 3.1 indicates the position of each of the sample collection points. Table 3.1 presents a description of each of these sampling points, and an inventory of both the water and the sediment samples (refer to Section 4.2) collected in each instance.

Transects WA and WM were introduced along the western arm of Lake Sibaya and across the mouth of this channel, respectively. The Mseleni River enters the lake at the western extent of this arm, in the vicinity of site WA1. Five sites, coinciding with varying lake depths, were sampled along each of transects SA and WM. Four sites were sampled along transect WA. An individual water sample was collected from both the lake surface and the bottom metre of the water column at each site, with the exception of sites WA1 and SA1, from which only one pelagial (open water) sample was collected in each instance.

Surface water samples were collected from Lake Sibaya in Nasco® PVC WHIRL-PAK™ collection bags, which had been sterilised by the ethylene-oxide process during production. Each sample bag was pre-rinsed several times on-site in order to equilibrate it with the water to be collected. Sample bags were tightly sealed so as to exclude air. Water samples were collected from within the bottom metre of the water column at each lake site, using a PVC Waterra™ 1litre disposable baler, which was lowered through the water column by means of a rope. A shot-line provided an accurate indication of depth at each sample site. Each of these waters was thereafter transferred to the above-mentioned PVC sampling bags for storage. The necessary equipment was not available to measure EC or pH in the field.

Figure 3.1: The study area from which water and sediment samples were gathered.

**Table 3.1:** Inventory of samples collected from the study area for geochemical characterisation.

| Transect | Geographical co-ordinates | Lake depth (m) | Surface water sample | Bottom water sample | Sediments (‘sed’) & sediment-contacted waters (‘ |
|---|---|---|---|---|---|
| **(a) Lake Samples** | | | | | |
| Western Arm (WA) | 27°21′15″ S; 32°33′40″ E | 2.9 | WA1s | WA1d | WA1$_{\text{sed \& eq}}$ |
| | 27°21′22″ S; 32°34′35″ E | 5.6 | WA2s | WA2d | WA2$_{\text{sed \& eq}}$ |
| | 27°21′02″ S; 32°35′15″ E | 8.9 | WA3s | WA3d | WA3$_{\text{sed \& eq}}$ |
| | 27°20′45″ S; 32°36′52″ E | 12.8 | WA4s | WA4d | WA4$_{\text{sed \& eq}}$ |
| Southern Arm (SA) | 27°25′03″ S; 32°42′03″ E | 0.5 | - | SA1d | SA1$_{\text{sed \& eq}}$ |
| | 27°24′48″ S; 32°42′07″ E | 4.9 | SA2s | SA2d | SA2$_{\text{sed \& eq}}$ |
| | 27°24′32″ S; 32°42′15″ E | 11.8 | SA3s | SA3d | SA3$_{\text{sed \& eq}}$ |
| | 27°24′19″ S; 32°42′22″ E | 19.2 | SA4s | SA4d | SA4$_{\text{sed \& eq}}$ |
| | 27°24′11″ S; 32°42′30″ E | 24.9 | SA5s | SA5d | SA5$_{\text{sed \& eq}}$ |
| Western Mouth (WM) | 27°21′45″ S; 32°40′0″ E | 0.9 | - | WM1d | WM1$_{\text{sed \& eq}}$ |
| | 27°21′34″ S; 32°40′07″ E | 5.1 | WM2s | WM2d | WM2$_{\text{sed \& eq}}$ |
| | 27°21′26″ S; 32°40′22″ E | 10.5 | WM3s | WM3d | WM3$_{\text{sed \& eq}}$ |
| | 27°21′08″ S; 32°40′25″ E | 15.2 | WM4s | WM4d | WM4$_{\text{sed \& eq}}$ |
| | 27°21′01″ S; 32°40′31″ E | 20.2 | WM5s | WM5d | WM5$_{\text{sed \& eq}}$ |
| **(b) River** | | | | | |
| Mseleni River | 27°20′45″ S; 32°31′58″ E | Water sample “River” was collected at 10cm water depth. Riverbed depth was 0.8 m. | | | |
| **(c) Aquifer** | | | | | |
| Community Garden | 27°19′05″ S; 32°33′34″ E | “Well 1” (2.4m) and “Well 2” (2.2m) shallow aquifer water samples | | | |
| Roadside Well | 27°19′51″ S; 32°32′53″ E | “Well 3” shallow aquifer (2.1m) water sample | | | |

**Plate 1:** Collection of the groundwater sample from well 3.
Photo: D. Scott.

**Plate 2:** The Van Veen grab being used to collect a shallow sediment sample ($SA1_{sed}$).
Photo: D. Scott.

A sub-sample of each of the collected waters was transferred to an airtight glass bottle for isotope analysis. All water samples were maintained at 4°C between analyses.

A near-surface water sample (10cm depth) was collected in PVC sample bags from the stream channel of the Mseleni River, approximately 1.5km WSW of its entry into the lake. Similarly, a water sample was collected from each of three shallow open wells – in use by the local community for subsistence agriculture. The Department of Water Affairs (DWAF) groundwater chemistry database for Mapping Unit 7 was used to supplement the sample data.

The Van Veen grab sampler which was used to collect lake sediments at each of the fourteen sampling sites, (refer to Section 4.2), also trapped waters immediately overlying these sediments. These combined sediment-water samples were stored in airtight PVC jars and placed on an horizontal shaker for two weeks, so as to enhance equilibration. The supernatant water was thereafter decanted and subjected to the various laboratory analyses performed on the above-mentioned waters. The water samples of this type are labelled by the subscript "sed".

## 3.3 ANALYTICAL METHODS

### 3.3.1 Laboratory analyses

The analytical methods used to characterise water samples collected from Lake Sibaya, the Mseleni River, three shallow aquifer wells and waters in direct contact with lake sediments are presented in Table 3.2. The author conducted the majority of these analyses, using the facilities available within the Department of Geological Sciences at the University of Cape Town. Standard methods of water analysis (APHA, 1995) were observed conscientiously where possible. Stable isotopes ($\delta^{18}O$ and $\delta D$) within groundwater well and lake waters were analysed within the FRD/UCT Isotope Facility of the above-mentioned department. Dissolved organic carbon (DOC) was determined by the analytical laboratories of the Cape Water Program, CSIR, in Stellenbosch. The reader is referred to Appendix A for further details of the analytical methods employed, and for the results of replicate measurements to gauge precision.

**Table 3.2:** Methods used in the analysis of water samples, specified as per APHA (1995).

| Analyte | Method Description | Method Number | Instrumentation |
|---|---|---|---|
| EC | Conductivity Meter | 2520 B | CRISON microCM meter |
| pH | Electrometric: pH meter | 4500-$H^+$ B | Metrohm 691 pH meter |
| Alkalinity | Potentiometric Titration (Gran Method) | 2320 B | Radiometer DTS 800 multi-titration system |
| Major ions | Ion Chromatography (IC) | 4110 B | Dionex ion chromatograph |
| Silica | Molybdosilicate Method | 4500-Si D | Sequoia-Turner 340 spectrophotometer |
| Phosphorus | Murphy and Riley (1962) Ascorbic Acid Method | 4500-P E | |
| Trace Elements | ICP-MS | 3120 B | Perkin-Elmer ELAN 6000 ICP-MS |
| DOC | Persulphate-ultraviolet Oxidation | 5310 C | Autoanalyser |
| Fluoride | Ion-selective Electrode | 4500-$F^-$ C | Corning Solid State Ion Selective Electrode |
| Stable Isotopes ($\delta^{18}O$ and $\delta D$) | Mass spectrometry | Socki *et al.* (1993) | Finnigan Mat 252 spectrometer |

### 3.3.2 Department of Water Affairs and Forestry databases

#### *3.3.2.1 National Groundwater Database*

The results were obtained of groundwater analyses carried out within Mapping Unit 7 by the CSIR and the Department of Water Affairs and Forestry (DWAF). For the purpose of this study, only those 20 groundwaters collected from the drainage region W70 were considered (Figure 3.2). All of these samples were analysed during the period 9th April 1994 to 26th October 1994. The full data set is presented in Appendix C.

The Department of Water Affairs and Forestry initiated the KwaZulu-Natal geohydrological-mapping project in 1993. A total of 706 chemical analyses had been conducted at the time when this data was retrieved, each of the results having been entered into the HYDROCOM data base set up for the Zululand coastal plain. The province of KwaZulu-Natal was subdivided into 11 mapping units, the boundaries of which are based mainly on geological reasoning. The area covered by Mapping Unit 7 is underlain by essentially unconsolidated to semi-consolidated fine sands containing varying amounts of clay and silt. Discontinuous clay lenses of varying thickness occur frequently throughout the sequence (Meyer, 1995).

A comprehensive account of the analytical methods adopted by the DWAF is presented in van Vliet *et al.* (1988). In summary, chloride and alkalinity are determined by titration, TDS and sulphate are determined gravimetrically, and metals are determined by atomic absorption spectrophotometry. In addition to pH, EC, TDS and total alkalinity, the following dissolved analytes were determined for many of the samples: Na, Mg, Ca, F, Cl, $SO_4$, Si and K. Phosphate (determined as orthophosphate) and nitrogen ($NH_4^+$, $NO_3$+ $NO_2$) were also determined within these groundwaters.

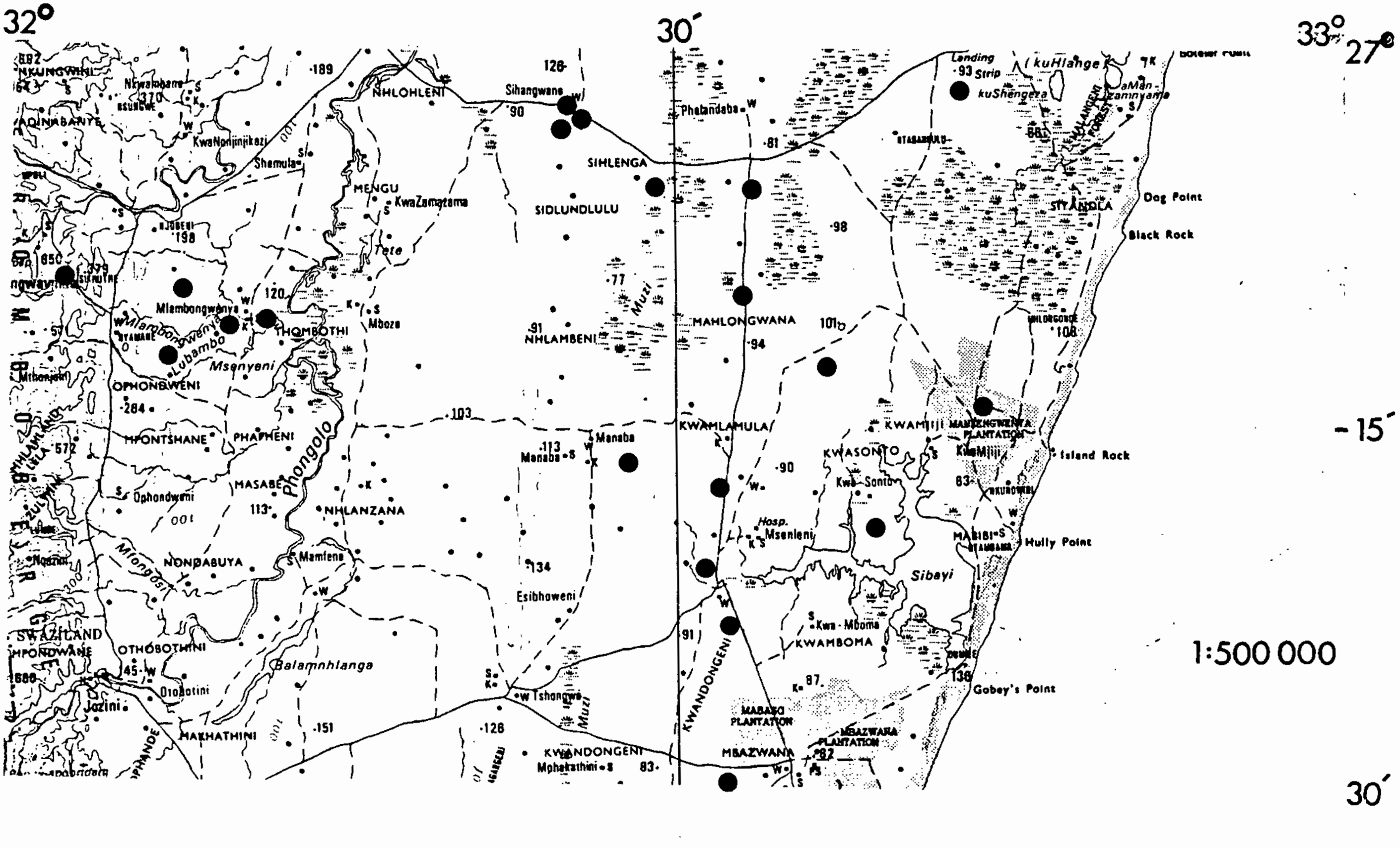

**Figure 3.2**: Selected boreholes and wells located within the region of Mapping Unit 7.

### 3.3.2.2 Lake level and lake water chemistry database

Measurements of water level and major ion chemistry of Lake Sibaya, conducted by the DWAF over the period 5 July 1980 to 5 November 1998, were obtained from the DWAF hydrological and chemical databases. Each of the samples was collected from station W7R001Q01 at Banda Banda bay in the south basin. Allanson (1979) notes that fluctuation in lake levels may be exaggerated at this station, due to its position at the apex of this narrow bay. Lake levels are reported relative to the fixed datum of 18.65m above geodetic mean sea level. The time period between successive measurements varied considerably. All samples were collected from within two metres of the surface of the water column. The water samples analysed in this particular study show that water chemistry is practically constant throughout the various regions and depths of the lake (*cf.* Section 3.4). Of the total of 201 samples collected, 144 were preserved with $HgCl_2$ prior to analysis. Water chemistry determinations were as per description in Section 3.3.2. This database is easily obtainable via the DWAF Head Office in Pretoria.

## 3.3.3 Chemical modelling

### *3.3.3.1 MINTEQA2 chemical speciation model*

Ionic speciation and mineral saturation indices were calculated for all analysed water samples, using the geochemical equilibrium speciation model MINTEQA2, (Allison *et al.*, 1991) developed for dilute aqueous systems. The complementary interactive program PRODEFA2 was used to create the necessary input files.

MINTEQA2 uses an approach of iterative guesses at the activity of each chemical component to calculate the equilibrium concentration of each species. The Davies equation was chosen to calculate activity coefficients for all charged species based on the ionic strength of all the collected water sample solutions. The Davies equation is an extension of the Debye-Hückel equation, in which the ion size-dependent parameters are the same for each charged ion (Lumsdon and Evans, 1995.) A further description of the MINTEQA2 model is presented in Appendix D. The problems associated with the inclusion of organic matter and Al in the MINTEQA2 model is also presented in the latter appendix.

### *3.3.3.2 PHREEQC model*

The computer program PHREEQC was used to model the effects which progressive evaporation would exert on the solute composition of the Lake Sibaya waters. The program is written in the C programming language, and uses ion-association and Debye-Hückel expressions to account for the non-ideality of solutions. This type of aqueous model is adequate for the waters of Lake Sibaya, which are known to be of low ionic strength. The MINTEQA2 database is supported by this package, and was used, to achieve consistency with previous speciation and mineral solubility modelling. Input to PHREEQC is completely free format, data being arranged in keyword data blocks. A series of evaporative concentration scenarios (or 'simulations') were run for sample WM2d, in which progressively increasing quantities of water (ranging from twice to one thousand times present concentration) were removed from the solution. Each of these simulations contained calculations to determine the initial solution speciation, as well as the chemical composition, associated with the removal of water. The 'EQUILIBRIUM_PHASES' data block was used to specify that supersaturated solids would precipitate from solution. Further description of the PHREEQC computer program is presented in Parkhurst (1995).

#### *3.3.3.3 STASOFT model*

The Stasoft (Version 3.0) chemical conditioning computer program (Friend and Lowenthal, 1992) was used to calculate the calcite precipitation potential of two representative Lake Sibaya waters (WA1s and WM4d) and the groundwaters of wells 1 and 2. The model calculates the activities of calcium, magnesium, sodium, chloride and sulphate, based on their entered concentrations. Further parameters entered into the model to enable calculation of the calcite precipitation potential include pH, temperature (assumed to be 20°C in each instance), alkalinity and EC. The intention is to interpret the output in terms of the practical ramifications of scaling or corrosion of the pipelines used to convey this water to the local community, and in the hypothetical use of this water by light industry in the region.

## 3.4 RESULTS AND DISCUSSION

Analysis of electrical conductivity (EC) and pH for the open (pelagial) waters of Lake Sibaya (refer to Table 3.3) revealed minimal variation in either of these properties, with respect to either depth or geographical locality. Regression of EC and pH against the water depth for each of the transects at which samples were collected yielded insignificant correlations ($R^2 < 0.6$; n=26) in each instance. This appears to confirm the proposal (Allanson, 1979) that the waters of Lake Sibaya are, to a large extent, homogenous as a result of relatively intense mixing initiated by wind action. In light of this fact, and with due consideration of time and logistical constraints, five lake samples were chosen as representative of Lake Sibaya pelagial waters, and were subjected to further chemical analyses. These samples were deliberately chosen to cover a range of depths, and each of the three sampling transects established throughout the lake.

Results of water analyses conducted on the selected pelagial waters of Lake Sibaya, the three groundwater wells, and the Mseleni River water sample are provided in Table 3.4 (a-c). The results of similar analyses conducted on waters in contact with Lake Sibaya sediments are presented in Table 3.5 (a-c).

### 3.4.1 pH and alkalinity

The pH of the Lake Sibaya open waters covered a narrow range of 8.0 to 8.3. This range is in accordance with the findings of previous studies conducted throughout the past three decades (Allanson and van Wyk, 1969; Bowen, 1976, 1978; Bruton, 1980, *In*: Bruton and Cooper, 1980) and coincides fairly closely with the average pH of 7.8 observed for the DWAF lake database. Indications are, therefore, that the open waters of Lake Sibaya are regulated by the $CO_2$-$HCO_3^-$-$CO_3^{2-}$ buffering system, and fall roughly within the upper range of pH (approximately 6.5 to 8) considered to be 'typical' of natural waters.

The bicarbonate ion is expected to constitute the predominant carbonate species in solution under the pH conditions prevalent within the lake waters. Accordingly, the MINTEQA2 chemical speciation model predicts that ≥ 97% of all carbonate in Lake Sibaya waters will occur as bicarbonate. Expressing all solution carbonate in this form, the molar concentration of $HCO_3^-$ averages 2.26mmol$_c$/l, with a standard deviation of 0.01. The low standard deviation suggests that the lake is thoroughly mixed to a depth of at least 25m (the maximum sampling depth).

**Table 3.3:** EC and pH analyses of all open water samples collected from the water column of Lake Sibaya. Mean EC and pH values and the upper and lower 95% confidence limits to this data are shown.

| Site | Lake depth (m) | Lake surface waters | | Lake bottom waters | |
|---|---|---|---|---|---|
| | | EC (µS/cm) | pH | EC (µS/cm) | pH |
| WA1 | 2.9 | 547 | 8.0 | 556 | 8.0 |
| WA2 | 5.6 | 558 | 8.0 | 546 | 8.1 |
| WA3 | 8.9 | 545 | 8.0 | 550 | 8.0 |
| WA4 | 12.8 | 543 | 8.0 | 548 | 8.1 |
| SA1 | 0.5 | - | - | 566 | 8.0 |
| SA2 | 4.9 | 558 | 8.1 | 559 | 8.0 |
| SA3 | 11.8 | 560 | 8.1 | 555 | 8.1 |
| SA4 | 19.2 | 553 | 8.1 | 546 | 8.1 |
| SA5 | 24.9 | 547 | 8.3 | 545 | 8.2 |
| WM1 | 0.9 | - | - | 550 | 8.2 |
| WM2 | 5.1 | 547 | 8.2 | 565 | 8.2 |
| WM3 | 10.5 | 550 | 8.3 | 556 | 8.3 |
| WM4 | 15.2 | 551 | 8.3 | 543 | 8.2 |
| WM5 | 20.2 | 547 | 8.2 | 543 | 8.3 |
| Mean | | 550.5 | 8.13 | 552.0 | 8.13 |
| ±95% Conf. | | 546.9 – 554.1 | 8.06 – 8.21 | 547.6 – 556.4 | 8.07 – 8.19 |

The waters appear to approach equilibrium with atmospheric $CO_2$, through the action of waves and water currents set up by prevailing winds. The invasion rate of $CO_2$ from the air into lakes of the Canadian Shield was shown (Emerson *et. al.*, 1973) to increase with the decay of the stagnant boundary layer (initially 300µm in thickness), as wind velocities increased, especially above 1.5 m/s. Carbon dioxide presumably undergoes dissolution in the Lake Sibaya waters, to produce carbonic acid, which subsequently dissociates, initially into bicarbonate ions, and thereafter into the carbonate ion. The pathway described above is presented in the following equation:

$$\underset{\phantom{x}}{CO_{2(g)} + H_2O} \rightarrow \underset{\textit{carbonic acid}}{H_2CO_3} \rightarrow \underset{\textit{bicarbonate}}{H^+ + HCO_3^-} \rightarrow \underset{\textit{carbonate}}{2H^+ + CO_3^{2-}}$$

The groundwater pH values determined for the three well water samples are in relatively close agreement with the average pH ($\bar{x}$=7.6, s.d.=0.7) of eighteen groundwaters analysed from the drainage region by the DWAF. The application of the Shapiro-Wilks' *W* test demonstrated that pH was normally distributed within the DWAF samples (W=0.98; p=0.90). The fact that the three groundwater wells analysed in this study display almost identical pH and alkalinity values to those of the lake waters suggests that the percolation of rain through the aquifer may also represent a significant control over the alkalinity of the lake waters. This control is hypothesised to occur through the past and present dissolution of $CO_2$ (as described above), carbonate minerals (refer to Section 4.4.4), and the weathering of primary silicate minerals from the aquifer sands.

In the former instance, the metabolic activity of roots, micro-organisms and other living organisms in the soil may generate $CO_2$, soluble organic acids and acidic organic residues, all of which behave as weak acids in the soil, displacing base cations from exchange sites (McBride, 1994). The base cations may then be leached from the soil into the groundwater (and subsequently into the lake), in the form of salts of bicarbonate and organic anions. This process is particularly favoured by high content of $CO_2$ in the soil atmosphere, which may reach levels as high as 1 to 5 percent $CO_2$ by volume (McBride, 1994).

The weathering of silicate minerals contained in the shallow aquifer of the Zululand coastal plain, under humid climatic conditions, is a non-reversible process, that the author proposes to have provided a significant source of alkalinity in solution over the past few thousand years. The source of this alkalinity is the silicate anion, liberated from the mineral by hydrolysis of the structure. This anion is a very strong base, reacting with protons from solution to form weak monosilicic acid (McBride, 1994). The alkalinity thus formed, (generated in the form of $OH^-$) reacts with $CO_2$ dissolved in the soil solution, to convert the alkalinity into the bicarbonate form, which is then carried to coastal groundwaters:

$$OH^- + \underset{carbonic\,acid}{H_2CO_3} \quad = \quad H_2O + \underset{bicarbonate}{HCO_3^-}$$

This reaction may therefore have boosted the bicarbonate alkalinity of the Lake Sibaya waters, through the inflow of these coastal groundwaters to the lake.

The substantially elevated alkalinity of the sediment waters may similarly be related to raised levels of soluble organic acids and acid organic residues associated with the incorporation of fine organic lacustrine mud (gyttja) into the sediment fraction. This would serve to justify both the lower pH of the sediment waters, in comparison with the open lake waters, and the increased alkalinity of such waters. The waters in direct contact with the sediments are expected to have approached equilibrium with the minerals (including mineralised phytoplankton assemblages) which have precipitated into the sediments. Microbial reduction associated with anaerobic conditions in the sediments may be producing $H_2S$, the accumulation of which would be expected to lower the pH of waters in direct contact with the sediment. A final explanation for the elevated alkalinity status of the sediment-contacted waters relates to the fact that, in accordance with standard methods (APHA, 1995), none of the water samples were filtered, prior to alkalinity measurement. Consequently, organic acids and colloidal silicates and oxyhydroxides may contribute significantly to the alkalinity determination, through providing negative surfaces at which $H^+$ ions may be held.

### 3.4.2 EC

As mentioned previously, the electrical conductivities (EC's) of the waters of Lake Sibaya were shown to be highly consistent (543-566 µS/cm) throughout various depths in the water column, and throughout various localities in the lake. This suggests thorough mixing to all depths of the water column. The long-term (1980-1998) average EC for the lake was determined from the DWAF chemistry database as 613µS/cm (s.d.=10.6).

For means of comparison with previous studies, electrical conductivities were converted to total dissolved solids (TDS) using the following empirically-derived equation (Dallas and Day, 1993):

$$TDS\,(mg/l) = EC\,(\mu S/cm)\ x\ 66$$

**Table 3.4**: Analysis of Lake Sibaya, groundwater well and Mseleni River bulk waters.

**(a)** General characteristics

| Sample No. | pH | EC (µS/cm) | Alkalinity (mg $HCO_3^-$/l) | DOC (mg/l) | ♦$SiO_2$ (mg/l) | Charge Balance (%) (excluding DOC) |
|---|---|---|---|---|---|---|
| WA1s | 8.0 | 547 | 139 | 3 | 8.3 | 5.0 |
| WA3d | 8.0 | 550 | 137 | 3 | 7.8 | 6.2 |
| SA5d | 8.2 | 559 | 139 | 3 | 8.9 | 8.2 |
| WM2d | 8.2 | 565 | 138 | 2 | 8.0 | 5.9 |
| WM4d | 8.2 | 543 | 138 | 3 | 8.5 | 6.1 |
| WELL 1 | 8.1 | 313 | 139 | 13 | 10 | 28.9 |
| WELL 2 | 7.8 | 362 | 139 | 16 | 12 | 6.9 |
| WELL 3 | 8.4 | 655 | 134 | 10 | 5.4 | 31.0 |
| RIVER | 8.2 | 699 | 136 | 4 | 9.7 | 24.5 |

**(b)** Major ion concentrations (mg/l)

| Sample No. | Na | $NH_4$ | K | Mg | Ca | Cl | $SO_4$ | ■$F^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| WA1s | 92 | 0.05 | 7.9 | 14 | 42 | 143 | 20 | 0.13 |
| WA3d | 87 | 0.05 | 6.6 | 14 | 35 | 130 | 9.2 | 0.14 |
| SA5d | 95 | 0.05 | 9.5 | 18 | 41 | 147 | 11 | 0.14 |
| WM2d | 91 | 0.05 | 8.1 | 17 | 45 | 150 | 19 | 0.13 |
| WM4d | 95 | 0.05 | 8.7 | 18 | 38 | 151 | 14 | •< 0.1 |
| WELL 1 | 83 | 0.05 | 10 | 13 | 85 | 88 | 14 | 0.14 |
| WELL 2 | 78 | 0.05 | 8.3 | 15 | 30 | 80 | 47 | 0.16 |
| WELL 3 | 76 | 0.6 | 17 | 10 | 86 | 57 | 40 | 0.15 |
| RIVER | 135 | 0.05 | 7.7 | 20 | 71 | 145 | 22 | 0.15 |

**(c)** Trace element concentrations (ppb)

| Sample | Li | Al | Cr | Mn | Ni | Cu | Zn | Se | Rb | Sr | Ba | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| WA1s | 1.9 | 3.9 | 2.3 | 0.5 | 1.0 | 1.5 | 5.3 | 1.6 | 10 | 151 | 123 | 64 |
| WA3d | 1.3 | 1.0 | 2.2 | 0.7 | 0.9 | 1.5 | 9.7 | 1.7 | 14 | 144 | 120 | 62 |
| SA5d | 1.2 | 5.4 | 1.9 | 0.3 | 1.2 | 2.3 | 3.6 | 1.7 | 13 | 146 | 127 | 65 |
| WM2d | 1.2 | 8.6 | 2.3 | 0.6 | 3.3 | 6.5 | 27 | 1.5 | 12 | 137 | 124 | 61 |
| WM4d | 1.0 | 18 | 2.2 | 0.5 | 1.1 | 5.5 | 13 | 1.5 | 13 | 159 | 127 | 52 |
| WELL 1 | 11 | 252 | 4.2 | 11 | 3.4 | 4.4 | 4.5 | 0.8 | 11 | 123 | 74 | 135 |
| WELL 2 | 12 | 364 | 4.3 | 2.7 | 2.7 | 4.3 | 9.9 | 0.9 | 6.6 | 86 | 72 | 218 |
| WELL 3 | 1.8 | 13 | 6.1 | 0.4 | 3.8 | 2.4 | 14 | 6.4 | 27 | 172 | 103 | 180 |
| RIVER | 4.6 | 8.1 | 4.4 | 0.5 | 1.5 | 2.0 | 3.2 | 1.7 | 6.5 | 176 | 101 | 102 |

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♦ Silica determined by the Molybdosilicate method (Standard Method 4500-Si D; In: APHA, 1995).

■ Fluoride determination by Ion Selective Electrode

• Fluoride detection limit as specified by Standard Methods (APHA, 1995).

**Table 3.5**: Analysis of waters in contact with Lake Sibaya sediments.

**(a)** General characteristics

| Sample No. | pH | EC (µS/cm) | Alkalinity (mg $HCO_3^-$/l) | DOC (mg/l) | ♦$SiO_2$ (mg/l) | Charge Balance (%) |
|---|---|---|---|---|---|---|
| WA1eq | 7.5 | 702 | 334 | | 41 | 0 |
| WA2eq | 8.0 | 868 | 389 | | 33 | 8 |
| WA3eq | 8.2 | 691 | 329 | | 33 | 10 |
| WA4eq | 7.9 | 869 | 402 | | 33 | 10 |
| SA1eq | 7.5 | 782 | 339 | | 39 | 10 |
| SA2eq | 7.5 | 1026 | 557 | 21 | 41 | 0 |
| SA3eq | 7.7 | 743 | 303 | 13 | 45 | 11 |
| SA4eq | 7.3 | 880 | 341 | | 24 | 10 |
| SA5eq | 8.1 | 763 | 330 | | 32 | 4 |
| WM1eq | 7.5 | 936 | 336 | | 37 | 15 |
| WM2eq | 7.8 | 990 | 361 | 10 | 40 | 20 |
| WM3eq | 7.4 | 627 | 319 | 29 | 33 | 2 |
| WM4eq | 7.5 | 772 | 320 | | 32 | 14 |
| WM5eq | 7.6 | 709 | 319 | | 26 | 5 |

**(b)** Major ion concentrations (mg/l)

| Sample No. | Na | $NH_4$ | K | Mg | Ca | Cl | $SO_4$ | ■$F^-$ |
|---|---|---|---|---|---|---|---|---|
| WA1eq | 78 | 3.4 | 11 | 16 | 62 | 121 | 16 | •< 0.1 |
| WA2eq | 82 | 14 | 15 | 28 | 56 | 106 | 22 | < 0.1 |
| WA3eq | 89 | 3.5 | 10 | 25 | 74 | 127 | 30 | 3.34 |
| WA4eq | 99 | 6.5 | 10 | 34 | 76 | 113 | 25 | 3.36 |
| SA1eq | 86 | 12 | 11 | 23 | 65 | 115 | 21 | < 0.1 |
| SA2eq | 88 | 21 | 16 | 28 | 83 | 111 | 17 | 3.48 |
| SA3eq | 86 | 7.8 | 11 | 25 | 57 | 114 | 23 | 3.36 |
| SA4eq | 81 | 23 | 12 | 19 | 70 | 113 | 22 | 3.45 |
| SA5eq | 99 | 7.3 | 11 | 24 | 57 | 129 | 21 | 3.37 |
| WM1eq | 94 | 14 | 16 | 33 | 77 | 120 | 1.7 | 3.83 |
| WM2eq | 87 | 19 | 17 | 35 | 77 | 115 | 25 | < 0.1 |
| WM3eq | 86 | 2.7 | 10 | 20 | 48 | 118 | 24 | 3.47 |
| WM4eq | 91 | 8.7 | 12 | 29 | 66 | 117 | 26 | 3.38 |
| WM5eq | 82 | 6.7 | 9 | 24 | 54 | 116 | 24 | 3.31 |

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♦ Silica determined by the Molybdosilicate method (Standard Method 4500-Si D; In: APHA, 1995).

■ Fluoride determination by Ion Selective Electrode

• Fluoride detection limit as specified by Standard Methods (APHA, 1995).

**Table 3.5 (continued):**

**(c)** Trace element concentrations (ppb)

| Sample No. | Li | Al | Cr | Mn | Ni | Cu | Zn | Se | Sr | Ba |
|---|---|---|---|---|---|---|---|---|---|---|
| Wa1eq | 2.1 | 46 | 2.7 | 1001 | 2.7 | 5.2 | 15 | 1.4 | 226 | 181 |
| Wa2eq | 1.0 | 65 | 3.3 | 872 | 3.9 | 6.5 | 24 | 11 | 324 | 774 |
| Wa3eq | 1.5 | 75 | 3.7 | 52 | 2.3 | 4.5 | 12 | 3.7 | 260 | 198 |
| Wa4eq | 1.0 | 27 | 4.2 | 68 | 4.0 | 6.9 | 15 | 3.5 | 368 | 306 |
| Sa1eq | 1.4 | 26 | 3.7 | 1485 | 2.5 | 5.3 | 20 | 3.0 | 293 | 342 |
| Sa2eq | 1.7 | 19 | 4.1 | 2956 | 2.5 | 87 | 14 | 3.6 | 448 | 492 |
| Sa3eq | 1.2 | 20 | 2.7 | 27 | 2.8 | 14 | 16 | 3.0 | 290 | 502 |
| Sa4eq | 6.1 | 28 | 45 | 35 | 5.6 | 16 | 16 | 2.9 | 285 | 348 |
| Sa5eq | 1.1 | 37 | 2.8 | 23 | 4.4 | 35 | 7.9 | 3.4 | 278 | 239 |
| Wm1eq | 1.7 | 34 | 4.3 | 5635 | 3.3 | 3.2 | 9.2 | 3.8 | 435 | 599 |
| Wm2eq | 1.2 | 56 | 3.5 | 2246 | 3.3 | 115 | 19 | 5.8 | 428 | 897 |
| Wm3eq | 1.2 | 34 | *< 0.02 | 9.3 | 1.7 | 1.3 | 9.4 | 2.4 | 211 | 220 |
| Wm4eq | 1.1 | 23 | 1.5 | 9.7 | 2.9 | 3.5 | 12 | 5.3 | 300 | 416 |
| Wm5eq | 1.1 | 91 | 1.2 | 29 | 2.5 | 2.4 | 18 | 5.0 | 261 | 300 |

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* Cr detection limit as specified by Horlick *et al.* (1992).

Total dissolved solids (TDS) represent the quantity of dissolved material, organic and inorganic, ionised and un-ionised, in a water sample. Measurement of low quantities of TDS by direct means (gravimetry) is subject to inaccuracy associated with experimental error. Since electrical conductivity is a function of the number of charged particles (ions) in solution, and since the majority of dissolved material in most waters are ionic, EC is often used as a surrogate for TDS. Note, however, that the mathematical relationship between TDS and EC quoted above is tenuous and should be treated with due caution (Dallas and Day, 1993).

Substituting average EC values into the above-mentioned formula yields a TDS value of 364 mg/l for lake waters (EC = 551.3µS/cm), and a value of 461 mg/l for the Mseleni River. The sediment-contacted waters show a TDS range of 456 - 677 mg/l, with an average value of 535mg/l. TDS values of 207, 239 and 432 mg/l are obtained for wells 1,2 and 3 respectively. Wells 1 and 2 fall within the group of 53% of DWAF groundwater samples in the catchment that had EC values in the range 200-400µS/cm. The Shapiro-Wilks' *W* value was highly significant ($W$=0.71; p=0.00) indicating that EC was not normally distributed within the latter samples, but rather positively skewed (skewness =1.98) and leptokurtic, or peaked (kurtosis=3.46). Mseleni River waters fall within the upper bracket of the TDS range (50-660 mg/l) recorded for local Zululand coastal plain rivers (Dallas and Day, 1993), and were elevated above lake or groundwater levels. This suggests slight contamination of the river waters.

The reported TDS of marine-isolated coastal lakes of the Zululand coastal plain are, without exception, slightly lower than those noticed within the free waters of Lake Sibaya. Lake Mzingazi (50-100 mg/l; Fowles and Archibald, 1987), Lake Cubhu (200 mg/l; Cyrus and Martin, 1988), Lake Mgobozeleni (300mg/l; Bruton and Appleton, 1975) and Lake Bhangazi South (220-290 mg/l; Crass, 1963; English, 1980) are examples of such lakes. These lakes fall within a region extending to 170 km south of Lake Sibaya. They constitute shallow lakes (less than 6m average depth) with direct outflows, but with no tidal exchanges (Hart, R.C., In: Cowan, 1995).

The EC of Lake Sibaya pelagial waters is approximately 60% to 70% greater than that of wells 1 and 2, respectively. The increase in EC, upon entering the lake, is proposed to arise primarily as a result of the evaporative concentration of the latter waters. This hypothesis will be tested further, at a later stage in this report. The EC level in well 3 is raised relative to that of the remaining two wells, with elevated $NH_4^+$ and $K^+$ concentrations indicating possible contamination of well 3 waters.

### 3.4.3 Major ions and the control thereof

#### *3.4.3.1 Major ions in solution*

A comparison of the average concentrations of the major ions determined in the open waters of Lake Sibaya in this study versus the longer-term average concentration of these ions (DWAF database: 1980-1998) is presented in Table 3.6. Fairly considerable variations exist between the two data sets with regard to the measured concentrations of various major ions in the lake waters, most notably those of Ca and Mg. It is not known to what extent this disparity relates to actual geochemical differences, to differences in analytical method, or to analytical error. The charge balance obtained for the DWAF data averaged 3.3%, indicating that the major ions were generally well accounted for in the laboratory analyses. Each of the ions was normally distributed within both sets of analyses, as determined from the examination of the relevant histograms (not shown) and the Levene test of homogeneity of variances.

The proportional concentration of major ions in the waters analysed in this study, in addition to those of the sediment-associated waters of each transect, the three groundwater wells, and the Mseleni River are represented by means of STAR diagrams in Figure 3.3. These plots were created using the FORTRAN 77 based programme 'STARS' (Willis and Hill, 1992). Each circle is divided into eight equal sectors, each representing one of the major ions in solution.

Within, or extending from, each is a quadrilateral whose area is proportional to the molar concentration of that ion, normalised to 100. These diagrams allow for the rapid and efficient comparison of up to nine variables (in this instance the major ions in solution) per sample, through the identification of significant pattern changes (Willis and Hill, 1992).

The Lake Sibaya pelagial water samples analysed in this study group into 'category 3' waters established for South African river waters by Day and King (1995). Within such waters, $Na^+$ constitutes the dominant cation, while $Cl^-$ and (to a lesser extent) $HCO_3^-$ comprise the dominant anions, although significant quantities of $Ca^{2+}$ and $Mg^{2+}$ are also present. Day and King note that category 3 waters are fairly widespread throughout the country, and appear not to be confined to, or excluded from, any particular geological formation.

The waters in direct contact with sediments collected from each of the three sampling transects are remarkably similar to each other in terms of major ion chemistry, each displaying the "butterfly-shaped" type STAR plot, dominated by $HCO_3^-$. The reason for the elevated bicarbonate concentrations was discussed in Section 3.4.1. The milliequivalent levels of $Cl^-$ and $Na^+$ are high, indicating a marine signature. The ions $HCO_3^-$, $Ca^{2+}$ and (to a lesser extent) $Mg^{2+}$ also show a significant presence within these waters, the first two ions occurring in roughly equivalent proportions in solution. The proportions of K, $SO_4^{2-}$, and $PO_4^{3-}$ in these aqueous solutions are minimal, as indeed they are within all the analysed water samples, with the possible exception of $SO_4^{2-}$ in well 2 and well 3 (not shown).

#### *3.4.3.2 Control over major ion dominance*

The relationship between TDS and the ratio $[Na^+]:([Na^+] + [Ca^{2+}])$ in Lake Sibaya pelagial waters is illustrated in Figure 3.4, as a means of assessing the controls over major ion proportions. Gibbs (1970) identified such a relationship within river waters. The predominant controls over ion dominance in these waters appear to be atmospheric precipitation and evaporative concentration, as opposed to the leaching of ions from the substratum (i.e. atmospheric rather than geological control). This suggests that the alkali metals (particularly $Ca^{2+}$ and $Mg^{2+}$) are present in low proportion in the Pleistocene to Recent aeolian sands of the lake catchment and groundwater aquifer. Consequently, the process of dissolution of these ions (by $HCO_3^-$ and protons produced by the dissolution of $CO_2$) is insufficient to significantly influence major ion chemistry. Alkali metals (particularly Na and K) are not easily dissolved from the substratum, even in the presence of the $HCO_3^-$ buffering system. Low levels of electrolytes in precipitation waters generally render surface waters relatively dilute. The wet- and dry-atmospheric deposition of cyclical salts onto the Zululand coastal plain by salt-laden on-shore winds is, however, undoubtedly raising solution ionic strength, and imparting to the coastal plain waters a relatively strong marine signature. This is evidenced by the millimolar charge ratio of 0.98 obtained for the $Na^+:Cl^-$ ion pair.

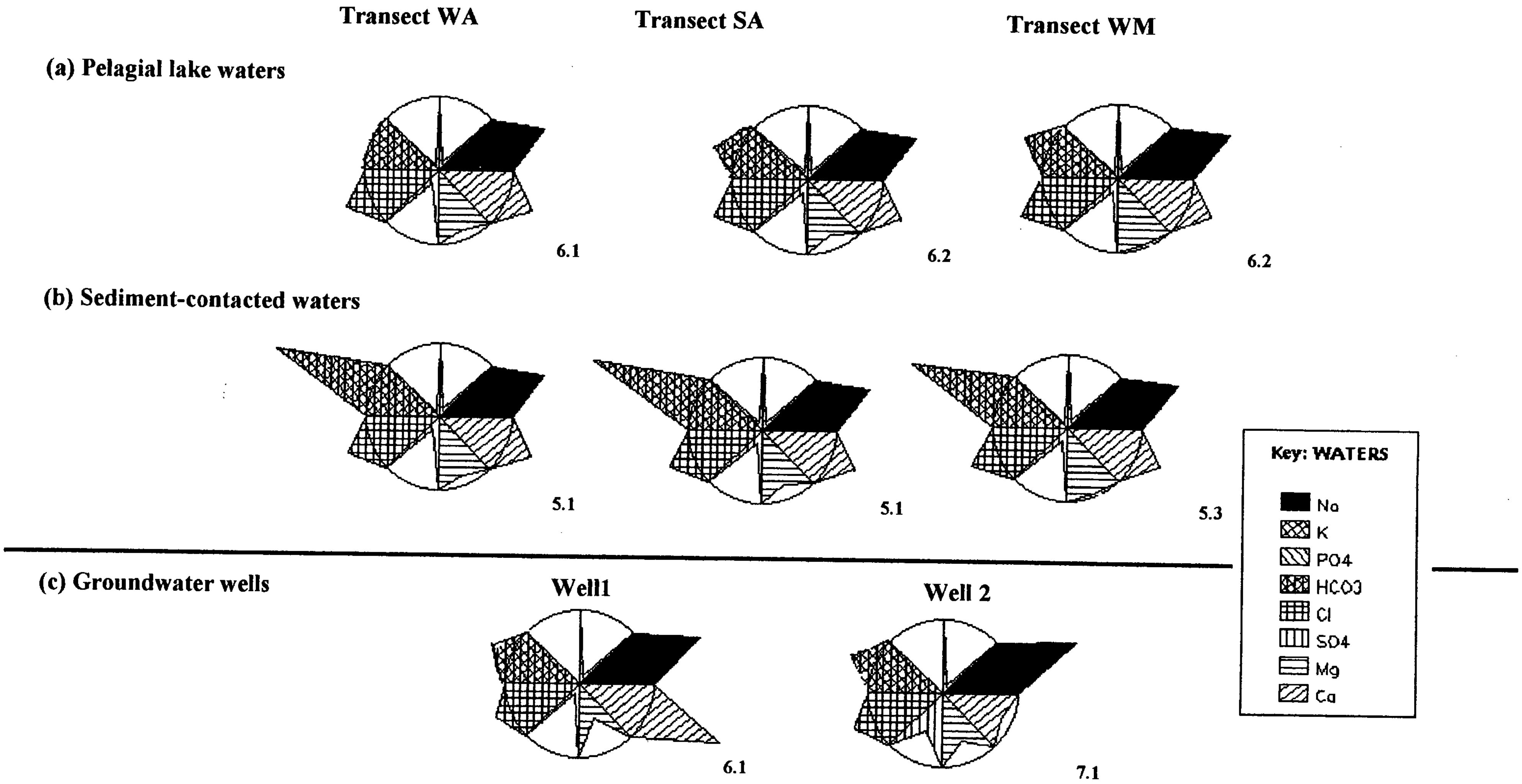

**Figure 3.3:** STAR diagrams displaying patterns of ionic dominance in water samples collected from Lake Sibaya, groundwater wells and waters in contact with Lake Sibaya sediments. Normalisation factors are indicated to the lower right of each plot.

**Table 3.6:** The average concentrations of major ions in the open waters of Lake Sibaya.

| Ion | Ion concentrations: this study (mg/l) | (mmol$_c$/l) | Average conc. (mg/l) and (s.d.) DWAF (1980-1998) | % Difference |
|---|---|---|---|---|
| Cations | | | | |
| $Na^+$ | 92 | 4.0 | 81 (30) | 6.4 |
| $Ca^{2+}$ | 40 | 2.0 | 23 (2.0) | 27 |
| $Mg^{2+}$ | 16 | 1.3 | 8.6 (0.8) | 30 |
| $K^+$ | 8.1 | 0.2 | 6.6 (0.7) | 10 |
| Anions | | | | |
| $HCO_3^-$ | 138 | 2.3 | 122 (99) | 6.2 |
| $Cl^-$ | 144 | 4.1 | 116 (8.4) | 11 |
| $SO_4^{2-}$ | 15 | 0.3 | 11 (4.2) | 15 |

Charge balance = 5.6% (calculated as $\frac{\sum cations - \sum anions}{\sum cations + \sum anions} x\,100$)

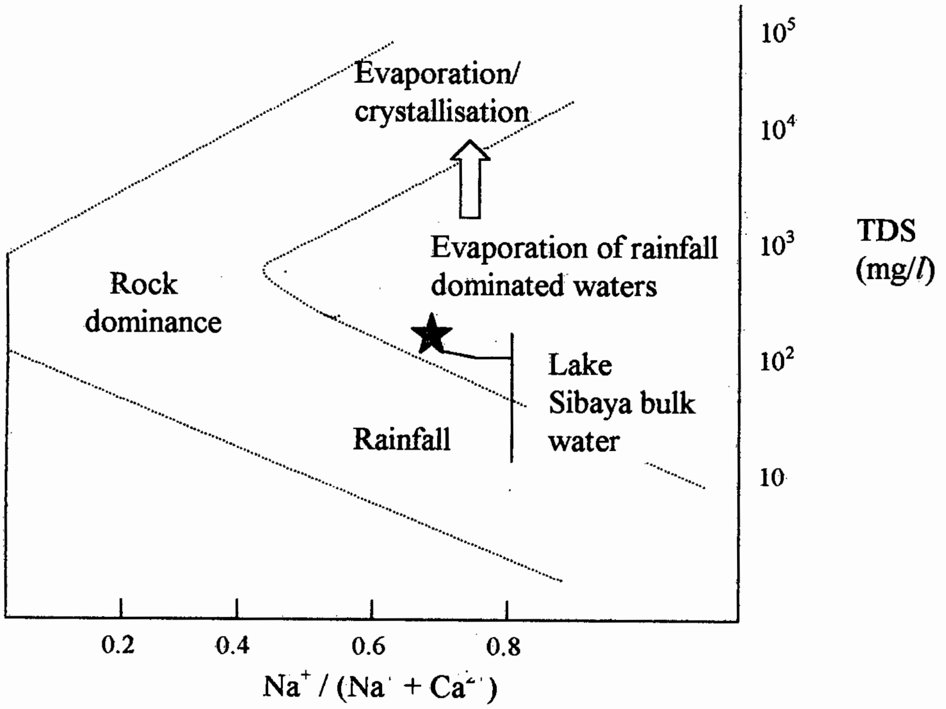

**Figure 3.4**: An investigation of the ratio [$Na^+$]: ([$Na^+$] + [$Ca^{2+}$]) versus TDS in Lake Sibaya bulk waters, as an indication of the processes controlling major ion dominance. (Modified after Day and King, 1995).

A previous assertion by Allanson and van Wyk (1969) that $Na^+$:$Cl^-$ proportions in Lake Sibaya (and other northern Zululand lakes) do not correspond with those of seawater, was incorrectly based on the percentage proportions of these ions in solution, rather than comparison of their ion ratios on a milliequivalent basis. Fairbridge (1972) specifies that approximately 50% of $Na^+$, and probably all of $Cl^-$, in coastal surface waters are derived from sea spray and recycled through the atmosphere. The ratios of other major components of surface and seawater ($Mg^{2+}$, $K^+$, $Ca^{2+}$, $SO_4^{2-}$, $HCO_3^-$ and $H_4SiO_4^{\circ}$) are subject to varying mechanisms and rates of removal, and are consequently not investigated here as evidence of a marine influence.

The slight salinity measured in Lake Sibaya waters is apparently sufficient to allow the occurrence of various euryhaline benthic and/or planktonic estuarine invertebrates, along with typical freshwater components in Lake Sibaya. Similar estuarine relicts are encountered in several Zululand lakes lacking tidal connections, such as Mgobezeleni, Mzingazi and Cubhu (Reavell and Cyrus, 1989).

The levels, and the relative molar proportions, of both $Na^+$ and $Cl^-$, are elevated in the bulk lake waters, relative to each of the three well waters sampled (refer to Figure 3.3). A three-fold explanation is offered. Firstly, a decrease in the concentrations of these constituents in atmospheric precipitation is to be expected with increasing distance from the coast, as outlined in Chapter 2. Secondly, groundwaters may become progressively enriched in these constituents with increasing flow distance along the catchment (as the groundwaters approach the lake), owing to the dissolution of salts at the soil surface, and from the aquifer sands. It appears unlikely, however, that fossil marine sources of $Cl^-$, which were speculated to be feeding Lake Sibaya waters (Hart, R.C. In: Cowan, 1995), would have persisted within the Tertiary sands underlying Lake Sibaya, given the intensive leaching regime and the ready solubility of NaCl. Finally, it is proposed that enrichment of these (and other) ions in Lake Sibaya bulk waters may be achieved through evaporative concentration of solutes associated with the excess of evaporation over atmospheric precipitation.

Figure 3.5 shows the monthly water level of Lake Sibaya for the period 1980 to 1998. The water level is reported relative to the fixed datum of 18.65m above geodetic mean sea level, which was established as the chart datum at Banda Banda. Unfortunately both the DWAF and the Weather Bureau meteorological stations at Mbazwana and at Sodwana Bay were closed down in late 1980, owing to infrequent and generally unreliable data (*pers. comm.* Mr. P. Vorster, DWAF, Durban). Consequently lake level cannot, here, be compared to the balance between evaporation and precipitation for the region over this period. Allanson (1979) noted relatively strong relationships between the level of the lake and both precipitation (1972-1977) and evaporation (1972-1974).

Figure 3.6 shows a statistically significant inverse relationship to exist between the TDS, measured within the Lake Sibaya pelagial waters between 1980 and 1998, and the lake depth over this period (which is here considered as a proxy for the degree of dilution or concentration). Several outliers ($\bar{x} \pm 3$ s.d.) were removed from the data set, prior to statistical analysis. This relationship highlights the importance of dilution and concentration processes in controlling the total solute concentration within the lake waters. Note, however, that the TDS spans a concentration range of barely 100 mg/l over the 19-year period in which these readings were measured. Since the lake has no substantial surface water inflow, and relatively minimal (<2.5% of lake volume) seepage to the coast (refer to Section 2.3), the volume of the lake is determined primarily by the balance achieved between atmospheric precipitation and evaporation, both directly over the lake surface, and indirectly by groundwater inflow. Accordingly, the ionic strength of the Sibaya waters appears to derive, primarily, from the balance between atmospheric precipitation and evaporation, and from the dissolution of minerals within the aquifer sands of the groundwater catchment. For reasons already discussed, the concentration of dissolved solutes arising from these sources is low. The latent potential for the reduction of mineral solubility, through the process of evaporative concentration of the Lake Sibaya waters, may therefore be largely unrealised, due to the dilute nature of these waters.

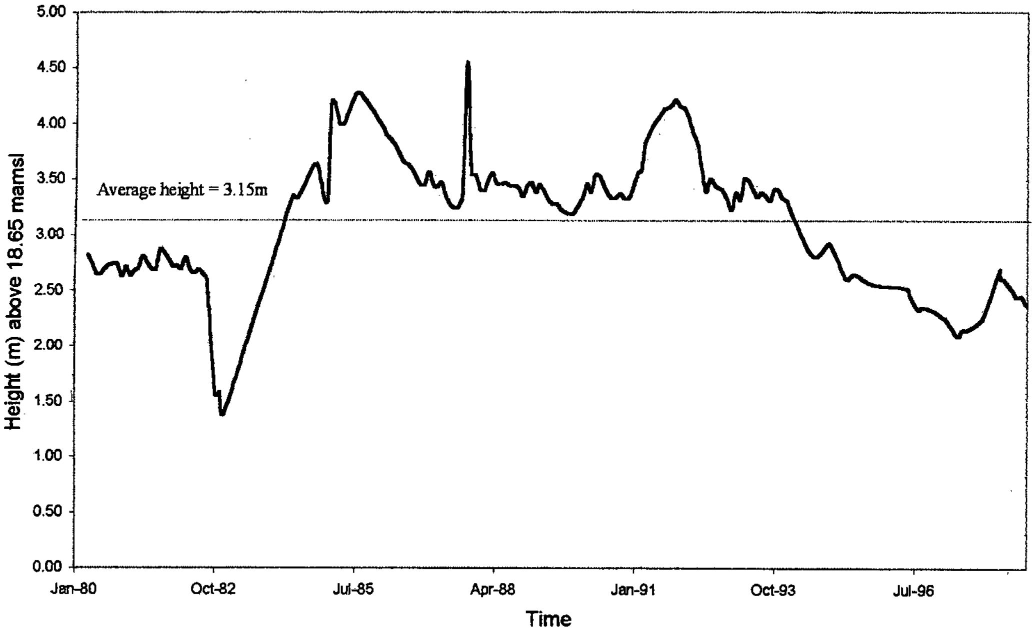

**Figure 3.5:** Monthly water level of Lake Sibaya for the period May 1980 to November 1998. Water level is recorded as the height above the 18.65 metre fixed datum at the recording station at Banda Banda. Evaporation and rainfall figures are not available for the region.

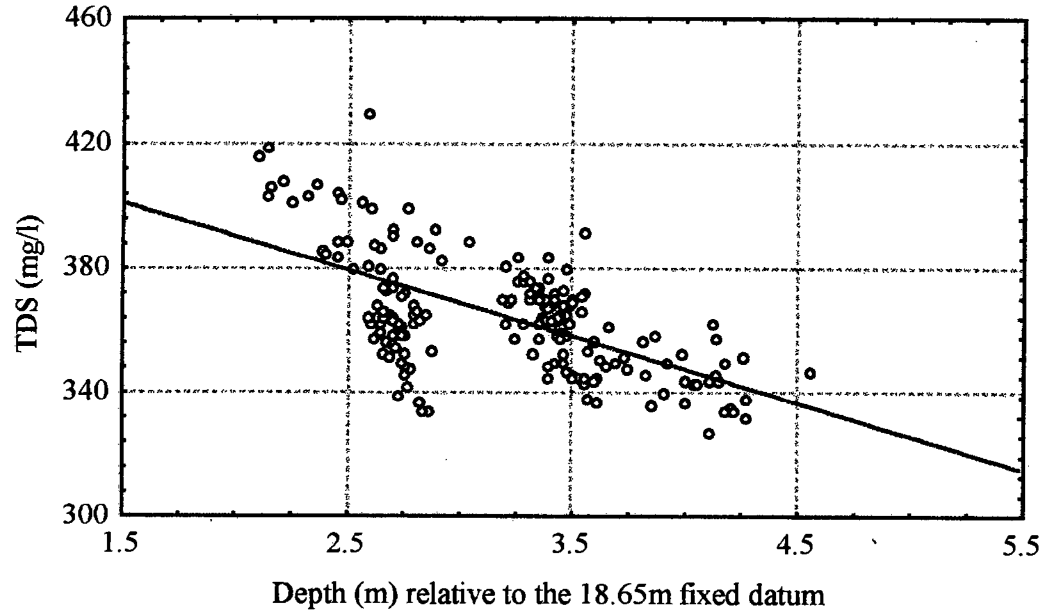

**Figure 3.6:** Variation in TDS concentration with water level in Lake Sibaya over the period 1980-1998. A correlation coefficient of -0.62 (p=0.000; N=189) was obtained for these two variables.

In the following section, stable isotope ratios will be used to verify the proposal that the lake waters are being evaporated above that of global meteoric waters. Thereafter, in Section 3.4.4, the results of mineral solubility modelling of water sample WM2d are presented, both for the time of collection, and for greater (hypothetical) degrees of evaporation of these waters.

### *3.4.3.3 Stable isotopes as indicators of evaporative concentration*

The important stable isotopes of oxygen are $^{16}O$ and $^{18}O$, and the stable isotopes of hydrogen are $^{1}H$ and $^{2}H$, the latter commonly being referred to as deuterium (D). When water undergoes evaporation, the residual water becomes progressively enriched in the heavier isotopes, $^{18}O$ and D. Analyses of the isotope ratios $^{18}O/^{18}O$ and $^{1}H/D$ in the waters of the Lake Sibaya system may therefore provide an indication as to whether these waters are undergoing a process of evaporative concentration.

Figure 3.7 shows that the oxygen and hydrogen isotopes in the two well samples plot approximately on the Global Meteoric Water Line (MWL), represented by the equation: $\delta D = 8 \bullet \delta^{18}O + 10$. Craig (1961) found that the stable isotopes of approximately 400 Northern Hemisphere riverine, lacustrine and rainwater samples fell along the line defined by this equation. The isotope ratios are expressed as the per mil (or ‰) difference in the ratio of the less abundant isotope to the most abundant isotope in a sample, relative to the same ratio in SMOW (Standard Mean Ocean Water) originally defined by Craig (1961). The slightly shallower gradient demonstrated by the regional Mseleni well sample waters is to be expected, since the Zululand coastal plain defines a region which is tropical, oceanic, and, furthermore, located within the Southern Hemisphere (Dansgaard, 1964).

The closeness of the Lake Sibaya catchment to the coast, and its low elevation, is likely to ensure that precipitation does not substantially alter the proportion of $\delta D$ or $\delta^{18}O$ as a result of progressive rainout (Sonntag *et. al.*, 1979). Evapo-transpiration of groundwater is not expected to occur to such a degree that it would alter, to any significant extent, the isotope ratios in waters which have entered the subsurface environment (Drever, 1992). The oxygen and hydrogen isotopes do not fractionate in shallow groundwater systems, and the $\delta^{18}O$ and $\delta D$ values are normally preserved after the precipitation enters the groundwater flow system (Hackley *et al.*, 1996). The $\delta D$ is generally unaffected by reaction with aquifer materials at low temperatures. Similarly, $\delta^{18}O$ is generally unaffected by reaction with silicates at low temperatures, for periods of time up to approximately one million years at temperatures below 50°C (Drever, 1997). No correlations are therefore expected to occur between chemical and isotopic data, as isotope values are influenced by processes occurring before the water enters the geohydrological system, whereas the chemical parameters are strongly influenced by interaction of the waters with the matrix with which they are in contact (Drever, 1997).

Upon entering Lake Sibaya, the groundwaters appear to undergo isotopic fractionation, becoming enriched in the heavier isotopes, $^{18}O$ and D (*cf.* Figure 3.7). Fractionation is any process that causes the isotopic ratios in particular phases or regions to differ from one another, as a result of minor mass differences between the isotopes (Drever, 1997). The composition of the residual water does not follow the meteoric water line, but rather evolves along a line of shallower gradient. This suggests physical fractionation during evaporation. The vapour pressure of an element is inversely proportional to its atomic mass, with the result that lighter isotopes of an element or compound will preferentially evaporate or diffuse, while the remaining liquid will be progressively enriched in the heavier isotopes as evaporation proceeds (Dansgaard, 1964). The temperature and relative humidity at which the evaporation takes place determine the precise slope of the residual water composition line. Water samples WA1s, WM2d and SA5d plot to the right of the meteoric water line, suggesting that they are undergoing evaporation. This is consistent with the approximately 390 mm/yr excess of evaporation over precipitation over the surface of the lake, as recorded by Pitman and Hutchinson in 1975. High evaporation from the lake is to be expected, owing to its high surface-area to depth ratio and its substantial wind fetch.

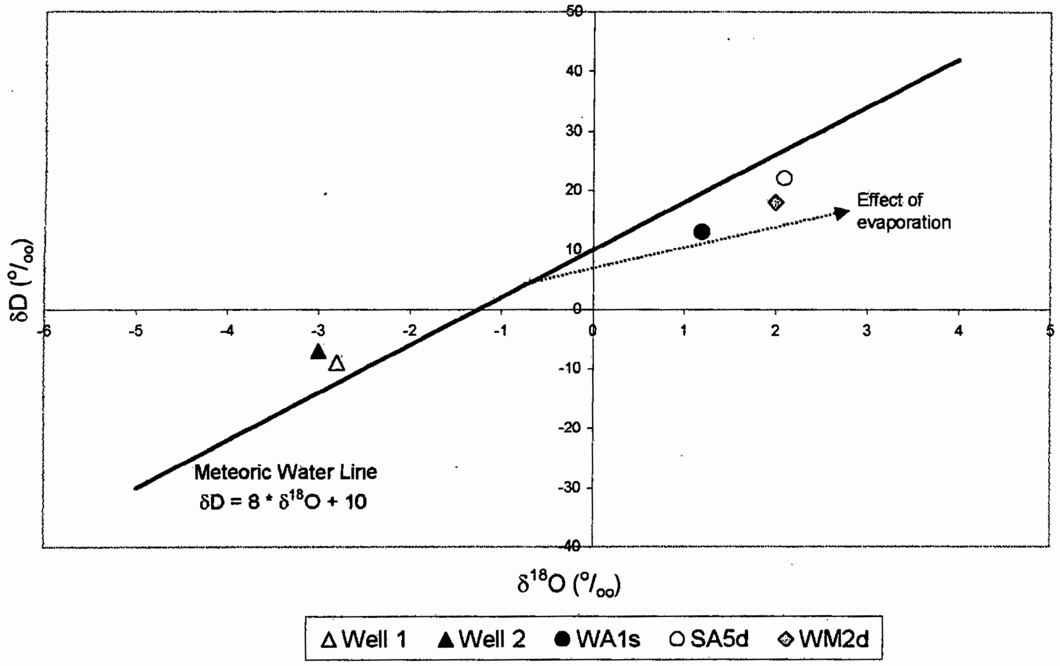

**Figure 3.7:** The isotopic composition of Lake Sibaya open waters and its adjacent groundwaters. The dotted line indicates the general trend observed in stable isotope ratios upon evaporation, as documented by Dansgaard, 1964.

## 3.4.4 Mineral solubility equilibria

### *3.4.4.1 Contemporary mineral solubilities*

The MINTEQA2 model was used to investigate the stability relationships that may exist between minerals in the Lake Sibaya sediments and the waters with which they are in contact. The thermochemical database incorporated within the model is used to predict mineral stability sequences, based on the premise that the minerals with the lowest free energy are those which are least soluble. It is important to note that the MINTEQA2 model is based solely on equilibrium thermodynamics. Owing to the slow reaction kinetics involved, minerals predicted to reach levels of oversaturation in aqueous solution might not, in reality, precipitate from, or indeed even approach equilibrium status within, the Lake Sibaya waters over a meaningful time frame. For this reason, only selected minerals, the formation of which is generally acknowledged to be favoured by the reaction kinetics acting in natural systems will be investigated to any extent. The calculated saturation index (SI) values of such minerals in the sample waters are presented in Table 3.7. Such mineral solid phases may exert a substantial control over the concentration of a particular element in solution.

In Section 3.4.3 evidence was presented to suggest that the process of evaporation of Lake Sibaya water might be acting to control the dominance of major ions in solution. In the event of the evaporative concentration of these waters, the first mineral expected to precipitate out would, most likely, be calcite (Eugster and Hardie, 1978).

**Table 3.7:** Saturation indices of selected minerals possibly occurring within waters collected from Lake Sibaya and groundwater wells of the Zululand coastal plain. Values of SI = 0 represent mineral solubility equilibrium, whereas positive values (in bold font), and negative values, indicate oversaturation and undersaturation, respectively, of waters with respect to the particular mineral. SI values were calculated by the MINTEQA2 model. Crystalline mineral forms are represented by (C) and amorphous forms by (A).

| | Calcite (C) $CaCO_3$ | Aragonite (A) $CaCO_3$ | Quartz (C) $SiO_2$ | $SiO_2$ (A) | Gypsum (C) $CaSO_4 \cdot 2H_2O$ | Sepiolite (C) $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$ |
|---|---|---|---|---|---|---|
| **Pelagial water** | | | | | | |
| WA1s | -0.29 | -0.43 | **0.14** | -0.85 | -2.78 | -2.71 |
| WA3d | -0.27 | -0.40 | **0.12** | -0.87 | -3.15 | -2.52 |
| SA5d | -3.27 | -3.41 | **0.18** | -0.81 | -4.71 | -3.41 |
| WM2d | **0.15** | **0.01** | **0.12** | -0.87 | -2.58 | -1.67 |
| WM4d | -0.01 | -0.15 | **0.15** | -0.84 | -2.93 | -1.42 |
| **Sediment-associated waters** | | | | | | |
| WA1eq | -1.05 | -1.19 | **0.84** | -0.15 | -3.31 | -2.80 |
| WA3eq | -2.00 | -6.47 | **0.74** | -0.25 | -2.96 | **0.06** |
| SA5eq | -1.47 | -1.61 | **0.74** | -0.25 | -4.31 | -1.85 |
| WM2eq | -0.55 | -0.69 | **0.83** | -0.16 | -2.98 | -0.97 |
| WM4eq | -1.25 | -1.39 | **0.73** | -0.26 | -3.32 | -2.86 |
| **Wells** | | | | | | |
| Well 1 | -0.55 | -0.69 | **0.24** | -0.75 | -3.47 | -2.65 |
| Well3 | -0.15 | -0.29 | -0.05 | -1.04 | -2.81 | -2.45 |
| Well3 | -0.15 | -0.29 | -0.05 | -1.04 | -2.81 | -2.45 |

The solubility of calcite in the waters of the Lake Sibaya system, together with its less stable polymorph (at 1 atmosphere), aragonite, is therefore investigated here, as an indication of the extent to which these waters have already been evaporated. At 20°C the solubility product of calcite is $10^{-8.45}$, whereas that of aragonite is $10^{-8.31}$ (Drever, 1997).

It is important to realise, as is pointed out in Appendix D, that the particular value for the molar site density of dissolved organic matter (DOM) which is entered into the MINTEQA2 model, will have a profound influence on the calculated SI value for calcite. This is demonstrated in Figure 3.8, in which the SI of calcite is shown to decrease in response to the progressively increasing complexation of Ca at DOM binding sites. The interpretation of solubility indices calculated by the MINTEQA2 model should therefore be treated with a due degree of uncertainty. In this instance, the saturation index of calcite remained relatively constant throughout a DOM site density range of up to twice that which was entered for solubility and speciation modelling purposes. At five times this concentration, however, MINTEQA2 predicted a considerable degree of undersaturation of these waters with respect to calcite. Owing to the generally low levels of DOC in these waters, therefore, it would appear as if calcite solubility is fairly resilient to 'realistic' estimations of the DOM site density that are entered into the model.

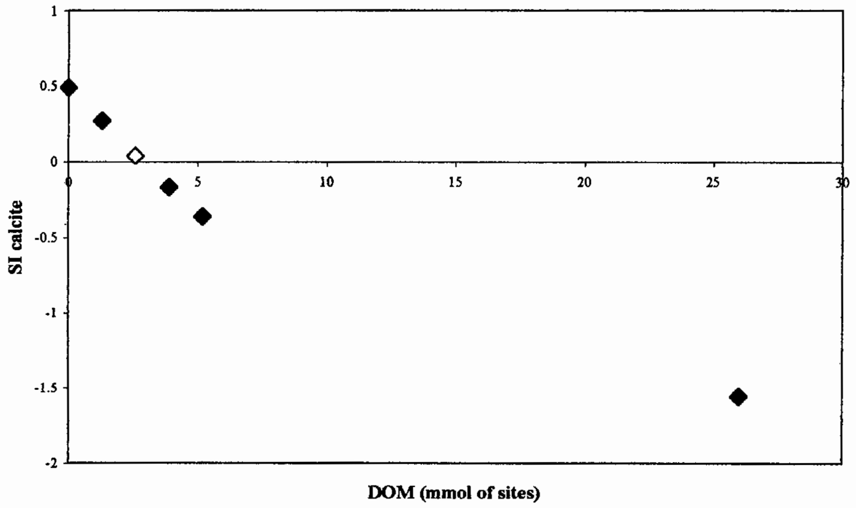

**Figure 3.8:** Calcite saturation index (SI) for sample WM2d (as calculated by MINTEQA2), as a function of various hypothetical DOM site densities. The hollow data point marker represents the binding site density entered for speciation and solubility modelling purposes.

The MINTEQA2 model calculated calcite saturation indices in the vicinity of zero in the pelagial lake waters (with the exception of sample SA5d), suggesting that these waters approach equilibrium with the mineral phase. The amorphous polymorph of $CaCO_3$ (aragonite) showed greater solubility in these waters, as could be expected from its greater state of entropy. No calcite or dolomite could be detected in the sediments (refer to Section 4.4.4), suggesting that even if these waters do, in fact, reach levels of oversaturation in some instances, the reaction kinetics involved may not be sufficient to favour their crystallisation at the present time. This theory is supported by the fact that the average Mg:Ca ratio of the 30 most dilute pelagial lake waters analysed by the DWAF over the period 1980-1998 is marginally higher than that obtained for the 30 most concentrated samples (refer to Table 3.8). The Mg:Ca ratio would be expected to increase with total solute concentration (EC), following the precipitation of calcite at increased levels of evaporative concentration.

The occurrence of calcareous outcrops in the vicinity of the western bank of the lake set an historical precedent for the precipitation of calcite from the lake waters, albeit at lower lake levels during Isotope Stage 2 of the Last Glacial Maximum (refer to Section 2.2.2). These outcrops justify, to some extent, the proposal that the calcite saturation index may, with progressive evaporative concentration of the lake waters, again reach a sufficient level of oversaturation to kinetically favour the precipitation of calcite into the sediments.

The greater degree of undersaturation of calcite in the sediment-associated waters, relative to the pelagial waters, probably relates to their slightly lower pH, or increased partial pressure of $CO_2$, under the reducing conditions present within the sediments. Within the organic gyttja accumulations, the anaerobic decay of organic material with sulphate reduction yields bicarbonate alkalinity, as per the general equation: $SO_4^{2-} + 2C_{org} + 2H_2O = H_2S + 2HCO_3^-$. Under these conditions the potential solubility of $CaCO_3$ would be increased in these waters, given the presence of solid phase calcium carbonate. In the absence of distinguishable quantities of calcite or aragonite in the sediments, however, the ion activity product of these waters would be increased, whilst the solubility product would remain constant. Since the saturation index is defined as the quotient of these parameters $(SI = \log\{IAP/K_{sp}\})$, the net result of the lowered pH is a decrease in the saturation index of these minerals within the sediment-associated waters.

In the absence of evidence to the contrary, the near-equilibrium status of the three well water samples, is interpreted as being the result of the dissolution of carbonate minerals within the aquifer sands. The Ca source in this instance is likely to be carbonaceous marl, which was shown to occur in diatomite deposits exposed in the incised Mseleni River valley adjacent to the wells (*cf.* Section 2.2.2). The groundwater sample collected from well 1 shows a low Mg:Ca ratio, thus supporting the idea of the dissolution of calcite from the aquifer sands. The Mg:Ca ratios of the 201 groundwaters from the drainage region show extensive variation ($\bar{x}$ = 0.94, std. dev. = 0.64), perhaps highlighting the important control which localised sources of Ca may exert over the solubility of calcite. The aquifer is likely to act as an open system, with gaseous transfer of $CO_2$ to replace that which is lost due to the dissolution of calcite. The partial pressure of the sediment waters was estimated at $10^{-3.76}$, based on the following formula (after McBride, 1994):

$$\frac{a_{Ca^{2+}}\, a^2_{HCO_3^-}}{P_{CO_2}} = \frac{K_{calcite}\, K_{H_2CO_3}\, K_{CO_2}}{K_{HCO_3^-}},$$

where *a* and K represent the activities and dissociation constants of their associated species.

It would appear as if the Lake Sibaya waters are on the verge of entering the first of a succession of chemical divides that typify the evolution of natural waters undergoing evaporation (Eugster and Hardie, 1978). According to the Hardie-Eugster model (Eugster and Hardie, 1970), the precipitation of calcite represents the first chemical divide, thereby determining the subsequent pathway along which the water will evolve with evaporation. Saturation indices calculated by MINTEQA2 suggest the incipient precipitation of calcite in the lake system. Bicarbonate alkalinity (2.3 mmol$_c$/l) narrowly exceeds milliequivalents of calcium (2.0 mmol$_c$/l) in solution. Consequently, the Hardie-Eugster model predicts that the precipitation of calcite would see the removal of all Ca from solution during evaporation, with the result that the Lake waters would tend towards an alkaline carbonate brine dominated by Na, $SO_4^{2-}$, $Cl^-$, $Mg^{2+}$ and $HCO_3^-$ (Drever, 1997). The next chemical divide would most likely be caused by the precipitation of sepiolite, which would remove $Mg^{2+}$, $HCO_3^-$ and $H_4SiO_4$ from this suite of solutes (Eugster and Hardie, 1978). In the Lake Sibaya waters, only 0.3 $\text{mmol}_c$ of bicarbonate alkalinity is anticipated to remain in the new volume of solution, following the precipitation of calcite. The milliequivalent amount of Mg in this same solution, by comparison, would be 1.3 $\text{mmol}_c$. The alkalinity would therefore represent the limiting component in the new solution, and would therefore be entirely removed from solution. Mg, by contrast, occurs in greater relative concentration in solution than alkalinity, and would be expected to exhibit an increase in relative concentration with the precipitation of sepiolite, as per the principles of the Hardie-Eugster model. Sepiolite is considerably undersaturated in each of the three groups of waters analysed in this study (refer to Table 3.7), reinforcing the observation that calcite crystallisation has not yet been achieved to any substantial degree. The solutes Na, Mg, $SO_4$ and Cl predominating in the new volume of solution, after the precipitation of sepiolite, are expected to occur in the respective molar charge ratio 4: 1:0.3:4.1. The resulting water would therefore be highly dominated by Na and Cl, with minor quantities of both Mg and $SO_4$.

**Table 3.8:** Mg:Ca molar ratios for selected waters of the extended Lake Sibaya system. The DWAF data represent the average of the most concentrated, and dilute, lake water samples analysed over a period of 19 years.

| | Dilute: DWAF (1980-1998) | Concentrated: DWAF (1980-1998) | Bulk lake: This study | Sed. water: This study | Well 1: This study |
|---|---|---|---|---|---|
| **EC (µS/cm)** | | | | | |
| Average | 518 | 722 | 553 | 811 | 313 |
| Std. dev. | 73 | 218 | 9.0 | 115 | - |
| Sample size | 30 | 30 | 5 | 14 | 1 |
| **Mg:Ca** | | | | | |
| Average | 0.631 | 0.625 | 0.656 | 0.653 | 0.242 |
| Std.dev. | 0.052 | 0.086 | 0.084 | 0.116 | - |

In the event that the calcium concentration (in equivalents) was greater than the alkalinity in the Lake Sibaya pelagial waters (following calcite crystallisation upon evaporation), gypsum would constitute the next mineral to precipitate from solution. This would constitute a chemical divide which would favour the build-up of Na, Ca, Mg, Cl and $SO_4^{2-}$ (Drever, 1997). The lake waters are shown in Table 3.7 to be even more undersaturated with respect to gypsum than they are with respect to sepiolite, suggesting that this pathway would not be favoured.

The dissolution of (crystalline) quartz is represented by the equation (Drever, 1997): $SiO_{2\,(quartz)} + 2H_2O = H_4SiO_{4(aq)}$, where $K_{eq} = a_{H4SiO4} = 1 \times 10^{-4}$ at 25°C (assuming that $a_{H2O}=1$). The solubility constant for the corresponding dissolution of amorphous silica, again at 25°C, is $2 \times 10^{-3}$ (Drever, 1997). Since the activity of silica, calculated from the Davies equation, is approximately 0.14 mmol/l in the pelagial lake waters (sample WA1s), these waters are calculated by MINTEQA2 to be very slightly oversaturated with respect to quartz (SI range of 0.12 to 0.18), yet undersaturated with respect to amorphous silica. The elevated solubility of amorphous silica (≈ 50– 60 mg Si/l), relative to quartz (≈ 3–7 mg Si/l), relates primarily to the decrease in the solubility of silica minerals as a function of increasing packing density on the silica tetrahedra and long-range crystal order (Drees *et al.*, 1989).

Consequently silica is expected to exist in solution in the form of monomers of silicic acid, under the existing solution pH regime (refer to Figure 3.9). The fact that Si determined by colorimetry was consistently between 2.5 and 4.5 times greater than that determined by ICP-MS (not shown) suggests, however, that the water samples contain significant quantities of Si present in forms other than monomeric Si. The molybdate-reactive Si concentrations determined by colorimetry were entered into the MINTEQA2 model. In view of the fact that Al was probably overestimated by the ICP-MS technique (through its association with colloidal aluminosilicates which passed through the 2µm filter), interpretation of the lake water composition in terms of aluminosilicate solubility equilibria would be fundamentally flawed, and is not attempted here. The fact that the three well waters are expected to approach equilibrium with quartz does suggest, however, that the dissolution of silicate minerals contained within the aquifer sands is acting to increase the activity of Si in solution to some extent, particular in the case of incongruent dissolution of aluminosilicates.

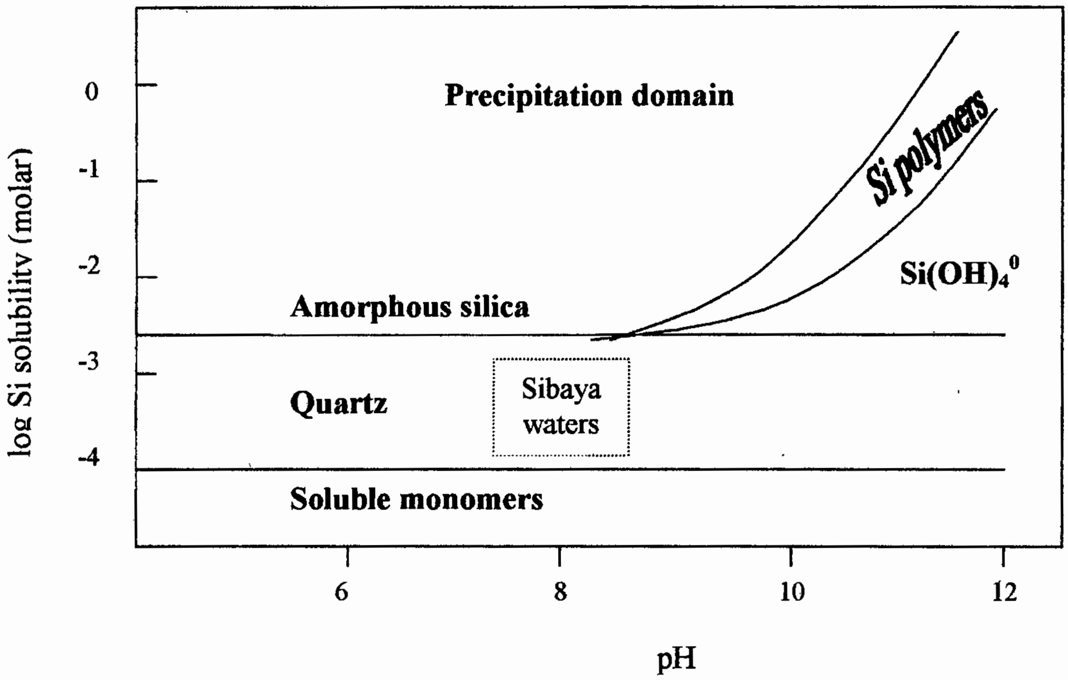

**Figure 3.9:** Schematic solubility diagram of Si as a function of pH, assuming equilibrium with amorphous silica. The approximate position of Lake Sibaya waters is shown. The region of the graph labelled as 'Si polymers' indicates conditions promoting soluble silica polymer formation (after McBride, 1994: pp219).

MINTEQA2 calculates higher saturation index values for quartz within sediment-associated waters (SI range 0.73 to 0.84) than within the pelagial Lake Sibaya waters. The dissolution rate of quartz from the Lake Sibaya sediments may be influenced by the particle size of these generally fine sands (Miller, 1998), with the weathering rate being directly correlated with increased surface area (Iler, 1958). The predicted near-equilibrium status of the sediment-associated waters with respect to quartz is encouraging in terms of interpreting sediment-water interactions, in that the waters may be expected to reach equilibrium with other less stable minerals. In this regard, the waters collected from immediately above the lake sediments, following intense mixing with the solid phase in the laboratory, would be expected to approach the equilibrium composition of the interstitial waters. It is important to note, however, that although both the pelagial and sediment-associated waters of Lake Sibaya are predicted to be slightly oversaturated with respect to quartz, the reaction kinetics involved in its crystallisation would act so slowly as to be practically ineffectual over the short term. Drees *et. al.* (1989) note that the concentration of soluble silica in soil systems is undoubtedly dynamic, where equilibrium conditions are the exception rather than the rule. For this reason the solubility of amorphous silica undoubtedly sets the upper limit of dissolved silica in the Lake Sibaya waters.

The dissolution of amorphous silica is, in turn, likely to be controlled by diatom assimilation of silicon contained within orthosilicate. Ehrlich (1981) reports that Si uptake by diatoms may readily occur to the extent of 1 500 to 20 000 ppm. Uptake is primarily in the form of hydrated, amorphous silica, a polymerised silicic acid (Werner, 1967). More highly polymerised forms of silica are apparently unavailable to these diatoms (Ehrlich, 1981). Upon senescence, the diatom frustules are expected to undergo partial dissolution before reaching the sediments. As discussed in Section 2.6, this biochemical condensation of dissolved silica greatly exceeds inputs to the sediments from abiogenic sources. This is likely to be true in Lake Sibaya, where the diatom population is predominant.

MINTEQA2 calculated positive gibbsite saturation indices for each of the pelagial, sediment-associated and groundwater well samples in which Al was added to the input file as a constituent. The saturation indices for gibbsite (0.12 to 0.97) were substantially higher than for its amorphous counterpart (-0.64 to –1.87). The magnitude of these saturation indices, particularly in the latter two groups of waters, suggests that the ICP-MS technique may well have overestimated Al concentration, by determining Al associated with fine (<2μm diameter) colloidal aluminosilicate materials in solution, rather than simply dissolved Al. Although gibbsite may well occur in the bulk sediments, the interpretation of its solubility equilibria in the Lake Sibaya system, based on the MINTEQA2 output, is subject to error. This is true of all the Al-containing minerals listed in the MINTEQA2 output files, with the consequence that their solubility equilibria will not be investigated further.

### *3.4.4.2 Forward modelling of evaporative concentration*

The evaporative concentration of Lake Sibaya appears to progress at an exceedingly slow rate, in response to low solute concentrations, and the continual throughflow of water through the lake by groundwater influx and coastal seepage. In view of this fact, PHREEQC was used to model an hypothetical series of evaporations of the representative pelagial water sample WM2d. A successive number of moles of water were conceptually removed from this solution, such that the water became evaporated to within the range of twice, to one thousand times, that of the present level. The use of the Davies equation to calculate activity coefficients may be inappropriate at the high levels of ionic strength attained in the later evolving brines. The Pitzer equation, or equivalent, may be more suited to such solutions (Smith *et al.*, 1995).

Based on an excess of evaporation over precipitation of 390 mm/y over the surface of Lake Sibaya, and a surface area ranging between 776 to 981 x $10^6$ $m^3$ (Hill, 1979), the lake is here calculated to diminish in volume at a rate of approximately 3% per year. The time required to evaporate the lake to any required volume can be approximated from the equation:

$$\ln\frac{V_t}{V_0} = -kt,$$

where $V_0$ and $V_t$ represent the initial and final lake volumes, respectively; k represents the rate (3%) of evaporation; and t represents time. If groundwater influxes to, and discharges from, the lake are ignored, the lake could be expected to evaporate to half of its present volume within a period of 23 years, based on the present climatic regime. Note that this is a gross simplification, which ignores the influence of diminishing lake surface area on evaporation, as well as ignoring the substantial source of groundwater influx from the coastal aquifer and the loss of water from the lake by seepage to the coast. Seepage of water from the lake to the ocean, via a palaeochannel (refer to Section 2.3.1), was calculated as being approximately 2.5% of lake volume, based on an average permeability of 4 m/d (Meyer and Godfrey, 1995). It is not known to what extent the influence of parameters such as solution ionic strength on clay dispersion and flocculation were accounted for in the derivation of this value. Neither has a confident estimation of the volume of groundwater recharge to Lake Sibaya been attempted. For the sake of simplicity, therefore, only the direct atmospheric controls over lake volume were considered in this preliminary estimation of the degree of concentration of Lake Sibaya waters by evaporation. It is hoped that a more representative water budget for the Lake Sibaya system will be calculated in future studies. This will allow for more accurate prediction of the future rate of evaporation of Lake Sibaya and the chemical pathway by which its waters are expected to evolve.

Figure 3.10 shows that the PHREEQC model yields the expectation that the precipitation of calcite will commence with the onset of additional evaporation of the Lake Sibaya waters. This is to be anticipated, given that the waters were shown to be in near equilibrium with calcite at the time of laboratory analysis. The initiation of quartz precipitation is, similarly, expected after three times evaporation of these waters. Amorphous $SiO_2$ does not precipitate from these waters, even upon extreme evaporation.

The slight excess of $HCO_3^-$ remaining after calcite precipitation, is not expected, by the PHREEQC model, to precipitate out as sepiolite [$MgSi_3O_6(OH)_2$], but rather to react with the excess $Mg^{2+}$ to form insoluble magnesite ($MgCO_3$) precipitating out after 100x evaporation. Drever (1997) states that, in terms of chemical divides, it would not make much difference whether $Mg^{2+}$ precipitated as a carbonate or a silicate. Since the Mg concentration (in equivalents) is greater than the alkalinity remaining after calcite precipitation, the computer model predicts the level of bicarbonate alkalinity to plateau following magnesite precipitation (Figure 3.11). The fact that alkalinity is not completely lost from solution presumably relates to considerations, within the model code, of equilibration of the lake waters with atmospheric $CO_2$.

Slightly contrary to the expectations of the Hardie-Eugster model, the model does not predict that Ca will be completely lost from solution through the precipitation of calcite (refer to Figure 3.11). Rather, the model calculates that a fraction of the Ca will react with the relatively abundant $SO_4^{2-}$ in solution, thereby precipitating out as gypsum ($CaSO_4{\cdot}2H_2O$) at 150x evaporation, according to the following reaction (Drever, 1997):

$$Ca^{2+} + SO_4^{2-} + 2H_2O = CaSO_4 \bullet 2H_2O_{gypsum} \qquad K_{sp} = 2.4x10^{-5}.$$

According to the law of mass action, the value of the equilibrium-constant expression $K_c$ (in this instance being equivalent to $K_{sp}$, assuming $a_{H2O}$=1), is constant for a particular reaction at a given temperature, irrespective of the equilibrium concentrations which are substituted (Ebbing, 1985). The activity of $SO_4^{2-}$ in solution might be sufficiently high, so as to raise the ion activity product (IAP) of $CaCO_3$ above this solubility constant ($K_{sp}$), and thereby induce the precipitation of gypsum. The PHREEQC model incorporates a complex series of algorithms to explain the equilibrium behaviour of solutes, and might not necessarily consider precipitation of calcite and gypsum to proceed independently of each other upon evaporation. By contrast, the conceptual Hardie-Eugster model is based on the simple precept that the precipitation of either gypsum or sepiolite minerals will not proceed until all alkalinity or calcium has been precipitated out of waters which are supersaturated with respect to $CaCO_3$.

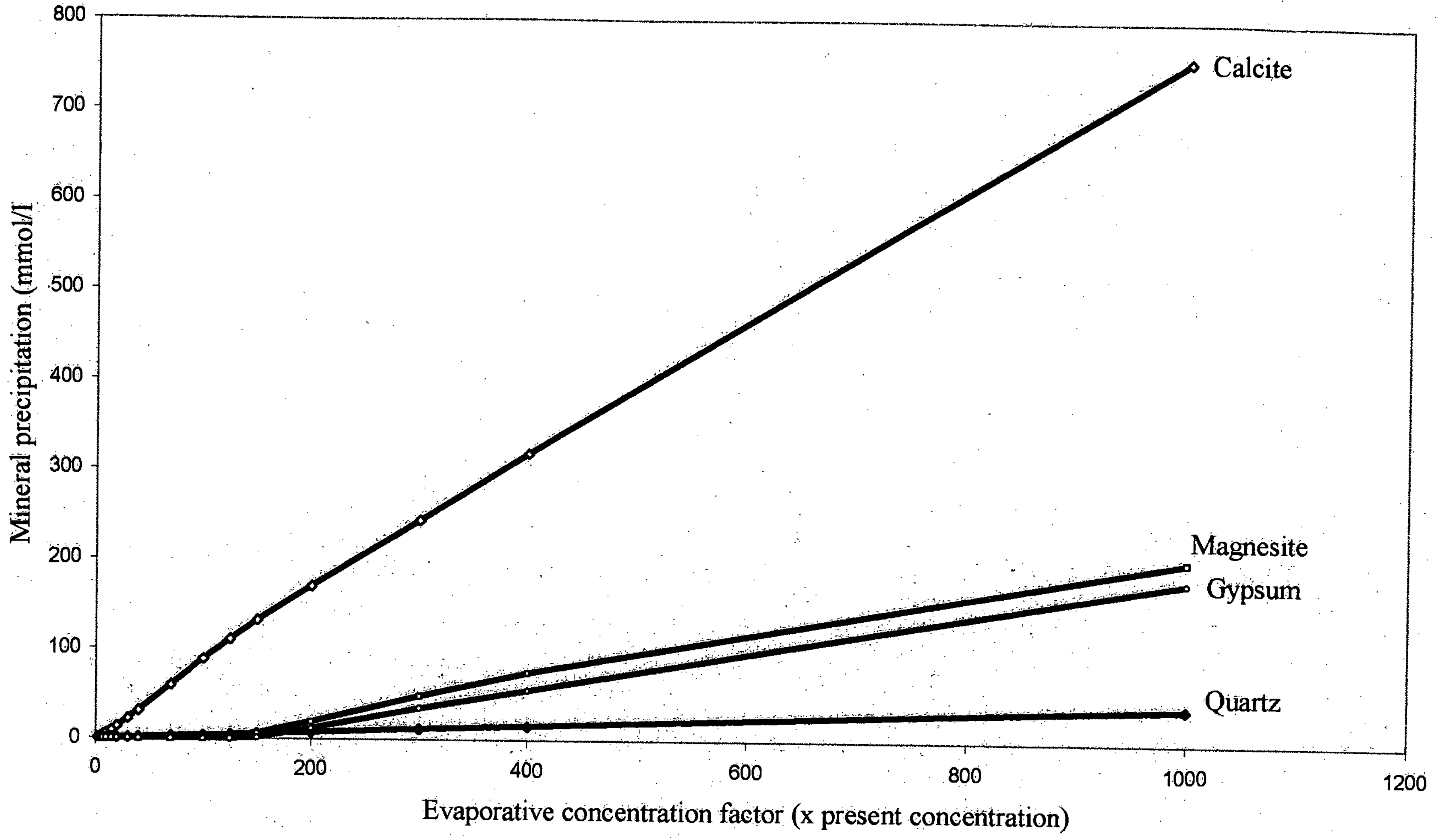

**Figure 3.10:** Minerals calculated by the PHREEQC model to precipitate as a result evaporation.

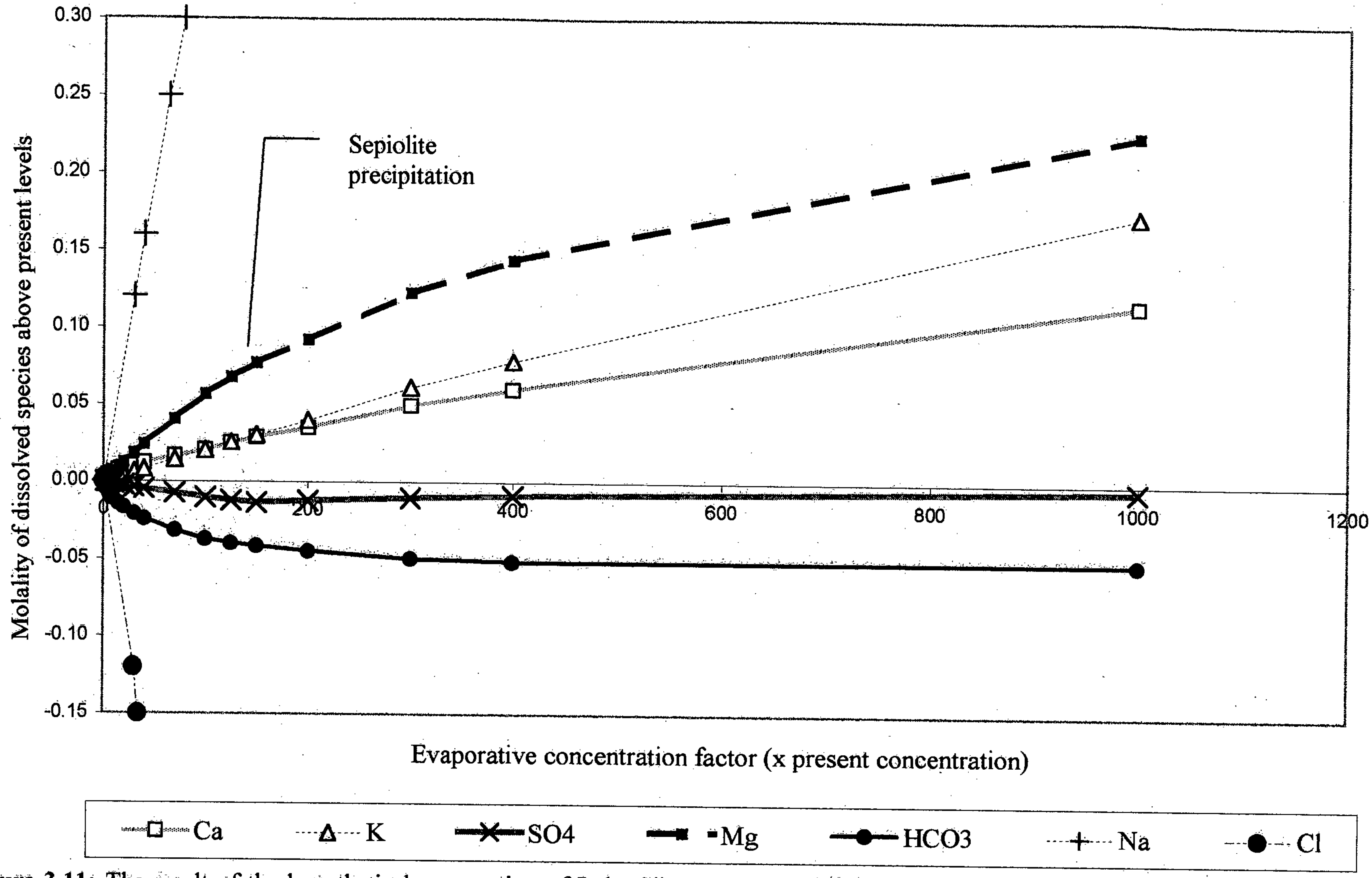

**Figure 3.11:** The result of the hypothetical evaporation of Lake Sibaya water at 25°C and $CO_2$ partial pressure of $10^{-3.5}$; as calculated by the PHREEQC model. No $H_4SiO_4$ was predicted to precipitate from the waters.

Figure 3.11 shows the behaviour of $Na^+$, $Cl^-$ and $K^+$ to be expected to be conservative upon evaporative concentration, in accordance with theoretical expectations. $Na^+$ and $Cl^-$ are modelled to constitute the overwhelming ions in the evaporated solution, the final solution therefore representing a carbonate-free chloride brine. Similar waters are generally encountered in highly saline endorheic lakes situated in arid regions (e.g. Great Salt Lake, Utah and Saline Valley, California). It is highly unlikely that Lake Sibaya will evaporate to such an extent within a reasonable geological timescale, given the present climatic regime and the diluting influence of the coastal groundwaters.

### 3.4.5 Chemical speciation modelling

The study of metal binding by naturally occurring complexants is of primary importance in understanding their behaviour and fate in aquatic systems. The distribution, lability and biological availability of these chemical elements within the extended Lake Sibaya system is undoubtedly dependent not only on their concentrations in solution, but also, fundamentally, on the chemical and physical associations of which they are a part. Particularly important in this regard are the controlling variables of pH, redox potential, and the availability of complexing ligands and sorption surfaces.

In view of this fact, the geochemical speciation modelling program MINTEQA2 was employed to predict the forms in which elements are most likely to occur under the specific aqueous conditions present in Lake Sibaya bulk and sediment-contacted waters. The speciation of selected elements within the waters of sample site WA3 is presented in Figure 3.12. The patterns of speciation and complexation observed in these latter samples was observed to be representative of the lake as a whole. The MINTEQA2 charge balances for all samples modelled, with the inclusion of dissolved organic matter (DOM) were generally less than 5% prior to speciation, and in only one instance ($WM2_{eq}$ = 11%) were values in excess of 10%. This suggests that the concentrations of the bulk of the major ions had been successfully accounted for. All samples demonstrated a charge balance below 8% following speciation, confirming the success of the process of iterative guesses at the activity of each charged species. The incorporation of dissolved organic matter (DOM) into the model as sites of charge is discussed in Section 3.3.3.

MINTEQA2 predicted that the majority of calcium in both the bulk lake water (65%) and the sediment-contacted waters (85%) would complex with organic matter dissolved in solution (DOM). The remaining calcium would be expected to occur as the labile free aqueous ion, $Ca^{2+}$. The proportion of $CaSO_4^o$ was not expected to exceed 1% of the total calcium species in solution. This is probably due to the reduction of sulphate to sulphide in the sediments during the anaerobic decay of organic matter in the sediments (e.g. gyttja), represented such:

$$SO_4^{2-} + 2C + 2H_2O = H_2S + 2HCO_3^-.$$

Anaerobic decay within the lake sediments could be expected to increase saturation with respect to carbonate minerals.

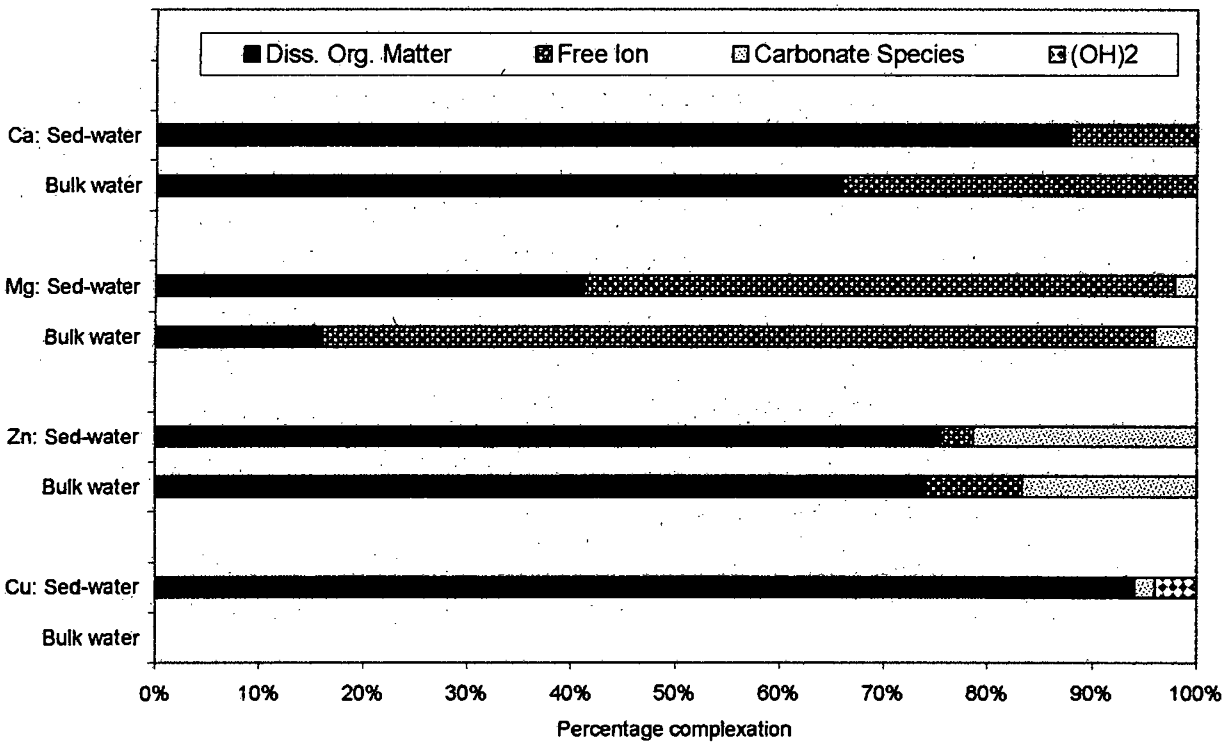

**Figure 3.12**: Element speciation predicted by the MINTEQA2 model for Lake Sibaya bulk and sediment-contacted waters. Samples WA3d and WA3eq were chosen as representative of these waters, respectively.

By contrast with calcium, Mg was predicted to exist predominantly as the free ion in the bulk- (82%), and sediment-contacted waters (55%). This is to be anticipated, owing to the enhanced solubility of Mg compounds, relative to their corresponding Ca counterparts (Wetzel, 1983). A lesser fraction of the total aqueous Mg (15% and 40% in these respective water types) was expected to undergo complexation with organic matter in solution. The relative extent to which organo-metallic complexation occurs in the lake waters is predicted (by the MINTEQA2 model) to follow the ascending sequence: Mg < Zn < Ca < Cu. This order conforms to the order of affinity of divalent metal ions for organic matter observed by McBride (1994). A variety of functional groups which are generally present in organic matter may act as Lewis bases in these metal bonding reactions in solution, including carboxylic, phenolic, amine, carbonyl, and possibly sulfhydryl groups (McBride, 1994).

### 3.4.6 The status of Lake Sibaya waters

The biota inhabiting the Lake Sibaya system are undoubtedly inseparably coupled with the dynamics of many chemical elements, in particular the distribution of nutrients and their biogeochemical regulation. Extensive studies have been conducted on the ecology of the lake over the past few decades. Levels of $NO_3$ (N) and soluble reactive phosphorus (SRP) were found, by Allanson and van Wyk (1969) and Hart and Hart (1977), to be uniformly low (17-32 µg/l and 10-25 µg/l, respectively) throughout the water column. The low concentrations of these essential elements is reflected in the low levels of algal standing crop and primary productivity

(Allanson, 1979). The reader is referred to Allanson (1979) for details of nutrient studies conducted on Lake Sibaya.

The intention here is not to repeat or revisit these earlier studies, but rather to focus attention on the possible broad-scale biotic implications of nutrient bioavailability in the lake. As mentioned in the introduction to this report, the application of the inductively coupled mass spectrometry (ICP-MS) technique allows for innovative insight into the trace element dynamics of natural waters. Owing to the novelty of such techniques, knowledge of the impacts of trace elements on biotic systems is largely limited to heavy metal toxicity, as opposed to micronutrient deficiency. It is therefore hoped that more thorough interpretation of the trace elements in the Lake Sibaya waters (as determined in this study) will be conducted in the future, with particular regard to the biotic implications for taxa identified within these waters.

### *3.4.6.1 Major elements*

The chemistry of freshwaters is generally dominated by $Na^+$, $Cl^-$, $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$, $HCO_3^-$ and $K^+$. Of the cations, Mg, Na and K demonstrate relatively conservative behaviour under typical freshwater conditions. Although these cations are generally readily available to biota at the required nutritional levels, K is not infrequently limiting to plants in very dilute waters. Calcium, which is more reactive, may exhibit marked seasonal and spatial dynamics within a lake system.

Macan (1961) specifies that hardly a group of freshwater animals exists in which the distribution of some species has not been related to calcium concentration. Calcium is an essential nutrient in the metabolism of all organisms, being essential for maintenance of the structural and functional integrity of cell membranes (Wetzel, 1983). The distribution of certain algae has been correlated to differing concentrations of calcium. Ca is also essential for muscle contraction, nervous activity, energy metabolism, as well as constituting a structural component of mollusc shells and crustacean carapaces. Wetzel (1983) draws a division between 'hard-water species' (≥ 20 mg Ca/l) of molluscs and crustaceans, and those that can tolerate less than this concentration.

The amount of calcium utilised by the biota of Lake Sibaya is expected to be so small, in comparison with existing levels, that depletion by biota would not be seen in normal analyses. Consequently, in the context of low biological productivity, and in the absence of a recognisable hypolimnion, calcium concentrations are not expected to exhibit recognisable seasonal variations with depth (Wetzel, 1983). Although the pelagial waters of Lake Sibaya are low in Ca, total levels of this element are not such that they would be expected to result in limitations to the lake biota. Furthermore, since the $Ca^{2+}$ free ion is expected to constitute 35% of the element in solution, the remainder being complexed to dissolved organic matter, the calcium in solution is expected to be readily bioavailable. The absence of detectable calcite in the sediment sands of the lake bed will be discussed in Section 4.4.4, as will the possible involvement of the dissolution of metamict Ca titanosilicate minerals as a slow release mechanism for Ca. As with all of the nutrients discussed, buffering of Ca solute levels by sediment contact is potentially important in terms of determining its availability.

Sodium and potassium are involved primarily in ion transport and exchange in all organisms, and in the transmission of nervous impulses and in muscle contraction in animals. An absolute sodium requirement has been demonstrated in only a few aquatic plants. Certain blue-green algae have been found to have sodium requirements ranging between 4 and 40 mg/l (Wetzel, 1983). Mg supply in the freshwaters of Lake Sibaya, as with Na and K, is likely to exceed metabolic requirement by organisms. Förstner and Witman (1981) describe these metals as non-critical. The

MINTEQA2 model predicts that Mg will occur in the lake waters predominantly in the labile divalent ion form, the remainder being complexed to DOM, which may, or may not, increase its lability. Na and K are expected to occur wholly as their respective free monovalent ions, and should therefore be readily bioavailable.

$CO_2$ and its equilibrium products (notably $HCO_3^-$ in the Lake Sibaya waters) are unlikely to limit photosynthesis in the Lake Sibaya aquatic ecosystem. As discussed in Chapter 2, $CO_2$ penetration of the lake waters is expected to be high as a result of intense wind mixing. Owing to the moderate contribution made by aquatic macrophytes to the total dry matter production in Lake Sibaya [only 11% of that produced by the phytoplankton community (Allanson, 1979)], the quantity of $HCO_3^-$ which they assimilate is expected to be negligible in the context of the lake system.

Chloride concentrations in Lake Sibaya are high, for reasons discussed in Section 3.4.3.1. The ion behaves as a conservative solute, and its distribution both spatially and seasonally is not significantly affected by its metabolic utilisation for the maintenance of an osmotic salinity balance or the exchange of ions within organisms (Wetzel, 1983). The importance of the raised $Cl^-$ levels in Lake Sibaya waters, relative to other freshwater lakes on the KwaZulu-Natal coastal plain, is reflected in the surprising number of estuarine faunal relict species which appear in the lake. This aspect is discussed later in this section, in relation to TDS.

The distribution and cycling of sulphur involve (a) the chemical species under various conditions, (b) biotic influences on the transformations of sulphur species, and (c) sulphur transport in the system (Wetzel, 1983). Approximately 90% of all dissolved sulphur in the Lake Sibaya waters is expected, according to the MINTEQA2 model, to occur as the free $SO_4^{2-}$ ion, the remainder occurring as the species $CaSO_4$, $MgSO_4$ and $NaSO_4$. The usual range of sulphate in freshwater lake waters is about 5 to 30 mg/l, with an average of about 11 mg $SO_4^{2-}$/l (Wetzel, 1983). This is the range in which $SO_4^{2-}$ occurs in the Lake Sibaya waters. Since nearly all assimilation of S is as $SO_4^{2-}$, S is present in Lake Sibaya in quantities which are sufficient to meet the high requirements by organisms for protein and $SO_4^{2-}$ ester synthesis (Wetzel, 1983), particularly given the low standing stock of organisms in Lake Sibaya.

During decomposition of organic matter by heterotrophic bacteria, S is released largely as $H_2S$. Decomposition of particulate organic matter synthesised in the trophogenic zone would be expected to be almost complete within the water column of lakes such as Sibaya, prior to reaching the sediments (Jewell and McCarthy, 1971). However, colloidal sulphur-containing organic compounds are degraded considerably more slowly than other organic compounds (Jewell and McCarthy, 1971), with the result that degradation of this material may not be complete upon reaching the sediments. The determination of S in the bulk Lake Sibaya sediments, by XRFS, may represent an underestimation of total S, as is noted in Section 4.4.4. Owing to the oligotrophic nature of Lake Sibaya, and the rapid oxidation of $H_2S$ under the oxic conditions prevalent within the water column, it is anticipated that minimal $H_2S$ will occur within the water column. Close to the sediments, as the redox potential declines to less than about 100mv as a result of bacterial decomposition of this material, much of the $H_2S$ may react with metal ions to form insoluble metal sulphides (Wetzel, 1983). In this manner, the redox potential of the $H_2S$-$SO_4$ couple plays a significant role in the modification of conditions for mobilisation of phosphate and numerous other nutrients, effectively acting as a 'catalyser' of limnetic nutrient cycling (Ohle, 1954).

Silica occurs in natural waters as dissolved silicic acid and particulate silica. Biotic requirements for Si are fundamentally limited to diatoms, although significant Si uptake may be achieved by other microbial forms (such as silicoflagellates and xanthophytes); radiolarians and actinopods; wetland plant forms (such as *Equisetum*); insects, and even vertebrates (Ehrlich, 1981). In addition to utilising Si to compose their skeletons (frustules), diatoms may require Si for the synthesis of chlorophyll (Werner, 1967), DNA (Darley, 1969) and DNA polymerase (Sullivan, 1971). Levels of Si are high within both the pelagial and the sediment-associated waters of Lake Sibaya, and they are unlikely to represent a limiting resource to diatoms. In the absence of any substantial stratification of the water column, the utilisation of silica by diatoms is not expected to induce any seasonal succession of diatom species relating to Si limitation.

When the concentration of Si is reduced to below about 0.5mg/l, many diatom species become outcompeted by non-siliceous algae. Si appears to be substantially elevated above such levels in the lake. Furthermore, the ratios of monovalent to divalent cations in the pelagial lake waters were less than 1.5 in all five samples (ranging between 1.2 and 1.4), suggesting (Wetzel, 1983) that diatoms would be favoured over desmid algae in the lake system.

Levels of $NH_4^+$ were consistently below the lower limit of detection (0.05 mg/l) in all Lake Sibaya pelagial waters. The ammonia concentration of the Lake Sibaya waters may have been under-represented to some extent, due to the fact that colloidally bound ammonia would have been removed by filtration through 0,2 µm Micropore filters prior to IC analysis. This particulate ammonia, which is generally associated with microscopic seston, is believed to be of considerable importance in the nitrogen cycle in lake systems (Hutchinson, 1975). The low levels of $NH_4^+$ determined in this study are consistent with the average of 0.04 mg $NH_4^+$/l determined by the DWAF (and expressed as N) for the period 1980-1998. DWAF state their lower limit of detection for ammonium as 0.02 mg $NH_4^+$/l. Wetzel (1983, p231) notes that $NH_4^+$ levels of unpolluted surface waters generally fall within the range of 0-5 mg/l, although concentrations are generally at the lower end of this range within oxygenated surface waters.

MINTEQA2 predicted that >93% of all ammonia would occur as $NH_4^+$ within all the Lake Sibaya waters. The decomposition of organic matter as an energy source for heterotrophic microbes, in both aerobic and anaerobic environments, results in the release of N compounds, including ammonia ($NH_3^+$), which subsequently protolyses to form ammonium in the aquatic environment. A considerable amount of ammonia in the sediment-contacted waters may, in fact, be produced directly from proteins during the decomposition of organisms, without the formation of soluble intermediate products (Von Brand, Rakestraw and Zabor, 1942, cited in Hutchinson, 1975). The elevated levels of $NH_4^+$ in transect SA sediments coincide with the greater numbers of hippopotami inhabiting this arm of the lake (*per. comm.* Mr. V. Dlamini, local resident). $NH_4^+$ constitutes a significant excretory product of vertebrate animals (Hutchinson, 1975). $NH_4^+$ is readily assimilated by plants in the photic zone, thereby rendering $NH_4^+$ concentrations low in these aerobic waters (Wetzel, 1983). Additionally, $NH_4^+$ may be oxidised in these waters through bacterial nitrification to $NO_2^-$ by (for example) *Nitrosomonas* or methane oxidisers, and through further oxidation of $NO_2^-$ to $NO_3^-$ by genera such as *Nitrobacter*. Since the water column of Lake Sibaya is well mixed throughout its depth, nitrification and denitrification are expected to occur in close proximity to the oxic-anoxic boundary, which presumably lies near the sediment-aqueous interface. The gyttja accumulations overlying all of the collected sediments may accommodate an oxidised microzone, capable of absorbing any ammonia that might have diffused from the mud into the free water. Only upon the reduction of this oxidised microzone will it lose its adsorptive power, thereby liberating any sorbed ammonia and destroying any barrier to the free passage of ammonia to the overlying water (Drever, 1997).

Both $NO_3$ and $NO_2$ were below the detection limit of the HPIC (≈ 0.1 mg/l) in both the pelagial and the sediment-contacted waters analysed in this study. The average concentration of the sum of these two species was calculated from the DWAF database as 0.06 mg N/l, with a standard deviation of 0.2 mg N/l, and a minimum detection limit of 0.04 mg N/l. $NO_2^-$ levels in natural lakes fall fairly predictably within the range 0-0.01 mg/l, whereas $NO_3^-$ levels are highly variable, fluctuating from undetectable levels to nearly 10 mg/l in fresh waters (Wetzel, 1983). In general, fresh water organisms are said to be capable of utilising nitrate under a wider range of conditions and at greater dilutions than they can use ammonia, the latter substance never comprising a better source of nitrogen than the former (Hutchinson, 1975).

In the process of the decomposition of organic matter in the reduced Lake Sibaya sediments, facultative anaerobic bacteria could be expected to utilise nitrate or nitrite as the terminal electron acceptor during the oxidation of organic carbon. In this way, $NO_3^-$ exerts a role as an electron acceptor in the reduction of $NO_3^-$ and $NO_2^-$ to gaseous $N_2$ and $N_2O$. The burrowing and ventilating activities of benthic animals which were identified by Hart (1979) as occurring in Lake Sibaya, may maintain an anoxic but potentially high redox potential zone around their burrows, thereby favouring denitrification. Such a postulation was made by Binnerup *et al.*, (1992) with reference to estuarine sediments. Since $NO_3^-$ appears to be limiting within the pelagial waters of Lake Sibaya, denitrification is expected to be largely limited to the sediment. Relatively high rates of denitrification could be expected within the sandy sediments of Lake Sibaya, owing to their porosity, which facilitates migration of nitrate to denitrifying zones.

The absence of detectable nitrate in well 1 and 2 water samples may be related to the fact that these groundwaters were collected during the dry season. Nitrate migration in soils is comparable to the rate of groundwater movement, and nitrate undergoes little or no adsorption in the aquifer (Loeb and Goldman, 1979). It is unlikely that denitrification would occur to any significant extent in the aquifer because, although conditions are reducing, carbon (Pooley, 1996; Ceruti, in prep) and nitrate availability are expected to be limiting to potential denitrifying microbial populations within these sands.

The minimal levels of dissolved N in the water column are quite predictable and expected. For all practical purposes the nitrogen cycle in lakes is microbial in nature: bacterial oxidation and reduction of nitrogen compounds are coupled with photosynthetic assimilation and utilisation by algae and larger aquatic plants. Photoautotrophic cyanobacteria (blue-green algae), photoautotrophic anaerobic bacteria, aerobic and anaerobic heterotrophic bacteria and chemotrophic bacteria occurring in the Lake Sibaya system would all presumably be capable of fixing nitrogen from the atmosphere, by means of the enzyme nitrogenase (Howarth *et al.*, 1998). This source of planktonic nitrogen fixation was shown to contribute between 0 and 82% of the total N input to various aquatic systems (Howarth *et al.*, 1998). Since $NH_4^+$ is usually found in greater concentrations in sediments than in the water column, and since high concentrations of $NO_3^-$ and $NH_4^+$ suppress the synthesis of nitrogenase, N-fixation in aquatic sediments is generally at the lower end of this scale (Howarth *et al.*, 1998). The rate of N-fixation in oligotrophic lakes generally ranges between 0.0003 and 2.0 g $N/m^2/yr$ (Howarth *et al.*, 1998).

In the context of $NH_4^+$ being limiting as a source of nitrogen for the synthesis of biomass, bacteria in Lake Sibaya would preferentially reduce species such as $NO_3^-$ and $NO_2^-$, either aerobically or anaerobically, through catalysis by reductase enzymes. The bacterial assimilation of $NH_4^+$ thus formed is related to the C:N ratio, both of the substrate and within the bacterial cells. If carbon is in excess in the substrate then the assimilation of $NH_4^+$ is rapid, and all available $NH_4^+$

is used up (Blackburn and Henriksen, 1983). Since the C:N ratio was shown to generally exceed 20:1 in the deeper gyttja sediments, rapid assimilation of $NH_4^+$ could be expected within the Lake Sibaya sediments. Harck (1995) demonstrated that the removal of $NO_3^-$ and $NH_4^+$ is considerably more substantial in organically-rich sediments of Verlorenvlei coastal lake (11% mass organic C) than in organically-poor (1% mass organic C) sediments. $NO_2^-$ was shown to be an intermediate in cycling between $NO_3^-$ and $NH_4^+$, accumulating in organically-rich sediments which were incubated and pre-dried by Harck, but not in these organically-rich sediments when maintained continuously wet throughout incubation.

Bowen (1976) noted the deep sediments of Lake Sibaya to be high in Kjeldahl nitrogen (427 mg/kg, n=3) relative to the littoral sediments (4.2-62.5 mg/kg, n=16) due to a high subsieve fraction that is largely organic in origin (gyttja). The littoral sediments are known to be wave washed, with surface organic debris being rapidly transferred to the deeper sediments. Nevertheless, Bowen (1976) demonstrated a highly significant loss in protein content of detritus with depth, claiming that the overall low level of protein in the pelagial waters undoubtedly inhibits the growth of fish, particularly *Oreochromis mossambicus* after their first year (*cf.* Section 2.6, page 2-29). His studies showed that the elevation of protein in shallow water detritus was due, not only to diatoms, but to dense concentrations of bacterial cells. Indeed, he proposed that the diatom cells are primarily responsible for the production of DOM, upon which the bacterial flora depends. The reduction in DOM as depth increases could be explained in terms of a corresponding decrease in diatom density and bacterial flora.

Similarly $PO_4^{3-}$ levels were below the detection limit of the HPIC in this study, and showed an average concentration of 0.02 mg P/l (s.d. = 0.06 mg P/l) within the DWAF database. Both phosphorus and nitrogen levels therefore appear to be limiting to the functioning of the lake ecosystem. Accordingly, Hart (1979) correlated low levels of soluble reactive phosphorus (SRP) with both low levels of productivity in Lake Sibaya, and rapid rates of nutrient cycling.

### *3.4.6.2 Trace elements*

The metabolic demands for iron and manganese are usually sufficiently low that the biota does not materially deplete these metals in lake systems (Wetzel, 1983). Both Fe and Mn are, however, essential micronutrients of microflora, plants and animals. Iron is required in the enzymatic pathways of chlorophyll and protein synthesis, in cytochromes, haemoglobin and in respiratory enzymes of all living organisms. Fe and Mn are furthermore functional components of nitrate assimilation, they participate in the Hill reaction of photosynthesis, and they comprise essential catalysts of numerous enzyme systems in plants, animals and bacteria. Although the requirements for Fe and Mn as micronutrients are low, their reactivity, very low concentrations, and restricted availability in the trophogenic zones of lakes suggest that under certain conditions, their availability may limit photosynthetic productivity (Wetzel, 1983).

Under oxidising conditions, ferric iron in solution would likely display a high affinity for hydroxide ligands in the alkaline lake waters, and thereby largely precipitate out as low solubility oxyhydroxides (Drever, 1997). The water column of Lake Sibaya has been shown to be well mixed (Section 3.4.1), and well saturated with dissolved oxygen at all depths (Allanson, 1979) during the cooler months when the samples investigated in this study were collected. The measured concentrations of dissolved Fe exceed those which would be expected if all Fe was in the ferric form at a pH > 5. It may be deduced that either a significant proportion of the iron is present as the more soluble $Fe^{2+}$, or insoluble $Fe^{3+}$, in the form of colloidal ferric hydroxides, may have passed through the 0.2μm filter. The determination of dissolved Fe by ICP-MS is also commonly complicated by argon interference (*pers. comm.* Dr. A. Späth, Department of Geological Sciences, U.C.T.). For this reason, any further interpretation of iron availability becomes tenuous.

Fe was not determined in the Lake Sibaya sediment-associated waters, due to technical problems experienced with the ICP-MS equipment. The dissolution of Fe oxyhydroxides, under the reducing conditions prevalent in the sediments, may promote Fe mobility significantly.

Extremely low levels of Mn were determined within the open pelagial waters of Lake Sibaya, the mean concentration being determined as 0.7μg/l. Since water samples were filtered through 0.2μm filters prior to analysis by ICP-MS, it is likely that colloidal Mn was excluded from the analysis, and that the element was primarily in the form of the soluble $Mn^{2+}$ ion. Mn concentrations of <50μg/l have been shown to inhibit the development of blue-green and green algae in streams, and to strongly favour diatom growth (Patrick *et al.*, 1969). Correspondingly, diatoms have been noted to exhibit a general dominance in the lake.

As shown in Tables 3,4c and 3.5c, the difference in Mn concentrations between the pelagial waters and the sediment-associated waters of Lake Sibaya is immense (mean concentrations of 0.52ppb versus 1032ppb, respectively). Furthermore, the contrast between the Mn concentrations in individual samples of these latter waters is astounding. No significant correlation was found to exist [correlation coefficient (C) =-0.11, p=0.7] between organic carbon content of the sediment solid phase and Mn concentration within the sediment-contacted waters. Support for this comes by way of the observation that the waters in contact with the gyttja sediments ($WA1_{eq}$ and $SA4_{eq}$) show vast differences in Mn concentration, of 1001 μg/l versus 35 μg/l, respectively. This is despite the fact that Mn concentrations in the solid phase of these two gyttja samples were the highest of all the sediments (Table 4.4). Rather, a significant trend was noticed between Mn concentration and lake depth, indicating that redox equilibria constitute the predominant control over Mn availability. Howard and Chisolm (1975) showed that nearly all of the total Mn in anaerobic water of the hypolimnion of a small eutrophic lake in New York was in soluble form, compared to less than 13 per cent in the aerobic water strata, thereby lending support to this observation.

Within the first 6 metres of lake depth, the sediment-associated waters (sample numbers 1 and 2 of each transect) show a range in Mn concentration of 872 to 5635μg/l. By contrast, waters in contact with the deeper sediments show average Mn concentrations of 60 μg/l (s.d.=11), 28 μg/l (s.d.=6) and 16 μg/l (s.d.=11) within transects WA, SA and WM, respectively. A Students' t-test for dependent samples revealed that waters in contact with sediments collected from less than 6m depth could be segregated from those collected from deeper levels with 98% confidence, when based on aqueous Mn concentration (t = 3.18; d.f.=5). These findings suggest intense photoreduction of manganese oxyhydroxides in the surface sediments of Lake Sibaya. The 1% photosynthetically active radiation (PAR) level (representing the most penetrating, green wavelength component of the visible energy), was determined at 7-8m depth in the Lake Sibaya water column during the winter months (Allanson, 1979). The penetration of this energy is likely to be influenced by factors such as Secchi disc transparency and colouration of the water. An effective light penetration depth of approximately 6m is therefore plausible in the winter months, when sampling was conducted.

Reducing conditions in the Lake Sibaya sediments would conceivably boost Mn mobility within their pore waters. Correspondingly, the waters in direct contact with the sediments appear to be enriched in Mn, relative to the pelagial waters, probably representing a near-equilibrium condition between the solid and aqueous phase. Enhanced dissolution of Mn oxyhydroxides in the shallower sediments, through photoreduction, appears to enrich the sediment-associated waters in Mn relative to their deeper counterparts. Patrick *et al.* (1969) noted that concentrations of Mn in excess of 1 mg/l, in the absence of high levels of calcium (which undergoes antagonistic reactions with Mn), are very inhibitory to blue-green and green algae, and can induce marked changes in their development and morphology. It is not known to what extent isolated pockets of high Mn concentration are influencing the autotrophic algal population in waters immediately overlying the shallow lake sediments.

**Zn, Cu and Ni**

As mentioned earlier in this section, quantitative information on the dynamics of the essential metallic micronutrients Zn, Cu, Co, Mo, V and Se is limited. All of these micronutrients (in addition to Fe and Mn already discussed) are required for the nutrition of plants and many animals (Wetzel, 1983). Most of the information on micronutrient requirements is obtained from studies of physiological deficiencies in cultures, which present an array of experimental difficulties, particularly involving contamination. Requirements are further complicated by observed differences that depend on the composition and concentration of other minerals, and an antagonism among these elements. The question of requirement concerns the availability of the micronutrient within the constraints of other ionic components of salinity, the extent of organic complexing of the micronutrient, and the metabolic demands of varying species (Patrick, 1978).

Concentration and availability of micronutrients in most aerated natural surface waters are generally very small, yet adequate to sustain active populations of algae within the constraints of light, temperature and macronutrient availability (Wetzel, 1983). Within oligotrophic aquatic systems such as Lake Sibaya, a paucity of the total amount and the bioavailable fraction of these elements may limit photosynthesis to some degree (Goldman, 1972). It is not yet known to what extent the low concentrations of various micronutrients in Lake Sibaya may be limiting the levels of biological productivity and diversity within the Lake Sibaya system. This control could conceivably be quite transitory, and effective only on certain algal species, thereby indirectly influencing algal succession and productivity (Wetzel, 1983). The low concentrations of Cr (should it occur in the hexavalent form), and probably also of V (which was not analysed in any of the water samples collected), may be partly responsible for favouring the development of diatoms over green and blue-green algae in the Lake Sibaya waters.

Micronutrient availability is controlled principally by redox conditions and pH, and by the extent of complexation with dissolved organic compounds and other inorganic ions. A large proportion of each of the micronutrients (>70%) occurs in the form of crystalline solids, adsorbed solid phases, organic complexes or dead seston, with very little prevailing as the free ion in solution (Wetzel, 1983). This would appear to be true of each of Zn, Ni (speciation not shown) and Cu, based on the element speciation output from the MINTEQA2 model (refer to Section 3.4.5). The potential importance of dissolved organic matter (DOM) in regulating the availability of Cu and Zn is notable in the Lake Sibaya waters. The apparently ready complexation of these micronutrients by dissolved organic compounds, probably through the formation of chelate-type complexes, is likely to lead to unexpectedly high concentrations of metals in solution (Drever, 1997). The dynamics of Zn, in particular, are expected to be closely related to microbial metabolism and transport of seston, and to the effectiveness of complexing with organic compounds (Wetzel, 1983).

### 3.4.7 Potential domestic/industrial use

Calcium carbonate precipitation potential (CCPP) values ranging between 6.3 and 7.6 mg $CaCO_3$ were determined by the Stasoft model (*cf.* Section 3.3.3.2) for Lake Sibaya pelagial waters at 20°C. From an engineering viewpoint, these constitute ideal waters, in that they are expected to precipitate an "egg-shell" calcite scale layer within domestic water pipes and industrial equipment, which is of sufficient thickness to prevent corrosion, yet not so thick as to clog flow in the pipes (Loewenthal and Marais, 1976). Either of these extremes is deleterious to engineering applications. The groundwaters of wells 1, 2 and 3 are similarly expected to be suited to piping, and to use by light industry. Waters from well 1 (CCPP=14 mg $CaCO_3$/l) and well 3 (CCPP=12 mg $CaCO_3$/l) may, however, pose a slight problem in terms of excessive scaling. It is important to realise that although the model predicts these waters to be supersaturated with respect to calcite, this is not necessarily the case in reality, nor will the reaction kinetics involved necessarily favour the precipitation of calcite, even under conditions of oversaturation.

Maintenance and replacement of pipes and machinery affected by scaling and corrosion is both costly and impractical in the context of the Zululand coastal plain. Corrosion may present a particularly important problem as a result of the proximity to the coast. Given one of the stated aims of the Reconstruction and Development Programme (RDP) to supply piped water to within 50m of each dwelling, and the proposed boom in light secondary industry linked to the new Spatial Development Initiative (SDI), further research in this field is warranted.

## 3.5 CONCLUSIONS

As suggested in the literature, the pelagial waters of Lake Sibaya were shown to be well mixed, both vertically and horizontally. These waters appear to be buffered within a pH range of 8.0 to 8.3, through equilibration of the lake waters with atmospheric $CO_2$, driven by intensive wind mixing. The MINTEQA2 model calculated that $HCO_3^-$ would constitute the predominant carbonate species (≥97%) in solution. The higher alkalinity and slightly lower pH of the sediment-associated waters would likely relate to the greater concentration of soluble organic acids in gyttja, the production of $H_2S$ by microbial reduction under anaerobic conditions, and the contribution of colloidal silicates and oxyhydroxides, which contribute negative surfaces for $H^+$ adsorption. The alkalinity of the coastal groundwaters presumably relates to the weathering of primary silicates and carbonates. Microbial activity in the soil may also produce soluble organic acids and carbonate species that contribute to the alkalinity of the coastal groundwaters.

The EC of the pelagial waters occupies the narrow range of 543-566 µS/cm. The cation suite is dominated by $Na^+$, and the anion suite by $Cl^-$, with the strong suggestion of an indirect maritime influence (wet and dry deposition). The level of $HCO_3^-$ is also relatively high in these waters. A disparity arose between the concentrations of Ca and Mg, in particular, measured by the Department of Water Affairs and Forestry (DWAF) over the period 1980 to 1998, and the concentrations of these elements determined in this study. The source of this discrepancy is not entirely known. Any interpretation of the geochemical data is therefore made within only a certain window of confidence.

The author proposes that atmospheric control (effected through the balance between precipitation and evaporation) constitutes the primary determinant of major ion dominance in these waters. Evidence to support the notion that the pelagial lake waters may be evaporated to a greater degree than their source groundwaters comes by way of:

- Climatic data (evaporation and precipitation)
- Stable isotope ratios ($\delta^{18}O$ and $\delta D$)
- The inverse relationship between TDS and lake level
- Mineral solubility equilibria (MINTEQA2 model)
- An historical precedent for calcite deposition, in the form of calcareous outcrops

Since low proportions of alkali earth metals occur in the Pleistocene and Recent aeolian sands of the coastal aquifer, due to intense leaching, the geological control over ion dominance by mineral dissolution is largely suppressed. The dilute nature of the pelagial waters may further be explained by the generally low concentrations of solutes in atmospheric precipitation. Under these conditions of low ionic strength, the effect of evaporation on the concentrating-up of solute ions appears to be largely stifled.

The MINTEQA2 chemical model predicted that the lake waters are presently in near equilibrium, or slightly oversaturated, with respect to calcite. The fact that calcite was not observed in any of the sediments (refer to Chapter 4) suggests that the reaction kinetics might not be presently favourable to its crystallisation. The incipient precipitation of calcite would herald the onset of the first chemical divide of the Hardie-Eugster model, whereby all Ca (and the majority of bicarbonate alkalinity) would be removed from solution. Forward modelling using PHREEQC predicts, however, that a fraction of the dissolved $Ca^{2+}$ would undergo complexation with $SO_4^{2-}$ after 150x evaporation above the present, thereby precipitating out of solution as gypsum. The PHREEQC model was therefore shown to differ from the conceptual Hardie-Eugster model, through its capability to allow the simultaneous precipitation of two or more oversaturated mineral species.

The PHREEQC model calculated that magnesium should begin to precipitate out as magnesite ($MgCO_3$) after 100x evaporation, thereby inducing the second chemical divide of the Hardie-Eugster model (which is more commonly achieved through the precipitation of sepiolite). Bicarbonate alkalinity was not calculated to be entirely used up in this reaction, as per Hardie-Eugster model expectations, but was rather allowed, by the model, to attain equilibrium with atmospheric $CO_2$. Sodium and chloride could be expected to dominate the residual water remaining after the additional evaporation of Lake Sibaya water, with minor contributions of $Mg^{2+}$ and $SO_4^{2-}$. Given the effect of groundwater dilution of the lake, it is unlikely that the Lake Sibaya waters will undergo such intensive evaporative concentration of solutes in the foreseeable future.

The waters of the extended Lake Sibaya were calculated by MINTEQA2 to be slightly oversaturated with respect to quartz. Owing to the slow reaction kinetics involved in the crystallisation of quartz, however, amorphous silica undoubtedly set the upper limit on the activity of dissolved silica in the lake. Geochemical models calculated that lake waters were undersaturated with respect to amorphous silica, both at present (MINTEQA2), and upon further hypothetical evaporation of the lake waters (PHREEQC). Rapid cycling of silicic acid, released into solution from the frustules of senescing diatoms, may feasibly set the solubility control on amorphous silica. The level of Si appears to be sufficiently high to favour the dominance of diatoms over non-siliceous algae in the lake. Aluminosilicate solubility equilibria were not interpreted, because of the great uncertainty involved in the determination of dissolved Al.

MINTEQA2 calculated that dissolved organic matter (DOM) constitutes the primary complexant of divalent metal ions, the relative extent of organo-metallic complexation following the ascending sequence: Mg < Zn < Ca < Cu. The majority of calcium in both the pelagial lake water (65%) and the sediment-contacted waters (85%) is predicted to complex with organic matter dissolved in solution (DOM). The remaining calcium would be expected to occur as the labile aqueous ion, $Ca^{2+}$. The bioavailable fraction of Ca is expected to be sufficiently great so as to prevent deficiency within the lake biota. Magnesium, by contrast, was predicted to exist predominantly as the free ion in the pelagial (82%) and sediment-contacted waters (55%).

Sodium, potassium and chloride are expected to occur exclusively as the conservative free ions in solution. As with magnesium, the supply of these non-critical elements to the freshwaters of Lake Sibaya is likely to exceed metabolic requirement by organisms. Approximately 90% of all dissolved sulphur in the Lake Sibaya waters is expected, according to the MINTEQA2 model, to occur as the labile $SO_4^{2-}$ ion. The sulphate concentration of the Lake Sibaya waters falls within the range characteristic of lake systems. Sulphate deficiencies are, therefore, not to be expected in the lake waters. Close to the sediments, however, much of the $H_2S$ released from organic matter upon decomposition, might react with metal ions to form insoluble metal sulphides.

Levels of $NH_4^+$ in Lake Sibaya pelagial waters were consistently below the lower limit of detection (0.05 mg/l). Both $NO_3^-$ and $NO_2^-$ were also below detection limit (≈0.1 mg/l) in both the pelagial and the sediment-contacted waters of the lake. Nitrate is expected to be limiting to productivity in the lake system, as indeed might be phosphate. Hart (1979) has correlated low levels of $NO_3$-N and soluble reactive phosphorus (SRP) with both low levels of productivity in Lake Sibaya, and rapid rates of nutrient cycling. Should any of the lake sediments be anaerobic, loss of nitrate could be expected to proceed as a result of reduction to ammonium, or via the process of denitrification. More work is required to validate this proposal.

Both Fe and Mn are essential micronutrients of microflora, plants and animals. The total Fe measured within the pelagial waters approximates the international drinking water average of 50μg/l (WHO, 1992). Nevertheless, oxidising conditions, and the low solubility of the hydrated ferric hydroxide, $Fe(OH)_3$, may still render Fe deficient in terms of bioavailability. In the absence of direct measurements of redox potential, and in light of the inaccuracies associated with Fe determination by ICP-MS, any interpretation of Fe solubility becomes highly speculative.

Manganese occurred at low concentrations (0.7μg/l) in the pelagial waters, thereby favouring the occurrence of diatoms above that of blue-green and green algae. On the basis of Mn concentration, waters in direct contact with shallow sediments (lake depth ≤6 m) could be segregated from those collected from deeper locations. A theoretical explanation for these disparities could relate to the intense photoreduction of manganese oxyhydroxides in the surface sediments, thereby serving to enrich their associated solutions in Mn, relative to their deeper counterparts. Since levels of dissolved oxygen have previously been shown to substantially exceed 50% throughout the water column, the majority of this released Mn would, however, be expected to re-precipitate into the sediments.

The data presented in this chapter characterise Lake Sibaya as a large freshwater lake falling within the oligotrophic category, namely low in nutrients with low organic production (Wetzel, 1983). Atmospheric control over the lake water composition appears to be in favour of evaporative concentration, but with slow rates of solute enrichment being observed over the past 19 years. This is presumably linked to low initial solute concentrations, which arise through minimal dissolution from intensely leached, unreactive aquifer sands and lake sediments. The area of surface contact between the minerals of the lake sediments and the pelagial water is also minimal in comparison with the lake volume, thereby minimising the effects of mineral dissolution on solute activity. Thorough mixing of the water column ensures that there are no significant nutrient pulses, either seasonally or at any level in the water column. In the absence of a hypolimnion, the bulk of the nutrients in the lake system are expected to be largely stored in the biomass, and consequently the cycling of nutrients through the food chain should be rapid. The primary value of the data presented in this chapter probably lies in the fact that it comprises a benchmark against which the results of future monitoring activities can be compared. Given the current advancement of the Spatial Development Initiative (SDI) linking Zululand to Mozambique, the present farming methods, and the developmental efforts required in order to meet Reconstruction and Development Project (RDP) objectives in the region, the possibility of pollution of the lake system in the near future is not inconceivable.

# CHAPTER 4: THE GEOCHEMISTRY OF LAKE SIBAYA SEDIMENTS

## 4.1 INTRODUCTION

As in the water column, organic productivity within the sediment medium is regulated by the rate of supply of energy and nutrients (Mortimer, 1949). In most lake systems the accumulation of nutrients within the bottom sediments due to sedimentation processes is considerably greater than the rate at which they are returned to the water column by biological, physical, chemical and mechanical processes (Förstner and Wittman, 1981). The concentrations of trace elements in the top few centimetres of bottom sediment are therefore generally far greater (by orders of magnitude) than their concentration in the water column (Horowitz, 1991). For this reason alone, any attempt at understanding the geochemical character of the Lake Sibaya system clearly relies upon an investigation of the chemical and mineralogical character of its bed sediments.

The purpose of this chapter is therefore three-fold, namely: to present an account of the methods employed in the collection and analysis of sediment samples; to present the analytical results obtained; and to interpret these findings in terms of potential processes affecting the chemical behaviour and availability of various elements.

## 4.2 SAMPLING

Lake Sibaya sediment samples were collected by boat from each of fourteen sample sites situated along the three lake transects. These sample sites correspond with the stations at which water samples were collected from the lake water column. The geographical location of each of these sites is shown in Figure 3.1, and their geographical co-ordinates and depth are presented in Table 3.1 (Section 3.2).

Sediment samples were collected by means of a Van Veen grab sampler (Plate 2, page 3-4). The hinged jaws of the instrument remain open, by means of a restraining mechanism, as it is lowered through the water column. On contact with the lake bottom, tension on the rope is removed, thereby releasing the restraining mechanism. Re-applying tension to the rope causes the jaws to "bite through" the sediment and close. The jaws remain firmly locked, as the sampler is withdrawn through the water column. In this manner, it was possible to collect sample to a sediment depth of approximately 10cm (Van Veen, 1936).

The sediments and the sediment-associated waters collected by the Van Veen grab were emptied into pre-rinsed screw-top plastic jars, which were filled to the brim to minimise the possibility of oxidation. The solid:aqueous ratio was approximately 3:4 within each of the samples. The sediment samples were thoroughly mixed on a horizontal shaken over a period of two weeks, after which time much of the supernatant water was decanted for routine water analysis (refer to Section 3.2). The remaining sediments were passed twice through a riffle-splitting device, which ensured that all four sub-samples remained representative of the original sediment sample. All sediment samples were transferred to a 4°C storage facility and remained stored therein between sample treatments and analyses.

## 4.3 ANALYTICAL METHODS

Geochemical characterisation of Lake Sibaya sediment samples was conducted primarily within the Department of Geological Sciences at the University of Cape Town. The general literature suggested that the sediments might be deficient with respect to various nutrients generally considered as requisite for biological functioning within freshwater lake systems. Accordingly, analyses were conducted at INFRUITEC, a division of the Agricultural Research Council, Stellenbosch, to determine availability indices for a suite of major and trace elements occurring within the sediments. Biological examination of four Lake Sibaya sediments was conducted in conjunction with the Freshwater Research Unit at the University of Cape Town. Details of the methods employed in the analysis of lake sediments are discussed in detail in Appendix B. A list of the analyses conducted is presented in Table 4.1.

**Table 4.1:** Analytical methods used to characterise Lake Sibaya sediments

| Sediment Property | Analytical Method | Reference |
|---|---|---|
| Colour | Colour matching | Munsell ® soil colour chart (1992). |
| Organic carbon | Dichromate oxidation-titration | Walkley and Black (1934) |
| Particle size distribution | Wet sieving: 0.053mm<br>Dry sieving: nested sieves | Gee and Bauder (1986) |
| Clay mineralogy | X-ray diffraction (XRD) | Whittig and Allardice (1986)<br>Jackson (1969)<br>Kinter and Diamond (1966) |
| Major and trace elements | X-ray fluorescence (XRF) | Willis (1995) |
| Availability indices | Extraction (various) and ICP | |
| | • $(NH_4)_2$ EDTA extraction: Cu, Zn | Baker and Amacher (1982) |
| | • Bray 2 extraction: P, K | P: Bray and Kurtz (1945);<br>K: Schulte and Olsen (1970) |
| | • Hot water extraction: B | Bingham (1982) |
| | • $NH_4OAc$ extraction: Na, Ca, Mg | Na: Knudsen *et al.* (1982)<br>Ca, Mg: Lanyon and Heald (1982) |
| Diatom genera | Frustule identification | Metting (1994) |

## 4.4 RESULTS AND DISCUSSION

### 4.4.1 Colour

Of the fourteen sediment samples collected from the Lake Sibaya bed, only two ($SA4_{sed}$ and $WA1_{sed}$) appeared, visually, to represent significant accumulations of the gyttja (fine organic-rich lacustrine mud) identified in the Lake Sibaya literature (refer to Chapter 2). By definition gyttja is very soft and hydrous in the fresh state, with a dark greenish-grey to black colour (Wetzel, 1983). In the dry state, some gyttjas are hard and black, while others are more friable and lighter in colour, depending on the main constituent (Wetzel, 1983). The organic carbon content of gyttja approaches, but does not exceed, 50%. Soil and sediment organic matter, as a whole, is a dark brown to black pigment (Bigham, and Ciolkosz, 1993), the darker colours frequently being derived predominantly from a high molecular- weight humic fraction (Stevenson, 1985).

Three independent observers determined the moist and dry colour of all the sediment samples, under natural light. The estimated precision of the method for one person is 0.5 units of hue, 0.1 units of value and 0.1 units of chroma (Bigham and Ciolkosz, 1993). Precision is expected to improve quite substantially with an increase in the number of observers. As seen from Table 4.2, the two above-mentioned samples were distinguished from the others by way of their darker grey/black colours in the moist state and their darker greyish-brown colour in the dry state. Based on their colour and on the strong visual suggestion of relatively high organic matter content, these two sediments appear to represent accumulations of gyttja collecting within the peripheral, sheltered regions of Lake Sibaya (refer to Section 2.2.2).

The remaining samples generally displayed relatively pale colours in the dried state, indicating a strong quartz component. Quartz is usually colourless and transparent or white, and has a vitreous lustre (Drees *et al.,* 1989). Any estimation of the organic matter content of the sandy sediments based purely on moist colour would be exaggerated, since sand-sized particles are poor scatterers of visible light, and will appear darker than silty sediments with the same quantity of black organic pigment (Bigham and Ciolkosz, 1993). A thin veneer (1mm to 10mm) of gyttja overlay each of the sandy sediments collected.

### 4.4.2 Particle size

Grain size constitutes the primary factor controlling sediment capacity for concentrating and retaining trace elements (Thorne and Nickless, 1981). A highly significant, positive correlation has been shown to exist between decreasing grain size and increasing trace element concentrations, arising as a result of both physical and chemical factors (Horowitz, 1991; Jones and Bowser, 1978). Fine-grained sediments, because of their large surface areas, are the main sites for the collection of inorganic constituents.

The combined silt-clay (mud) fraction remaining after removal of the sand fraction (< 0.053 mm) by wet-sieving was less than 6%, in all but the two samples resembling gyttja (refer to Table 4.2). These sediments are categorised as 'pure sand/sand' according to the Wentworth soil texture classification scheme (Wentworth, 1922). Further differentiation of the sand fraction into its composite Wentworth sand texture classes revealed that these sediments fall within the fine sand category (0.25-0.106mm), with the exception of samples collected from SA1 and SA2, which constitute medium grade sands.

This is consistent with the findings of Miller, (1998), who explained the occurrence of the medium-grained sand exposures in wind-exposed regions in terms of wind-induced current and wave activity, acting to winnow the finer sand fraction from these areas. There is a general decrease in grain size with increasing water depth (Figure 4.1), with statistically significant correlations exhibited for the two finer sand fractions plotted against depth. This pattern suggests that the winnowing of ex-channel lag deposits may indeed represent a control over the sediment size distribution (Section 2.2.2), as would the slow rate of sedimentation to the lakebed. Förstner and Wittman (1979) state that this general pattern of decreasing sediment grain sizes from the shore towards the basin is to be expected within lakes, which exhibit a relatively continuous (albeit slow in this instance-) accumulation of sediment materials. A more thorough interpretation of the sedimentology of Lake Sibaya can be found in Miller (1998), a basic summary of which is presented in Chapter 2.

**Table 4.2**: General characterisation of Lake Sibaya sediment samples. Colour categorisation is according to the Munsell Soil Colour Chart (1992). The combined silt + clay fraction (%) represents the mass fraction remaining after wet-sieving (0.53µm aperture). (Sediments did not effervesce upon addition of concentrated HCl, indicating minimal, or no, carbonate content.)

| Sample | Moist Munsell Colour | Dry Munsell Colour | Org. C (%) | Silt+clay % |
|---|---|---|---|---|
| WA1sed | 5Y 2.5/1: Black | 2.5Y 4.5/2: Greyish brown-dark greyish brown | 24 | 73 |
| WA2sed | 5Y 5/2: Olive grey | 2.5Y 6.5/3: Pale yellow-light yellowish brown | 1.4 | 1 |
| WA3sed | 2.5Y 5/2: Greyish brown | 2.5Y 6.5/3.5: Light yellowish brown | 0.4 | 6 |
| WA4sed | 5Y 4/2: Olive grey | 2.5Y 6.5/3: Pale yellow - light yellowish brown | 0.3 | 2 |
| | | | | |
| SA1sed | 5GY 5/1: Greenish grey | 5GY 7/1: Light greenish grey | 2.0 | 2 |
| SA2sed | 5GY 5/1: Greenish grey | 5GY 7/1: Light greenish grey | 1.7 | 2 |
| SA3sed | 2.5Y 5/2: Greyish brown | 2.5Y 6.5/3: Pale yellow-light yellowish brown | 2.0 | 1 |
| SA4sed | 3/N3: Very dark grey | 2.5Y 3/1.5: Very dark grey- very dark greyish brown | 22 | 63 |
| SA5sed | 5Y 5/2: Olive grey | 2.5Y 7/4: Pale yellow | 1.5 | 2 |
| | | | | |
| WM1sed | 5Y 6/3: Pale olive | 5Y 7/3: Pale yellow | 3.8 | 2 |
| WM2sed | 2.5Y 5/2: Greyish brown | 2.5Y 7/2.5: Light grey-pale yellow | 0.4 | 1 |
| WM3sed | 2.5Y 5/3: Light olive brown | 2.5Y 7/4: Pale yellow | 0.4 | 3 |
| WM4sed | 2.5Y 5/3: Light olive brown | 2.5Y 7/4: Pale yellow | 1.4 | 2 |
| WM5sed | 2.5Y 5/3: Light olive brown | 2.5Y 7/4: Pale yellow | 0.6 | 4 |

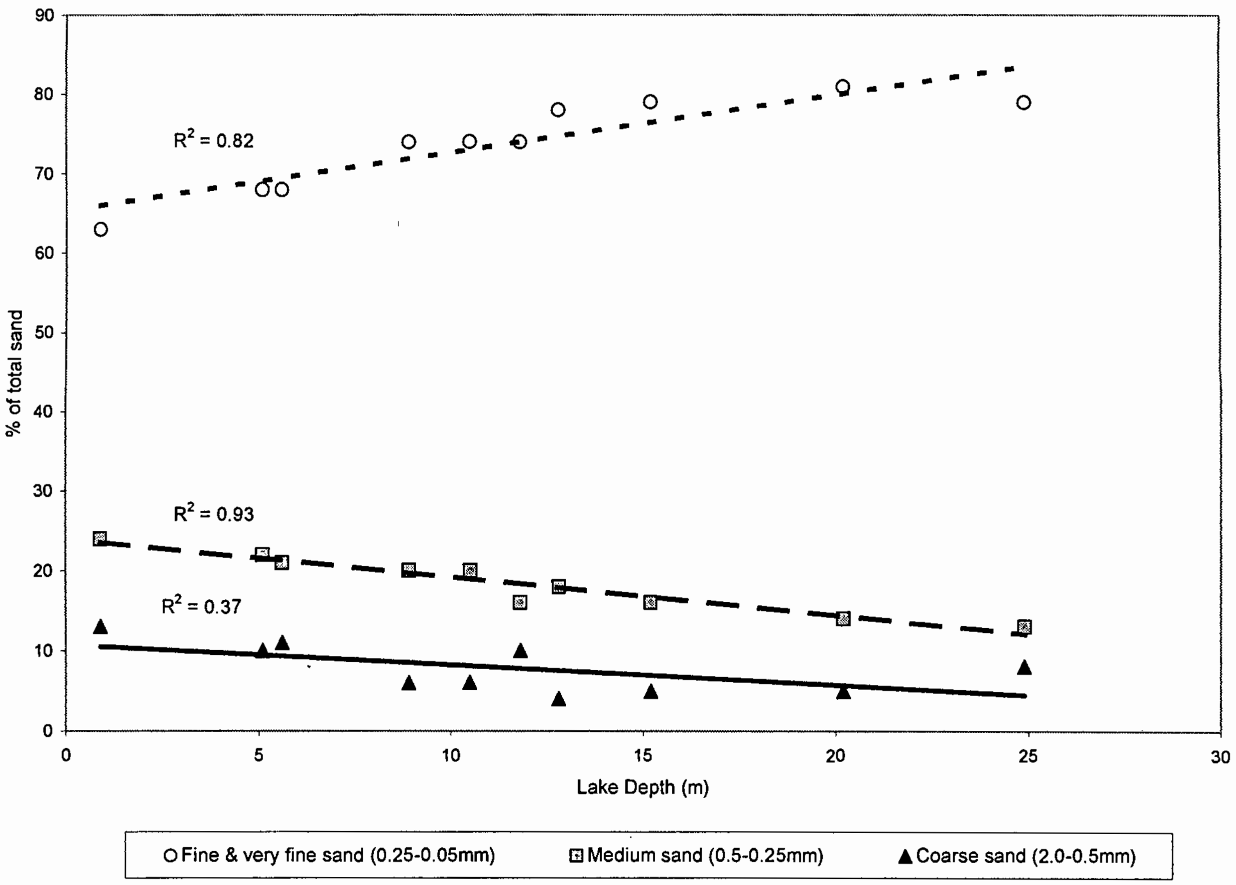

**Figure 4.1:** Sand grade of Lake Sibaya sediments as a function of lake depth.

Cation exchange capacity is expected to be relatively low within these sandy sediments, because of their low surface area to volume ratio. Owing to the extreme dominance of the sand fraction on particle size within the former sediments, further separation of the muds into their component fractions was not conducted. The methods required to achieve such separation (refer to Appendix A) are generally time-consuming and fraught with complications (*pers. comm.* Dr. P.J. Holmes, Engeo Department, University of Cape Town).

### 4.4.3 Clay mineralogy

X-ray diffractograms of the untreated Na-saturated clay fractions extracted from selected sediment samples collected from transects WA, SA and WM are shown in Figure 4.2. All samples show almost identical diffraction patterns. The following discussion of clay mineralogy therefore applies to all of the Lake Sibaya sediment samples.

Kaolinite, quartz and mica were positively identified as occurring within the clay fraction of all fourteen sediment samples. The first order peak for kaolinite featured prominently at a d-spacing of 7.10Å, with further significant kaolinite peaks occurring at d-spacings of 3.59Å (90%) and 2.51Å (70% intensity). A major quartz ($\alpha$-$SiO_2$) peak was positively identified at a d-spacing of 3.44Å (100%). Minor quartz peaks were identified at diffraction spacings of 4.33Å (35%) and 2.15Å (6%). Weak first and second order mica peaks were identifiable at 10.08Å and 5.04Å, respectively. The presence of mica group minerals was confirmed by the retention of the 10.08Å peak upon Mg-saturation, glycerol solvation, K-saturation and heating to 500°C of the XRD sample slides (Figures 4.3. and 4.4). A series of strongly overlapping peaks was evident between 10 - 18Å (5 – 9° 2θ), these peaks being more pronounced in some sediment samples relative to others. These peaks suggest the presence of undifferentiated 2:1 layer silicate material.

The presence of quartz in both the sand- (*cf.* Section 4.4.2), (presumably) silt-, and clay fractions of the Lake Sibaya sediments is not surprising, given its status as the second most common mineral, after feldspars, in the earth's crust. Furthermore, quartz is highly resistant to weathering (Goldich, 1938). Dense packing of the crystal structure, and the high activation energy required to alter the Si-O-Si bonds, are major factors contributing to the high stability of quartz (Drees *et al.*, 1989). Bonding forces become progressively stronger with decreasing particle size, until a size is reached at which the bonding forces limit further subdivision (Krinsley and Smalley, 1972). According to the literature, nearly all of the quartz in the total clay fraction (< 2μm) of the Lake Sibaya sediments is expected to occur in the coarse-clay fraction (Drees *et al.*, 1989; Allen and Hajek, 1989).

The low physiochemical activity of quartz will serve as a diluent to more reactive clay mineral components in the Lake Sibaya sediments. The highly closed structure of quartz inhibits the degree to which impurities can enter the crystal structure by atomic substitution and interstitial elemental occlusion, thereby rendering quartz extremely pure (Drees *et al.,* 1989). Silica minerals consequently lack significant isomorphous substitution for Si, are electrically balanced, and thus exhibit negligible surface charge (Grim, 1968; McBride, 1994). Very small amounts of anion and cation exchange are expected to arise from broken Si-O bonds and Si-OH (silanol) groups around the particle edges (Krinley and Smalley, 1972). Silica surfaces are not highly hydrated - only weak adhesive forces bond polar $H_2O$ molecules to the essentially uncharged, non-ionic silica surface. Few, if any, adsorbed cations are available for solvation, and cation solvation is negligible (Drees *et al.*, 1989). The extent to which organic matter and/or sesquioxides may form coatings on Lake Sibaya quartz grains - and thereby influence their cation exchange capacity (refer to Chapter 2) – is investigated in Section 4.4.4.

Rai and Kittick (1989) claim that thermodynamic data generally support the empirical observation that primary minerals dissolve to form clay minerals. The weathering of a mineral is affected by its composition, coefficients of expansion, cleavage, hardness, specific surface, and the original defects in the crystals. Additional external factors are the physical, biological and chemical (oxidation-reduction, hydration, hydrolysis, pH, chelation, cation exchange, carbonation) conditions of the weathering environment (Rai and Kittrick, 1989). Kaolinites are predicted (from thermodynamic data) to be stable in solutions of moderate $H_4SiO_4$ activity (being generally of well drained environments), whereas montmorillonites should remain stable in solutions with high $H_4SiO_4$ activity (characteristic of poorly drained conditions) (Rai and Kittick, 1989).

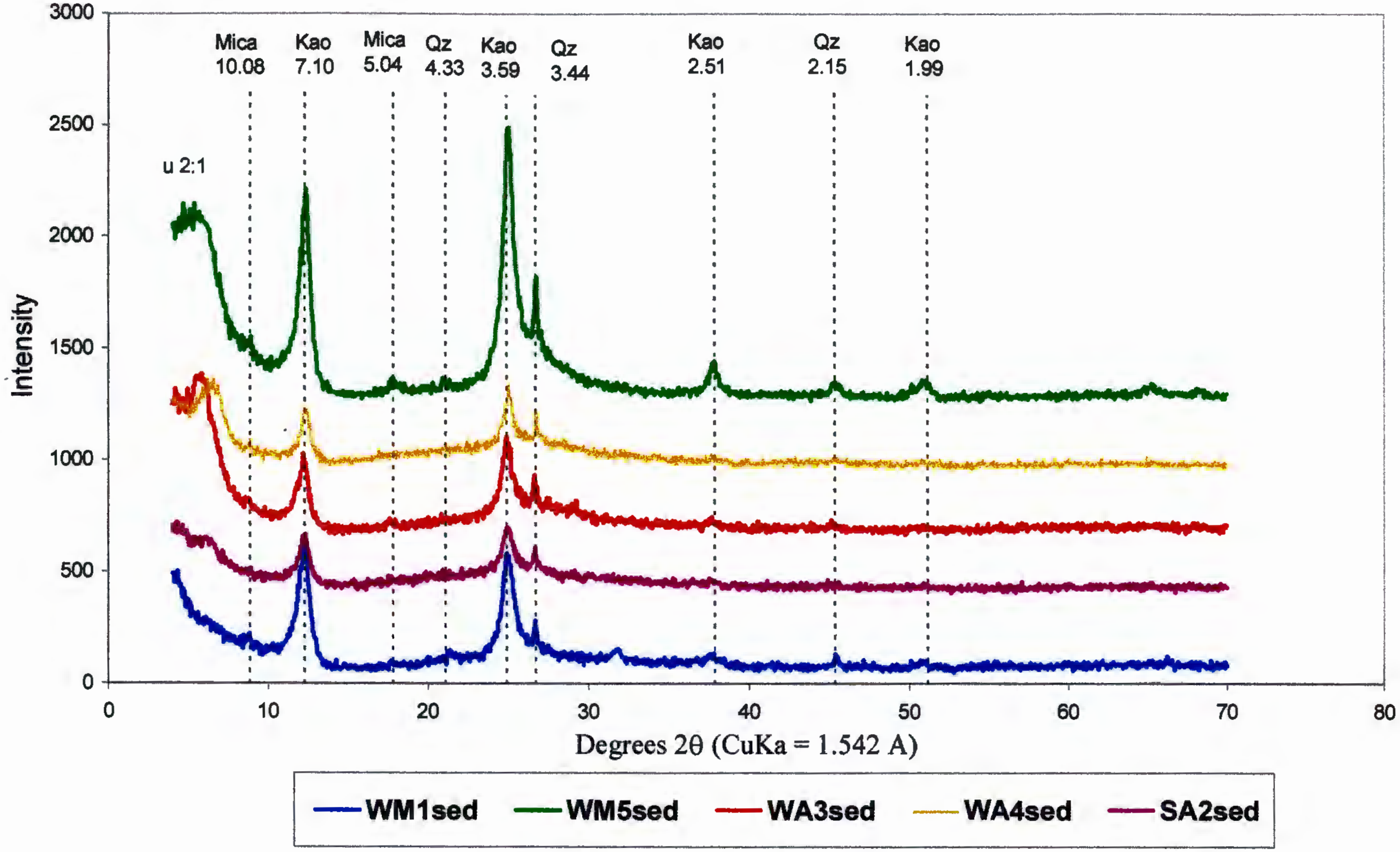

**Figure 4.2:** X-ray diffractograms showing the clay mineralogy of selected sediments collected from each of transects WA, SA and WM in Lake Sibaya. 'Kao' indicates kaolinite, 'Qz' represents quartz, and 'u 2:1' indicates undifferentiated 2:1 layer phyllosilicates. All d-spacings are labelled.

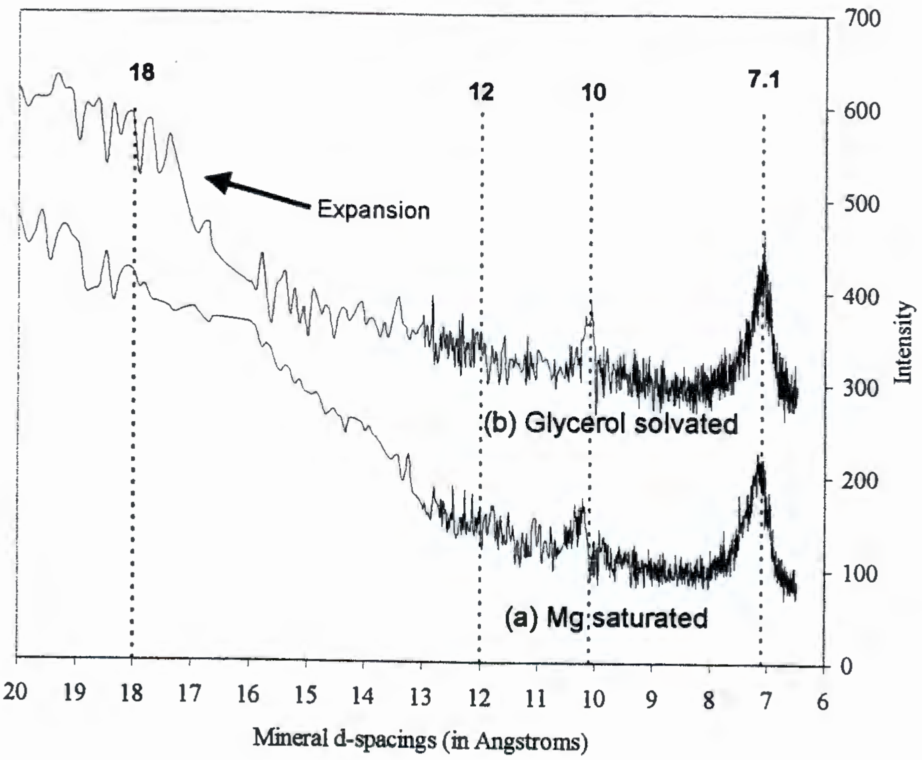

**Figure 4.3:** Diffractograms showing (a) Mg-saturation and (b) glycerol solvation pre-treatment of sample WM5$_{sed}$. Refer to the main body text for explanation.

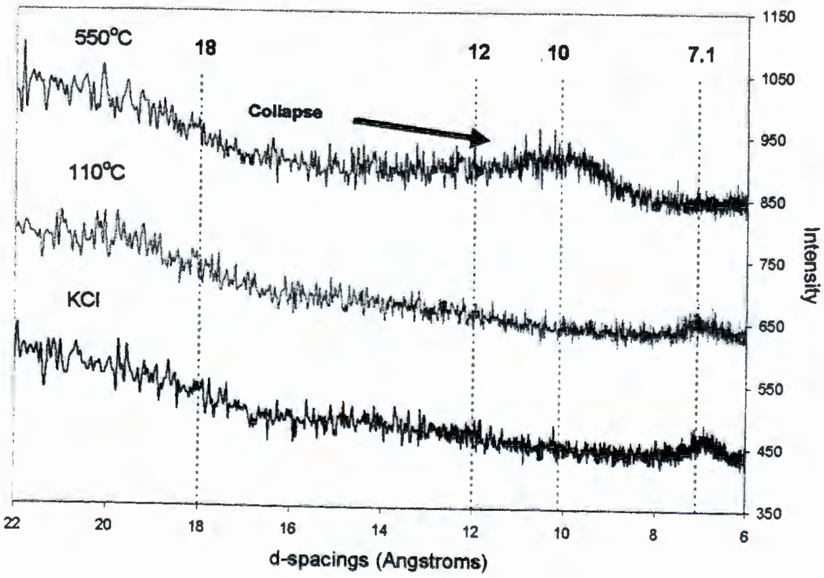

**Figure 4.4:** Diffractograms showing K-saturation and subsequent heat pre-treatment of sample WM5$_{sed}$ to 110°C and 550°C. Refer to the text in the report for details.

Although concentrated in the clay fraction, kaolinite might also be expected to occur as fine silt (5-2μm) and even as medium-silt (20-5μm) particles within the Lake Sibaya sediments. Larger amounts of kaolinite are usually present in the coarse clay (2-0.2μm) than in the fine clay (<0.2μm) (Allen and Hajek, 1989). The formation of kaolinite is favourable within the humid tropical/subtropical environment of the Zululand coastal plain, which has exhibited conditions of alternate wet and dry seasons and relatively unimpeded drainage within its recent geomorphological history. Under such conditions, primary silicate minerals - predominantly those that are arkosic (feldspathic) – will undergo weathering reactions in the direction of kaolinite formation (Garrels and Christ, 1965). The advanced stage of weathering of these sediments is indicative of the intensive leaching and/or oxidising environment experienced along the Zululand coastal plain. The synthesis of significant quantities of kaolinite in the soils/sediments of the coastal plain (pedogenic kaolinite) seems unlikely, given the slow reaction kinetics of this process. At the soil ambient temperatures experienced along this region, kaolinite dominance is generally not expected within soils younger than 10 000 years (Loveland, 1984; Glenn, 1960).

Negative charge associated with isomorphous substitution within the structures of layer silicate minerals is generally the major contributor to the exchange capacities of mineral soils (Sposito, 1989). Schofield and Samson, (1954) have postulated that kaolinite retains permanent negative charge, commonly through isomorphous substitution of $Fe^{3+}$ (and possibly $Fe^{2+}$). If this is indeed the case, the magnitude of permanent layer charge is, in any instance, minimal ($\approx$ -1.0 cmol/kg), and CEC is related largely to 'edge sites', rather than to permanent layer charge sites (McBride, 1994). The silanol group is the most likely edge site to adsorb cations (electrostatically) at the pH values present in the Lake Sibaya sediments. Both Weiss and Russow (1963) and Follett (1965) demonstrated that exchangeable cations were bound only on the tetrahedral basal plane of kaolinite, and that substitution of $Al^{3+}$ for $Si^{4+}$ was confined to the outer tetrahedral sheet. The kaolinites within the Lake Sibaya clay fraction are expected to show negligible inner-sphere, or co-ordination, bonding within the pH range of the ambient waters. The CEC of kaolinite is consequently confined to only about 3-5 meq/100g (Appelo and Postma, 1994).

The edge sites of kaolinite are proposed as the first ones to sorb both sulphate and phosphate anions (Rao and Sridharan, 1984, cited in Dixon and Weed, 1989). The anion exchange capacity of kaolinite is, however, dependent on the protonation of these edge sites. Since Lake Sibaya solutions are well pH buffered, and fall outside of the acid pH range, the discussion of anion exchange capacity with respect to the kaolinite content of the sediments is not relevant.

Close to igneous and metamorphic rock source types, macroscopic mica, occurring in flakes, is common in coarse-textured sediments (Fanning *et al.*, 1989). Because micas are softer than most of the other minerals with which they are commonly associated, however, they tend to be readily broken down, physically, during transport and sedimentation processes. This would serve to explain the limited presence of these micas in the clay fraction of Mseleni soils (Pooley, 1996) and Lake Sibaya sediments. These micas are anticipated to accumulate within the coarse clay (0.2-2μm) fraction of the lake sediments because (a) they are less resistant to physical disintegration than quartz, which accumulates in the coarser sediment fractions; (b) micas in the fine (<0.2μm) clay fraction are expected to have undergone more transformation to expansible 2:1 layers; and (c) neoformed minerals such as smectite (*cf.* below) tend to occur preferentially in the finer clay fractions (Fanning, *et al.*, 1989).

The amount and kind of mica occurring in more recent unconsolidated sediments depend upon the origin of the sediments (Frye *et al.*, 1962). The subdued intensity of the mica peaks suggests that micas do not constitute a major component of the Lake Sibaya sediment clay fraction. Since micas originate mainly from soil parent materials, and tend to weather to other minerals with time, they are expected to be less prevalent in these highly weathered sandy sediments (Jackson, 1964). The weak intensity of the 5.04Å mica peak in the lake sediments, relative to that at 10.08Å, suggests, to some extent, that these are Fe-rich micas (such as biotite, glauconite and lepidomelane), rather than aluminous micas (Fanning *et al.*, 1989).

The CEC of micas is relatively small because the interlayer cations are tightly held, non-hydrated, and balance a high layer charge. The total area for ion exchange in these micas is restricted to external surfaces. These micas will not retain anions on the edge surfaces under the pH regime of the Lake Sibaya waters.

The micas in the Lake Sibaya sediments may have served as precursors to the expansible 2:1 minerals, which are apparently present within the clay fraction. This transformation involves the replacement of the 'non-exchangeable' interlayer cations (usually $K^+$) by hydrated exchangeable cations (Fanning *et al.*, 1989). This results in both an increase in CEC, and a possible source of K for macrophyte plants in the lake. Interlayer cation exchange sites have a very high selectivity for $K^+$ and other weakly hydrated cations such as $NH_4^+$, $Rb^+$ and $Cs^+$ (Fanning *et al.*, 1989). Thus, for other more strongly hydrated cations to replace K from a mica interlayer, they must occur in the sediment-contacted and pore waters at an activity many times the activity of K. Perhaps more likely is the neoformation of the undifferentiated 2:1 layer silicates in the environment of the sediments, through the recombination of silica, aluminium, iron and the various base cations released as a consequence of primary mineral dissolution. Smectites are expected to form rapidly in alkaline solutions, arising through restricted drainage and/or evaporative salt accumulation, such that the normally mobile alkaline and alkaline earth ions (Na, Ca, K, Mg) accumulate, along with silica (McBride, 1994). Neoformation of smectites from Na-rich saline water is favoured under these conditions. The formation of these new, low temperature, secondary minerals could therefore be reached through high intensity leaching of the coastal plain sediments, and subsequent accumulation of the more soluble leaching products (silica and the base cations) within the local environment of the lake sediments. (McBride, 1994). The reducing environment likely within the Lake Sibaya sediments is expected to assist mineral crystallisation.

Resolution of the undifferentiated 2:1 layer silicates was achieved by means of rendering the clay homoionic, (via Mg-saturation of the clay exchange complex) and subsequently solvating the treated clay with glycerol. Figure 4.3 shows the resultant expansion of the 001 spacing of the clay towards 18Å upon glyceration, thereby suggesting the presence of smectite. Corresponding patterns of increased concavity of the 12-18Å portion of the diffractogram, and of sharpening of the 10.1Å mica peak upon glyceration, are also observed. The fact that the 14Å peak (which is not visibly pronounced, due to background noise) does not collapse to 12Å upon initial heating (110°C) of the K-saturated clay (*cf.* Figure 4.4), yet subsequently undergoes collapse to 10Å with more intense heating to 550°C (*cf.* arrow Figure 4.4), further suggests the presence of smectite. Despite the high CEC of smectite (as described in Chapter 2), the relatively low mineral intensities obtained from the diffractograms suggest that it occurs in minimal quantities within the clay fraction of the Lake Sibaya sediments.

The physical and chemical properties of any sediment are controlled, to an immense extent, by the mineralogy of the clay fraction. The unreactive mineralogy of the clay fraction of the Lake Sibaya sediments is likely to translate into low cation exchange capacities. It is proposed that this will exert significant consequence in terms of ion exchange, sorption capacity, elemental speciation and nutrient availability.

### 4.4.4 Chemical composition

The concentrations of major and trace elements within the Lake Sibaya sediments, as determined by X-ray fluorescence spectrometry, are presented in Tables 4.3 and 4.4, respectively. The sum of the weight percentages of the major elements (expressed as their individual oxides) fell within the range 99.7-101.7% for each of the samples, indicating acceptable analytical accuracy. The relative abundance of the major elements (on a milliequivalent basis) is demonstrated graphically by means of STAR diagrams in Figure 4.5. Since patterns of major ion (and organic carbon) abundance were shown to be transect specific, only a few representative samples from each transect are shown as STAR diagrams. The overwhelming silica dominance in these sediments has been artificially suppressed in these plots, through the introduction of a multiplication factor. The use of these diagrams is described in Section 3.4.

The fate of the major elements within lake sediments is well documented in the literature (Degens, 1965; Brownlow, 1979; Butcher *et al.*, 1992; McBride, 1994). Silica concentrates predominantly in the resistate sediments, and alumina in the hydrolysates (primarily the clay minerals). Potassium shows a proclivity towards being adsorbed by the clays, forming minerals such as glauconite and illite in the process. Calcium and magnesium commonly accumulate in the carbonates, whilst iron and manganese are generally associated with the oxidates. Sodium is likely to remain predominantly in solution within the Lake Sibaya system. In view of such associations expected during sedimentation, the silicon content of the sediments (expressed as the $SiO_2$ percentage of the total sediment, determined by XRF) is here considered as a suitable proxy for the occurrence of quartz. Similarly, calcium, aluminium and iron (expressed as their oxides) are deemed suitable surrogates for the distribution of carbonates, the mud/clay mineral fraction, and oxides, respectively. The organic carbon content of the lake sediments is presented in Table 4.2. The significant correlations calculated between major sediment fractions and trace elements, and between individual members of these groups, are presented in Table 4.5.

Immediately obvious from the comparison of the gyttja accumulations with the siliceous sandy sediments is the substantially greater contribution of organic carbon to the bulk of the gyttja muds. The organic carbon contents of the two sediments sampled from sites WA1 and SA4 were of the same order of magnitude ($\bar{x}$=23%, *cf.* Table 4.2) as the average value (27%) reported by Miller (1998) for Lake Sibaya gyttja accumulations. As discussed in Chapter 2, the wind strength is sufficiently reduced, and the bathymetry sufficiently complex within the peripheral water bodies of Lake Sibaya, so as to allow for the local accumulation of the breakdown products of organic matter.

The meagre organic carbon content of the siliceous Lake Sibaya sediment samples attests to both the low level of primary activity, and an unusually rapid rate of recycling of organic matter through the food chain. This is reflected in the relatively high turnover rates of the invertebrate organisms studied by Hart (In: Allanson, 1979). Most (75 to >99 percent) of particulate organic matter synthesised in the trophogenic zone of lakes of moderate depth is decomposed in the water column by the time it reaches the sediment interface (Wetzel, 1983). The dissolved organic matter (DOM) which is thus released is rapidly utilised by bacteria. Decomposition is expected to be virtually complete in the water column of larger, oligotrophic lakes (such as Lake Sibaya). This is because of the amount of time required for decomposition of refractory materials of algal cells, and the distance (and time) through which a particle travels during sedimentation (Jewell and McCarthy, 1971). Once reaching the sediments of Lake Sibaya, large quantities of organic matter may be further lost to methanogenesis, under anaerobic conditions, during which process they are converted quantitatively to methane and carbon dioxide. The documenting of dome-shaped gyttja deposits on the lakebed, by Miller (1996), would appear to substantiate this proposal. The extent to which this methane escapes to the atmosphere is presumably determined by the presence and activity of methane-oxidising bacteria in the overlying water (ZoBell, 1964).

The quantity of organic carbon shows significant correlations (at the 95% confidence level) with $Al_2O_3$, suggesting that specific organic molecules are bonding with the clays, either through the formation of ionic bonds (through simple ion exchange), or through adsorption-type van der Waals' bonds (Degens, 1965). This interaction is likely to occur to a higher degree with the smectite (identified by XRD) and possible randomly interstratified clay minerals, than with the (dominant) kaolinite clay fraction (Turchenek and Oades, 1978). As discussed in Chapter 2, mutual accumulation of the clay sized fraction, and of organic matter, is expected to arise in regions of the lake fed by sediment slumping and retarded current flow. Various trace metals (Cr, Cu, Mn, Mo, Ni, U, and V) were proposed by Curtis (1966) to complex with dissolved organic matter in solution, and to subsequently concentrate, through adsorption, onto clay mineral surfaces. The absence of significant correlations between organic carbon content of the siliceous sediments and any of the trace elements suggests that this is not the case in this system.

Positive correlations are observed between the quantities of $Al_2O_3$ and each of Sr, Zr, Nb, Cr, V and Y (Table 4.5). Although statistically significant at the 95% confidence level, the strength of the correlation is relatively low in each instance, thereby reinforcing the proposal that the clay fraction of the sediments is of generally low reactivity (Section 4.4.3). Furthermore, the explanation for each of these relationships is not necessarily founded on ion exchange or sorption processes. Cr appears to occur in the $Cr^{3+}$ form, which is readily immobilised through chemisorption by the silicate clays. The correlation observed between vanadium and clay content (represented by $Al_2O_3$) probably relates to the substitution of the vanadate ion into the structures of layer silicates, thereby severely limiting its bioavailability (McBride, 1994). A strong positive correlation is observed between $Al_2O_3$ and $K_2O$. It is feasible that a large proportion of the $K^+$ ions is trapped in a non-exchangeable form in the structure of the supposed illite (and possibly vermiculite) clay fraction, through the collapse of the interlayer regions of the mineral structure. The strong correlations observed between each of $Al_2O_3$, $K_2O$ and Rb suggest isomorphous substitution of $K^+$ and $Rb^+$ within the clay fraction of the sediments.

Cu and Zn displayed a lack of significant correlation with clay content in the Lake Sibaya siliceous sediments. Shuman (1991) reported that clays are capable of sorbing both Cu and Zn in excess of CEC at near-neutral or alkaline pH levels, attributing the excess retention to either surface precipitation or sorption of the univalent $M(OH)^+$ form. Wakatsuki and Kawaguchi (1975, cited in: Dixon, 1989: p506) found that Cu and Zn were sorbed by kaolinitic soil clays at solution ion activities lower than those required for oxide/hydroxide precipitation. Contrary to these findings, Zn appears to be immobilised by the limited solubility of Fe and Mg oxides and hydroxides, above that of adsorption by the clay fraction.

**Table 4.3:** Major elemental concentrations (weight percentages of the individual oxides) within Lake Sibaya sediments, as determined by X-ray fluorescence spectrometry.

| Sample | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO | $K_2O$ | $P_2O_5$ | $SO_3$ | $H_2O$- | LOI | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| WA1sed | 53 | 0.19 | 4.14 | 2.27 | 0.24 | 1.88 | 0.32 | 0.14 | 0.56 | 6.6 | 31.8 | 101.0 |
| WA2sed | 98 | 0.16 | 0.62 | 1.26 | 0.02 | 0.06 | 0.30 | 0.02 | <0.02 | 0.1 | 0.5 | 101.0 |
| WA3sed | 97 | 0.20 | 0.59 | 1.84 | 0.05 | 0.10 | 0.26 | 0.02 | <0.02 | 0.3 | 0.7 | 101.5 |
| WA4sed | 95 | 0.23 | 0.86 | 2.78 | 0.09 | 0.13 | 0.32 | 0.02 | <0.02 | 0.5 | 1.2 | 101.2 |
| SA1sed | 96 | 0.91 | 1.04 | 1.51 | 0.12 | 0.25 | 0.37 | 0.01 | <0.02 | 0.1 | 0.8 | 101.5 |
| SA2sed | 96 | 0.42 | 1.11 | 1.46 | 0.06 | 0.15 | 0.44 | 0.01 | <0.02 | 0.1 | 0.5 | 100.6 |
| SA3sed | 96 | 0.48 | 1.19 | 1.61 | 0.1 | 0.14 | 0.44 | 0.02 | <0.02 | 0.0 | 0.2 | 99.9 |
| SA4sed | 24 | 0.21 | 4.56 | 2.99 | 0.28 | 0.87 | 0.36 | 0.15 | 0.03 | 7.7 | 58.6 | 99.7 |
| SA5sed | 96 | 0.37 | 1.02 | 1.49 | 0.07 | 0.12 | 0.45 | 0.02 | <0.02 | 0.1 | 0.3 | 100.1 |
| WM1sed | 97 | 0.23 | 1.15 | 1.23 | 0.05 | 0.04 | 0.35 | 0.01 | <0.02 | 0.2 | 1.0 | 101.3 |
| WM2sed | 99 | 0.14 | 0.71 | 1.09 | 0.04 | 0.06 | 0.35 | 0.01 | <0.02 | 0.1 | 0.4 | 101.7 |
| WM3sed | 98 | 0.16 | 0.73 | 1.15 | 0.03 | 0.02 | 0.35 | 0.01 | <0.02 | 0.1 | 0.3 | 101.0 |
| WM4sed | 96 | 0.16 | 0.85 | 1.42 | <0.01 | 0.03 | 0.36 | 0.01 | <0.02 | 0.2 | 0.2 | 99.8 |
| WM5sed | 96 | 0.18 | 0.93 | 1.54 | <0.01 | 0.04 | 0.37 | 0.02 | <0.02 | 0.2 | 0.4 | 99.7 |

**Table 4.4**: Trace element concentrations (mg/kg) within Lake Sibaya sediments, as determined by X-ray fluorescence spectrometry.

| Sample | Zn | Co | V | Cu | Mn | Cr | Mo | Zr | Sr | Nb | Y | Rb | [1]Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| WA1sed | 25 | 9 | 32 | 10 | 435 | 58 | <1 | 97 | 45 | 2 | 9 | 17 | 16 |
| WA2sed | 2 | 2 | 13 | 7 | 331 | 45 | 5 | 186 | 11 | 2 | 3 | 9 | 16 |
| WA3sed | 5 | 4 | 14 | 7 | 577 | 46 | 4 | 204 | 12 | 3 | 3 | 8 | 24 |
| WA4sed | 7 | 6 | 18 | 7 | 450 | 55 | 5 | 236 | 15 | 3 | 4 | 10 | 16 |
| SA1sed | 5 | 3 | 32 | 6 | 167 | 80 | 3 | 884 | 24 | 12 | 8 | 12 | 24 |
| SA2sed | 4 | 2 | 21 | 7 | 157 | 70 | 5 | 471 | 22 | 7 | 5 | 13 | 24 |
| SA3sed | 4 | 1 | 23 | 7 | 264 | 67 | 4 | 578 | 22 | 6 | 5 | 14 | 16 |
| SA4sed | 27 | 7 | 37 | 11 | 439 | 75 | <1 | 117 | 65 | 5 | 16 | 33 | 7.9 |
| SA5sed | 4 | 2 | 21 | 6 | 184 | 59 | 4 | 412 | 20 | 5 | 5 | 13 | 16 |
| WM1sed | 3 | 1 | 14 | 5 | 157 | 42 | 3 | 342 | 11 | 3 | 4 | 12 | 16 |
| WM2sed | 2 | 1 | 12 | 7 | 157 | 44 | 4 | 168 | 11 | 2 | 3 | 10 | 16 |
| WM3sed | 2 | 1 | 13 | 6 | 149 | 44 | 5 | 213 | 11 | 2 | 3 | 11 | 24 |
| WM4sed | 3 | 1 | 15 | 8 | 190 | 55 | 6 | 223 | 13 | 2 | 3 | 12 | 31 |
| WM5sed | 2 | 2 | 14 | 8 | 312 | 59 | 6 | 249 | 12 | 3 | 3 | 12 | 24 |

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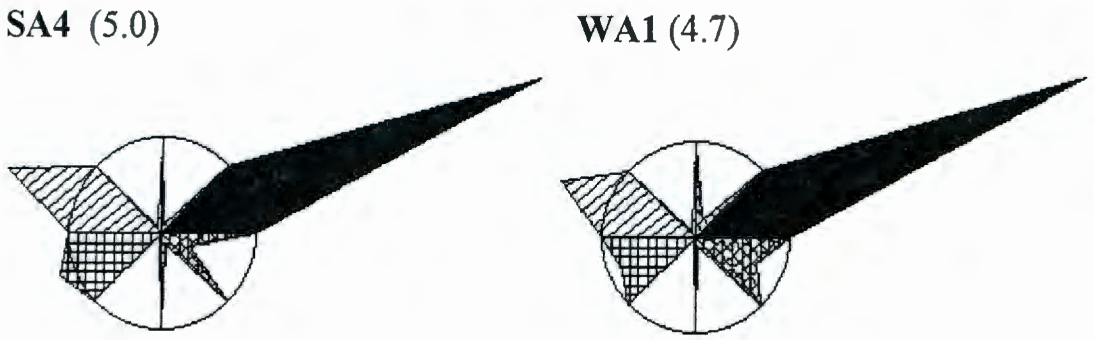
[1] Ni (mg/kg) converted from NiO concentration (weight %) of fusion discs

(a) Organic-rich muds (gyttja)



(b) Siliceous sediments

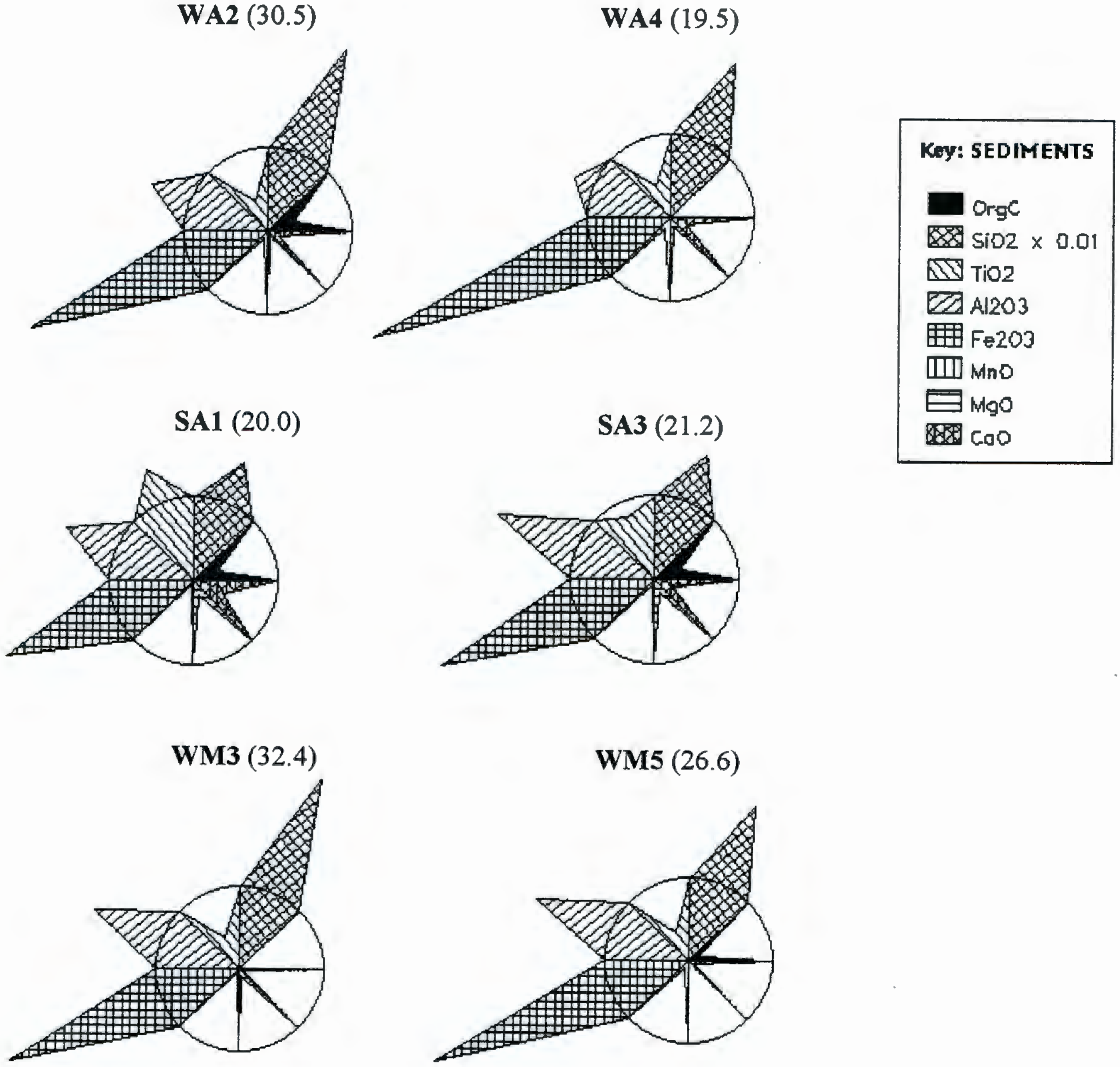


**Figure 4.5:** Star diagrams demonstrating the predominant fractions comprising selected Lake Sibaya bulk sediments. Major elements, determined by XRF, are expressed as their oxides (refer to text). A scaling factor of 0.01 has been applied to silica. Normalisation factors are displayed alongside sample numbers.

**Table 4.5:** Significant correlations (at the 95% confidence level) between (a) individual trace elements; (b) major sediment fractions; and (c) major sediment fractions versus trace elements in Lake Sibaya sediments.

(a)

| | Sr | Zr | Nb | Mo | Cr | Ni | Mn | Cu | V | Co | Zn | Rb | Y |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sr** | | | | | | | | | $0.94^1$ | | | $0.66^2$ | |
| **Zr** | | | | | | | | | $0.96^1$ | | | $0.59^2$ | |
| **Nb** | | | | | | | | | $0.97^1$ | | | | |
| **Mo** | | | | | | $0.79^1$ | | $0.82^1$ | | | | | |
| **Cr** | | | | | | | | | $0.91^1$ | | | | |
| **Ni** | | | | | | | | $0.85^1$ | | | | | |
| **Mn** | | | | | | | | | | $0.75^2$ | | $-0.65^2$ | |
| **Cu** | | | | | | | | | | | | | |
| **V** | | | | | | | | | | | | | $0.95^1$ |
| **Co** | | | | | | | | | | | $0.83^1$ | | |
| **Zn** | | | | | | | | | | | | | |
| **Rb** | | | | | | | | | | | | | |
| **Y** | | | | | | | | | | | | | |

(b)

| | $SiO_2$ | Org. C | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO | $P_2O_5$ | $K_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| **$SiO_2$** | | | | | | | | | |
| **Org. C** | | | | | | | | | |
| **$TiO_2$** | | | | | | | | | |
| **$Al_2O_3$** | $-0.64^2$ | $0.74^2$ | | | | | | | |
| **$Fe_2O_3$** | $-0.68^2$ | | | | | | | | |
| **MgO** | | | $0.79^1$ | | | | | | |
| **CaO** | | | $0.90^1$ | | | $0.88^1$ | | | |
| **$P_2O_5$** | | | | | $0.76^1$ | | | | |
| **$K_2O$** | | | | $0.79^1$ | | | | | |

(c)

| | Sr | Zr | Nb | Mo | Cr | Ni | Mn | Cu | V | Co | Zn | Rb | Y |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$SiO_2$** | $-0.62^2$ | | | | $-0.67^2$ | $-0.63^2$ | | | | | $-0.68^2$ | | |
| **Org. C** | | | | | | | | | | | | | |
| **$TiO_2$** | $0.87^1$ | $0.98^1$ | $0.99^1$ | | $0.86^1$ | | | | $0.97^1$ | | | | $0.98^1$ |
| **$Al_2O_3$** | $0.68^2$ | $0.69^2$ | $0.58^2$ | | $0.62^2$ | | | | $0.61^2$ | | | $0.87^1$ | $0.66^2$ |
| **$Fe_2O_3$** | | | | | | | $0.68^2$ | | | $0.89^1$ | $0.88^1$ | | |
| **MgO** | $0.78^1$ | $0.77^1$ | $0.76^1$ | $-0.63^2$ | $0.61^2$ | | | | $0.83^1$ | | $0.70^2$ | | $0.79^1$ |
| **CaO** | | $0.85^1$ | $0.90^1$ | | $0.82^1$ | | | | $0.92^1$ | | $0.68^2$ | $0.88^1$ | $0.89^1$ |
| **$P_2O_5$** | | | | | | | $0.90^1$ | | | $0.79^1$ | | | |
| **$K_2O$** | $0.70^2$ | | | | $0.62^2$ | | $0.65^2$ | | | | | $0.91^1$ | |

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[1] $p \leq 0.005$

[2] $p \leq 0.05$

Mn oxyhydroxides would appear to occur in insufficient quantity to significantly affect the lability of either ion. Cu and Zn might be expected to immobilise, through the formation of sulphides, which should remain insoluble across all pH ranges under the reducing conditions experienced in the lake sediments. This aspect is addressed at a later stage in this section.

Given the intense weathering regime on the coastal plain, it is expected that the lake sediments would contain substantial accumulations of Fe and Ti oxides, associated with a clay mineral suite characteristically dominated by 1:1 layer silicates (Milnes and Fitzpatrick, 1989). The latter minerals possess a relatively small isomorphous substitutional negative charge, which interacts with the positive charge associated with the surfaces of the metal oxides to produce a low net electric charge. In fact, no significant correlations were observed between the predominantly kaolinite clay fraction and either Fe or Ti in the Lake Sibaya sediments. Instead, a strong positive correlation ($R^2 = 0.90$, $p<0.005$) was observed between Ti (expressed as $TiO_2$) and Ca (as CaO), suggesting the possible presence of minerals such as the Ti oxide mineral perovskite ($CaTiO_3$) and/or the Ca titanosilicate, sphene (or titanite), ($CaTiSiO_5$). Geological and climatic conditions would likely favour the occurrence of sphene, above that of perovskite, along the Zululand coast (*pers. comm.* Dr. H. Frimmel, Department of Geological Sciences, University of Cape Town).

Sphene is likely to occur as a residual mineral in the Zululand soils and Lake Sibaya sediments as a result of the weathering of intermediate and acid plutonic rocks, in which it may constitute the dominant Ti mineral (Bonneau and Souchier, 1982; Claridge and Weatherhead, 1978). Sphene has a monoclinic structure, in which the dominant units are tilted $TiO_6$ octahedra linked into kinked chains by sharing corners (Speer and Gibbs, 1976). The Ti atoms are displaced from the centres of the octahedra. The chains of $TiO_6$ octahedra are cross-linked by $SiO_4$ tetrahedra to produce a $[TiOSiO_4]^{2-}$ framework, encompassing large cavities in which Ca atoms are placed in irregular pentagonal coordination. The Ca content of sphene was reported (Deer *et al.*, 1992) as being approximately 18 to 19%. Many elements may substitute for the hepta-coordinated Ca atoms, including alkalis, alkaline earths and rare earths (Ribbe, 1982). In the absence of detectable levels of calcium carbonate, the strong relationship between Ca and Sr in the Lake Sibaya sediments may relate, in part, to chemisorption (specific adsorption) of these divalent cations by the inner coordination layer of Ti minerals, as suggested by Milnes and Fitzpatrick (1989). Mg may similarly be substituting for Ti in the sphene structure, in line with the strong correlation that exists between the two components in the Lake Sibaya sediments.

Owing to their high specific gravity, Ti and Zr minerals are highly resistant to weathering. They have consequently been observed (Beus, 1971) to undergo progressive concentration in the sand and silt fractions of sandy sediments, from the Precambrian to the present, due to repeated cycling. Owing to the overwhelming silica dominance in the Lake Sibaya sediments, only the clay fraction was investigated by XRD. The possible occurrence of traces of the radioactive elements Th and U in sphene may aid in its chemical degradation to, at least, an X-ray amorphous (metamict) state (Ribbe, 1982). Consequently, metamictic sphene may, in any instance, be insufficiently crystalline in soils or sediments to be detected by standard mineralogical techniques, such as the XRD technique applied in this study (Gleadow and Lovering, 1978; Milnes and Fitzpatrick, 1989).

Excluding the two gyttja samples, the average molar ratio Ca:Ti in the Lake Sibaya sediments ranges from 0.68 (std. dev.=0.14) for Transect WA, to 0.45 (std. dev.=0.05) for Transect SA, and to 0.32 (std.dev.=0.17) for Transect WM. If it is assumed that all Ca in the sediments arises from sphene and perovskite, between 32% and 68% of all Ti in the sediments would, therefore, be required to occur as these minerals in order to account for the entire Ca content in the sediments. Although sphene is generally acknowledged to occur within the sands of the Zululand coastal plain (Milnes and Fitzpatrick, 1989), a perusal of the literature revealed no account of its relative abundance. In the absence of supporting data, it is suggested that sphene and, to a lesser extent, perovskite are likely to co-occur with numerous other Ca-bearing minerals (e.g. clinopyroxines) in the coastal sands. Neither perovskite nor sphene constitute important economic sources of Ti, by contrast with rutile ($TiO_2$) and ilmenite ($FeTiO_3$), which are mined from the Richards Bay coastal dune sands approximately 180 km south of Lake Sibaya.

The possible association of Ca with Ti tectosilicates may be significant in terms of the lability of Ca within the waters of Lake Sibaya and the shallow coastal aquifer. In the context of severe nutrient deficiency, the levels of Ca in the adjacent soils of the Fernwood form, though correctly classified as being suboptimal for crop growth, were found by Pooley (1996) to be elevated relative to other plant nutrients. This is surprising, given the coarse textured, acid nature of these soils, the low levels of weatherable calcium-containing minerals in the parent material, and the high propensity for leaching of Ca under the humid climatic regime. In the apparent absence of substantial quantities of carbonate (in the lake sediments, at least), the slow release of Ca from weathering Ca-bearing Ti oxides and tectosilicates in the coastal sands may provide a significant source of calcium to the lake, when viewed in the context of overall Ca deficiency in the Lake Sibaya catchment. Opinion is divided as to whether the Ti that is dissolved through the decomposition of these Ti silicates or Ti-bearing silicates will accumulate locally, or migrate through the soil profile. Milnes and Fitzpatrick (1989) are of the opinion that the Ti that is initially dissolved will rapidly precipitate as an hydrous oxide that crystallises as anatase or rutile. By contrast, Correns (1978) and Dumon and Vigneaux (1979) have postulated that organic acids act as the transporting agent for the migration of the dissolved Ti through the soil profile. In any event, the Ca that is presumably liberated through the dissolution of the Ca Ti-silicates in the sands of the Zululand coastal aquifer is proposed to leach through to the shallow groundwaters of the Lake Sibaya catchment. These waters could therefore be expected to constitute a source of calcium to Lake Sibaya, which, as discussed previously in this report, is considered to represent a surface expression of the shallow groundwater table.

A further probable source of calcium to the extended Lake Sibaya system comprises the calcareous material blown into the region from the adjacent coastline by the prevailing north-easterly and south-westerly winds. Dry deposition of suspended Ca-bearing particles, and saltation of biogenic and terrigenous material, provide a boost to the Ca concentration of the Lake Sibaya water mass and its catchment. Ca enrichment of rainwater may also occur, through the dissolution of calcareous dust of terrigenous origin, as described in Chapter 2. Evidence also exists (*pers. comm.* Dr. R. Maud of Drennan Maud & Associates) to suggest the presence of a grey calcareous (40% CaO) marl layer, "sandwiched" within the aeolian sands of the KwaMbonambi Formation underlying the bottom sediments of Lake Sibaya and the catchment sands in its immediate vicinity. As evidenced by the diatomite exposures near the lake (*cf.* Section 2), this calcitic layer was formed contemporaneously with the progressive shallowing of the lake during the Last Glacial Maximum. The calcareous matter was doubtless derived, in part, from the Upper Cretaceous rocks, which underlie the Pleistocene and Recent deposits upstream of the Mseleni River diatomite deposits. Wind deflation of the dry, sediment-starved portion of the lake basin, between 18 000 to 8 000 years BP, served to redistribute this calcareous material over the lake catchment. This process continued until the subsequent stabilisation of sea level to its present level 7 000 – 6 000 years BP (Miller, 1998). Ensuing dissolution of calcareous sediment by rainwater and groundwaters, percolating through the aquifer sands of the catchment, has provided a progressively diminishing source of calcium to the Lake Sibaya system, as these carbonates are gradually leached from the sands.

The elevated levels of the heavy minerals of Ti, Zr, Sr, Nb, Rb and Y within transect SA sediments (in general), and sediment $SA1_{sed}$ (in particular) are to be expected, as a result of their proximity to the coastal dune cordon. Progressive removal of the fine sand fraction to deeper waters, by the action of waves and water currents, is likely to result in a concentration of the heavier minerals in the shallower lake waters. The sample size was insufficient to show this depth-concentration relationship to hold true statistically. The strong positive correlation between $TiO_2$ and Zr ($R^2$=0.98, p=0.00) suggests, however, the presence of a coarser refractory fraction remaining after sorting. Zirconium is likely to occur as the stable silicate mineral, zircon ($ZrSiO_4$). Average levels of the six above-mentioned heavy elements within the SA transect sediments ranged between approximately double and triple those of the remaining two sampling transects. Vastly similar, and statistically robust, correlations were obtained when each of the heavy elements Zr, Nb, and Y was regressed against either Ti or Ca. This further supports the proposal that Ca is caught up primarily within the heavier mineral fraction of the sediments, as Ca-Ti oxides and Ca-Ti tectosilicates.

The lack of significant correlations (at the 95% confidence level) between Zr and each of $Fe_2O_3$ and $P_2O_5$, indicates that, within Lake Sibaya sediments, Fe and P do not substitute for Si in the tetrahedral sites of the zircon structure, as is suggested by Milnes and Fitzpatrick (1989) to frequently occur. Specific adsorption of phosphate by Ti oxide mineral particles has been previously observed in soils (Milnes and Fitzpatrick, 1989), but does not appear to occur in the case of the Lake Sibaya sediments.

In the Lake Sibaya sediments, Fe determined by XRFS is presumed to represent, for the most part, the range of polyhydroxy species or polycations, hydroxides, oxyhydroxides and oxides, any of which may form when Fe cations hydrolyse at pH>3. In the strongly leached siliceous sediments of Lake Sibaya, where the colloid fraction is dominated by low charge kaolinite clays, and where organic content is limited, these Fe species may be expected to control the electrochemistry of the sediments to a significant extent. Fe (reported as $Fe_2O_3$) constitutes the second most dominant fraction (after silica) of all siliceous Lake Sibaya sediment samples, when considered on a molar basis (*cf.* Figure 4.5). By contrast, Fe represents a relatively small proportion of the total composition of the gyttja sediments, being outweighed considerably by the content of organic carbon, silica, and the clay fraction (represented by $Al_2O_3$). The lower relative contribution of Fe to the composition of the gyttja samples is likely related to the dissolution of Fe oxides under increased reducing conditions. Intensified reduction is likely to occur in these organic-rich samples because of $O_2$ deficiency associated with greater microbial activity, which is linked, in turn, to an abundant carbon energy source. Owing to the high stability of $Fe^{3+}$ oxides ($K_{sp}$ ranges of $10^{-39}$ to $10^{-44}$) (Schwertmann and Taylor, 1989), their re-dissolution by purely protolytic reaction will not proceed within the pH regime of the Lake Sibaya sediments.

Fe oxides may or may not be associated with clay surfaces in nature (Oades, 1984). The poor correlation between $Al_2O_3$ and $Fe_2O_3$ suggests that the presence of hydrous iron oxides is not causally related with that of Lake Sibaya clay particles. Furthermore, Al would appear not to replace Fe in these oxides, despite the fact that Al commonly substitutes for structural Fe at much higher levels than any other cation under natural conditions (Schwertmann and Taylor, 1989).

$Fe_2O_3$ showed negligible correlation with organic carbon in the siliceous Lake Sibaya sediments. According to the pertinent literature (Schwertmann and Taylor, 1989), humic and fulvic acids associated with organic matter are commonly associated with the amphoteric surfaces of iron oxides, transferring a net negative charge to the oxides and lowering PZC values. It might be conceivable to consider that the weak relationship between organic matter and Fe relates to a strong decrease in the adsorption of the organic acids by Fe oxides with increasing pH (Schwertmann and Taylor, 1989). If this is true, it would appear from the chemical correlations (Table 4.5) as if specific adsorption of phosphates is outcompeting that of organic ions, as well as of other anions such as silicate, molybdate, and possibly sulphate, for available adsorption sites on Fe-oxides. Surface charge on Fe oxides is amphoteric, and dependent upon both pH and ionic strength (refer to Section 2.5, Chapter 2). P may therefore also undergo specific adsorption onto neutral, or even negative, surfaces as the polyvalent anion $HPO_4^{2-}$, thereby increasing the CEC of Fe oxides through the creation of additional negative charges (Schwertmann and Taylor, 1989). This would serve to reduce phosphate availability to the lake biota.

Perhaps more feasible, however, is the proposal that Fe oxides are generally absent from the lake sediments, given the low pe expected in such environments. Retention of metal ions by oxide surfaces is inversely dependent on the degree of crystallinity (Okazaki *et al.*, 1986) and (since the oxides have variable charge) the pH of the solution (Barrow, 1987). The dissolution of Fe oxides, under reducing conditions and alkaline pH, would therefore initiate the release of metal ions.

The substantial correlation ($r=0.76$, $p\leq0.005$) calculated between Fe and P indicates the possible occurrence of the ferric phosphate, strengite ($Fe[HPO_4]\bullet2H_2O$), or the ferrous phosphate mineral, vivianite [$Fe_3(PO_4)_2\bullet8H_2O$]. A further 49 phosphorus minerals contain Fe as a constituent (Lindsay *et al.*, 1989). Vivianite, in particular, is could be expected to remain stable in the sediments under the likely reducing conditions (Black, 1967). Oxidation will then cause a continuous compositional change in vivianite, $Fe^{2+}$ being isomorphously replaced by $Fe^{3+}$, with valency being compensated by replacement of $H_2O$ by OH (Lindsay, *et al.*, 1989). With the onset of greater oxidation, vivianite will dissolve, releasing P in some other form, most likely Fe and/or Al phosphate (Lindsay *et al.,* 1989). The occurrence of either vivianite or strengite in the Lake Sibaya sediments is, at this stage, purely speculative. Further investigation would be required to confirm their presence.

Sulphur (expressed as $SO_3$ in Table 4.3) was below detection limits in all but the two gyttja sediment samples ($WA1_{sed}$ and $SA4_{sed}$). Only two calibration standards were used in the XRF analysis of fusion discs for major element abundance, both of which were of considerably higher S concentration than the lake sediments (*pers. comm.* Prof. J. Willis, Department of Geological Sciences, U.C.T). The calibration may therefore have been out at the lower end of the analytical range occupied by the Lake Sibaya samples. Time constraints prevented the repeat determination of S using more appropriate calibration standards. It appears likely that, where S does occur in the Lake Sibaya sediments, it will occur in the form of sulphides covalently bonded to metal cations and/or complexed with organic matter, particularly within the reduced, organic-rich gyttja muds. The mobility of chalcophilic elements such as Zn, Cu and Fe may be significantly reduced through the precipitation of insoluble sulphides. The extreme insolubility of the ZnS complex may represent a substantial control over the mobility of $Zn^{2+}$ released through the dissolution of Fe oxides in the relatively high pH regime of the Lake Sibaya waters. Owing to the small sample size, these hypotheses are not amenable to be either substantiated or disproved statistically.

### 4.4.5 Nutrient availability

Solid components in sediments influence the levels of trace elements in solution, via sorption-desorption and dissolution-precipitation reactions. Much of the micronutrients associated with the solid phase are not available for plant uptake. In fact, <10% generally are in soluble and labile forms (Lake *et al.,* 1984). Consequently, knowledge of sediment composition in terms of merely the total element content is usually not very useful for understanding the processes and dynamics of element availability and cycling.

The results of chemical soil extraction tests conducted on two siliceous sands ($SA5_{sed}$ and $WM2_{sed}$) and two gyttja samples ($WA1_{sed}$ and $SA4_{sed}$) collected from the Lake Sibaya bed are presented in Table 4.6. These tests use various solvents and complexants to extract a quantity of the particular element from the solid phase, which then correlates statistically to the size of the "available pool" observed, empirically, to be taken up by plants. The biological extractability of different elements depends on their properties, such as their tendency to complex with organic matter, to chemisorb on minerals, to precipitate as insoluble sulphides, carbonates, phosphates or oxides, or to co-precipitate in other minerals (McBride, 1994).

The procedure to extract part, or all, of the "bioavailable pool" involves bathing the sediment in a solution of complexing, acidifying, or reducing chemicals. Consequently the properties of the sediment which control the solubility of the element, the redox potential, the pH, and the solubility of minerals and organic matter may all be modified. Some information regarding elemental speciation and availability is therefore lost in the process (Shuman, 1991). Nonetheless, extractability tests generally provide a more realistic account of the 'window' of available forms of nutrients which can potentially be assimilated by biota. In the general absence of literature pertaining to the availability of element fractions to aquatic biota, much of the interpretation of available nutrient fractions is based on experience relating to terrestrial ecosystems. Given the commercial incentives linked to crop research, the nutrient availability database for terrestrial crops is in many cases substantially greater than for limnetic systems.

**Table 4.6:** Nutrient availability indices (mg/kg) determined for selected Lake Sibaya sediments.

| **Extractant** | **Element** | **Gyttja samples** | | **Siliceous sediments** | |
|---|---|---|---|---|---|
| | **(mg/kg)** | **WA1sed** | **SA4sed** | **SA5sed** | **WM2sed** |
| Bray-2 | P | 14 | 38 | 12 | 7 |
| | K | 334 | 515 | 22 | 20 |
| 1*M* $NH_4OAc$ | Na | 872 | 881 | 30 | 39 |
| | Ca | 8312 | 11868 | 644 | 488 |
| | Mg | 1269 | 1640 | 75 | 83 |
| 0.02*M* $(NH_4)_2$ EDTA | ♦Cu | 1 | 2.5 | <0.01 | <0.01 |
| | Zn | 2.7 | 4.7 | 0.2 | 0.2 |
| Hot water | B | 16 | 5.1 | 0.7 | 0.4 |

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♦ Cu lower limit of detection for the ICP-MS technique, as specified by Standard Methods (1995).

#### *4.4.5.1 Boron*

Boron is of limnological interest, because it is a micronutrient required by many algae and other lake organisms. Boron additions to aquatic angiosperms have been found to stimulate photosynthesis to levels of 100 mg/l, beyond which inhibitory responses occurred (Wetzel, 1983).

Shuman (1991) highlights an almost complete lack of selective extraction data relating to B. Jin *et al.* (1987) found that up to 0.34% of the total B in terrestrial soils existed in the water-soluble form, 0 to 0,23% was non-specifically adsorbed (exchangeable), 0,05 to 0,30% was specifically adsorbed, 0,23 to 1,52% was in the Mn oxide form, 2,8 to 34,4% was in the amorphous Fe-oxide form, 17,5 to 73,9% was in the crystalline Fe oxide form, and 2,4 to 79,2% was in the residual form. Kabata-Pendias and Pendias (1985) similarly report that less than 5% of the total B is usually available to plants. The critical minimum levels for B in soil systems, using the hot water extraction method is 0.1-0.3 mg/kg (Kabata-Pendias and Pendias, 1985). This level is exceeded in all four samples analysed, suggesting that B is not likely to be limiting to the growth and metabolism of algae in Lake Sibaya. Pooley (1996) similarly showed concentrations of B extracted from the grey sands of the Mseleni region adjacent to the lake to be low (0.25 to 0.91 mg/kg), but apparently adequate for normal plant growth.

The degree of general prevalence of boron in the Lake Sibaya sediments is likely the product of two principal patterns of behaviour, namely (a) accumulation as a residual element, or (b) release through dissolution and desorption, under an intense weathering regime. To some extent, B may be accumulating as a residual element in the clastic fraction of the Lake Sibaya sediments, owing to the resistance of B-bearing minerals (such as tourmaline within the igneous granitic source rocks) to chemical breakdown. This accumulation in the solid fraction is likely countered, however, by the release of B (as the highly mobile species $H_3BO_3$), arising from the dissolution of less stable primary silicates, in which it occurs as a trace element (Chesworth, 1991). In the absence of substantial amounts of either decayed organic matter or fine mineral material in the siliceous Lake Sibaya sediments, adsorption of the highly mobile boric acid ($H_3BO_3$) is expected to be low. Furthermore, since the coastal plain sands (and to a lesser extent, the lake sediments), are below the pH range (8 to 9) at which B is most effectively adsorbed on Al and Fe oxides and silicate minerals (McBride, 1994), the low availability of B may be explained through the leaching of the coarse sediments. The raised levels of B in the two gyttja samples ($WA1_{sed}$ and $SA4_{sed}$) presumable occur as a result of greater contents of each of the silicate clay fraction, decayed organic matter and the sesquioxides of aluminium and iron (Kabata-Pendias and Pendias, 1985).

#### *4.4.5.2 Phosphorus*

Compounds containing P play major roles in nearly all phases of metabolism, particularly in the energy transformation of phosphorylation reactions during photosynthesis (Wetzel, 1983). P is required in the synthesis of nucleotides, phospholipids, sugar phosphates, and other phosphorylated intermediate compounds. Further, phosphate is bonded, usually as an ester, in a number of low-molecular-weight enzymes and vitamins essential to algal metabolism (Wetzel, 1983). Phosphorus commonly constitutes the least abundant element, in solution, of the major nutrients required for algal growth, and is therefore frequently the limiting nutrient in ecosystems. Ionised inorganic $PO_4^{3-}$ constitutes the most important form of P for plant nutrition. Phytoplankton species vary in their ability to utilise organic phosphate esters, and to obtain phosphate groups enzymatically or by release of exoenzymes to the water for catalytic dissociation (Wetzel, 1983). Consequently, a majority of the inorganic soluble phosphate and organic esters released to water during active growth of algae is very rapidly recycled.

The specified minimum guideline for soil extractable P (by the Bray-II method), in terms of the nutritional status of sands (<10% clay) for orchards, is ≥30 mg/kg (Infruitec, 1998). In the absence of a more suitable availability index for the nutrient, the P status will be interpreted with reference to this guideline. This level of extraction is attained in only one ($SA4_{sed}$) of the four sediment samples that were analysed, implying that the low lability of P is limiting to ecological functioning. Hart and Hart (1977) correlated low concentrations of $NO_3(N)$ and soluble reactive phosphorus (SRP) in Lake Sibaya with a low algal standing crop and low overall primary productivity.

Levels of P extraction from the two gyttja samples were greater than those from the siliceous sediments. This presumably relates to the high content of dead and decaying plants fringing the lake, which are accumulated into the sediments as gyttja during high lake levels. The $PO_4^{3-}$ ions liberated into the water from such material, as SRP, will be readily assimilated by developing algal and bacterial masses during flooding of the marginal swamps near the sample sites WA1 and SA4. Howard-Williams and Allanson (1978) demonstrated the rapidity with which phosphate was lost from senescent hydrophyte material and subsequently taken up by an epiphyte association in another South African coastal lake, Swartvlei (Western Cape). An equivalence with the inundated littoral plants of Lake Sibaya can reasonably be expected. Much of the allocthonous material from the littoral regions is expected to pass quickly, by wave action and sediment slumping, into deeper water, where decay of the resultant gyttja will continue.

### *4.4.5.3 Sodium and potassium*

The monovalent cations sodium and potassium are involved primarily in ion transport and exchange within limnetic organisms. Owing to the high solubility of Na, the element is unlikely to be limiting to lake biota. As with Ca and Mg, Na exchange levels were enormously elevated in the gyttja samples relative to the siliceous sands, thereby confirming a higher CEC in the former sediments. Such accumulations of fine sapropelic mud therefore represent an abundant source of nutrients, in what is otherwise a nutrient-stressed environment.

The levels of exchangeable K are presumably sufficient in the gyttja samples to prevent nutrient deficiencies. By way of reference, concentrations of K in the range of 30-50 mg/kg are specified as being minimum guidelines for the establishment of fruit orchards (Infruitec, 1998). By comparison, the levels of K that are reversibly exchanged from the siliceous sediments, by the Bray-II method, may feasibly reflect K deficiencies within much of the lake ecosystem.

Exchangeable Na and K constituted 6-12% and 3% (consistently) of sediment CEC (determined in $1N\ NH_4Cl$), respectively, in the four sediments analysed.

### *4.4.5.4 Copper and zinc*

Zn and Cu are important essential elements in both the plant and animal kingdoms. Fairbridge (1972) reports that the high mobility of both copper and zinc during weathering processes causes the not-infrequent appearance of deficiency diseases. Higher plants predominantly absorb Zn as the divalent cation, which acts as either metal component of enzymes, or as a functional, structural, or regulatory cofactor of a large number of enzymes. Through its requirement in the activity of these various enzymes, Zn is fundamentally involved in carbohydrate and protein metabolism. Cereals grown on soils derived from highly leached sediments are particularly susceptible to these deficiency diseases, undergoing interveinal chlorosis (generally in monocotyledons), stunted growth and malformation of stems and leaves (Kiekens, 1995). $Cu^+$ is found in enzymes capable of carrying oxygen as haemoglobin does, and is actually required in the formation of haemoglobin (Förstner and Wittmann, 1981, p11). Animals therefore also generally show rapid response to copper deficiencies. The recommended dietary intake of Zn for humans is around 15 mg/day (Kiekens, 1995).

Most of the Zn in soils and sediments exists in unavailable forms. The percentage of Zn in the more plant-available forms, such as water-soluble, exchangeable, and organic, is low compared with less plant-available forms in the oxide and residual fractions (Hickey and Kittrick, 1984). Zn that is extractable with di-ammonium EDTA is often correlated with the more available fractions, such as exchangeable and organic fractions, and thus is considered plant-available (Shuman, 1986). Kiekens (1995) recognises a very significant relationship to exist between the uptake of Zn by plants and the amounts of Zn solubilised at different pH levels as the soil-water suspension is progressively acidified. $Zn^{2+}$, in particular, appears to be the predominating form in which Zn is absorbed by plant root (Kiekens, 1995). Field calibrations of the di-ammonium EDTA extraction technique, conducted by the Cedara Grain Crops Institute in Natal, indicated a critical value of 1.5mg Zn/l for plant growth requirements (cited in Pooley, 1996). Considering the density of the sediments, this translates to approximately 1mg Zn/kg of sediment. This value falls within the range of 0.8-1.4 mg/kg generally specified in the international literature for similar methods (Martens and Lindsay, 1990). These levels are only met within the two gyttja samples.

As anticipated, total Zn levels in the highly leached acid sediments and sands of the coastal plain (Pooley, 1996) are very low, thereby contributing to low available contents. Further explanations for the low availability of Zn in the siliceous sediments would appear to include its reduced solubility at alkaline pH, due to increasing adsorption of Zn by negatively charged colloidal soil particles, and the low content of organic complexing or chelating ligands. The generally low level of extractable Zn suggests that much of the Zn pool might be caught up in residual forms, which are nonlabile or nonavailable, according to LeClaire *et al.* (1984). A relatively strong correlation was calculated between Zn and Ca (expressed as CaO) determined by XRFS. Given the absence of effervescence in the sediments, following treatment with HCl, it would appear as if solid phase carbonate minerals would not occur in significant quantity in the sediments to govern Zn mobility. As discussed earlier in this section, the insolubility of metal sulphides within the reducing sediments is expected to set an upper limit on Zn lability.

The range of copper concentrations in lake sediments would appear to vary from 7 to 68 mg Cu/kg dry (Hutchinson, 1975). The Lake Sibaya sediments fall at the lower end of this scale. As with Zn, Cu is found largely in unavailable forms, according to fractionation techniques. Cu in the water-soluble and exchangeable forms are considered to be plant-available, whereas that associated with organic matter may be so tightly bound as to be relatively unavailable (Shuman, 1986). The availability of copper to macrophyte algae in the Lake Sibaya sediments will relate to the readiness with which the available ion $Cu(OH)_2^0$ is absorbed by these plants in the alkaline sediments (Kiekens, 1995). Copper is specifically adsorbed or "fixed" in sediments, rendering it one of the least mobile trace elements. Rates of adsorption of Cu are amongst the lowest of the essential elements. The Cu in the rhizosphere zone is predominantly in the form of

Cu organically complexed by root exudates or soil humus. Uptake and translocation, however, is a function of the activity of $Cu^{2+}$ in true solution at the active absorption sites (Baker and Low, 1970). Cu functions in plants as part of the prosthetic groups of enzyme systems, and as a facultative activator of enzymatic systems (Kiekens, 1995).

An investigation of limnological literature revealed minimal data with regard to the Cu and Zn requirements of freshwater species. The concentration of di-ammonium EDTA extractable Cu was found to be below the detection limit capabilities of the ICP-MS technique in the siliceous sediments. This would appear to suggest that Cu may approach levels that are suboptimal for biological requirement and ecological functioning within the siliceous sediments of Lake Sibaya. By contrast, Cu was relatively bioavailable from the gyttja samples, falling comfortably above the critical values of 0.4-1 mg/kg specified by Sims and Johnson (1990) for plant crops. In Section 4.4.4, it was shown that copper was not significantly correlated with any of the major solid fractions in the sediments.

Given the low levels of available Cu and Zn in the siliceous sediments of Lake Sibaya, it would seem feasible that other trace elements might also occur at levels which are suboptimal to ecological functioning. This view is consistent with the nutrient deficiencies observed in the adjacent Mseleni coastal sands by Pooley (1996) and Ceruti (in prep).

#### *4.4.5.5 Calcium*

As discussed in Section 3.4.6, Ca is a requisite nutrient for normal metabolism of higher plants, as well as possibly for algae. Exchangeable Ca, constituted between 68-76% of the total CEC of the Lake Sibaya sediments, thereby approximating the value of 70% of CEC which has been suggested as the minimum level suitable for the growth of fruit trees (Infruitec, 1998). Melsted (1953) found that extractable Ca concentration <400 mg/kg in acid, sandy soils caused deficiency in maize. The Ca exchanged from the sediments by 1*M* $NH_4OAc$ exceeded this concentration in each of the sediments. As could be expected from the dominant mineralogy of the sediment types, the concentration of Ca that was exchanged from the siliceous sands was barely one-quarter of that exchanged from the gyttja samples. Pooley (1996) noted Ca to be suboptimal, but not necessarily deficient to plants, within the Fernwood form soils adjacent to the lake. This condition might well also describe the siliceous sediments of the Lake Sibaya bed.

### 4.4.6 Diatom populations

A preliminary investigation of the diatom content of the sediments revealed large-scale disparities within both their total number, and their diversity, in the various sediments. The diatoms were identified to the genus level, and a qualitative account of their prevalence was provided.

A wide number and diversity of diatoms were present within gyttja sample $WA1_{sed}$, all individuals being of considerable size. Representatives of the following genera were noted: *Melosira, Tabellaria, Eunotia, Cocconeis, Gomphrena, Rhodalopia, Synedra, Meridion, Fragilaria* and *Navicula.* The diatom population density within this sample was amongst the highest experienced by the analyst, Mrs. M. Joska. By contrast, the second gyttja sample $SA4_{sed}$ contained very few diatoms, the majority of which were very small. Representatives of the genera *Melosira*, *Tabellaria,* and *Cocconeis* were identified in this sample. Since silicon levels are uniformly sufficient for diatom requirements throughout the lake waters, it would appear as if the paucity of diatoms in the latter sediments relates to low photosynthetic production, due to the attenuation of light above the sample depth of 19.2m. Low energy fixation was recorded below 10m depth by Allanson (1979), apparently for the same reason. The former sample, by contrast, falls within the zone (2-3m depth) which Allanson recognised as exhibiting the maximum production. Data collected by Bowen (1978) hinted strongly that the terrace littoral of Lake Sibaya could be an important zone of energy fixation. The presence of faecal pellets in the $SA4_{sed}$ sediment sample suggests predation by small invertebrates (*pers. comm.* Mrs. M. Joska, Zoology Department, U.C.T.), a possible further explanation for the observed disparity in diatom abundance.

The number and diversity of diatoms was considerably less within the two siliceous sediment samples than within either of the gyttja samples, particularly in the case of $WM3_{sed}$. Only one genus of diatom (*Tabellaria*) was (occasionally) observed in this sample, the presence of faecal pellets again suggesting that predation by some species might be partly responsible for their scarcity. In addition to *Tabellaria*, representatives of the diatom genera *Rhodalopia* and *Navicula* were observed in sample $WM1_{sed}$, although these were generally few in number (*pers. comm.* Mrs. M. Joska).

Hart and Hart (1977) report that the phytoplankton community in Lake Sibaya is dominated, from a cell volume and therefore total biomass viewpoint, by *Closterium spp., Synedra acus, Anabaenopsis sp., Melosira granulata* and *Anabaena sp,* in order of importance. Four of the ten diatom genera identified within sample $WA1_{sed}$ had not previously been included within the preliminary checklist of benthic and planktonic algae constructed by Allanson in 1979. Of the genera included in the above list, eight of the ten component species identified by Allanson were benthic only, one species (*S. acus v. augustissima*) was uniquely planktonic, and the final species (*S. ulna*) was both benthic and planktonic (Allanson, 1979). This would seem to highlight the fact that, upon senescence, the diatoms are largely dissolved within the water column, prior to reaching the sediments.

Further interpretation of the patterns of diatom distribution and diversity throughout the lake is beyond the scope of this study.

## 4.5 CONCLUSIONS

The range of Lake Sibaya sediments analysed in this study can be grouped into two main categories, based on their content: those that are siliceous, fine-medium grained sands; and those which represent accumulations of organic-rich (>20% organic C) mud (gyttja). The latter accumulations apparently derive primarily from decaying littoral material, submerged during periods of high lake level. These muds may subsequently be incorporated into the (generally) deeper sediments by sediment slumping and deposition, under relatively sheltered conditions. The gyttja accumulations have been shown to represent nutrient 'oases' within an otherwise nutrient-poor (oligotrophic) lake system. The meagre organic carbon content of the siliceous sediments probably relates to the greater degree of decomposition of refractory materials from algal cells, associated with longer periods of residence in the water column, prior to deposition. The soluble components of organic matter (DOM) are rapidly recycled through the food chain. None of the trace elements investigated appeared to be associated with organic carbon in the siliceous sediments, suggesting that many of the reactive organic ligands had been lost from the solid phase during decomposition. Specific organic molecules do, however, appear to be bonding with clay minerals, through the formation of ionic bonds (ion exchange) or adsorption-type van der Waal's bonds.

The low surface area to volume ratio of the sandy sediments, in addition to their predominant quartz component and the low reactivity of their clay fraction, translates into a low CEC. The clay fraction of the sediments is dominated by quartz and kaolinite, with a subdominant mica and 2:1 layer silicate component. Relatively weak, yet statistically significant, positive correlations were noticed between the clay fraction and each of Sr, Zr, Nb, Cr, V and Y. Not all of these associations are necessarily causal.

Calcium is apparently associated with Ti in the Lake Sibaya sediments, indicating the possible presence of the Ca titanosilicate mineral, sphene. If this is indeed the case, the weathering of metamict sphene may contribute a source of Ca which is slowly released into solution by the Lake Sibaya sediments and surrounding aquifer sands of the Zululand coastal plain. Ca appears to be suboptimal, but not necessarily deficient, within the siliceous sediments of the Lake Sibaya bed. Further sources of Ca to the extended lake system include contemporary windblown calcareous beach deposits, and the dissolution of calcareous sediments that were wind-distributed from the Lake Sibaya deflation basin during periods of reduced lake level. Outcrops of calcareous marl near the lake attest to calcite precipitation associated with diminishing lake levels during the Last Glacial Maximum.

The substantial correlation calculated between Fe and P in the siliceous sediments indicates the possible occurrence of the ferrous phosphate mineral, vivianite, although this requires confirmation. The low lability of P could potentially represent a major limit to ecological functioning in the lake. Gyttja samples are expected to represent a relatively abundant source of P, being associated primarily with decaying littoral plant material incorporated into the sediments, by wave action and sediment slumping, during periods of raised lake level.

The extent to which chalcophilic elements (Zn, Cu and Fe) are immobilised by the precipitation of metal sulphides, within the reducing sediments, may have been underestimated, due to the use of inappropriate calibration standards during bulk sediment analysis by XRFS. Levels of available Zn were low. Levels of bioavailable copper appear to be limiting to the aquatic ecosystem, although gyttja accumulations provide a relative abundance of bioavailable copper. Potassium, similarly, would appear to be limiting and may affect ion exchange processes within macrophytes.

# CHAPTER 5: GENERAL DISCUSSION

The northern region of the Zululand coastal plain is patently plagued by nutrient deficiency. This was the conclusion reached in recent studies, conducted by Pooley (1996) and Ceruti (in prep), of the nutrient status of soil and plant tissue, and this aspect is again highlighted in this geochemical investigation of the extended Lake Sibaya system. The recurrent trend in each instance would appear to be a general dearth of base cations remaining within the system, following a relatively short, yet intensive, period of leaching of the low reactivity siliceous sands. Pooley recognised mud pans to constitute the nutrient 'hotspots' of the coastal plain. Sapropelic gyttja, accumulated into the sediments of sheltered regions of the lake might, similarly, represent the only significant bounty of nutrients in what appears, otherwise, to be an oligotrophic-mesotrophic lake.

The possible association of Ca with the Ca titanosilicate mineral, sphene, may account for the fact that bioavailable Ca from the aquifer sands (Pooley, 1996) and the lake sediments (this study) would be sufficiently low so as to be suboptimal, yet, (perhaps surprisingly) not deficient to biological functioning and productivity. The weathering of metamict sphene in these sediments may well provide a mechanism for the slow release of Ca from the structure of the mineral. Further work is required to confirm the occurrence of sphene (or a likely Ca-containing mineral analog) in sufficient quantities to significantly influence the availability of calcium.

Atmospheric control over major ion composition has been proposed in this study to outweigh the control which may be exerted by the local geology. The influx of marine cyclical salts, borne by onshore winds, imparts to the lake a distinct maritime signature. Substantial evidence was presented to suggest that the waters of Lake Sibaya are evaporated above that of their influent groundwaters. Although the effect of this evaporation on the major ion composition of the lake water is largely masked by the low concentration of solutes, forward modelling of hypothetical further evaporation showed that the composition of the residual waters would converge towards an almost exclusively sodium and chloride dominated brine. An accurate investigation of the contemporary hydrology of the system is required before the net extent to which solutes are concentrated up in solution over time can be estimated.

Lake Sibaya presently exists in a near pristine condition, largely because of its relative geographical isolation and the low population density of the region. The mode of agriculture presently practised in its catchment is primarily subsistence-driven. The future trend may well be towards increasing population density and greater intensification of land use, particularly given Reconstruction and Development Programme (RDP) objectives and the initiation of the Spatial Development Initiative (SDI) to establish trade links between Mozambique and Zululand. Intensive use of nutrient fertilisers may well occur, in response to growing agricultural demands and the low fertility status of the coastal soils. In the light of this, the pollution of the lake and its catchment is deemed a distinct possibility in the near future. Owing to its position on low reactivity, relatively unbuffered, coastal sands, the lake is expected to be highly susceptible to overloading with allocthonous material. The data presented in this report may serve as a yardstick of the environmental quality of the lake system at any specific time. Williams *et al.* (1976) note that the eutrophication of formerly oligotrophic lakes represents, to all practical purposes, an almost irreversible process. It is hoped that the information presented here may be used to prevent the deterioration of the system from its presently near pristine state.

## REFERENCES

Allanson, B.R. 1979. Chapter 4: The physico-chemical limnology of Lake Sibaya. In: Allanson, B.R. (ed.). *Monographicae Biologicae* Volume 36: Lake Sibaya. W. Junk bv Publishers, The Hague.

Allanson, B.R. and Hart, R.C. 1975. The primary productivity of Lake Sibaya, Kwazulu, South Africa. *Verh. Internat. verein. Limnol.* **19**: 1426-1433.

Allanson, B.R., Hill, B.J., Boltt, R.E. and Schultz, V. 1966. An estuarine fauna (fish, invertebrates) in a freshwater lake in South Africa. *Nature* **209**: 532-533.

Allanson, B.R. and van Wyk, J.D. 1969. An introduction to the physics and chemistry of some lakes in Northern Zululand. *Trans. R. Soc. S. Afr.* **38**:217-239.

Allen, B.L. and Hajek, B.F. 1989. Mineral occurrence in soil environments. In: Dixon, J.B. and Weed, S.B. (eds.). 1989. *Minerals in soil environments, 2nd Edition.* Soil Science Society of America, Wisconsin, USA.

Allison, J.D., Brown, D.S. and Novo-Gradac, K.J. 1991. *MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems.* EPA/600/3-91/021. Environmental Protection Agency, Athens, GA.

American Public Health Association (APHA). 1995. *Standard Methods for the examination of water and wastewater (19th Edition).* Eaton, A.D., Clesceri, L.S., and Greenberg, A.E. (Eds).

Anderson, W. 1904. *Second report of the geological survey of Natal and Zululand.* Surveyor-General's Department (Natal). Newman and Co., London. 50-52.

Anonymous. 1980. *Mineral Powder Diffraction File Search Manual.* JCPDS International Centre for Diffraction Data, Swartmore, PA.

Appelo, C.A.J. and Postma, D. 1994. *Geochemistry, groundwater and pollution.* A.A. Balkema, The Netherlands.

Baker, D.E. and Amacher, M.C. 1982. Nickel, copper, zinc and cadmium. 323-336. In: Page, A.L., Miller, R.H. and Keeney, D.R. (eds.). *Methods of soil analysis, Part 2: Chemical and microbiological properties (2nd edition).* Soil Sci. Soc. of Am., Madison, Wisconsin.

Baker, D.E. and Low, P.F. 1970. *Soil Sci. Soc. Am. Proc.* **34**: 49-56.

Barnhisel, R.I. 1977. Chlorites and hydroxy interlayered vermiculite and smectite. . 331-356. *In*: Dixon, J.B. and Weed, S.B (ed.). 1977. Minerals in soil environments. *Soil Sci. Soc. Am. Monogr.*, Madison, WI.

Barrow, N.J. 1987. *Reactions with variable-charge soils.* Martinus Nijhoff Publ., Dordrecht, Netherlands.

Barshad, I. 1948. Vermiculite and its relation to biotite as revealed by base exchange reactions, x-ray analysis, differential thermal curves, and water content. *Am. Mineral.* **33**: 655-678.

Bayer, A.W. 1938. An account of the plant ecology of the coastbelt and midlands of Zululand. *Ann. Natal Mus.*, **8**: 371-455.

Benedetti, M.F., Milne, C.J., Kinniburgh, D.G., Van Riemsdijk, W.H. and Koopal, L.K. 1995. Metal ion binding to humic substances: Application of the non-ideal competitive adsorption model. *Environ. Sci. Technol.* **29**: 446-457.

Berner, R.A. 1978. Rate control of mineral dissolution under earth surface conditions. *Am. J. Sci.* **278**: 1235-1252.

Berner, R.A. 1980. *Early diagenesis – A theoretical approach.* Princeton University Press, Princeton, N.J., 241 .

Berner, R.A. 1984. Sedimentary pyrite formation: an update. *Geochem. Cosmochim. Acta* **47**: 855-862.

Beus, A.A. 1971. Titanium distribution in the lithosphere. *Chem. Geol.* **8**: 247-275.

Beyers, C.P. DE L. and Coetzer, F.J. 1971. Effect of concentration, pH and time on the properties of di-ammonium EDTA as a multiple soil extractant. *Agrochemophysica* **3**: 49-54.

Bigham, J.M. and Ciolkosz, E.J. 1993. *Soil Colour.* SSSA special publication Number 31. Soil Science Society of America, Inc. Madison, U.S.A.

Bingham, F.T. 1982. Boron. 431-448. In: Page, A.L., Miller, R.H. and Keeney, D.R. (eds.). *Methods of soil analysis, Part 2: Chemical and microbiological properties ($2^{nd}$ edition).* Soil Sci. Soc. of Am., Madison, Wisconsin.

Binnerup, S.J., Jensen, K., Revsbech, N.P., Jensem, M.H. and Sorensen, J. 1992. Denitrification, dessimilatory reduction of nitrate to ammonium, and nitrification in a bioturbated estuarine sediment as measured with $^{15}$N and microsensor techniques. *Applied and Environmental Microbiology* **58**: 303-313.

Birch, G.F. 1981. The Karbonat-Bombe: A precise, rapid and cheap instrument for determining calcium carbonate in sediments and rocks. *Trans. geol. Soc. S. Afr.*, **84**: 199-203.

Black, C.A. 1967. *Soil-plant relationships.* John Wiley and Sons, New York.

Blackburn, T.H. and Henriksen, K. 1983. Nitrogen cycling in different types of sediments from danish waters. *Limnology and Oceanography* **28**: 477-493.

Bolt, G.H. (ed.). 1982. *Soil chemistry, B: Physico-chemical models.* Elsevier, Amsterdam.

Boltt, R.E. 1969. The benthos of some South African lakes. Part II. The epifauna and infauna of the benthos of Lake Sibaya. *Trans. R. Soc. S. Afr.* **38**: 249-269.

Bonneau, M. and Souchier, B. 1982. *Constituents and properties of soils.* Academic Press, Ltd., London.

Boucher, K. 1975. *Global climate.* The English Universities Press Ltd., London.

Bowen, S.H., 1976. *Feeding ecology of the cichlid fish Sarotherodon mossambicus in Lake Sibaya, KwaZulu.* PhD. thesis. Rhodes University, Grahamstown.

Bowen, S.H., 1978. Benthic diatom distribution and grazing by *Sarotherodon mossambicus* in Lake Sibaya, South Africa. *Freshwater Biol.* **8**: 449-453.

Brand, W. 1966. D/H Ring Test Final Report. *Isogeochem. Internet Group.* Unpublished data.

Bray, R.H. and Kurtz, L. 1945. Determination of total, organic, and available forms of phosphorus in soils. *Soil Sci.* **59**: 39-45.

Breeuwsma, A., Wosten, J.H.M, Vleeshouwer, J.J., Van Slobbe, A.M. and Bouma, J. 1986. Derivation of land qualities to assess environmental problems from soil surveys. *Soil Sci. Soc. Am. J.* **50**: 186-190.

Brownlow, A.H. 1979. *Geochemistry.* Prentice-Hall, New Jersey.

Bruton, M.N. and Appleton, C.C. 1975. Survey of Mgobezeleni lake system in Zululand, with a note on the effect of a bridge on the mangrove swamp. *Trans. Roy. Soc. S. Afr.* **41**: 283-294.

Bruton, M.N. and Cooper, K.H. (Eds).. 1980. *Studies on the ecology of Maputaland.* Rhodes University, Grahamstown.

Burns, N.M. and Nriagu, J.O. 1976. Forms of iron and manganese in Lake Erie waters. *J. Fish. Res. Bd. Can.* **33**: 463-470.

Butcher, S.S., Charlson, R.J., Orians, G.H. and Wolfe, G.V. 1992. *Global biogeochemical cycles.* Academic Press, London.

Butlin, K.R. 1953. The bacterial sulphur cycle. *Research* **6**: 184-191.

Cassey, W.H. and Westrich, H.R. 1992. Control of dissolution rates of orthosilicate minerals by divalent metal-oxygen bonds. *Nature* **355**: 157-159.

Ceruti, P. (in prep). *Ameliorating nutrient deficient sandy soils of Maputaland.* MSc. Thesis (in prep): Environmental Geochemistry. Department of Geological Sciences, University of Cape Town.

Chesworth, W. 1991. Geochemistry of nutrients. :1-30. In: Mortveld, J.J., Cox, F.R., Shuman, L.M. and Welch, R.M. (eds.). *Micronutrients in agriculture (2nd Edition).* Soil Science Society of America, Inc. Madison, Wisconsin.

Claridge, G.G.C. and Weatherhead, A.V. 1978. Mineralogy of silt fractions in New Zealand soils. *N. Z. J. Sci.* **21**: 413-423.

Clarke, F.W. 1924. The data of geochemistry. 5th ed. *Bull. U.S geol. Surv.* **770**: 841.

Coetzee, F. 1975. Solution pipes in coastal aeolianites of Zululand and Mozambique. *Trans. geol. Soc. S. Afr.* **78**: 323-334.

Coplen, T.B. 1988. Normalisation of oxygen and hydrogen isotope data. *Chemical Geology,* **72**: 293-297.

Correns, C.W. 1978. Titanium. In: Wedepohl, K.H. (ed.). *Handbook of geochemistry, Vol II.* Sec 22B-220. Springer-Verlag, Berlin.

Coston, J.A., Fuller, C.C. and Davis, J.A. 1992. The search for a geochemical indicator of lead and zinc sorption in a sand and gravel aquifer, Falmouth, Massachusetts, U.S.A. In: *Water-Rock Interaction.* Kharaka and Maest (eds). Balkema, Rotterdam.

Craig, H. 1961. Isotopic variations in meteoric waters. *Science*, **133**: 1702-1703.

Crass, R.S. 1963. *The fishery potential of Lake Bhangazi, Zululand.* Unpublished report of the Natal Parks Board.

Curtis, C.D. 1966. Ther incorporation of soluble organic matter into sediments and its effect on trace element assemblages. In: *Advances in organic chemistry.* Hobson, G.D. and Louis, M.C. (eds.). Pergamon Press, Oxford.

Cyrus, D.P. and Martin, T.J. 1988. Distribution and abundance of the benthos in the sediments of Lake Cubhu: a freshwater coastal lake in Zululand, South Africa. *J. Limnol. Soc. Sth. Afr.* **14**: 93-101.

Dansgaard, W. 1964. Stable isotopes in precipitation. *Tellus,* **16**: 436-468.

Darley, W.M. 1969. *Silicon requirement for growth and macromolecular synthesis in synchronised cultures of diatoms.* University of California, San Diego, California.

Davis, J.A. and Kent, D.B. 1990. Surface complexation modeling in aqueous geochemistry. In: Hochella, M.F. and White, A.F. (eds). Mineral-water interface geochemistry. *Reviews in mineralogy* **23**, Mineral Soc. Am.

Day, J.A. and King, J.M. 1995. Geographical patterns, and their origins, in the dominance of major ions in South African rivers. *S. Afr. J. Sci.* **19**: 299-306.

Deer, W.A., Howie, R.A. and Zussman, J. 1992. *An introduction to the rock-forming minerals (2nd Edition).* Longman Scientific and Technical, Essex, England.

Degens, E.T. 1965. *Geochemistry of sediments: A brief survey.* Prentice-Hall, Inc., New Jersey.

De Wit, J.C.M., Van Riemsdijk, W.H. and Koopal, L.K. 1993. Proton binding to humic substances. *Environ. Sci. Technol.* **27**: 2005-2014.

Diamond, R.E. and Harris, C. 1997. Oxygen and hydrogen isotope composition of Western Cape meteoric water. *S. Afr. J. Sc.* **93**: 371-374.

Dixon, J.B. 1989. Chapter 10: Kaolin and serpentine group minerals. In: Dixon, J.B. and Weed, S.B. (eds.). 1989. *Minerals in soil environments, 2nd Edition.* Soil Science Society of America, Wisconsin, USA.

Dixon, J.B. and Weed, S.B. (eds.). 1989. *Minerals in soil environments, 2nd Edition.* Soil Science Society of America, Wisconsin, USA.

Domagalski, J.L. and Eugster, H.P. 1992. Controls on trace metal geochemistry at Walker, Mono, and Great Salt Lakes: p 635-638. In: *Water-Rock Interaction.* Kharaka and Maest (eds). Balkema, Rotterdam.

Drees, R.L., Wilding, L.P., Smeck, N.E., and Senyaki, A.L. 1989. Silica in soils: Quartz and disordered silica polymorphs. In: Dixon, J.B. and Weed, S.B. (Eds).. 1989. *Minerals in soil environments, 2nd Edition.* Soil Science Society of America, Wisconsin, USA.

Drever, J.I. 1988. *The geochemistry of natural waters: surface and groundwater environments – 2nd ed.* Prentice Hall, New Jersey.

Drever, J.I. 1997. *The geochemistry of natural waters: surface and groundwater environments – 3rd ed.* Prentice Hall, New Jersey.

Drischell, H. 1940. Chlorid-, Sulfat-, und Nitrtagehalt der atmosphärischen Niederslage in Bbad Reinerz und Oberscreiberhau im Vergleich zu bisher bekannten Werten andere Orte. *Balneologe,* **7**: 321-334. (Unseen reference).

Driscoll, C.T. 1989. The chemistry of aluminium in surface waters. In: Sposito, G. (ed.). *The environmental chemistry of aluminium.* CRC Press, Florida. 241-277.

Dumon, J.C. and Vigneaux, M. 1979. Evidence for some mobility of titanium in podzols and under laboratory conditions as a result of the action of organic agents. *Phys. Chem. Earth* **11**: 331-337.

Dunlevey, J.N. 1997. The Berea Red Sands. *Heavy Minerals 1997.* South African Institute of Mining and Metallurgy, Johannesburg.

Du Toit, A.L. 1954. *The Geology of South Africa.* Oliver and Boyd: Edinburgh.

Du Toit, S.R. 1977. The Mesozoic history of the Aghulas Bank in terms of plate-tectonic theory. *Geokongres 77 Abstracts.* 17th Congress of the Geological Society of South Africa, Rand Afrikaans University, Johannesburg.

D.W.A. F. (Department of Water Affairs and Forestry). 1995. *South African Water Quality Guidelines. Volume 7: Aquatic Ecosystems.*

Dyer, T.G.J. 1976. Expected future rainfall over selected parts of South Africa. *S. Afr. J. Sci.* **72**: 237-249.

Dyer, T.G.J. 1979. Pseudo-periodicities in lake level changes. In: *Lake Chilwa.* Eds: Kalk, M., Howard-Williams, C. and MacLachlan, A.J. Dr W. Junk. The Hague.

Ehrlich, H.L. 1981. *Geomicrobiology.* Marcel Dekker, Inc. New York.

Emerson, S., Broecker, W. and Schindler, D.W. 1973. Gas-exchange rates in a small lake as determined by the radon method. *J. Fish. Res. Bd. Canada* **30**:1475-1484.

Emiliani, C. 1987. *Dictionary of the physical sciences.* Oxford University Press, Oxgord.

English, J.M. 1980. *Investigation into the origins, bathymetry and physical limnology of Lkae Bhangazi.* Unpublished Honours project Report, University of Natal. 51.

Erlank, A.J., Smith, H.S., Marchant, J.W., Cardoso, M.P., and Ahrens, L.H. 1971. Zirconium. In: Wedepohl, K.H. (ed.). *Handbook of geochemistry, Vol II-4,* Sec. 4. Springer-Verlag, New York.

Eugster, H.P. and Hardie, L.A. 1978. Saline lakes. In: Lerman, A (ed.). *Lakes: Chemistry, geology and physics.* Springer-Verlag, New York.

Eugster, H.P. 1980. Geochemistry of evaporitic lacustrine deposits. *Ann. Rev. Earth Planet Sci.* **No. 8**: 35-63.

Eyrolle, F., Benedetti, M.F., Benaim, J.Y. and Fevrier, D. 1996. The distribution of colloidal and dissolved organic carbon, major elements and trace elements in small tropical catchments. *Geochim. Cosmochim. Acta* **60** No. 19. 3643-3656.

Fairbridge, R.W. (ed.). 1972. *The encyclopaedia of geochemistry and environmental sciences.* Van Nostrand Rheinhold Company, U.S.A.

Fanning, K.A. and Pilson, M.E.Q. 1973. On the spectrophotometric determination of dissolved silica in natural waters. *Anal. Chem.* **45**:136.

Fanning, K.A, Keramidas, V.Z. and El-Desoky, M.A. 1989. Micas. In: Dixon, J.B. and Weed, S.B. (Eds.). 1989. *Minerals in soil environments, 2nd Edition.* Soil Science Society of America, Wisconsin, USA.

Feltz, H. 1980. Significance of bottom material data in evaluating water quality. *In*: Baker, R. (ed.). *Contaminants and sediments.* Ann Arbor, Mich., Ann Arbor Science Publishers Inc.

Fitzpatrick, R.W., Le Roux, J. and Schwertmann, U. 1978. Amorphous and crystalline titanium and iron titanium oxides in synthetic preparations at near ambient conditions, and in soil clays. *Clays Clay Miner.* **26**: 189-201.

Follett, E.A.C. 1965. The retention of amorphous, colloidal ferric hydroxides by kaolinites. *J. Soil Sci.* **16**: 334-341.

Förstner, U. and Wittman, G. 1981. *Metal pollution in the aquatic environment, 2nd Edition.* Springer-Verlag, New York.

Fowles, B.K. and Archibald, C.G.M. 1987. Zooplankton and estuarine relict (benthic) fauna in Lake Mzingazi, a freshwater coastal lake of Natal. *Journal of the Limnological Society of Southern Africa* **13**: 66-74.

Friend, F. and Lowenthal, R.E. 1992. *Stasoft III: Computer program for chemical conditioning of low and medium salinity waters.* Water Research Commission, Pretoria, South Africa.

Frye,J.C., Glass, H.D., and Willman, H.B. 1963. *Stratigraphy and mineralogy of the Wisconsin loesses of Illinois, Ill.* State Geol. Surv. Circ. **334**.

FSSA, 1974. *Manual of soil analysis methods. FSSA Publication no. 37.* Fertilizer Society of South Africa.

Gee, G.W. and Bauder, J.W. 1986. Particle Size Analysis. In: Klute, A. (ed.). *Methods of Soil Analysis: Physical and Mineralogical methods. Part 2 (2nd Ed.).* Am. Soc. Agron. Madison, Wisconsin.

Gibbs, R.J. 1970. Mechanisms controlling world water chemistry. *Science* **170**: 1088-1090.

Gleadow, A.J.W. and Lovering, J.F. 1974. The effect of weathering on fission track dating. *Earth Planet. Sci. Lett.* **22**: 163-168.

Glenn, R.C. 1960. Chemical weathering of layer silicate minerals in loess-derived Loring silt loam of Mississippi. *Trans. Int. Congr. Soil Sci.*, 7th, 1960 (Madison, Wisconsin) **IV**: 523-531.

Goldich, S.S. 1938. A study in rock weathering. *J. Geol.* **46**: 17-58.

Goldman, C.R. 1972. The role of minor nutrients in limiting the productivity of aquatic ecosystems. In: Likens, G.E. (ed.). *Nutrients and eutrophication: The limiting-nutrient controversy.* Special symposium: Amer. Soc. Limnol. Oceanogr. **8**: 313-322.

Griffioen, J. 1992. *Cation exchange and carbonate chemistry in aquifers following groundwater flow.* Ph. D. thesis, Free University, Amsterdam.

Grim, R.E. 1968. *Clay mineralogy, 2nd Ed.* McGraw-Hill Publishers, New York.

Gunnison, D. and Alexander, M. 1975. Resistance and susceptibility of algae to decomposition by natural microbial communities. *Limnol. Oceanogr.* **20**: 64-70.

Hackley, K.C., Liu, C.L. and Coleman, D.D. 1996. Environmental isotope characteristics of landfill leachates and gases. *Ground Water*, **34**: 827-836.

Hammer, U.T. 1986. *Saline lake ecosystems of the world.* Dr. W. Junk Publishers, Dordrecht.

Handa, B.K. 1975. Geochemistry and genesis of fluoride containing ground waters in India. *Ground Water*, **13**: 275-281.

Hansen, K. 1959. Sediments from Danish lakes. *J. Sediment. Petrol.* **29**: 38-46.

Harck, T.R. 1995. *A geochemical investigation of the aquatic sediments, groundwater and surface water of the Verlorenvlei coastal lake, with special reference to nitrate transformations.* Masters thesis (Environmental Geochemistry), Department of Geological Sciences, University of Cape Town.

Harck, T.R., Willis, J.P.W. and Fey, M.V. 1997. Denitrification of nitrate-rich ground water entering Verlorenvlei Lake on the west coast of South Africa. Conference proceedings: Wanty, R.B., Marsh, S.P. and Gough, L.P. (eds.). 4th International Symposium on Environmental Geochemistry, Vail, Colorado, (October 5 – October 10, 1997). Open File Report 97-496. United States Department of the Interior, Geological Survey.

Hardie, L.A. and Eugster, H.P. 1970. The evolution of closed-basin brines. *Mineral Soc. Am. Spec. Publ.* **3**: 273-290.

Harriss, R.C. 1967. Silica and chloride in interstitial waters of river and lake sediments. *Limnol. Oceanogr.* **12**: 8-12.

Hart, R.C. 1979. Chapter 7: The invertebrate communities: Zooplankton, zoobenthos and littoral fauna. In: Allanson, B.R. (ed.). *Monographicae Biologicae* Volume 36: Lake Sibaya. W. Junk bv Publishers, The Hague.

Hart, R.C. 1995. Chapter 7: South African coastal lakes. In: *Wetlands of South Africa.* Cowan, G.I. (ed.). 1995. Department of Environmental Affairs and Tourism, Pretoria.

Hart, R.C. and Hart, R. 1995. The seasonal cycles of phytoplankton in subtropical Lake Sibaya: A preliminary investigation. *Arch. Hydrobiol.* **80**: 85-107.

Harter, R.D. 1983. Effect of soil pH on adsorption of lead, copper, zinc and nickel. *Soil Sci. Soc. Am. J.* **47**: 47-51.

Harter, R.D. 1991. Micronutrient adsorption-desorption reactions in soils. In: Mortveld, J.J., Cox, F.R., Shuman, L.M. and Welch, R.M. (eds.). *Micronutrients in agriculture (2nd Edition).* Soil Science Society of America, Inc. Madison, Wisconsin.

Harwood, J.E. 1969. The use of an ion-selective electrode for routine analysis of water samples. *Water Res.* **3**: p. 273.

Hattingh, R.P. 1991. Hydrogeochemistry of the Zululand Coastal Plain. In: Botha, G.A. (ed.). *Field guide and abstracts 19-26 April, 1997: Maputaland - Focus on the Quaternary evolution of the south-east African coastal plain.* International Union for Quaternary Research, Commission on Quaternary Shorelines (Africa Subcommission).

Hickey, M.G. and Kittrick, J.A. 1984. Chemical partitioning of copper, cadmium, nickel and zinc in soils and sediments. *J. Environ. Qual.* **13**: 372-376.

Hill, B.J. 1975. The origin of southern African coastal lakes. *Transactions of the Royal Society of South Africa* **41**: 225-240.

Hill, B.J. 1979. Bathymetry, morphometry and hydrology of Lake Sibaya. In: Allanson, B.R. (ed.). *Monographicae Biologicae* Volume 36: Lake Sibaya. W. Junk bv Publishers, The Hague.

Hobday, D.K. 1979. Chapter 1: Geological evolution and geomorphology of the Zululand coastal plain. In: Allanson, B.R. (ed.). *Monographicae Biologicae* **36**: Lake Sibaya. W. Junk bv Publishers, The Hague.

Horlick, G., Tan, S.H., Vaughan, M.A. and Shao, Y. 1992. Chapter 10: Inductively Coupled Plasma-Mass Spectrometry. In: *Inductively coupled plasmas in analytical atomic spectrometry.* Montaser, A. and Golightly, D.W. (eds.). 1992. Blackie & Son Limited, Glasgow.

Horowitz, A.J. 1991. *A primer on sediment-trace element chemistry* (*2nd Ed.*). Lewis Publishers, Inc., U.S.A.

Horowitz, A., Elrick, K., and Hooper, R. 1989. *The prediction of aquatic sediment-associated trace element concentrations using selected geochemical factors: Hydrological Processes* **3**: . 347-364.

Howard, H.H. and Chisolm, S.W. 1975. Seasonal variation of manganese in a eutrophic lake. *Amer. Midland Nat.* **93**:188-197.

Howard-Williams, C. 1979. Chapter 6: Distribution, biomass and role of aquatic macrophytes in Lake Sibaya. In: Allanson, B.R. (ed.). *Monographicae Biologicae* Volume 36: Lake Sibaya. W. Junk bv Publishers, The Hague.

Howard-Williams, C. and Allanson, B.R. 1978. *Swartvlei project report: Part II. The limnology of Swartvlei, with special reference to production and nutrient dynamics in the littoral zone.* Institute for Freshwater Studies Special Report No. 78/3. Rhodes University.

Howarth, R.W., Marino, R., Lane, J. and Cole, J.J. 1988. Nitrogen fixation in freshwater, estuarine and marine systems. 1. rates and importance. *Limnology and Oceanography* **33**: 669-687.

Hunter, I.T. 1988. Climate and weather off Natal. In: Schumann, E.H. (ed.). Coastal Ocean Studies off Natal, South Africa. *Lecture notes on coastal and marine studies*, **26**: 81-100.

Hutchinson, G.E. 1975. *A treatise on limnology: Volume I, Part 2 – Chemistry of lakes*. John Wiley & Sons, New York.

ILEC Lake Database. Online. International Lake Environmental Committee Foundation for Sustainable Management of World Lakes and Reservoirs. Available: http://www.biwa.or.jp/ilec/top.html. 30 Oct 1998.

Iler, R.K. 1955. *Colloid chemistry of silica and silicates*. Cornell Univ. Press, New York.

Infruitec. 1998. Guidelines for the evaluation of the nutritional status of soils for fruit orchards. Unpublished summary, ARC – Fruit, Vine and Wine Research Institute, Stellenbosch. p1.

Jackson, M.L. 1964. Chemical composition of soils. In: Bear, F.E. (ed.). *Chemistry of the soil.* Rheinhold Publishing Corp., New York.

Jackson, M.L. 1969. *Soil chemical analysis – advanced course*. Department of Soils, Univ. of Wisconsin, Madsion, WI.

Jacobs, L., Emerson, S., and Skei, J. 1985. Partitioning and transport of metals across the $O_2/H_2S$ interface in a permanently anoxic basin: Framvaren Fjord, Norway. *Geochim. Cosmochim. Acta*, **49**: 1433-1444.

Jenny, H. 1932. Studies of the mechanism of ionic exchange in colloidal aluminium silicates. *J. Phys. Chem.,* **36**: 2217-2258.

Jewell, W.J. and McCarthy, P.L. 1971. Aerobic decomposition of algae. *Environ. Sci. Technol.* **5**: 1023-1031.

Jones, B. and Bowser, C. 1978. The mineralogy and related chemistry of lake sediments. *In: Lehman, A. (ed.). Lakes: Chemistry, geology, physics*. Springer-Verlag, New York.

Junta, J.L., Hochella, M.F., Harris, D.W. and Edgell, M. 1992. Manganese oxidation at mineral-water interfaces, a spectroscopic approach. . In: *Water-Rock Interaction.* Kharaka and Maest (eds). Balkema, Rotterdam.

Kabata-Pendias, A. and Pendias, H. 1985. *Trace elements in soils and plants.* CRC Press Inc., Boca Raton, Florida.

Kersten, M. and Forstner, U. 1995. Chapter 9: Speciation of trace metals in sediments and combustion waste. In: Chemical speciation in the environment. Ure, A.M. and Davidson, C.M. (eds.). *Chemical speciation in the environment.* Chapman and Hall, Glasgow.

Kiekens, L. 1995. Chapter 13: Zinc. In: Alloway, B.J. (ed.). 1995. *Heavy metals in soils (2nd edition).* Blackie Academic and Professional, London.

King, L.C. and King, L.A. 1959. A reappraisal of the Natal Monocline. *S. Afr. Geog. J.* **41**: 15-30.

Kinter, E.B. and Diamond, S. 1966. A new method for preparation and treatment of oriented-aggregate specimens of soil clays for x-ray diffraction analysis. *Soil Sci.* **81**:111-120.

Kitano, Y. 1975. *Geochemistry of water.* Dowden, Hutchinson and Ross, Inc., Pennsylvania.

Klages, M.G. and White, J.L. 1957. A chlorite-like mineral in Indiana soils. *Soil Sci. Soc. Am. Proc.* **21**:16-20.

Klute, A. (ed.). 1986. *Methods of soil analysis. Part 1: Physical and mineralogical methods, 2nd Edition.* Soil Science Society of America, Wisconsin, USA.

Knesl, O. 1996. *A geochemical investigation of the water and sediments of the Barber's Pan, North West Province.* Masters Thesis, Department of Geological Sciences, University of Cape Town.

Knudsen, D., Peterson, G.A. and Pratt, P.F. 1982. Lithium, sodium and potassium. 225-246. In: Page, A.L., Miller, R.H. and Keeney, D.R. (eds.). *Methods of soil analysis, Part 2: Chemical and microbiological properties (2nd edition).* Soil Sci. Soc. of Am., Madison, Wisconsin.

Kohnke, H. 1968. *Soil Physics.* McGraw-Hill Book Company, New York.

Krauskopf, K.B. 1956. Dissolution and precipitation of silica at low temperatures. *Geochim. Cosmochim. Acta.,* **10**: 1-26.

Krauskopf, K.B. 1967. *Introduction to Geochemistry.* McGraw-Hill Inc., New York.

Krinsley, D.H. and Smalley, I.J. 1972. Sand. *Am. Sci.* **60**: 286-291.

Lake, D.L., Kirk, P.W. and Lester, J.N. 1984. Fractionation, characterisation, and speciation of heavy metals in sewage sludge and sludge-amended soils. *J. Environ. Qual.* **13**: 175-183.

Lanyon, L.E. and Heald, W.R. 1982. Magnesium, calcium, strontium and barium. 247-262. In: Page, A.L., Miller, R.H. and Keeney, D.R. (eds.). *Methods of soil analysis, Part 2: Chemical and microbiological properties (2nd edition).* Soil Sci. Soc. of Am., Madison, Wisconsin USA.

LeClaire, J.P., Chang, A.C., Levesque, C.S. and Sposito, G. 1984. Trace metal chemistry and arid-zone field soils amended with sewage sludge: IV. Correlations between zinc uptake and extracted soil zinc fractions. *Soil Sci. Am. J.* **48**: 509-513.

Lind, C.J. and Anderson, L.D. 1992. Trace metal scavenging by precipitating Mn and Fe oxides. In: *Water-Rock Interaction.* Kharaka and Maest (eds)., Balkema, Rotterdam.

Lindsay, W.L., Vlek, P.L. and Chien, S.H. 1989. Chapter 22: Phosphate minerals. In: Dixon, J.B. and Weed, S.B. (eds.). 1989. *Minerals in soil environments, 2nd Edition.* Soil Science Society of America, Wisconsin, USA.

Loeb, S.L. and Goldman, C.R. 1979. Water and nutrient transport via groundwater from Ward Valley into Lake Tahoe. *Limnology and Oceanography* **24**: 1146-1154.

Loewenthal, R.E. and Marais, G. v. R. 1976. Carbonate chemistry of aquatic systems: Theory and application. *Ann Arbor Science*, Michigan.

Loveland, P. 1984. The soil clays of Great Britain, I. England and Wales. *Clay Miner* **19**: 681-707.

Lubbe, A.M., Elphinstone, C.D. and Fellingham, S.A. 1973. Mseleni joint disease: food and water supplies. *S.A.Med.J.* **47**: 25225-2233.

Lumsdon, D.G. and Evans, L.J. 1995. Predicting chemical speciation and computer simulation. In: Ure, A.M. and Davidson, C.M. (eds.). *Chemical speciation in the environment.* Blackie Academic and Professional, London.

Macan, T.T. 1961. Factors that limit the range of freshwater animals. *Biol. Rev.* **36**: 151-198.

MacEwan, D.M.C. 1946. The identification and estimation of the montmorillonite group of minerals, with special reference to soil clays. *J. Soc. Chem. Ind.* **65**:298-305.

Mackenzie, F.T, Vink, S., Wollast, R. and Chou, L. 1995. Comparative geochemistry of marine saline lakes. In: Lerman, A., Imboden, D. and Gat, J.R. (eds.). *Physics and chemistry of lakes.* Springer-Verlag, Berlin.

Maest, A.S., Pasilis, S.P., Miller, L.G. and Nordstrom, D.K. 1992. Redox geochemistry of arsenic and iron in Mono Lake, California, USA. In: *Water-Rock Interaction.* Kharaka and Maest (eds). Balkema, Rotterdam.

Martens, D.C. and Lindsay, W.L. 1990. Testing soils for copper, iron, manganese and zinc. In: Esterman, R.L. (ed.). *Soil testing and plant analysis (3rd edition).* SSSA, Madison, WI. 229-260.

Maud, R.R. 1968. Quaternary geomorphology and soil formation in coastal Natal. *Z. Geomorph. N.F.* **7**: 155-199.

Maud, R.R. 1980. The climate and geology of Maputaland. In: *Studies on the ecology of Maputaland.* Bruton, M.N. and Cooper, K.H. (eds.). Cape and Transvaal Printers (Pty) Ltd., Cape Town.

Maud, R.R., Partridge, T.C., Alhonen, P., Donner, J. and Vogel, J.C. 1993. *A preliminary assessment of the environmental conditions represented by the Mbaswana diatomite (Zululand coast).* Conference abstract, SASQUA XIth Conference, Kimberley, July 1993.

McBride, M.B. 1994. *Environmental chemistry of soils.* Oxford University Press, Oxford.

McCall, P.L. and Tevesz, M.J.S. 1982. *Animal-sediment relations.* Plenum Press, New York.

McKnight, D.M. and Bencala, K.E. 1990. The chemistry of iron, aluminium, and dissolved organic material in three acidic, metal-enriched mountain streams, as controlled by watershed and in-stream processes. *Water Resources Res.,* **26**: 3087-3100.

Melsted, S.W. 1953. Some observed calcium deficiencies in corn under field conditions. SSSA Proc., v17: 52-54.

Mengel, K. and Kirkby, E.A. 1978. *Principles of plant nutrition.* International Potash Institute, Bern, Switzerland.

Metting, B.L. 1994. Algae and cyanobacteria. 427-459. In: Weaver, R.W., Angle, J.S. and Bottomley, P.S. (eds.). *Methods of soil analysis, Part 2: Microbiological and biochemical properties.* Soil Science Society of America, Inc. Madison, Wisconsin, USA.

Meyer, R. 1991. Geological information from geohydrological investigations on the Zululand Coastal Plain. In: Botha, G.A. (ed.). *Field guide and abstracts 19-26 April, 1997: Maputaland - Focus on the Quaternary evolution of the south-east African coastal plain.* International Union for Quaternary Research, Commission on Quaternary Shorelines (Africa Subcommission).

Meyer, R. and Kruger, G.P. 1988. A sedimentological model for the northern Zululand coastal plain. *Extended Abstract: 22nd Earth Science Congress of the Geological Society of South Africa.* University of Natal, Durban. 423-425.

Meyer, R., Talma, A.S. and Botha, J.F. 1993. *Ground water survey of the Zululand coastal aquifer.* Africa Needs Ground Water International Convention, Johannesburg. Paper 3, Vol. 1.

Meyer, R. and Godfrey, L. 1995. *Characterisation and mapping of the groundwater resources, KwaZulu-Natal Province, Mapping Unit 7. CSIR Report No. EMAP-C-95024.* Pretoria.

Meyer, R., Talma, A.S., Duvenhage, A.W.A., Eglington, B.M., Taljaard, J., Botha, J.F., Verwey, J.P., Buys, J., and Van Der Voort, I. 1995. *Geohydrological investigation and evaluation of the Zululand coastal aquifer.* Water Research Commission Report.

Miller, W.R. 1996. *Sequence stratigraphy of the latest Mesozoic and Cenozoic sediments below Lake Sibaya, Northern KwaZulu-Natal.* Council for Geoscience Geological Survey Report No. 1996-0318.

Miller, W.R. 1998. *The sedimentology of Lake Sibaya, Northern KwaZulu-Natal.* Council for Geoscience, Geological Survey Report No. 1998-0139.

Miller, W.R. 1998b. *The bathymetric, sedimentological and seismic stratigraphy of Lake Sibaya, Northern KwaZulu-Natal.* MSc. Thesis. University of Natal, Durban.

Miller, W.R., Alhonen, P. and Vogel, J.C. 1997. A late Pleistocene diatomite exposure on the western shores of Lake Sibaya. *Maputaland focus on the Quaternary evolution of the south-east African coastal plain.* Botha, G.A. (ed.). International Union for Quaternary Research Workshop Abstracts, Council for Geoscience, Pretoria.

Milnes, A.R. and Fitzpatrick, R.W. 1989. Titanium and zirconium minerals. In: Dixon, J.B. and Weed, S.B. (Eds).. 1989. *Minerals in soil environments, 2nd Edition.* Soil Science Society of America, Wisconsin, USA.

Moll, E.J. 1970. *Vegetation studies in the Three Rivers Region, Natal.* Ph.D. thesis, Department of Botany, University of Natal, Pietermaritzburg.

Morad, S. and Aldahan, A.A. 1982. Authigenesis of titanium minerals in two Proterozoic sedimentary rocks from southern and central Sweden. *J. Sediment. Petrol.* **52**: 1295-1305.

Mörner, N.A. 1970. The position of the ocean level during the interstadial at about 30 000 years B.P. – a discussion from a climatic-glaciologic point of view. *Canadian Journal of Earth Sciences,* **8**: 132-143.

Mortimer, C.H. 1942. The exchange of dissolved substances between mud and water in lakes. *J. Ecol.* **29**: 280-329.

Mortimer, C.H. 1949. Underwater 'soils': A review of lake sediments. *Journal of Soil Science* **1**: 63-73.

Mortveld, J.J., Cox, F.R., Shuman, L.M., and Welch, R.M. (eds.). 1991. *Micronutrients in agriculture (2nd edition).* SSSA, Madison, WI.

*Munsell ® Soil Colour Chart.* 1992. Macbeth ® Division of Kollmorgen Instruments Corp., New York.

Murray, K. and Wade, P. 1996. Checking anion-cation balance of water quality analyses: Limitations of the traditional method for non-potable waters. *Water SA* **22**: 27-32.

Nelson, D.W. and Sommers, L.E. 1982. Total carbon, organic carbon, and organic matter. In: Page, A.L., Miller, R.H. and Keeney, D.R. (eds*). Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties* (*2nd edition*). *Agronomy Monograph* **9**: 539-579.

Nishimura, M., Nakaya, S. and Tanaka, K. 1973. Boron in the atmosphere and precipitation: Is the sea the source of atmospheric boron? In: *Proc. Symposium on Hydrogeochemistry and Biogeochemistry.* Clarke Company, Washington, D.C. 547-557.

Nkedi-Kizza, P., Rao, P.S.C., Jessup, R.E. and Davidson, J.M. 1982. Ion exchange and diffusive mass transfer during miscible displacement through an aggregated oxisol. *Soil Sci. Soc. Am. J.* **46**: 471-476.

Noble, R.G. and Hemens, J. 1978. Inland water ecosystems in South Africa – a review of research needs. *South African National Scientific Programmes Report* No 34. 150 .

Nordstrom, D.K., Plummer, L.N., Wigley, T.M., Wolery, T.J., Ball, J.W., Jenne, E.A., Bassett, R.L., Crerar, D.A., Florence, T.M., Fritz, B., Hoffman, M., Holdren, G.R., Lafon, G.M, Mattigod, S.V., McDuff, R.E., Morel, F., Reddy, M.M., Sposito, G. and Thrailkill, J. 1979. A comparison of computerised chemical models for equilibrium calculations in aqueous systems. In: Jenne, E.A. (ed.). *ACS Symp. Ser. 93*: p 857-892.

Norrish, K. and Rosser, H. 1983. Mineral phosphate. 335-361. In: Div. Soils, CSIRO (ed.). *Soils: An Australian viewpoint.* CSIRO Melbourne, Academic Press, London.

Nriagu, J.O. 1978. Dissolved silica in pore waters of Lakes Ontario, Erie and Superior sediments. *Limnol. Oceanogr.* **23**: 53-67.

Odum, E.P. 1971. *Fundamentals of ecology.* W.B. Saunders Co., London.

Ohle, W. 1954. Sulfat als "katalysator" des limnischen stoffkreislaufes. *Vom Wasser* **21**: 13-32.

Ohle, W. 1964. Kolloidkomplekxe als Kationen- und Anionenaustaucher in Binnengewässern. *Vom Wasser* **30**: 50-64.

Okazaki, M.K., Takimodah, K. and Yamane, I. 1986. Adsorption of heavy metal cations on hydrated oxides and oxides of iron and aluminium with different crystallinities. *Soil Sci. Plant Nutr.* (Tokyo) **32**: 523-533.

Oom, B.M. 1997. *The potential for using stable isotopes for solving urban geohydrological problems in the Cape Town area.* Masters thesis (Environmental Geochemistry), Department of Geological Sciences, University of Cape Town.

Parkhurst, D.L. 1995. *Users guide to PHREEQC – a computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations.* Water-Resources Investigations Report 95-4227. U.S. Geological Survey, Lakewood, Colorado.

Patick, R. 1978. The effects of trace metals in the aquatic ecosystem. *Amer. Sci.* **66**: 185-191.

Philips (Analytical). 1992. *X'Pert System User Guide*: 2nd Edition, June 1992.

Pitman, W.V. and Hutchinson, I.P.G. 1975. *A preliminary hydrological study of Lake Sibaya.* Report No. 4/75, Hydrological Research Unit.

Pooley, J.J. 1996. *Nutrient deficiencies in soils of the Mseleni area, Kwazulu-Natal.* MSc. Thesis: Environmental Geochemistry. Department of Geological Sciences, University of Cape Town.

Rai, D. and Kittrick, J.A. 1989. Mineral equilibria and the soil system. In: Dixon, J.B. and Weed, S.B. (Eds.). 1989. *Minerals in soil environments, 2nd Edition.* Soil Science Society of America, Wisconsin, USA.

Ramsar Data Sheet: Lake Sibaya. Online. Department of Environmental Affairs and Tourism. Kyle, R. and Ward, M.C. http://water.ccwr.ac.za/wetlands/sibaya.html.. 30 Oct 1998.

Ramsay, P.J. 1991. *Sedimentology, coral reef zonation, and late Pleistocene coastline models of the Sodwana Bay Continental Shelf, Northern Zululand.* PhD thesis. Department of Geology and Applied Geology, University of Natal, Durban.

Reavell, P.E. and Cyrus, D.P. 1989. Preliminary observation on the macrocrustacea of coastal lakes in the vicinity of Richards Bay, Zululand, South Africa. *Sth.Afr.J. aquat. Sci.* **15**: 103-128.

Reynolds, R.C. 1980. Interstratified clay minerals. .249-303. *In*: Brindley, G.W. and Brown, G. (ed.). Crystal structures of clay minerals and their x-ray identification. *Mineral. Soc. Monogr.* **5**. Mineralogical Society, London.

Ribbe, P.H. 1982. Titanite (sphene). 137-154. In: Ribbe, P.H. (ed.). Reviews in mineralogy, Vol 5: Orthosilicates. *Mineralog. Soc. Amer.*, Washington, DC.

Riffenberg, H.B. 1925. Chemical character of ground waters of northern Great Plains. *Wat. Supp. Pap., Wash.,* **560B**: 31-52. (unseen reference).

Russell-Hunter, W.D. 1970. *Aquatic productivity: an introduction to some basic aspects of biological oceanography and limnology.* Collier-MacMillan, London.

Schofield, R.K. and Sampson, H.R. 1954. Flocculation of kaolinite due to the attraction of oppositely charged crystal faces. *Discuss. Faraday Soc.* **18**: 135-145.

Schulte, E.E. and Olsen, C.C. (eds.). 1970. *Wisconsin soil testing and plant analyses procedures.* Soil Fertility Series **6**. Dept. of Soil Sci., Univ. of Wisconsin, Madison.

Schwertmann, U. and Taylor, R.M. 1989. Iron oxides. 379-438. In: Dixon, J.B. and Weed, S.B. (eds.). 1989. *Minerals in soil environments, 2nd Edition.* Soil Science Society of America, Wisconsin, USA.

Selivanov, L.S. 1946. Géochimie et biogéochimie du brome dispersé. *Trav. Lab. Biogéochim. URSS,* **8**: 5-72. (Unseen reference, Russian text).

Seymour, A. and Seward, P. 1996. *Groundwater harvest potential of the Republic of South Africa.* (Unreferenced 1:8 500 000 Albers' equal area projection map). Department of Water Affairs and Forestry. Government Printer, Pretoria.

Shapiro, J. 1969. Iron in natural waters – its characteristics and biological availability as determined with the ferrigram. *Verh. Int.Ver. Limnol.* **17**: 456-466.

Shelford, V.E. 1918. Conditions of existence. In: *Freshwater Biology*. Ward, H.B. and Whipple, G.C. (eds.). John Wiley & Sons Inc. New York. 21-60.

Shuman, L.M. 1986. Effect of liming on the distribution of manganese, copper, iron and zinc among soil fractions. *Soil Sci. Soc. Am. J.,* **50**: 1236-1240.

Shuman, L.M. 1991. Chemical forms of micronutrients in soils. 113-144. In: Mortveld, J.J., Cox, F.R., Shuman, L.M. and Welch, R.M. (eds.). *Micronutrients in agriculture (2^nd^ Edition).* Soil Science Society of America, Inc. Madison, Wisconsin.

Simpson, Sir. G.C. 1941. On the formation of cloud and rain. *Quart. J. R. met. Soc.,* **67**: 163-169.

Sims, J.T. and Johnson, G.V. 1991. Micronutrient soil tests. In: Mortveld, J.J., Cox, F.R., Shuman, L.M., and Welch, R.M. (eds.). 1991. *Micronutrients in agriculture (2$^{nd}$ edition).* SSSA, Madison, WI.

Slater, J.M. and Capone, D.G. 1987. Denitrification in aquifer soils and nearshore marine sediments influenced by groundwater nitrate. *Applied and Environmental Microbiology* **53**: 1292-1297.

Smith, G.R., Tanji, K.K., Jurinak, J.J. and Burau, R.G. 1995. Applications of a Pitzer equations-based model to hypersaline solutions. In: Loeppert, R.H., Schwab, A.P. and Goldberg, S. (eds.). 1995. *Chemical equilibrium and reaction models.* SSSA Special Publication Number 42. Soil Science Society of America, Inc. Madison, Wisconsin.

Smith, R.M. and Martell, A.E. 1989. *Critical stability constants. Vol. 6. 2$^{nd}$ supplement.* Plenum Press, New York.

Socki, R.A., Karlsson, H.R, and Gibson, E.K. 1992. Extraction technique for the determination of oxygen-18 in water using pre-evacuated glass vials. *Anal. Chem.* **64**: 829-831.

Sonntag, C., Klitzch, E., Lohnert, E.P., Ee-Shazly, E.M., Munnich, K.O. Junghans, C.H., Torweihe, U., Weisstroffer, K. and Swailem, F.M. 1979. Palaeoclimatic information from deuterium and oxygen-18 in carbon-14 dated North-Saharan Groundwaters. *Isotope Hydrology*, IAEA, Vienna, **2**: 569-581.

Speer, J.A. and Gibbs, G.V. 1976. The crystal structure of synthetic titanite, $CaTiSiO_4$, and the domain textures of natural titanites. *Am. Mineral.* **61**: 238-247.

Sposito, G. 1984. *The surface chemistry of soils.* Oxford University Press, New York.

SSSA. 1990. *Handbook of standard soil testing methods for advisory purposes.* The Non-Affiliated Soil Analysis Work Committee, Soil Science Society of South Africa, Pretoria.

Stevenson, F.J. 1985. Geochemistry of soil humic substances. In: Aiken *et. al.* (ed.). *Humic substances in soil, sediment and water.* John Wiley and Sons, New York.

Stevenson, F.J. and Ardakani, M.S. 1972. Organic matter reactions involving micronutrients in soils. 79-114. *In:* Mortveld, J.J. *et. al.* (eds.). *Micronutrients in agriculture.* SSSA, Madison, WI.

Stumm, W. and Morgan, J.J. 1980. *Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters.* Wiley and Sons, New York.

Stumm, W. and Morgan, J.J. 1981. *Aquatic Chemistry, 2$^{nd}$ Edition.* New York: John Wiley and Sons.

Sugawara, K. 1948. Distribution of fine particles of salts in the air. *J. Jap.Chem.,***82**: 341.

Sullivan, C.W. 1971. *A silicic acid requirement for DNA polymerase, thymidylate kinase and DNA synthesis in the marine diatom.* University of California, Berkeley, California.

Talma, A.S. 1992. *Natural isotope ratio differences as tracers of the sources of water and carbon.* Proc. Seminar on stable isotopes in plant nutrition, soil fertility and environmental studies. Inst. Soil, Climate and Water, Pretoria, 72-78.

Tankard, A.J. 1976. Cenozoic sea-level changes: a discussion. *Ann. S. Afr. Mus.,* **71**: 1-17.

Taylor, R.M. and Schwertmann, U. 1974. The association of phosphorus with iron in ferruginous soil concretions. *Aust. J. Soil Res.* **12**: 133-145.

Thiesen, A.A., and Harward, M.E. 1962. A paste method for preparation of slides for clay mineral identification by x-ray diffraction. *Soil Sci. Soc. Am. Proc.* **26**:90-91.

Thorne, L, and Nickless, G. 1981. The relation between heavy metals and particle size fractions within the Severn Estuary (U.K) inter-tidal sediments. *The Science of the Total Environment*, **19**: 207-213.

Tinley, K.L. 1976. *The ecology of Tongaland.* Wildlife Soc., Natal Branch, Durban.

Tinley, K.L. and van Riet, W.R. 1981. *Tongaland: zonal ecology and rural land use proposals*, unpublished report. Department of Co-operation and Development, Pretoria.

Turchenek, L.W. and Oades, J.M. 1978. Organo-mineral particles in soils. In: Emerson *et. al.*, (eds.). *Modification of soil structure.* John Wiley & Sons, Chichester, U.K.

Tyson, P.D. 1978. Rainfall changes over South Africa during the period of meteorological record. In: *Biogeography and ecology of Southern Africa.* Werger, M.S.A. (ed.). . 53-69. Dr W. Junk bv. Publishers.

US EPA. 1991. *Summary of modifications and new features in MINTEQA2 and PRODEFA2 versions 3.10, 3.11.* U.S. Environmental Protection Agency, Env. Res. Laboratory: Athens, Georgia.

Van Veen, J. 1936. *Onderzoekingen in de Hoofden.* Algemeene Landsdukkerij, 'S-Gravenhage.

Van Vliet, H.R.P., Kempster, P.L., Sartory, D.P., Gerber, F.A. and Schoonraad, I.J. 1988. Analytical methods manual. *Hydrological Research Institute Report No. TR136.* South African Department of Water Affairs, Pretoria.

Viner, A.B. 1975. The supply of minerals to tropical rivers and lkaes (Uganda). In: Hasler, A.D. (ed.). Coupling of land and water systems. *Ecological studies* **10**: 227-261.

Walker, G.F. 1950. Vermiculite-organic complexes. *Nature* **166**: 695-697.

Walker, G.F. 1957. On the differentiation of vermiculites and smectites in clays. *Clay Miner. Bull.* **3**: 154-163.

Walkley, A. and Black, I.A. 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Science* **37**: 29-38.

Weaver, R.W., Angle, J.S. and Bottomley, P.S. (eds.). *Methods of soil analysis, Part 2: Microbiological and biochemical properties.* Soil Science Society of America, Inc. Madison, Wisconsin, USA.

Webster, J.G. 1992. Trace metals at the oxic/anoxic-$H_2S$ boundary in Lake Vanda, Antarctica. In: *Water-Rock Interaction.* Kharaka and Maest (eds). Balkema, Rotterdam.

Weiss, A. and Russow, J. 1963. Über titan im gitter von kaolin. *Proc. Int. Clay Conf. 1963 (Stockholm)* **1**: 203-213.

Wentworth, C.K. 1922. A scale grade and class terms for clastic sediments. *J. Geol.* **30**: 377-392.

Werner, D. 1966. *Arch. Microbiol.* **55**: 278-308.

Wetzel, R.G. 1983. *Limnology, 2nd Edition.* Saunders College Publishing, U.S.A.

Whittig, L.D. and Allardice, W.R. 1986. X-ray Diffraction techniques. 331-362. In: Klute, A. (ed.). 1986. *Methods of soil analysis. Part 1: Physical and mineralogical methods, 2nd Edition.* Soil Science Society of America, Wisconsin, USA.

WHO. 1992. Revision of the WHO Guidelines for drinking water quality: *Report on the Final Task Group Meeting.* 37p. WHO, Geneva.

Williams, J.D., Jaquet, H. J-M. and Thomas, R.L. 1976. Forms of phosphorus in the surficial sediments of Lake Erie. *J. Fish. Res. Can.,* **33**: 413-429.

Willis, J.P. 1995. *Instrumental parameters and data quality for routine major and trace element determinations by WDXRFS.* Information Circular No. 14. Department of Geological Sciences, University of Cape Town.

Willis, J.P. and Hill, D.R.H. 1992. "STAR" plots – diagrams with strong visual impact for simultaneously displaying variations in four to nine sample characteristics. *Int. Conf. Proceedings Elemental Analysis of Coal and its By-Products, 1992*: 75-79. World Scientific Publications, Singapore.

Woodcock, A.H. 1953. Salt nuclei in marine air as a function of altitude and wind force. *J. Met.,* **10**: 362-371.

Wright, I. 1997. A broad overview of the Cenozoic evolution of the Northern KwaZulu-Natal palaeodune cordons. In: Botha, G.A. (ed.). *Field guide and abstracts 19-26 April, 1997: Maputaland - Focus on the Quaternary evolution of the south-east African coastal plain.* International Union for Quaternary Research, Commission on Quaternary Shorelines (Africa Subcommission).

ZoBell, C.E. 1964. Geochemical aspects of the microbial modification of carbon compounds. In: Colombo, U. and Hobson, G.D. (eds.). *Advances in organic geochemistry.* Macmillan Co., New York.

# APPENDIX A: METHODS OF WATER ANALYSIS

## A.1: REPORTING OF RESULTS

In this report, results are expressed using significant figures, whereby all digits in the reported result are known definitely, except for the last digit, which may be in doubt due to unavoidable uncertainty. Digits that are not significant are dropped by rounding off.

The quality of the analytical data was checked using the recovery of known additions within the demonstrated linear range of the particular method. Reagent blanks were analysed as a monitor of the purity of reagents and the overall procedural blank. Where applicable (e.g. colorimetric methods), approximately 10% of the sample load was analysed as reagent blanks. Calibration was achieved by means of the use of standards within the linear range of the method. Where appropriate, the standard curve was then verified at regular time intervals over the period of analysis.

The precision of a particular method was assessed through the analysis of duplicate samples, in excess of 5% of the samples. The precision of a particular method is frequently expressed, in this report, through the use of the relative standard deviation (RSD) or coefficient of variation (CV), expressed as a percentage. This statistic normalises the standard deviation and is frequently stated in preference over the standard deviation in reporting precision, since it facilitates making direct comparisons among analyses that include a wide range of concentrations. RSD is calculated as follows:

$$RSD\,(\%) = 100 \times \frac{SD}{Mean}$$

## A.2: ELECTRICAL CONDUCTIVITY (EC)

The laboratory determination of electrical conductivity for all water samples collected was achieved by means of a CRISON microCM conductivity meter. The meter incorporates a temperature probe for automatic temperature compensation, in addition to a conductivity cell (cell constant: $C = 1.03\ \text{cm}^{-1}$.) Replication of EC measurement was conducted on random samples one week after initial readings were conducted. All measurements were conducted at room temperature (between 19.2 ° C and 20.3° C). The EC values determined for all open Lake Sibaya waters are presented in Section 3.4 of the main body of the report. The results of replicate EC measurements conducted on representative open lake waters, the three groundwater wells and a sample from the Mseleni River are presented in Table A.1.1.The statistical results of replicate EC readings conducted on waters in contact with Lake Sibaya sediments are presented in Table A.1.2. RSD values were, in each instance, $\leq 1.6\%$, indicating acceptable analytical precision.

**Table A1.1:** Results of replicate analyses conducted on representative open waters of Lake Sibaya, three groundwater wells, and the Mseleni River.

| | | EC (µS/cm) | | | pH | | | $SiO_2$ (mg/l) | | | P (mg/l) | | | F (mg/l) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | N | Mean | RSD (%) | N | Mean | RSD (%) | N | Mean | RSD (%) | N | Mean | RSD (%) | N | Mean | RSD (%) |
| WA1s | 3 | 550 | 0.6 | 2 | 8.1 | 0.2 | 2 | 8.3 | 4.0 | 2 | 0.08 | 10 | 2 | 0.14 | 7.1 |
| WA3d | 4 | 550 | 1.1 | 3 | 8.1 | 0.5 | 2 | 7.9 | 4.5 | 2 | 0.06 | 11 | 2 | 0.14 | 0.0 |
| SA5d | 4 | 559 | 0.5 | 2 | 8.2 | 0.2 | 2 | 7.8 | 1.5 | 2 | 0.05 | 11 | 2 | 0.14 | 7.1 |
| WM2d | 3 | 562 | 0.6 | 3 | 8.2 | 0.4 | 2 | 8.5 | 1.5 | 2 | 0.06 | 9.0 | 2 | 0.14 | 7.1 |
| WM4d | 3 | 548 | 0.8 | 3 | 8.3 | 0.2 | 2 | 8.7 | 2.1 | 2 | - | - | 2 | < 0.1 | - |
| Well 1 | 3 | 311 | 1.1 | 2 | 8.1 | 0.9 | 2 | 10 | 1.2 | 2 | 0.07 | 10 | 2 | 0.13 | 7.7 |
| Well 2 | 3 | 360 | 0.6 | 3 | 7.8 | 0.3 | 2 | 9.5 | 1.7 | 2 | 0.08 | 7.3 | 2 | 0.16 | 6.3 |
| Well 3 | 3 | 652 | 0.4 | 3 | 8.4 | 0.3 | 2 | 5.6 | 3.9 | 2 | 0.80 | 0.3 | 2 | 0.15 | 0.0 |
| River | 3 | 693 | 1.2 | 2 | 8.3 | 0.7 | 2 | 9.7 | 4.0 | 2 | 0.43 | 1.2 | 2 | 0.16 | 6.3 |

**Table A1.2:** Results of replicate analyses conducted on waters in equilibrium with Lake Sibaya sediments.

| | EC (μS/cm) | | | pH | | | $SiO_2$ (mg/l) | | | P(mg/l) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | N | Mean | RSD (%) | N | Mean | RSD (%) | N | Mean | RSD (%) | N | Mean | RSD (%) |
| $WA1_{eq}$ | 3 | 702 | 1.1 | 2 | 7.5 | 0.8 | 2 | 40 | 3.3 | 2 | 0.3 | 2.2 |
| $WA2_{eq}$ | 2 | 868 | 1.0 | 3 | 8.0 | 1.3 | 2 | 35 | 5.1 | 2 | 1.9 | 1.1 |
| $WA3_{eq}$ | 2 | 691 | 0.5 | 2 | 8.2 | 0.3 | 2 | 33 | 0.4 | 2 | 1.4 | 1.6 |
| $WA4_{eq}$ | 3 | 869 | 1.2 | 2 | 7.9 | 0.2 | 2 | 33 | 0.7 | 2 | 0.3 | 3.9 |
| | | | | | | | | | | | | |
| $SA1_{eq}$ | 3 | 782 | 1.0 | 3 | 7.5 | 0.3 | 2 | 39 | 0.8 | 2 | 0.4 | 2.6 |
| $SA2_{eq}$ | 2 | 1026 | 1.1 | 2 | 7.5 | 0.4 | 2 | 41 | 0.8 | 2 | - | - |
| $SA3_{eq}$ | 2 | 743 | 0.7 | 3 | 7.7 | 0.7 | 2 | 45 | 1.0 | 2 | 1.7 | 0.6 |
| $SA4_{eq}$ | 3 | 880 | 0.9 | 2 | 7.3 | 0.6 | 2 | 24 | 1.4 | 2 | 0.3 | 5.0 |
| $SA5_{eq}$ | 3 | 763 | 1.5 | 2 | 8.1 | 0.5 | 2 | 32 | 0.6 | 2 | 0.3 | 3.5 |
| $WM1_{eq}$ | 2 | 936 | 0.0 | 2 | 7.5 | 0.9 | 2 | 36 | 0.7 | 2 | 0.3 | 4.6 |
| | | | | | | | | | | | | |
| $WM2_{eq}$ | 2 | 990 | 1.6 | 2 | 7.8 | 0.5 | 2 | 40 | 0.4 | 2 | 3.4 | 3.0 |
| $WM3_{eq}$ | 2 | 627 | 1.6 | 3 | 7.4 | 0.7 | 2 | 33 | 0.1 | 2 | 4.5 | 0.5 |
| $WM4_{eq}$ | 2 | 772 | 0.5 | 4 | 7.5 | 0.7 | 2 | 32 | 0.3 | 2 | 2.0 | 4.6 |
| $WM5_{eq}$ | 3 | 709 | 0.7 | 2 | 7.6 | 0.7 | 2 | 26 | 0.7 | 2 | 1.9 | 2.9 |

## A.3: pH

A Metrohm 691 pH meter was used to determine the pH of all samples collected, following calibration with buffer solutions pH 7.02 and pH 4.00. The meter comprises a combined electrode, consisting of a glass indicator electrode plus reference electrode. Measurements were performed at room temperature (temperature range: 19.5°C to 20.6°C.) Replicate pH measurements were conducted at random, both immediately following initial measurement, and after the duration of one week. Relative standard deviation values of 0.17 and 0.19 were obtained for the measurement of pH buffers at regular intervals throughout the above-mentioned pH analysis of samples.

As with EC, the pH values determined for all open Lake Sibaya waters are presented in Section 3.4 of the main report. RSD values were $\leq$ 1.3% for replicate measurements on both representative lake, river and well waters (Table A.1.1), and waters in contact with the lake sediments (Table A.1.2). This indicates acceptable analytical precision.

## A.4: ALKALINITY

The alkalinity of selected representative water samples was determined by potentiometric titration, using the Gran method outlined by Stumm and Morgan, 1980. A Radiometer DTS 800 multi-titration system, (consisting of a TTT 85 titrator, and an ABU 80 autoburette linked to both a PHG201 glass electrode and a REF401 calomel reference electrode) was used for this purpose. Duplicate alkalinity measurements were conducted on samples, drawn at random, one week after initial measurements were conducted. Equivalent aliquots of Milli-Q ($M_Q$) water were read as blanks at regular intervals throughout the analysis.

The Gran method operates through the use of a series of functions designed to alleviate the complications involved in identifying the end-point pH in alkalinity titrations. Within a region of pH above and below the end-point, these functions plot linearly against the volume of strong acid added. Initially 10 ml aliquots of each sample were titrated to pH 4.00. Thereafter, small increments of 0.01*M* HCl were successively reacted with each sample, so as to reach various predetermined endpoints (viz. pH values: 4.00; 3.80; 3.60; 3.40 and 3.20.) The total volume of acid ($V_x$) required for each titration was recorded, as was the measured pH value at each endpoint. The values of $V_x$, pH and $V_s$ (the initial volume of sample) were substituted into the Gran function (Equation A1.1), to create a series of values for $F_x$.

$$F_x = (10^{-pH_x})(V_s + V_x)$$

Linear regression was performed on the linear portion of each of the plots of $V_x$ values against $F_x$ values, so as to determine the intersection with the x-axis. This point represents $V_f$, the volume of standard strong acid required to titrate the sample to the $H_2CO_3^*$ equivalence point. $HCO_3^-$ is the dominant carbonate species for waters with the pH range 6.4 to 10.33 (Drever, 1997.) All alkalinity readings were therefore calculated to mg $HCO_3^-$/l, through use of the following equation:

$$mg\,HCO_3^-/l = mmol_c\,H^+/ml * Atomic\,weight\,HCO_3^- * 1000$$

The results of the duplicate alkalinity measurements – conducted one week apart - for waters from Lake Sibaya, the Mseleni River and open wells in the vicinity of the lake are presented in Table A 1.3. Similarly, alkalinity measurements for waters in contact with lake sediments are presented in Table A.1.4. The equation for the best-fit line through the linear portion of the Gran Plot obtained for initial alkalinity measurement of each sample is also tabulated. All $R^2$ values were greater than 0.93, indicating a high goodness-of-fit of each regression line to the data. Machine sensitivities of 99.8% and 99.9%, respectively, were recorded for the successive measurement sittings.

**Figure A1.1: Alkalinity Gran Plot (Sample SA5d)**

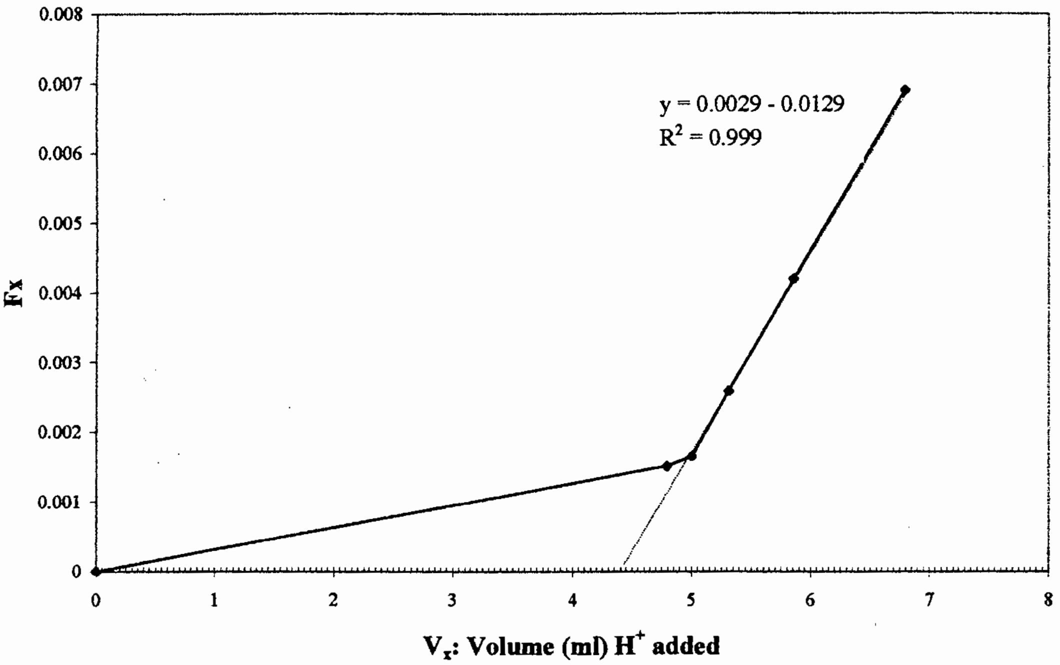

**Table A1.3:** Results of repeat alkalinity measurement of selected Lake Sibaya, well and river water samples. The equation and $R^2$ value for the best-line-of-fit to the Fx versus Vx data plot is presented for the initial alkalinity measurement in each instance.

| Sample | Linear Equation | $R^2$ value | Alkalinity (mg $HCO_3^-$ / l) 19/8/98 | 26/8/98 | Mean and (std. dev.) |
|---|---|---|---|---|---|
| WA3d | y = 0.003x - 0.020 | 1.00 | 137 | 138 | 137 (0.35) |
| SA2d | y = 0.002x – 0.013 | 0.99 | 137 | 140 | 138 (2.5) |
| SA5s | y = 0.003x - 0.013 | 1.00 | 135 | 137 | 136 (1.4) |
| SA5d | y = 0.002x – 0.013 | 1.00 | 139 | 142 | 140 (1.4) |
| WM3s | y = 0.002x – 0.013 | 0.99 | 137 | 140 | 138 (1.8) |
| WM4d | y = 0.002x – 0.013 | 0.99 | 138 | 138 | 138 (0.35) |
| WM5d | y = 0.002x – 0.013 | 1.00 | 138 | 138 | 138 (0.00) |
| Well 1 | y = 0.002x – 0.012 | 1.00 | 139 | 142 | 140 (1.8) |
| Well 2 | y = 0.002x – 0.008 | 0.99 | 139 | 140 | 139 (0.71) |
| Well 3 | y = 0.001x – 0.025 | 0.99 | 134 | 138 | 136 (2.5) |
| River | y = 0.001x – 0.020 | 1.00 | 136 | 137 | 136 (0.71) |

**Table A1.4:** Results of repeat alkalinity measurement of waters in contact with Lake Sibaya sediments. The equation and $R^2$ value for the best-line-of-fit to the Fx versus Vx data plot is presented for the initial alkalinity measurement in each instance.

| Sample | Linear Equation | $R^2$ value | Alkalinity (mg $HCO_3^-$ / l) 11/9/98 | 20/9/98 | Mean and (std. dev.) |
|---|---|---|---|---|---|
| $WA1_{eq}$ | y = 0.009 x – 0.047 | 0.95 | 167 | 174 | 171 (5.0) |
| $WA2_{eq}$ | y = 0.008 x – 0.096 | 0.94 | 195 | 198 | 196 (2.5) |
| $WA3_{eq}$ | y = 0.007 x - 0.039 | 0.93 | 165 | 171 | 168 (4.6) |
| $WA4_{eq}$ | y = 0.009 x - 0.110 | 0.95 | 201 | 209 | 205 (5.7) |
| $SA1_{eq}$ | y = 0.008 x - 0.087 | 0.94 | 170 | 165 | 167 (3.5) |
| $SA2_{eq}$ | y = 0.007 x - 0.129 | 0.96 | 279 | 286 | 282 (5.0) |
| $SA3_{eq}$ | y = 0.008 x - 0.078 | 0.94 | 152 | 159 | 155 (5.3) |
| $SA4_{eq}$ | y = 0.009 x - 0.095 | 0.95 | 171 | 177 | 174 (4.2) |
| $SA5_{eq}$ | y = 0.008 x - 0.088 | 0.94 | 165 | 170 | 168 (3.5) |
| $WM1_{eq}$ | y = 0.008 x - 0.055 | 0.95 | 168 | 171 | 170 (2.1) |
| $WM2_{eq}$ | y = 0.005 x – 0.031 | 1.00 | 181 | 187 | 184 (4.2) |
| $WM3_{eq}$ | y = 0.005 x – 0.032 | 1.00 | 160 | 168 | 164 (5.7) |
| $WM4_{eq}$ | y = 0.005 x – 0.032 | 1.00 | 160 | 160 | 160 (0.0) |
| $WM5_{eq}$ | y = 0.004 x – 0.030 | 1.00 | 160 | 168 | 164 (5.7) |

## A.5: ION CHROMATOGRAPHY (IC)

Ion chromatography (IC) was used to determine ion concentrations within representative lake water samples. Suspended solids were removed by filtration through 0.2μm Millipore membranes. The samples were thereafter diluted with Milli-Q de-ionised water, to obtain EC values in the range of 50 to 100μS/cm. A Dionex onguard-P filter cartridge was used to remove biological constituents in the final stage of sample preparation.

A Dionex ion chromatograph, housed within the Geological Sciences Department of the University of Cape Town, was used to perform analyses of anions ($Br^-$, $Cl^-$, $NO_2^-$, $NO_3^-$ and $SO_4^{2-}$) and cations ($K^+$, $Na^+$, $NH_4^+$, $Ca^{2+}$ and $Mg^{2+}$.) Detection was achieved by means of conductivity, with chemical eluant suppression. Cations were separated by means of an HPIC-CS12A column. Anions in lake waters were separated by means of an HPIC-AS4A column, whereas anions within waters in contact with lake sediments were separated with an HPIC-AS14 column. The conditions under which the instrument was operated are presented in Table A.1.5.

Determinations of two anion- and two cation- standards of known concentration were conducted at regular intervals throughout the analysis, so as to gauge the accuracy of the analytical method and the sample handling procedure. Standards were chosen so as to coincide with the approximate concentration ranges expected to occur within the collected samples. The difference between expected and measured values remained below 9% for all measurements of cation standards, and below 7% for all anion standards, indicating acceptable precision and repeatability. Calibration standards were also run on each day on which ion chromatography was performed.

**Table A1.5:** Conditions under which anions and cations within water samples were determined by ion chromatography (IC.)

| | Anions | Cations |
|---|---|---|
| Separator column | HPIC-AS4A / HPIC-AS14 | HPIC-CS12A |
| Guard column | HPIC-AG4A | HPIC-CG12A |
| Sample loop volume | 50μl | 25μl |
| Eluant | AS4A: 1.80 mM $Na_2CO_3$<br>AS14: 3.5 mM $Na_2CO_3$<br>1.70 mM $NaHCO_3$ | 22 mM $H_2SO_4$ |
| Suppressor | Anion MicroMembrane (AMMS) | Cation suppressor (CSRS-I 4mm) |
| Regenerant | 25 mN $H_2SO_4$ | 22 mM $H_2SO_4$ |
| Expected background conductivity | 15 to 20 μS | ≈ 30 μS |
| Approximate run time | 7 minutes | 15 minutes |

Ion concentrations for duplicate lake, river and well water sample IC analyses (refer to Table A.1.6) were generally below 5%, indicating good analytical precision. Similarly, within-laboratory precision appears to be good for ion chromatography analysis of the waters in contact with lake sediments (refer to Table A.1.7.) All cation concentration balances between successive IC measurements of the latter waters (with the exception of potassium in sample $SA4_{eq}$) were within six- percent difference, as were all anion concentrations (with the exception of $F^-$ and $NO_3^-$ in sample $WM3_{eq}$.)

The charge balance between major cation and anion concentrations (expressed as millimoles of charge per litre, $mmol_c/l$) was investigated for each of the representative water samples selected for comprehensive analysis (cf. Table A.1.8 and Table A.1.9.) Major ions considered in the balance include $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$, $F^-$, $NO_2^-$, $Br^-$, $NO_3^-$ and $SO_4^{2-}$ (all determined by ion chromatography); $PO_4^{3-}$ (by colorimetry) and $HCO_3^-$ (by Gran titration.) The following equation (Murray and Wade, 1996) was used to calculate anion-versus-cation charge differences in each instance:

$$Charge\ Balance\ (\%) = \frac{\sum mmol_c cations/l - \sum mmol_c anions/l}{\sum mmol_c cations/l + \sum mmol_c anions/l} * 100$$

Of the 23 water samples analysed by ion chromatography, 9 (39%) show ion charge differences in excess of 10%, of which 3 samples (13% of total samples considered) show differences exceeding 13%. The relatively high degree of conformity between the magnitude of anion and cation charge suggests acceptable data quality with respect to the detection of aqueous.

**Table A.1.6:** Duplicate IC analyses of selected Lake Sibaya, Mseleni river and well water samples.

| | $Na^+$ | $NH_4^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $Cl^-$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|
| WA1s | | | | | | | |
| 20/8/98 | 91.9 | <0.1 | 7.9 | 14.0 | 42.1 | 143.4 | 20.2 |
| 27/8/98 | 90.0 | <0.1 | 8.3 | 13.8 | 42.3 | 129.8 | 20.0 |
| % Difference | 2.1 | - | 5.4 | 1.3 | 0.7 | 9.4 | 1.3 |
| WA3d | | | | | | | |
| 20/8/98 | 87.3 | <0.1 | 6.6 | 13.7 | 35.3 | 109.5 | 9.2 |
| 20/8/98 | 84.8 | <0.1 | 6.6 | 13.7 | 34.9 | 108.8 | 9.4 |
| % Difference | 3.0 | - | 0.3 | 0.7 | 1.2 | 0.7 | 2.1 |
| SA5d | | | | | | | |
| 20/8/98 | 94.7 | <0.1 | 9.5 | 18.0 | 40.6 | 147.5 | 11.4 |
| 27/8/98 | 92.9 | <0.1 | 9.7 | 17.4 | 40.6 | 149.0 | 11.8 |
| % Difference | 1.9 | - | 1.9 | 3.6 | 0.1 | 1.1 | 3.1 |
| WM2d | | | | | | | |
| 20/8/98 | 91.1 | <0.1 | 8.1 | 16.6 | 44.9 | 150.4 | 19.0 |
| 27/8/98 | 90.9 | <0.1 | 8.2 | 16.5 | 44.4 | 143.9 | 18.9 |
| % Difference | 0.2 | - | 1.4 | 0.5 | 1.0 | 4.3 | 0.8 |
| WM4d | | | | | | | |
| 20/8/98 | 94.5 | <0.1 | 8.7 | 17.5 | 38.4 | 150.8 | 14.1 |
| 27/8/98 | 92.1 | <0.1 | 9.0 | 17.6 | 36.9 | 152.7 | 14.2 |
| % Difference | 2.5 | - | 3.9 | 0.9 | 3.9 | 1.3 | 1.1 |
| Well 1 | | | | | | | |
| 20/8/98 | 82.7 | <0.1 | 10.0 | 12.5 | 85.4 | 87.9 | 13.7 |
| 20/8/98 | 85.6 | <0.1 | 11.1 | 12.8 | 84.4 | 85.8 | 13.5 |
| % Difference | 3.4 | - | 11.2 | 1.8 | 1.2 | 2.5 | 1.8 |
| Well 2 | | | | | | | |
| 20/8/98 | 77.5 | | 8.3 | 14.9 | 30.3 | 79.6 | 47.0 |
| 27/8/98 | 77.9 | <0.1 | 8.6 | 15.2 | 32.3 | 78.1 | 46.8 |
| % Difference | 0.4 | - | 3.9 | 2.3 | 6.7 | 1.8 | 0.4 |
| Well 3 | | | | | | | |
| 20/8/98 | 75.5 | 0.6 | 16.7 | 10.1 | 85.8 | 57.2 | 39.7 |
| 20/8/98 | 79.1 | <0.1 | 17.5 | 10.6 | 89.8 | 55.1 | 37.7 |
| % Difference | 4.8 | - | 4.6 | 5.1 | 4.7 | 3.6 | 5.1 |
| River | | | | | | | |
| 20/8/98 | 135.3 | <0.1 | 7.7 | 19.5 | 70.5 | 144.7 | 22.1 |
| 20/8/98 | 134.2 | <0.1 | 8.0 | 19.3 | 70.8 | 145.0 | 22.2 |
| % Difference | 0.8 | - | 4.1 | 1.0 | 0.4 | 0.2 | 0.3 |

**Table A.1.7:** Duplicate IC analyses (conducted within the Department of Geological Sciences, University of Cape Town) of selected water samples in contact with Lake Sibaya sediments.

**(a) Cations**

| | $Na^+$ | $NH_4^+$ | $K^+$ | $Mg^{2+}$ | $Mn^{2+}$ | $Ca^{2+}$ |
|---|---|---|---|---|---|---|
| $WA2_{eq}$ | | | | | | |
| 16/9/98 | 81.5 | 14.2 | 14.9 | 27.5 | 15.7 | 56.0 |
| 16/9/98 | 81.9 | 14.2 | 15.2 | 27.9 | 16.6 | 55.9 |
| % Difference | 0.5 | 0.2 | 2.4 | 1.5 | 5.6 | 0.1 |
| $SA2_{eq}$ | | | | | | |
| 16/9/98 | 88.4 | 20.6 | 15.6 | 28.1 | <0.1 | 83.1 |
| 22/9/98 | 88.3 | 20.5 | 15.5 | 28.2 | <0.1 | 82.9 |
| % Difference | 0.2 | 0.2 | 0.9 | 0.6 | - | 0.3 |
| $SA4_{eq}$ | | | | | | |
| 16/9/98 | 81.0 | 23.0 | 11.5 | 19.1 | <0.1 | 69.9 |
| 16/9/98 | 78.8 | 22.8 | 9.8 | 18.1 | <0.1 | 66.3 |
| % Difference | 2.6 | 1.0 | 14.4 | 5.3 | - | 5.2 |
| $WM3_{eq}$ | | | | | | |
| 16/9/98 | 85.6 | 2.7 | 10.1 | 20.2 | 3.5 | 48.1 |
| 16/9/98 | 85.8 | 2.7 | 10.1 | 20.8 | <0.1 | 47.6 |
| % Difference | 0.1 | 0.7 | 0.4 | 2.9 | - | 1.0 |
| $WM5_{eq}$ | | | | | | |
| 16/9/98 | 81.8 | 6.7 | 9.2 | 24.2 | <0.1 | 54.2 |
| 22/09/98 | 81.7 | 6.9 | 9.2 | 24.1 | <0.1 | 54.1 |
| % Difference | 0.2 | 2.2 | 0.8 | 0.3 | - | 0.2 |

**(b) Anions**

| | $F^-$ | $Cl^-$ | $Br^-$ | $NO_3^-$ | $PO_4^{3-}$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|
| $WA2_{eq}$ | | | | | | |
| 16/9/98 | <0.1 | 105.5 | < 0.1 | < 0.1 | < 0.1 | 21.7 |
| 16/9/98 | <0.1 | 105.4 | <0.1 | <0.1 | <0.1 | 21.5 |
| % Difference | - | 0.1 | - | - | - | 1.1 |
| $SA2_{eq}$ | | | | | | |
| 16/9/98 | 3.5 | 111.1 | 4.9 | < 0.1 | 11.4 | 17.5 |
| 22/9/98 | 3.4 | 110.5 | 4.7 | <0.1 | 11.0 | 17.7 |
| % Difference | 3.2 | 0.6 | 3.5 | - | 2.8 | 1.3 |
| $SA4_{eq}$ | | | | | | |
| 16/9/98 | 3.5 | 112.7 | < 0.1 | 6.9 | 11.9 | 21.8 |
| 16/9/98 | 3.3 | 111.4 | <0.1 | 6.6 | 12.0 | 21.3 |
| % Difference | 5.5 | 1.1 | - | 3.2 | 1.4 | 2.2 |
| $WM3_{eq}$ | | | | | | |
| 16/9/98 | 3.5 | 117.8 | < 0.1 | 9.0 | 10.8 | 23.6 |
| 16/9/98 | 3.1 | 115.7 | <0.1 | 8.4 | 10.6 | 22.8 |
| % Difference | 9.5 | 1.8 | - | 6.2 | 2.6 | 3.5 |
| $WM5_{eq}$ | | | | | | |
| 16/9/98 | 3.3 | 116.3 | < 0.1 | 7.0 | 11.1 | 24.2 |
| 22/09/98 | 3.2 | 113.6 | <0.1 | 6.7 | 10.8 | 24.0 |
| % Difference | 2.7 | 2.3 | - | 4.8 | 2.3 | 0.9 |

**Table A.1.8:** Charge balances obtained for waters collected from Lake Sibaya, Mseleni River and groundwater wells in the region.

| Sample | Σ cations (mmol$_c$/l) | Σ anions (mmol$_c$/l) | Charge Balance (%) (excluding DOM) | Charge Balance (%) (including DOM*) |
|---|---|---|---|---|
| WA1s | 7.5 | -9.0 | -9.4 | -9.4 |
| WA3d | 6.9 | -8.3 | -9.5 | -9.5 |
| SA5d | 7.9 | -9.0 | -6.4 | -6.4 |
| WM2d | 7.8 | -9.2 | -8.2 | -8.2 |
| WM4d | 7.7 | -9.1 | -8.2 | -8.2 |
| Well 1 | 9.2 | -7.3 | 11.1 | 11.2 |
| Well 2 | 6.3 | -7.8 | -10.2 | -10.1 |
| Well 3 | 8.9 | -6.9 | 12.7 | 12.7 |
| River | 11.2 | -9.0 | 10.8 | 10.8 |

**Table A.1.9:** Charge balances obtained for waters in contact with Lake Sibaya sediments.

| Sample | Σ cations (mmol$_c$/l) | Σ anions (mmol$_c$/l) | Charge Balance (%) (excluding DOM) | Charge Balance (%) (including DOM*) |
|---|---|---|---|---|
| WA1$_{sed}$ | -8.3 | 8.3 | -0.4 | -0.5 |
| WA2$_{sed}$ | -8.9 | 10.3 | 7.5 | DOC not analysed |
| WA3$_{sed}$ | -8.3 | 10.1 | 10.0 | DOC not analysed |
| WA4$_{sed}$ | -9.4 | 11.5 | 10.0 | DOC not analysed |
| SA1$_{sed}$ | -8.1 | 9.9 | 10.0 | DOC not analysed |
| SA2$_{sed}$ | -11.8 | 11.8 | 0.2 | DOC not analysed |
| SA3$_{sed}$ | -7.5 | 9.4 | 11.3 | 11.2 |
| SA4$_{sed}$ | -8.2 | 10.2 | 10.5 | 10.4 |
| SA5$_{sed}$ | -9.0 | 9.8 | 4.2 | DOC not analysed |
| WM1$_{sed}$ | -9.1 | 12.2 | 14.5 | DOC not analysed |
| WM2$_{sed}$ | -8.8 | 13.1 | 19.6 | DOC not analysed |
| WM3$_{sed}$ | -8.0 | 8.3 | 1.7 | 1.6 |
| WM4$_{sed}$ | -7.8 | 10.4 | 14.1 | 14.0 |
| WM5$_{sed}$ | -7.9 | 8.9 | 5.5 | DOC not analysed |

## A.6: SILICA

Nine representative lake water samples, and all fourteen waters in contact with lake sediment samples, were filtered through 0.2μm Millipore filter membranes and analysed for molybdate-reactive silica, using the molybdosilicate method (Standard Methods, 1995: 4500-Si D.) Water samples were collected and stored in polyethylene prior to analysis. This method is recommended for relatively pure waters containing between 0.4 and 25 mg $SiO_2$/*l*. This range can be extended - if required - by diluting, by concentrating, or by varying the light path (Fanning and Pilson, 1973.) Advantages of using the molybdosilicate method include its speed and simplicity, and its freedom

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* Dissolved organic matter (DOM) calculated as: L (moles of binding sites) = (DOC x 2) (5 x $10^{-4}$), after US EPA, (1991).

from the constraint of requiring sample dilution. Minimum detectable limits of approximately 1 mg $SiO_2$/l are expected from the method when the precautions outlined below are followed (Standard Methods, 1995.) The method showed a relatively high degree of precision (relative standard deviation: 7.7%; relative error: 9.8%) when synthetic samples - of similar composition to those obtained for the Lake Sibaya waters - were analysed by 19 laboratories (Standard Methods, 1995. pp4-118.)

The primary principle underlying the molybdosilicate method involves the reaction of ammonium molybdate with silica - and any phosphate present - to produce heteropoly acids at a pH of approximately 1.2. The addition of oxalic acid solution ensures that molybdophosphoric acid is destroyed, whilst molybdosilicic acid remains unaffected. The intensity of the yellow colour produced in this reaction is then proportional to the concentration of molybdate-reactive silica. The extent to which forms of silica which are unreactive with molybdate occur in water is unknown (Fanning and Pilson, 1973.)

Shortfalls of this method include interference arising as a result of tannin, colour and turbidity; as well as the limited stability of the yellow colour produced by the method (Standard Methods, 1995.) Treatment with oxalic acid eliminates interference from phosphate and reduces interference from tannins. Photometric compensation - through the addition of all reagents except for ammonium molybdate to a duplicate of the sample against which the spectrophotometer was blanked – was made in the case of samples $SA4_{eq}$ and $WM4_{eq}$, so as to reduce interference effects due to colour and turbidity. A blank determination was made, to correct for any silica that may have been introduced to the sample via apparatus and reagents. The ionic strength of Lake Sibaya water is sufficiently low that the intensity of the yellow colour produced is unlikely to be affected by salt concentration (Standard Methods, 1995.)

The preparation of reagents was conducted using a batch of chemicals low in silica. Ammonium molybdate reagent was prepared through the dissolution of 10g of $(NH_4)_6Mo_7O_2\cdot 4H_2O$ in 100 ml deionised water, with subsequent adjustment of pH to between 7 and 8, through the addition of NaOH. Adjustment of the pH prevents the formation of a precipitate. Sodium metasilicate nonahydrate was dissolved in distilled water to obtain stock silica solution, which was subsequently diluted so as to obtain permanent colour standards for visual determination of silica. Both samples and reagents were stored in plastic containers to guard against high blanks.

The method required the addition – in rapid succession – of 1 ml 1:1 HCl and 2 ml ammonium molybdate reagent to 50 ml of each of the filtered water samples. Thorough mixing was ensured, whereafter the samples were allowed to stand for 5 to 10 minutes. A Sequoia-Turner 340 spectrophotometer was used to measure absorbance, (at 410 nm, with a light path of 1 cm) 10 minutes after the addition of 2 ml of oxalic acid solution. The yellow colour develops in accordance with Beer's law. Sample dilutions were made, where necessary, to reach compliance with the recommended concentration range specified for the method. Standard solutions (covering the optimum ranges: 0, 20, 40, 60, 80 and 100µg $SiO_2$/55 ml final volume) were used to prepare a calibration curve [absorbance=0.028 (mg $SiO_2$/l)+ 0.081; $R^2 = 0.99$] from which silica concentrations in the collected samples could be determined.

The results of duplicate analyses conducted on Lake Sibaya, well and Mseleni river water samples are presented in Table A1.1. The residual standard deviation (RSD) was below 5% for duplicate measurements on each sample, indicating good precision. The results of silicate determination on waters in direct contact with lake sediments are presented in Table A1.2. These waters, likewise, indicate relatively rigorous analytical precision, with all samples except one ($WA2_{eq}$) indicating RSD values below 5%.

## A.7: PHOSPHORUS

Phosphorus analyses involve two principle procedural steps, namely: (a) conversion of the phosphorus form of interest to dissolved orthophosphate, and (b) colorimetric determination of dissolved orthophosphate. The Murphy and Riley (1962) ascorbic acid method, (Standard Methods, 1995: 4500-P E), used for the colorimetric determination of dissolved orthophosphate in the collected water samples, is suitable for the range of 0.01to 6 mg P/*l*. Precision for the method was determined at approximately 4% relative standard variation for water samples in the applicable concentration range (Standard Methods, 1995: 4500-P A.) The lower limit of detection using this method is 0.01 mg P/l (Standard Methods, 1995.)

All glassware was soaked overnight in HCl and rinsed thoroughly with Milli-Q de-ionised water prior to use, so as to reduce phosphate contamination. Sample volumes were stored in glass at 4°C prior to analysis. These samples were filtered through 0.45 µm Millipore membrane filters, (so as to separate suspended from dissolved forms of phosphorus) and their pH tested against phenolphtalein indicator. Aliquots of 25 ml of sample were then treated with a range of standard phosphate solutions, in addition to 4.0 ml of a mixed reagent. This reagent comprises of the following volumetric proportions: 50% $5M$ $H_2SO_4$; 5% $0.01M$ potassium antimonyl tartrate solution; 15% $0.03M$ ammonium molybdate solution; and 30% $0.01M$ ascorbic acid solution. The ammonium molybdate and potassium antimonyl tartrate produce phosphomolybdic acid upon reaction with orthophosphate within an acid medium. The ascorbic acid within the reagent reduces this heteropoly acid, thereby yielding an intense blue colour. Samples were not subjected to either preliminary hydrolysis or oxidative digestion, owing to the fact that dissolved, reactive forms of phosphorus were to be determined.

A Sequoia-Turner model 340 spectrophotometer with a light path of 1 cm was used to measure absorbance at 880nm within each sample, 20 minutes after the addition of the mixed reagent. The spectrometer was zeroed against reagent blank in each instance. Standard phosphate solutions, (in the concentration range specified as suitable for the method) were read photometrically, in order to construct a calibration line [absorbance=0.546 (mg $PO_4^{3-}$/l) + 0.006; $R^2$ = 1.00), from which sample concentrations could be read. The analysis of relatively turbid sample blanks indicated that turbidity and colour interference were negligible in terms of influencing absorbance.

The P concentrations of the analysed water samples were calculated from the equation for the best line fit to the calibration, as per Equation 3:

$$mg\,P/l = \frac{absorbance - c}{m} \times dilution\,factor \qquad (3)$$

$where\ m\ and\ c\ represent\ the\ slope\ and\ y-\text{int}ercept, respectively, of\ the\ calibration line: y = mx + c$

The results of duplicate phosphorus determinations within the representative Lake Sibaya, well and Mseleni River water samples are presented in Table A1.1. Only two of these water samples (Well 3 and the Mseleni River sample) showed substantial levels of phosphorus. Residual standard deviation (RSD) values are high for the remaining samples, presumably since measured concentration values approach the lower limit of detection range for the method. The results of duplicate phosphorus determinations for waters in contact with Lake Sibaya sediments are tabulated in Table A.1.2. RSD values were acceptable (RSD < 5%) in each instance.

## A.8: INDUCTIVELY COUPLED PLASMA-MASS SPECTROSCOPY

A range of dissolved trace elements were determined in filtered and acidified water samples by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS.) An ELAN 6000 ICP-MS (Perkin-Elmer, Sicex, U.S.A) interfaced to appropriate software was used to perform the analysis, conducted within the Department of Geological Sciences at the University of Cape Town.

The coupling of an inductively coupled plasma source to a mass spectrometry detector constitutes a rapid, sensitive and convenient method for trace and ultra-trace analysis of water samples. The ICP source consists of a flowing stream of argon gas ionised by an applied radio frequency field. This field is inductively coupled to the ionised gas by a water-cooled coil surrounding a quartz torch, which confines the plasma. The water sample of interest is nebulised and the aerosol thus generated is carried into the plasma, through an injector tube located within the torch. The injection of sample aerosol directly into the ICP results in almost complete dissociation of molecules at temperatures of approximately 6000 to 8000$^{o}$K, thereby reducing chemical interference to a phenomenal extent (Standard Methods, 1995.) Sample atoms are thereafter directed into the mass spectrometer where electromagnetic fields separate the ions (based on different charge-to-mass ratios) for detection. Detection is possible down to parts per trillion (ppt) levels for some elements, provided that the relevant precautions of monitoring internal standards and standard concentration additions, and efforts to reduce matrix effects are adhered to. In such instances, and with a sample size ≥ 30, precision and reproducibility may approach 2% relative standard deviation for waters in the concentration range of 10 – 100 mg/l (*pers. comm.* J. Willis, Department of Geological Sciences, U.C.T.).

Samples were filtered and acidified (3ml sample: 27 ml of 2% nitric acid) prior to analysis. Samples were not acidified in the field because of the limitations that this would potentially place on determining the redox status of such waters. The choice of a 0.2μm Millipore membrane filter is unconventional, a 0.45μm Millipore membrane filter generally being considered standard in terms of defining suspended versus dissolved material. The rationale behind this decision was the likely greater effectiveness of the former filter at removing suspended material. One hundred microlitres of internal calibration standard, containing 10 ppb yttrium, rhodium and rhenium, were added to each sample. Periodic analysis of a NIST standard sample of known concentration provided a gauge of the accuracy of the analytical results. Samples and standards were prepared in the same acids, so as to minimise any matrix effects which might arise through suppression of analyte ionisation by matrix components.

The results of quantitative analysis of trace elements in lake, river and well waters; and in waters in contact with sediments are presented in Tables 3.4 (c) and 3.5 (c) of the main body of the report, respectively. In each instance the stated element concentrations represent the average of two duplicate measurements of each sample water. RSD values, based on triplicate measurement of NIST-1460 standard sample, were below 2% in all but three samples (Se: 2.32%; Cs: 5.63% and Tl: 9.81%) of the waters in contact with lake sediments.

## A.9: DISSOLVED ORGANIC CARBON (DOC)

Analysis of Dissolved Organic Carbon (DOC) was performed on 0.45μm filtered samples using the persulphate-ultraviolet oxidation method (Standard Methods, 1995: 5310 C.) This method constitutes a rapid, precise means of measuring trace levels of organic carbon in water. The analyses were conducted by the analytical laboratories of the Cape Water Programme, CSIR, in Stellenbosch. Samples were preserved at 4°C, with minimal exposure to light and atmosphere, prior to DOC determination.

Conceptually, the method involves the oxidation of organic carbon to carbon dioxide by persulphate in the presence of ultraviolet light. An autosampler was used to introduce samples serially into a continuously gas purged reactor, in which is submerged an ultraviolet light. The $CO_2$ produced is sparged continuously from the solution, and is carried in the gas stream to an infrared autoanalyser that is specifically tuned to the absorptive wavelength of $CO_2$. The instrument's microprocessor integrates the area of the peaks produced by the autoanalyser, compares them to the peak area of the calibration standard, and produces a printout of a calibrated organic carbon value in milligrams per litre.

It appears unlikely that any of the water samples analysed were sufficiently turbid so as to prevent complete oxidation to any significant degree. Large organic particles - or very large or complex organic molecules such as tannins, lignins, and humic acid - may interfere with DOC determination, through hindering oxidation rate (Standard Methods, 1995: pp 5-19). Mercuric nitrate added to the persulphate solution prevented potential preferential oxidation of chloride (and consequent inhibition of organic matter oxidation) in all samples analysed. With adequate attention given to minimising sample contamination and method background, minimum detectable concentrations of 0.2 to 0.3 mg/l can be expected (Standard Methods, 1995: pp 5-19.) Standard errors of 6% are reported for the method (Standard Methods, 1995: pp 5-20).

## A.10: FLUORIDE

Fluoride levels within collected water samples were determined by means of the ion selective electrode method (Standard Methods, 1995: 4500-$F^-$ C), which is reported to be suitable for fluoride concentrations ranging from 0.1 to more than 10 mg/*l*.

A Corning solid state ion selective electrode and voltmeter were used for fluoride determination. The electrode is an ion selective sensor consisting of a lanthanum fluoride doped crystal, across which a potential is established by fluoride solutions of different concentrations. The crystal contacts the sample solution at one face and an internal reference solution at the other. The fluoride electrode measures the ion activity of fluoride rather than the concentration, fluoride ion activity being dependent on the solution total ionic strength and pH, and on fluoride complexing species (Standard Methods, 1995). Addition of ionic strength adjustment buffer (Orion TISAB III) containing the complexing agent CDTA, to all sample and standard solutions, however, serves to ensure nearly uniform ionic strength background, adjusts pH, and breaks up potentially interfering ion complexes. In this manner optimum conditions are ensured, such that the electrode, in effect, measures concentration (Standard Methods, 1995).

Calibration of the fluoride electrode was achieved by means of recording the voltage output of the electrode within standard solutions of known fluoride concentrations. Orion Fluoride Standard 100 ppm (± 0.5 ppm) sodium fluoride solution was diluted with appropriate volumes of de-ionised water, so as to achieve standard solutions within the range of fluoride concentrations suited to the method. A ten percent dilution with concentrated ionic strength adjustment buffer was performed on all sample and standard solutions, for the reasons detailed above. Calibration of standard solutions yielded an $R^2$ value of 0.99 when fluoride readings were compared against known concentrations.

Chloride, phosphate and sulphate levels in the sample waters are all substantially below those listed (Standard Methods, 1995: pp4-59) as likely to result in detectable error (0.1 mg/*l*) due to ion interference. Furthermore, CDTA (cyclohexylenediamine-tetraacetic acid) present within the buffer will preferentially complex interfering polyvalent cations (notably aluminium and iron) and release free fluoride ions (Harwood, 1969.) Similarly, despite the fact that hydroxide ions are prevalent in the alkaline water samples analysed, the pH maintained by the buffer ensures that no hydroxide interference occurs (Standard Methods, 1995.) These measures reduce the potential for interference in fluoride determination by the ion selective electrode method. Under such conditions, fluoride determination by 111 laboratories, of a synthetic sample containing 0.75 mg $F^-$/*l* and 300 mg alkalinity/l, yielded a relative standard deviation of 4.8% and a relative error of 0.2% (Standard Methods, 1995: pp4-62.)

Duplicate measurements of fluoride levels - determined by the ion-selective electrode method - for the open waters of the lake, the Mseleni River and the groundwater wells are presented in Table A.1.1. In the case of the sediment-contacted waters, a t-test comparison for independent samples was conducted, so as to compare fluoride concentrations obtained by ion chromatography, and those obtained by the selective ion electrode method (refer to Table A.1.10). A p-level of $< 0.05$ was obtained for this comparison, indicating that the difference between the fluoride levels determined by the two analytical methods is significant. Fluoride levels determined in sediment waters by ion chromatography were possibly elevated, as a result of peak interference effects (notably the major negative contribution of the "water dip"), despite the use of the HPIC-AS14 anion column operating under weak eluent (3.5mM $Na_2CO_3$.) For this reason the fluoride levels quoted in the text are those measured by the ion-selective electrode method. In both batches of water samples, fluoride levels approached the lower limit of detection (0.1 mg/*l*) for the method.

**Table A.1.10**: A t-test comparison of fluoride levels determined by the ion-selective electrode method and ion chromatography (IC) for waters in contact with Lake Sibaya sediments.

| Sample | $F^-$ (mg/l) by ISE | $F^-$ (mg/l) by IC |
|---|---|---|
| $WA1_{eq}$ | 0.14 | <0.1 |
| $WA2_{eq}$ | 0.16 | <0.1 |
| $WA3_{eq}$ | 3.07 | 3.34 |
| $WA4_{eq}$ | 3.13 | 3.36 |
| $SA1_{eq}$ | 0.18 | <0.1 |
| $SA2_{eq}$ | 3.14 | 3.48 |
| $SA3_{eq}$ | 3.11 | 3.36 |
| $SA4_{eq}$ | 3.09 | 3.45 |
| $SA5_{eq}$ | 3.08 | 3.37 |
| $WM1_{eq}$ | 3.57 | 3.83 |
| $WM2_{eq}$ | 0.14 | <0.1 |
| $WM3_{eq}$ | 3.04 | 3.47 |
| $WM4_{eq}$ | 3.07 | 3.38 |
| $WM5_{eq}$ | 2.98 | 3.31 |

**t-Test for independent samples**

t-statistic: 3.55

p-level: 0.035 (i.e. $< 0.05$, reject $H\phi$ at 95% confidence level)

## A11: ISOTOPES

Water samples to be subjected to isotope analysis were tightly sealed in pyrex bottles to prevent evaporation. Oxygen and hydrogen isotope measurement was achieved through the use of a Finnegan MAT 252 mass spectrometer housed within the stable isotope laboratory in the Department of Geological Sciences, University of Cape Town. The internal isotope reference water standard Cape Town Millipore Precipitation water (CTMP) was used to convert the sample data to the international standards, Standard Mean Ocean Water (SMOW) and Standard Light Antarctic Precipitation (SLAP), according to the method of Coplen (1988). The fractionation factor between $CO_2$ and water at 25°C was assumed to be 1.0412 (Coplen, 1993). Data are reported in the familiar $\delta$ notation, where $\delta = (R_{sample}/R_{standard} - 1) \times 1000$, and $R = {}^{18}O/{}^{16}O$ or D/H. The average difference between duplicates of the CTMP internal water standard analysed in this laboratory over the period March 1995 to May 1997 was found to be 0.48‰ for hydrogen (n=23) and 0.1‰ for oxygen (n=18) (Diamond and Harris, 1997). These correspond to values of 2σ of 0.74‰ and 0.14‰, respectively. The CTMP internal water standard is run with each batch of samples and used to correct for drift in the reference gases. A recent test of analytical quality, in which 38 South African laboratories determined D/H deviations in two gases, relative to a third (Brand, 1966), revealed that the results obtained from the UCT Finnegan Mat 252 fell within the range of the standard deviations.

In the preparation of samples for oxygen isotope determination, a disposable vacutainer test tube was evacuated under vacuum and subsequently filled with approximately 0.5 atm of medical grade $CO_2$, in accordance with the method of Socki *et al.* 1992). Sample aliquots of approximately 2ml volume were injected into the vacutainer, via a hypodermic needle. The vacutainer was thereafter thoroughly shaken, and submerged into a 25°C bath for several hours to encourage equilibrium between the $H_2O$ and $CO_2$. The $H_2O$ and $CO_2$ present in the vacutainer were frozen by immersion in liquid $N_2$ for several minutes. Whilst the sample was still being kept frozen, the hypodermic needle was used to evacuate any non-condensable gases.

The vacuum line was then closed off and the vacutainer placed into a slush of frozen propan-2-ol, which vaporised the $CO_2$, allowing it to expand into the line, where it was re-frozen as a cold finger with liquid nitrogen. The above-mentioned process was repeated, namely pumping out the non-condensable gases, replacing the liquid nitrogen from the cold finger with the propan-2-ol slush, allowing the $CO_2$ to warm up and expand into the line, and subsequently re-freezing the sample with liquid nitrogen as a second cold finger. This latter cold finger was frozen against a pressure transducer, which allowed the voltage- (and hence, the $CO_2$ yield-) to be determined as a gauge of any $CO_2$ leakage from the vacutainer. The second cold finger was re-opened to the line, and liquid nitrogen was placed around a break-seal tube so as to ensure that the $CO_2$ remained frozen within the sample. The break-seal tube was thereafter sealed under vacuum with an oxygen-propane torch, prior to measurement by mass spectrometer.

# APPENDIX B: METHODS OF SEDIMENT ANALYSIS

## B.1: COLOUR

The moist and air dried colours of all collected sediment samples were measured by comparison to the Munsell ® soil colour chart (1992.) Three independent observers determined the moist and dry colour of the sediments, under conditions of natural light. The classification of soil colour is by three variables: hue, value and chroma. The hue notation of a colour indicates its relation to red, yellow, green, blue and purple. The value notation indicates its lightness, and the chroma notation indicates its strength. The nomenclature for the colour of the Lake Sibaya sediments was according to two complementary systems: (i) colour names and (ii) the Munsell notation of colour.

## B.2: CARBONATE

Air-dried and moist sediment samples, when treated with concentrated HCl on a clean watchglass, showed no sign of effervescence. The Karbonat-Bombe technique has been shown to detect $CaCO_3$ levels to a lower limit of 2,5%, with a corresponding precision (RSD) of 3.6% (Birch, 1981). Given that the maximum concentration of Ca determined by XRFS (*cf.* Section B.6 of this Appendix) of the bulk sediment (after conversion from the stated CaO values) was approximately 1.3% ($WA1_{sed}$), the levels of $CaCO_3$ were deemed to be insufficient to detect with any certitude by the Karbonat-Bombe method.

## B.3: ORGANIC CARBON

The rapid dichromate oxidation-titration method of Walkley and Black (1934) was used to determine the organic C content of each the Lake Sibaya sediments. Air-dried sediments (1g) were thoroughly mixed with 10 ml of 0.167*M* $K_2Cr_2O_7$ solution and 20 ml of concentrated $H_2SO_4$. To ensure that the oxidation of organic matter reaches completion, 1 gram aliquots of swing-milled sediment (-300 #) were used in each instance. The reaction proceeds according to the following equation:

$$2Cr_2O_7^{2-} + 3C + 16H^+ = 4Cr^{3+} = 3CO_2 + 8H_2O$$

The Erlenmeyer flask containing the solution was allowed to cool for 30 minutes, after which time 150ml de-ionised water, 10 ml concentrated ortho-phosphoric acid, and 1 ml barium diphenylamine sulphonate indicator were added. The excess dichromate was titrated, by drop-wise addition of 0.5*M* iron (II) ammonium sulphate hexahydrate solution, until the green endpoint was reached. The reduced dichromate is taken to be equivalent to the organic C present in the sample, assuming that soil organic matter has an average valence of zero. The iron (II) ammonium sulphate solution was standardised against 10 $cm^3$ 0.167 mol/L $K_2Cr_2O_7$ solution, according to the method described above.

The carbon content of each sample was calculated according to the following equation:

$$\%C = \frac{[ml\,Fe(NH_4)_2(SO_4)_2\,in\,blank - ml\,Fe(NH_4)_2(SO_4)_2\,in\,sample]\ x\ M\ x\ 0.3\ x\ f}{soil\,mass\,(g)}$$

$$where: M = \text{molar concentration of } \mathrm{Fe(NH_4)_2(SO_4)_2} = \frac{10\,\mathrm{ml\,K_2}Cr_2O_7\,x\,0.167\,x\,6}{ml\ \mathrm{Fe(NH_4)_2(SO_4)_2}}$$

$$and\ f = average\ recovery\ factor = 1.3$$

The recovery factor specified above is designed to compensate for organic carbon, which remains unrecovered by the method. Empirical investigation of 20 soils by Walkley and Black showed an average of only 76% of the organic C in these soils to be recovered by heat of dilution. Nelson and Sommers (1982) argue that unless an appropriate f value is determined experimentally for each particular soil or sediment, the Walkley Black method will provide only approximate or semi-quantitative estimates of soil organic C content. Further factors affecting the accuracy of the method include interference by other soil constituents (e.g. $Cl^-$, $Fe^{2+}$ and $MnO_2$), and the assumption that the average oxidation state of the organic C is zero.

Duplicate organic carbon determinations conducted on sediments $WA4_{sed}$, $SA4_{sed}$ and $WM5_{sed}$ revealed residual standard deviation (RSD) values of less than 8% in each instance, suggesting good analytical precision. Organic carbon content was minimal (< 4%) for all lake sediment samples, except for $SA4_{sed}$ and $WA1_{sed}$, which each exceeded 20% organic carbon. These two samples appeared visually to contain considerably greater amounts of organic matter than the other samples.

## B.4: PARTICLE SIZE DISTRIBUTION

The particle size distribution of a sediment expresses the proportions of the various sizes of particles it contains. Fractionation and particle size analysis were determined for the coarser particle size fractions through sieving procedures. It is theoretically possible to further extract particles in the silt and clay size fraction, in accordance with settling velocities of spherical particles determined by Stokes Law (Kohnke, 1968). The sand-sized fraction showed great dominance over the combined latter fraction in all but two samples. For this reason, and in view of the complications and time demands associated with the sedimentation method, the mud sized fraction was not subjected to further separation.

The weight percentage of the coarse gravel fraction (>2 mm) of Lake Sibaya sediments was determined by passing wet sediment through a 2mm sieve. The mass of the dry coarse particles was determined, and expressed as a percentage of the entire sample (with due correction for the original mass percentage of water, determined by evaporative loss following heating.) The sediment size fraction (≤ 2 mm) passing through the wet-sieving procedure described above was dialysed against distilled water (to remove excess salts) and air-dried. The precise weight of a representative sample of this size fraction (± 100 g) was determined. Siliceous cementing agent, which might exist within these sediments, was removed by soaking overnight in 0.1 mol/*l* NaOH, and thereafter washing the sediment free of salts by centrifugation. Earlier analyses (refer to Sections B.2 and B.3) revealed that organic carbon- and carbonate- levels within Lake Sibaya sediment samples (with the exception of $\mathrm{WA1_{sed}}$ and $\mathrm{SA4_{sed}}$) were sufficiently low that their cementing and/or flocculating potential would be minimal.

Ten millilitres of Calgon dispersing solution was added to the pre-treated oven-dried sediment. The suspension was made up to approximately 150 ml with de-ionised water and shaken on a horizontal reciprocating shaker overnight. The dispersed sample was thereafter washed quantitatively on a 0.053mm sieve until the percolate showed clear. The sand was then transferred to a tared evaporation dish and dried at 105°C to constant mass. The dried sand was transferred to a nest of sieves arranged in decreasing size from top to bottom in the following order: 0.5; 0.25; 0.106; 0.053 mm. The sieves were well shaken and the mass of each sand fraction (and the residual silt plus clay that passed through the 0.053 mm sieve) was determined. A precision of 0.01 g was achieved.

## B.5: CLAY MINERALOGY (X-RAY DIFFRACTION)

Both the physical and chemical properties of any sediment are controlled to an immense extent by the mineralogy of such sediment, and particularly by that of the clay fraction. The clay fractions of sediments are commonly composed of mixtures of one or more secondary phyllosilicate minerals, co-occurring with primary minerals inherited directly from the parent material. One of the most informative techniques of positively identifying such mineral species and estimating their proportions is x-ray diffraction analysis. This technique relies upon the principles of the periodicity of arrangement of atoms within crystals, and upon the wave nature of x-rays.

In brief, the principle of x-ray diffraction involves the scattering of a collimated beam of monochromatic x-rays by atoms of a crystal, and the reinforcement of scattered rays in definite directions away from the crystal. Reinforcement of scattered rays is quantitatively related to the distance of separation of atomic planes, as defined by Bragg's law:

$$n\lambda = 2d\sin\theta$$

Each crystalline species contains planes of atoms separated by a constant distance characteristic of that species. Since no two minerals possess exactly the same interatomic distances in three dimensions, the angles at which diffraction occurs will be distinctive for a particular mineral. The interatomic distances within a mineral crystal therefore result in an unique array of diffraction maxima, which serve to identify that mineral (Whittig and Allardice, 1986.)

## B.5.1: Sample preparation

### *B.5.1.1 Clay isolation and slide mounting*

To ensure detection of mineral species in a clay sample by x-ray diffraction analysis, it is highly advantageous to concentrate the individual species as far as possible. Segregation and concentration of mineral species present in the clay fraction (< 0.2μm) of Lake Sibaya sediments was achieved by means of dispersion in a dilute $Na_2CO_3$ solution of pH 10. The supernatant solution was repeatedly siphoned off after various time intervals, and at various depths, in accordance with settling rates determined by Stokes' Law. The clay fraction which remained was flocculated, via the adjustment of solution pH to approximately 5 (through the addition of 0.1*M* HCl) and the introduction of sodium chloride. These flocculated clays were concentrated-up by centrifugation, and were thereafter successively dialysed against tap water and distilled water, so as to remove excess salinity. The clay concentrations within the resultant solutions were each adjusted to approximately 20 mg/l.

The clay sample extracts obtained by the method described above were mounted as an oriented aggregate, to encourage preferential orientation of layer-silicate species. An advantage of this method over random-powder samples is the enhancement of basal (00*l*) diffraction maxima, thereby allowing detection of small quantities of phyllosilicate species, which might otherwise be obscured among more crystalline or more perfect diffracting species in the sample (Whittig and Allardice, 1986.) As little as 1% smectite has been detected in polycomponent mixtures using such a mount (MacEwan, 1946.)

Porous ceramic-plate mounted aggregate was prepared according to the method specified by Kinter and Diamond (1966.) Clay extracts were mounted on unglazed tiles cut to appropriate dimensions (approximately 5.0cm diameter and 0.5 cm depth) and smoothed by wet grinding on a glass plate with fine-grade corundum abrasive. A dilute suspension (containing approximately 20 mg of clay) was added to the surface of each porous tile. The liquid was separated from the clay by suction (applied to Buchner Funnel apparatus via a vacuum pump), leaving clay oriented on the surface. The surface of each moist mounted sample was smoothed with a glass slide held at an angle to the sample. This smoothing technique has been shown by Thiesen and Harward (1962) to markedly increase the basal (00*l*) x-ray diffraction maxima from phyllosilicate species in many instances. Diffraction intensities from (00*l*) planes are normally highest per unit of clay for phyllosilicate mineral species (Whittig and Allardice, 1986.)

A significant benefit to mounting the clay extracts on a porous plate is the fact that they may be treated, prior to each stage of analysis, by applying successive portions of the appropriate solution to the surface, and pulling the solution through the plate by suction. The use of single mounted samples therefore negates the need for preparation of a separate mount for each treatment and x-ray diffraction analysis.

### *B.5.1.2 Saturation of the clay exchange complex*

Phyllosilicates possess many similar or identical structural features which render their differentiation and identification more complex than most mineral species. Selected sediment samples that showed significant peak intensities in the d-spacing range characteristic of phyllosilicate minerals, were therefore exposed to various treatments and analysed by x-ray diffraction, so as to aid in their identification. Both the distances between crystal layers, and the intensity of diffraction from expansible phyllosilicates, vary with the nature of the liquid present between layers.

Since expansible phyllosilicates may retain different amounts of interlayer water - depending upon the nature of interlayer exchangeable cations - it is imperative that a clay sample prepared for diffraction analysis be homoionic, to ensure that expansion as a result of hydration will be uniform within all crystals of a species. Furthermore, since clay samples are commonly analysed after air-drying, it is advisable to exchange-saturate the clay with a cation that will minimise changes in interlayer water adsorption due to fluctuations in relative humidity (Whittig and Allardice, 1986). Magnesium (which allows relatively uniform interlayer adsorption of water by expansible phyllosilicates) and potassium (which specifically restricts interlayer adsorption of water by vermiculite) are most commonly used for exchange-saturation (Walker, 1957.) The methods of reaching saturation of the exchange complex in the selected clay suspensions chosen for analysis of layer silicates are those described by Jackson (1969.) Brief descriptions of the methods followed are presented below..

**Magnesium saturation**

The formation of a stable, two-layer water complex between layers of air-dried, Mg-saturated members of the smectite and vermiculite series allows for the differentiation of these 2:1 phyllosilicates from those of their non-expansible counterparts. The expansion of layers in the former members results in an inter-atomic spacing of approximately 1.4-nm between (00*l*) planes, as opposed to the non-expansible members which maintain an inter-atomic spacing of approximately 1,0-nm.

The pH of an aliquot of dispersed clay suspension containing approximately 20 mg of clay was adjusted to approximately 6, through drop-wise addition of 0.1*M* HCl. Sufficient 5*M* $MgCl_2$ was pulled through the porous ceramic tiles so as to render each clay suspension approximately 0.5*M* with respect to Mg. Each sample was further washed twice with approximately 10 ml of 0.5*M* $MgCl_2$. Excess salts were removed from the exchange-saturated samples by washing once with 50% methanol, once with 95% methanol, and finally with 95% acetone, until the clear percolate yielded a negative test for chloride with 0.1*M* $AgNO_3$.

**Glycerol solvation**

The diffraction spacing of approximately 1.4 nm obtained from a Mg-saturated air-dried sample may be contributed by smectite, vermiculite, chlorite, or by a mixture of these species (Whittig and Allardice, 1986.) Glycerol solvation is required in order to separate and positively identify smectite. The principle underlying this differentiation involves the ability of smectite members to absorb double sheets of glycerol molecules between adjacent layers, thereby yielding a basal spacing of approximately 1.77-nm. In contrast, the interlayer expansion of vermiculites with glycerol solvation is negligible, thus allowing differentiation to be made between these two groups (Walker, 1950.)

Mg-saturated samples, mounted on porous ceramic plates as oriented aggregate samples, were glycerol-solvated by twice passing a 1:1 glycerol-water solution through the sample by suction. Direct solvation of a sample in this manner essentially eliminates the uncertainty associated with determining the correct amount of glycerol to be added to each slide (Whittig and Allardice, 1986.)

### Potassium saturation

Detection of non-expansible 1.4-nm chlorites (2:2 phyllosilicates) requires further diagnostic tests for positive differentiation from 1.4-nm vermiculite. K saturation of vermiculites will result in their collapse to essentially non-expanded structures (1.0-nm), whereas most chlorites will remain unaffected (Barshad, 1948.)

Mounted clay samples containing approximately 20 mg of dispersed clay suspension were leached sufficiently often with 1*M* KCl so as to complete saturation of the clay with potassium. Excess salts were removed from the exchange-saturated samples in the same manner as that outlined for the magnesium saturation method.

### Heat treatment of clay slides

The mounted K-saturated clay samples referred to above were heated to 110°C overnight, and thereafter to 550°C for two hours, so as to accomplish two important functions, namely: (i) to effect collapse of vermiculite containing non-exchangeable interlayer hydroxy complexes and, (ii) to destroy the kaolin minerals (Whittig and Allardice, 1986.)

Hydroxy interlayers (Al, Fe or Mg) frequently occur in vermiculite and smectite species as randomly spaced islands between phyllosilicate layers (Klages and White, 1957.) In contrast, hydroxy interlayers in chlorites are continuous and fully polymerised (Barnhissel, 1977.) The presence of these hydroxy layers in the vermiculite structure, in particular, complicates the differentiation of smectites from chlorites (Whittig and Allardice, 1986.) Applying intense heat to K-saturated samples will collapse discontinuous hydroxy complexes, but will not affect most chlorites (Barnhissel, 1977.)

When chlorite is present in a sample, it normally yields a second-order maximum at virtually the same position as the first-order maximum of kaolinite (0.715 nm) or serpentine (0.71-0.73 nm.) However, if a 0.715 nm maximum, obtained from an unheated sample, disappears or decreases in intensity after heating at 550°C, this then serves to confirm the presence of kaolinite.

### B.5.2: Examination of clays by X-ray diffraction

Clay mineralogy was determined by scanning the slides using a Philips X'PERT SYSTEM PW 1390 X-ray diffractometer, controlled by a PW3710 diffractometer control unit. Analysis was conducted using a PW3020 vertical goniometer, a PW3011 proportional detector, a PW1386/55 automatic divergence slit, and a PW1752/00 curved graphite monochromator. Reproducibility using the vertical goniometer is specified as approximately 0.0001° at 2θ (Philips Analytical, 1992.) A PW2233/20 copper long fine focus (LFF) tube (Cu Kα = 1.542 Å) operating at 40 kV and 25 mA was used for the analysis. Copper radiation is not greatly affected in most cases by air or sample absorption, and it provides adequate resolution [typical energy detection resolution is 19% (Philips Analytical, 1992)] for most mineral analyses (Whittig and Allardice, 1986.)

The untreated clay samples were initially scanned, (in the step scan mode) through a range of 4.0 to 70.0° 2θ, operating at a step size of 0.05° 2θ and a counting time of 1 second/step. Treated samples (Mg- and K- saturation, glycerol solvation) were later scanned over a range of 4.0 to 25° 2θ, operating at a step size of 0.01° 2θ and a counting time of 0.5 seconds/step.

Where differentiation treatments were required to identify various phyllosilicates, diffractograms were examined in the following order (i) Na-saturated, air dried sample; (ii) Mg-saturated, air dried sample; (iii) Mg-saturated, glycerol-solvated sample; (iv) K-saturated, air-dried sample; (v) K-saturated sample heated to 110°C; and (vi) K-saturated sample heated to 550°C. Whittig and Allardice (1986) report this sequence of observation as being the most efficient in terms of identification and differentiation of species. The practical problem of the clay samples cracking up on the slides following each successive treatment, had the outcome that only one of the total of fourteen sediment clay fraction samples ($WM5_{sed}$) was successfully examined under the complete set of treatments. The likely cause of this is the incomplete segregation of the clay fraction from that of the silt fraction, leading to a coating of uneven thickness on the surface of the slide. Time constraints prevented the repeat of the clay segregation process.

### B.5.3: Interpretation of x-ray diffractograms

Qualitative interpretation of diffraction patterns was achieved by determining the interatomic spacings giving rise to the various maxima, and comparing these spacings-, and the intensity thereof-, with known spacings of minerals (Anon, 1980.) Since the geometry of the spectrometer-, and the wavelength of radiation- are fixed, the angle of diffraction from diffracting planes was directly dependent upon the interplanar distances. Diffraction angles were obtained (in terms of 2θ) from the spectrometer pattern, and were then converted to the corresponding diffraction spacings, through the implementation of the Bragg equation.

Since the intensities of diffraction maxima relate to the number of corresponding diffraction planes in a sample, the relative intensities of maxima theoretically provide a basis for the estimation of the concentrations of mineral species present. In reality, however, estimation of mineral percentages based on X-ray diffraction alone is, at best, semi-quantitative, owing to variations in chemical composition, crystal perfection, amorphous substance, and particle size (Jackson, 1969.)

In general, the X-ray diffractograms obtained for the clay fraction of the Lake Sibaya sediments show high levels of background radiation. Non-directional scatter of X-radiation from materials amorphous to X-rays (presumably principally organic matter and amorphous silica) served to lower the ratio of diffraction maxima to background, and thus decreased the sensitivity of the analysis.

## B.6: X-RAY FLUORESCENCE SPECTROMETRY (XRFS)

Major and trace element concentrations within all 14 sediment samples collected from Lake Sibaya were determined by X-ray fluorescence spectrometry (XRFS.) A Philips X'Unique II X-ray spectrometer, housed within the Department of Geological Sciences at the University of Cape Town, was used for the analysis. Analytical conditions for the XRF analysis were as stated in Willis (1995.) Calibration was by means of international reference materials (BHVO-1, BIR-1, JB-2, JG-1, JG-2, JR-2, STM-1, W-2, NIM-G, NIM-S and R16.)

Wet sediment was dialysed against distilled water to remove excess salts, and was thereafter oven-dried at 50°C. Approximately 80 grams of each dried sediment sample was ground to a particle size of –300 mesh (approximately 40μm) in a carbon-steel vessel, using a Siebtechnik swing mill. Powder briquettes consisted of 6 grams of crushed sample, combined with 6 drops of Mowiol binder (2% Hoescht Mowiol N 70-80 in distilled water.) Powder briquettes for two sediment samples which appeared to be rich in organic matter ($SA4_{sed}$ and $WA1_{sed}$) were formed by using Hoescht Wax as the binder (8g sample: 2g wax.) Briquettes were pressed in a 30 mm die under 10 tons of pressure, with boric acid acting as backing. The trace elements determined on powder briquettes included Co, Mn, Cr, V, Mo, Nb, Zr, Y, Sr, U, Rb, Th, Pb, Zn, Cu, Ni and S.

Fusion discs were prepared for the analysis of major elements by X-ray fluorescence spectrometry. Approximately 3 g of –300 # sample was dried at 110°C for 5 hours, to determine any residual water. The sample was then roasted at 1000°C overnight, so as to determine loss on ignition (LOI.) In the case of the organic rich samples alluded to above, a gradual stepwise ashing procedure (spanning the temperature range of 110°C to 1000°C) was followed, so as to minimise the production of smoke. Fusion discs were made by combining 0.7 g of roasted sample with 6 g of Sigma 12:22 flux and 4 drops of wetting agent (2.9*M* LiBr.) Discs were produced in automatic mode by a Claisse Fluxy instrument, operating under program 8. Major elements determined (as oxides) were $SiO_2$, $TiO_2$, $Al_2O_3$, $Fe_2O_3$, MnO, MgO, CaO, $K_2O$, $P_2O_5$, $Na_2O$ and $SO_3$. The lower limits of detection for the major elements (refer to Table B.1) were determined according to the formula overleaf (Willis, 1995).

$$LLD(in\,ppm) \;=\; \frac{6}{m}\sqrt{\frac{I_b}{T_{total}}}$$

where: m = net peak/concentration

$I_b$ = background count rate under the peak in cps

$T_{total}$ = counting time for peak in seconds ($T_p$) + total counting time for background in seconds ($T_b$)

**Table B.1:** Lower limits of detection for major elements determined by XRFS

| | Sensitivity (kcps/%) | Background (kcps) | LLD (ppm) |
|---|---|---|---|
| Ni | 3.40 | 0.015 | 3.45 |
| Al | 0.32 | 0.049 | 65.1 |
| Mn | 1.46 | 0.029 | 11.1 |
| Ti | 0.87 | 0.017 | 14.2 |
| K | 5.53 | 0.006 | 1.28 |
| P | 1.09 | 0.001 | 2.88 |
| Na | 0.02 | 0.001 | 106 |
| Si | 0.34 | | |
| Fe | 1.69 | 0.100 | 17.8 |
| Cr | 1.14 | 0.007 | 7.10 |
| Ca | 7.25 | 0.092 | 3.96 |
| S | 1.00 | 0.055 | 22.1 |
| Mg | 0.07 | | |

## B7 EXCHANGEABLE ELEMENTS

Exchangeable elements in the sediments were determined using standard methods described in the handbook compiled by the Non-Affiliated Soil Analysis Work Committee and published by the Soil Science Society of South Africa (SSSA, 1990). These methods are the standard against which the performance of laboratories participating in the control scheme of the Fertiliser Society of South Africa, (administered by the Department of Soil Science and Plant Nutrition, University of Pretoria) are evaluated.

### B7.1 Bray-2 extraction of P

Acid soluble, adsorbed or available, and reserve phosphates present in the Lake Sibaya sediments were extracted by means of the Bray-2 procedure developed by Bray and Kurtz (1945). The extraction of P by this method is based on the solubilisation effect of $H^+$ on soil P, and the ability of $F^-$ to lower the activity of $Al^{3+}$ and, to a lesser extent, that of $Ca^{2+}$ and $Fe^{3+}$ in the extraction system. $F^-$ also complexes $Al^{3+}$, thereby increasing the solubility of aluminium phosphate compounds and, by precipitation as CaF, releases P from calcium phosphate compounds. This method is suitable for the highly weathered sediments, of low to medium CEC, which underlie Lake Sibaya. The method is further suited to the two organic-rich gyttja sediments that were analysed.

Bray-2 solution, (consisting of 600 $cm^3$ $NH_4F$ stock solution and 200 $cm^3$ concentrated HCl, diluted up to 20 $dm^3$ with de-ionised water) was added to sediment sample and shaken thoroughly, before filtration through Whatman No. 2V filter paper. Phosphorus-free charcoal was added to the filtered suspension to remove interfering organic acids and to decolourise the extract, which was thereafter further shaken. This extract is thus not suitable for the determination of microelements. Superfloc N-100 flocculant was added to the suspension, which was then filtered through Whatman No. 40 paper. Determination of total phosphates in the extracts was by ICP.

### B7.2 Di-ammonium EDTA extraction of Cu and Zn

The extraction of the microelements Cu and Zn was by the di-ammonium EDTA method described by Beyers and Coetzer (1971). Air-dried soils were crushed to a fineness of ≤ 1mm in a porcelain mortar. To this sediment was added 0.02 mol/l $(NH_4)_2$ EDTA solution. The sample suspensions were thereafter shaken on a reciprocating shaker at constant temperature (20°C), whereafter they were centrifuged and filtered through Whatman No. 40 paper. Cu, Mn and Zn were determined by ICP, using respective calibration standards ranging between 1 to 10μg Cu/$cm^3$; 1 to 4μg Mn/$cm^3$; and 0.5 to 2μg Zn/$cm^3$, each prepared in 0.02 mol/$dm^3$ $(NH_4)_2$ EDTA.

### B7.3 Hot water extraction of B

Water-soluble boron (which is considered to be immediately available to plants) was extracted from the Lake Sibaya sediments by hot water, as described in FSSA (1974). Air dry sediment was placed into a soda glass Erlenmeyer flask, and thereafter well-mixed with de-ionised water, at a soil:water ratio of 1:2. The flask was stoppered, heated on a hotplate to 80°C, and subsequently placed in an oven, set at 80°C, for 5 minutes. Calcium chloride solution (0.05 mol/$dm^3$) was added to the flask, after which the contents were shaken and filtered through Whatman No. 542 paper. Hot water extractable B was determined by ICP, using de-ionised water as the blank.

### B7.4 Ammonium acetate (1 mol/$dm^3$, pH 7) extractable cations

The ammonium acetate method was used to determine extractable cations $Ca^{2+}$, $Mg^{2+}$, $K^+$ and $Na^+$ in the Lake Sibaya sediments, as an indication of their nutrient status. The method is described in SSSA (1990). Since $CaCO_3$ was shown to be negligible in, or perhaps absent from, these sediments, the cations $Ca^{2+}$, $Mg^{2+}$ and $Na^+$ are expected to be completely exchangeable by $NH_4AOc$. Extraction was performed on moist sediment samples at 20°C. $NH_4OAc$ solution (1 mol/$dm^3$, pH 7, 20°C) was added to the sediment, and thoroughly shaken on a reciprocating shaker. The extract was thereafter rapidly filtered through a Buchner funnel, to which suction was applied. The filtrate was refiltered until clear, and immediately analysed by ICP.

## B8 IDENTIFICATION OF DIATOMS

A basic investigation was conducted on the diversity of diatom genera within four of the collected sediment samples, being the two gyttja samples ($WA1_{sed}$ and $SA4_{sed}$) and two siliceous samples collected from the WM transect (samples $WM1_{sed}$ and

$WM4_{sed}$). The dominant genera in these waters were identified from their frustule (skeletal) morphology, and a qualitative indication of their relative abundance was provided. The investigations were conducted by Mrs M. Joska of the Freshwater Research Unit, University of Cape Town. None of the samples was preserved with formalin upon collection.

# APPENDIX C: GROUNDWATERS FROM DRAINAGE REGION W70 (DWAF DATABASE).

**Note: All values are in units of mg/l, with the exception of EC (mS/m) and pH (unit-less).**

| HOLE NO. | DATE | LATITUDE (decimal degrees) | LONGITUDE (decimal degrees) | PLACE NAME | EC | TDS | pH | Na | Mg | Ca | F |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 94007494 | 19940410 | -27.0161 | 32.14167 | RESERVE | 26.5 | 153 | 7.4 | 33 | 4 | 4.5 | 1 |
| 94022641 | 19941021 | -27.0192 | 32.70167 | SHANGEZA | 20.4 | 117 | 6.8 | 26 | 4.1 | 3.3 | 0.09 |
| 94022483 | 19941019 | -27.0422 | 32.42194 | SIHANGWANE | 498 | 2954 | 7.9 | 522 | 90.6 | 377.7 | 0.1 |
| 94022690 | 19941024 | -27.0475 | 32.44778 | MAHLASELA | 161 | 1179 | 7.9 | 292 | 10.2 | 47.2 | 0.2 |
| 94022495 | 19941019 | -27.0492 | 32.41722 | SIHANGWANE | 368 | 2200 | 7.6 | 413 | 60.2 | 247.9 | 0.1 |
| 94022562 | 19941020 | -27.0806 | 32.56333 | PELINDABA | 47.9 | 274 | 7.7 | 73 | 5.7 | 7.3 | 0.19 |
| 94022550 | 19941020 | -27.0808 | 32.56083 | PELINDABA | 69.9 | 510 | 8.1 | 48 | 15.8 | 65.4 | 0.24 |
| 94022549 | 19941020 | -27.0839 | 32.48556 | MDONINI GAT 6 | 57.6 | 324 | 7.4 | 74 | 7.1 | 18.3 | 0.36 |
| 94007500 | 19940409 | -27.1189 | 32.02639 | RESERVE | 68.7 | 578 | 8.7 | 161 | 1.7 | 3.7 | 5.55 |
| 94022574 | 19941020 | -27.1356 | 32.55917 | NDL. SCHOOL | 27.9 | 160 | 6.8 | 36 | 5.5 | 7.3 | 0.4 |
| 94022586 | 19941020 | -27.1564 | 32.15639 | MQH. PRIMARY | 21.1 | 120 | 6.7 | 23 | 2.6 | 7 | 0.18 |
| 94022665 | 19941022 | -27.1614 | 32.09972 | NJOBENI | 209 | 1365 | 7.9 | 318 | 35.8 | 70.5 | 0.61 |
| 94022598 | 19941020 | -27.1658 | 32.16583 | M VELABUSHA | 24.5 | 186 | 6.9 | 32 | 5.9 | 6.8 | 0.14 |
| 94022653 | 19941021 | -27.1869 | 32.65778 | PLANTATION | 17 | 113 | 7.6 | 10 | 2.8 | 9.5 | 0.11 |
| 94022689 | 19941022 | -27.2481 | 32.76083 | ROCKTAIL BAY | 20 | 102 | 6.4 | 26 | 3.8 | 2.5 | 0.15 |
| 94022847 | 19941026 | -27.2786 | 32.42889 | MANABA | 32.8 | 153 | 6.2 | 44 | 4.1 | 4.4 | 0.1 |
| 94022884 | 19941026 | -27.3103 | 32.60361 | KWA SONTE | 20.6 | 119 | 7.5 | 17 | 2.9 | 12.2 | 0.13 |
| 94022896 | 19941026 | -27.3192 | 32.73778 | MABIBI | 30 | 177 | 7.3 | 26 | 3.2 | 18.2 | 0.13 |
| 94022860 | 19941026 | -27.3603 | 32.53472 | MSELENI | 111 | 822 | 8.1 | 165 | 9.9 | 58.6 | 0.29 |
| 94022872 | 19941026 | -27.4003 | 32.56028 | KWAMBOMA | 23.1 | 131 | 7.7 | 27 | 4.6 | 5.4 | 0.16 |

**Continued overleaf**

**APPENDIX C… (Continued from previous page)**

**Note: All values are in units of mg/l.**

| HOLE NO. | PLACE NAME | Cl | $NO_3$+$NO_2$ (as N) | $SO_4$ | $PO_4$ (as ortho-P) | TAL (as $CaCO_3$) | Si | K | $NH_4$ (as N) |
|---|---|---|---|---|---|---|---|---|---|
| 94007494 | RESERVE | 38.2 | 4.6 | 11.2 | 0.026 | 31.4 | 18.29 | 2.69 | 0.051 |
| 94022641 | SHANGEZA | 37.7 | 1.916 | 6.7 | 0.14 | 19.6 | 5.31 | 5.9 | 0.001 |
| 94022483 | SIHANGWANE | 1291.9 | 8.129 | 327.5 | 0.007 | 237.5 | 16.52 | 18.05 | 0.038 |
| 94022690 | MAHLASELA | 243.6 | 0.026 | 19.8 | 0.049 | 454.6 | 23.11 | 11.59 | 0.008 |
| 94022495 | SIHANGWANE | 875.1 | 7.316 | 247.3 | 0.005 | 255.9 | 15.7 | 11.92 | 0.028 |
| 94022562 | PELINDABA | 112.1 | 0.005 | 9.5 | 0.023 | 51.1 | 10.44 | 3.59 | 0.008 |
| 94022550 | PELINDABA | 84.2 | 0.009 | 5 | 0.018 | 233.9 | 20.08 | 6.21 | 0.005 |
| 94022549 | MDONINI GAT 6 | 126.4 | 0.973 | 10.4 | 0.143 | 61.4 | 13.91 | 7.69 | 0.007 |
| 94007500 | RESERVE | 45.9 | 0.028 | 16.6 | 0.015 | 280.2 | 16.59 | 1.51 | 0.015 |
| 94022574 | NDL. SCHOOL | 54.3 | 1.071 | 22.1 | 0.013 | 22.4 | 4.72 | 2.6 | 0.026 |
| 94022586 | MQH. PRIMARY | 51.7 | 0.147 | 6.6 | 0.044 | 16.5 | 8.2 | 6.78 | 0.395 |
| 94022665 | NJOBENI | 400 | 0.051 | 69.6 | 0.008 | 383.3 | 22.3 | 3.3 | 0 |
| 94022598 | M VELABUSHA | 39 | 15.349 | 10.6 | 0.042 | 17 | 7.15 | 2.69 | 0.006 |
| 94022653 | PLANTATION | 21.3 | 1.275 | 8.6 | 0.285 | 34 | 5.12 | 12.46 | 0.009 |
| 94022689 | ROCKTAIL BAY | 28 | 3.175 | 16.1 | 0.036 | 8.9 | 3.62 | 0.46 | 0.014 |
| 94022847 | MANABA | 51.9 | 1.348 | 22.2 | 0.097 | 11.6 | 11.21 | 5.94 | 0.02 |
| 94022884 | KWA SONTE | 28.1 | 0.023 | 9 | 0.013 | 37.2 | 7.93 | 3.98 | 0.006 |
| 94022896 | MABIBI | 49.1 | 0.942 | 11.9 | 0.019 | 46 | 7.05 | 7.59 | 0.019 |
| 94022860 | MSELENI | 157.2 | 0.988 | 11.4 | 0.021 | 336 | 17.34 | 5.05 | 0.016 |
| 94022872 | KWAMBOMA | 40.7 | 2.233 | 5.1 | 0.018 | 29.5 | 8.98 | 1.82 | 0.016 |

## APPENDIX D: THE MINTEQA2 CHEMICAL SPECIATION MODEL

As discussed in Section 3.3.3.1, MINTEQA2 uses an approach of iterative guesses at the activity of each chemical component to calculate the equilibrium concentration of each species. In this study the Davies equation (an extension of the Debye-Hückel equation) was used to calculate activity coefficients for all charged species. This equation assigns equal ion size-dependent parameters for each charged ion (Lumsdon and Evans, 1995).

Aqueous phase equilibrium composition constitutes that set of species concentrations which gives a mass imbalance less than the pre-set tolerance level for each component. After equilibrating the aqueous phase, MINTEQA2 computes the saturation index (SI) for each possible solid with respect to the solution. This is achieved through comparing the logarithmic ratio of the ion activity product (IAP) of each solid with the corresponding formation constant (K) after the aqueous phase has been equilibrated, such:

$$Saturation\,Index = \log \frac{IAP}{K}$$

The solid with the most positive SI is allowed to precipitate by depleting the dissolved concentrations of those components comprising the solid, in accordance with the stoichiometry of each component. The reverse process occurs if an existing solid is found to be under-saturated with respect to the solution. The entire computational loop of iterating to equilibrium, checking for precipitation or dissolution, and shifting mass from the aqueous to the solid phase or vice versa is repeated until equilibrium is achieved and there are no over-saturated possible solids and no under-saturated existing solids. The user-defined option for disallowing the precipitation of solids was chosen for each of the water samples modelled, owing to the inherent assumption within the program code that no solid phase exists in the titrated solution possessing additional acid-neutralising capacity (as in the form of alkalinity).

A major source of uncertainty in the modelling of element speciation (and therefore mineral saturation indices) involves the incorporation of dissolved organic matter (DOM) into the model, and the resultant effect on speciation. DOM is largely composed of poorly defined, heterogeneous molecules of high molecular weight, constituting a complex amalgam of ligand types with varying affinity for protons and metal cations. DOM has a strong tendency to complex Al in particular and, in addition to its considerable effect on Al speciation, can significantly increase the total concentration of Al in solution (Driscoll, 1989). For this reason, the output obtained from any speciation and mineral solubility model should be treated with due scepticism, particularly with regard to predictions of the solubility of aluminium mineral species.

Binding site concentrations (L) were estimated, for input into the MINTEQA2 model, using the empirical relationship determined for Suwannee River fulvic acid (US EPA, 1991): $L(moles\,of\,sites) = (DOC\,x2)(5x10^{-4})$. The effect of various DOM concentrations on the mineral solubility modelled by MINTEQA2 is presented in Section 3.4.5.