

**GEOCHEMICAL AND LIMNOLOGICAL ASPECTS OF
PHOSPHOROUS CONTAMINATION IN THE NOORDHOEK
VALLEY, CAPE PENINSULA.**

by

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ABSTRACT

The Noordhoek Valley is situated on the Atlantic coast of the Cape Peninsula, South Africa (34°07'S, 18°22'E). Towards the east, the valley hosts numerous townships, while to the west it opens into a lowland marsh area, bordered by a five-kilometre beach. The wetland is subjected to various forms of anthropogenic pollution; the two most important being the discharge of urban runoff and treated effluent from the local sewage works. During the period of the study (Jan-Oct 1998), the occurrence of toxic cyanobacteria of the species *Microcystis aeruginosa* was reported for the two main water bodies within the wetland. The objective of this study was to conduct an investigation of geochemical and limnological aspects of phosphorus contamination within the wetland. The investigation concentrated on the two main waterbodies of the wetland: The Lake and Wildevölvlei.

Two sets of water samples were taken from The Lake and its stormwater drainage system, the Sun Valley/ Fish Hoek wetland, in May and August 1998. Data collected from previous water quality assessments were used to supplement this study in order to give an overall chemical characterisation of The Lake and to assess its suitability for blue-green algae. Sediment samples, collected from The Lake, the Sun Valley/Fish Hoek wetland and Wildevölvlei were analysed to determine the pollution status of the vleis and the relative phosphorus adsorption capacity of the vlei sediments. Geochemical modelling, using MINTEQA2 and PHREEQC, was used to deduce the operative geochemical reactions that are likely to govern phosphorus mobility in the wetland. In addition, the accumulation of the bluegreen algae toxin microcystin in Wildevölvlei sediment and fish was investigated.

The water column in The Lake appears to be generally well-mixed, due to its shallow basin morphometry and strong prevailing winds. Occasional fish kills suggest that under calm conditions stagnation does occur, resulting in the release of sediment H_2S . By the beginning of winter (May), after two successive blooms of dinoflagellates and blue green algae, the pH of The Lake was found to be neutral to alkaline, varying from 6.81 to 8.57. Total alkalinity was high with an average of $180 \text{ mg. CaCO}_3.\text{L}^{-1}$ in the vlei, whereas $46 \text{ mg CaCO}_3.\text{L}^{-1}$ was measured in the incoming stormwater. The average conductivity in The Lake was calculated to be 423 mS.m^{-1} , which characterises The Lake as saline. The ionic composition of The

Lake is that of diluted seawater, with Na being the dominant cation and Cl the dominant anion. The marine signature is explained by the proximity of The Lake to the Atlantic Ocean, as well its hydraulic conductivity with a saline aquifer.

The Lake is characterised by a local catchment, utilising only groundwater and winter runoff as recharge and is subjected to a seasonal water table fluctuation of approximately 1 m. Seasonal decalcification was observed, induced by high primary production and evaporation in summer. 70 % of the hydraulic winter input stems from urban stormwater runoff. The runoff is characterised by a higher relative Ca and HCO_3 concentration than The Lake.

The organic matter content measured as COD was found to be high, ranging from 32 to 114 mg.L^{-1} . The average COD concentration (96 mg.L^{-1}) of The Lake was found to be higher than the COD concentration measured in the incoming stormwater (63 mg.L^{-1}). A dense stand of *Potamogeton pectinatus* is considered to be the major source of organic material in The Lake. Nutrient concentrations in The Lake were high. NH_4 concentrations ranged from 0.22 to 0.37 mg.L^{-1} , whereas NO_3 concentrations were measured to be between 0.05 and 0.07 mg.L^{-1} . The source of the high NH_4 concentration is thought be decaying plant material within The Lake. Phosphorus concentrations were found to be between 0.25 and 0.10 mg.L^{-1} , and 0.02 and 0.21 mg.L^{-1} for TP and ortho-P (measured as soluble reactive P), respectively. P concentrations in the incoming stormwater were found to be twice as high as in The Lake and, therefore, P is being imported into The Lake from the catchment. An evaluation of annual (1998) P concentrations in The Lake showed that, according to the OECD classification, The Lake is eutrophic with respect to phosphorus.

Sediment samples were found to be distinctly different for the different vleis. The Lake and the Sun Valley/Fish Hoek wetland were characterised by calcareous, strongly reduced, very sulphur rich sediments, whereas sediments of Wildevoëlvlei displayed all the characteristics of sewage sludge. Diversity of benthic macrofauna was found to be very low, with only oligochaetes and diptera being found. Sediments of The Lake and the Sun Valley wetland were classified as loamy sand and sandy loam, whereas Wildevoëlvlei sediments were characterised as sand. The differences in particle size are linked to the positions of the vleis within the catchment.

Mineralogical data were only obtained for sediments of The Lake and the Sun Valley/Fish Hoek wetland. Diffractograms of the clay fractions showed the presence of kaolinite, pyrite and quartz. Significant amounts of kaolinite were only identified in samples from the Sun Valley/Fish Hoek wetland and the eastern part of The Lake, whereas pyrite is the dominant mineral in sediments from the eastern part of The Lake.

Analyses of readily available P using an alkaline extraction yielded 32 to 60 mg.kg⁻¹ for calcareous sediments (The Lake, SunValley wetland), whereas acidic P extraction of Wildevoëlvlei sediments resulted in values of 116 to 325 mg.kg⁻¹. Total P concentrations, as determined by XRFS, ranged from 160 mg.kg⁻¹ to 1667 mg.kg⁻¹ for sediments of The Lake, whereas P concentrations in Wildevoëlvlei sediments ranged from 525 to 4647 mg.kg⁻¹. A significant correlation ($p < 0.04$) between the total P concentration and the organic carbon content was found for all sediments.

Phosphorus adsorption isotherms obtained for sediments showed a saturation of the Wildevoëlvlei sediments with respect to P. P adsorption isotherms for sediments of The Lake and the Sun Valley/Fish Hoek wetland fitted the Freundlich equation. With the exception of Fish Hoek vleis sediments, the P adsorption capacity of sediments was estimated to be very high. The adsorption coefficient determined by the Freundlich equation ranged from 329 to 1660. It is hypothesised that the very high P adsorption capacity of the Noordhoek wetland sediments is an artefact of the analytical method that was used to determine the P adsorption isotherms. Due to the nature of the method applied, the number of adsorption sites was artificially increased, by a) aerating (oxidising) the sediments and b) increasing the specific surface area by dispersing the sediments. Geochemical modelling using the PHREECQ chemical model showed that the formation of Fe phosphates is a function of the O₂ content in the sediments. The higher the oxygen content in the sediments the more monosulphides are oxidised leading to an increase in Fe³⁺ in solution. The high affinity between Fe³⁺ and PO₄⁻ not only results in an overall decrease of free PO₄⁻ in solution, but also competes with the divalent Ca and Mg ions, leading to destabilisation of Ca phosphates.

Under natural conditions the dense growth of *P. pectinatus* is assumed to prevent resuspension of the sediments. It is hypothesised that the high S content and the strongly reducing conditions decrease the Fe³⁺ activity and prevent the formation of Fe phosphates.

The main mechanism of P removal from the water column is thought to be via formation of Ca phosphates.

Dissection of the fish *Liza richardsoni* collected during the *M. aeruginosa* bloom in Wildevoëlvlei showed that the fish were feeding on the algae. Toxin analysis carried out on livers from *L. richardsoni* did not yield any detectable microcystin concentrations. Accumulation of the toxin in the sediment of the vlei did not occur either. Adsorption experiments showed that microcystin-RR has a high affinity for Wildevoëlvlei sediments. It is proposed that the accumulation of microcystins depends mainly on two factors: the extracellular microcystin concentration in the water and the presence of a competent degradative microflora. In the context of Wildevoëlvlei accumulation of microcystin in either fish or vlei sediments is not considered a health risk.

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CHAPTER 1

BACKGROUND INFORMATION

1.1 Introduction

The Noordhoek Valley is situated on the Atlantic coast of the Cape Peninsula, South Africa (34°07'S, 18°22'E) (Figure 1.1). Towards the east the valley hosts numerous townships, while to the west it opens into a lowland marsh area, bordered by a five-kilometre beach. The marsh land gives rise to numerous seasonal vleis and two permanent water bodies of which one functions as an estuary, connecting the wetlands with the sea (Figure 1.2). Purselove (1998) describes this part of the valley as one of the most magnificent stretches of unspoiled landscapes on the Cape Peninsula and indeed, arguably, anywhere in the world. In 1999 an application will be made to declare the area a World Heritage Site.

In December, 1997, the Cape Metropolitan Council commissioned a study on the Noordhoek Wetlands to develop a catchment management plan for the area. Essential components of the study were to assess the present quality of existing wetlands and the development of sound ecological management guidelines. Analysis of surface waters and stormwater runoff within the catchment indicated that all of the permanent wetlands suffer from severe "cultural" eutrophication (Davies and Gassner, 1999). Eutrophication, the over - enrichment of receiving waters with mineral nutrients, leads to excessive production of undesirable algae and aquatic weeds, together with oxygen shortages caused by their senescence and decomposition.

The Noordhoek Wetlands are subjected to various forms of anthropogenic pollution; the two most obvious ones are the discharge of urban runoff and treated effluent from the local sewage works. During the period of the study (Jan-Oct 1998) the occurrence of cyanobacteria was reported for two vleis within the Noordhoek Valley. A dense bloom of toxic *Microcystis aeruginosa*, in the shallow coastal vlei, Wildevoëlvlei, in January 1998 lead to a tremendous human health risk and public awareness of the ongoing deterioration of the Noordhoek wetlands. The costs for the short-term eradication of the algae were approximately R 350000 (Wood, *personal communication*¹).

¹ Julia Wood: Environmental Officer, South Peninsula Municipality, Cape Town



Figure 1.1 Map of the Noordhoek Valley, showing the study site (1 : 50 000).

A toxic algal population, even though very small, was also present in an adjacent vlei, The Lake. The cyanobacterial toxins observed in both vleis were microcystins (Harding, *personal communication*²). Microcystins are extremely potent hepatotoxins, lethal to various wild and domestic animals and a health risk to humans in contact with contaminated water (Kellerman *et al.*, 1988, Harding *et al.*, 1995; Van Halderen *et al.*, 1995). Besides being the source of serious illnesses (hepatoenteritis, asymptomatic pneumonia, dermatitis) they are considered to be the strongest tumour promoters known to science (Yoshizawa *et al.*, 1990; Nishiwaki-Matsushima *et al.*, 1992).

Microcystins are normally present inside cyanobacterial cells and enter the surrounding water upon senescence of the population, leading to decomposing cyanobacterial scums and accumulation in sediments. Although numerous studies have investigated the rapid degradation processes of cyanobacterial toxins in the water column, little is known about their reaction with bottom sediments (Jones, 1990; Jones and Orr, 1994, Jones *et al.*, 1994). Rapala *et al.* (1994) reported loss of dissolved toxins due to adsorption on lake sediments, but biological decomposition of the sorbed form of a chemical tends to be slower than its dissolved counterpart (Schwarzenbach *et al.*, 1993).

It is well established that the limiting nutrient controlling freshwater algal growth is phosphorus, where the ratio between nitrogen and phosphorus plays an important role in determining the composition of the algal community (Wetzel, 1983; Reynolds, 1984). Phosphorus-rich conditions can favour cyanobacteria over other algae (Thornton and Mc Millan, 1989). In most lakes, reservoirs, and estuaries a concentration of 100 $\mu\text{g.L}^{-1}$ of P is regarded as unacceptably high (Vollenweider, 1968; Correll, 1998), and for typical Cape Peninsula vlei systems 40 $\mu\text{g.L}^{-1}$ is a problem (Vollenweider, 1968; Harding *personal communication*). In Wildevoël vlei and The Lake mean total phosphorus concentrations during the bloom event were 2200 $\mu\text{g.L}^{-1}$ and 300 $\mu\text{g.L}^{-1}$ respectively.

² Dr. William R. Harding: Head of Hydrology, Scientific Service, Cape Metropolitan Council

1.2 Objectives of the study

The aim of the study was to investigate the geochemical and limnological aspects of the formation of blue-green algal populations within the Noordhoek Wetlands. In order to accomplish this objective the following procedures were completed:

- I. A review of the relevant literature on proliferation and consequences of cyanobacteria (blue-green algae) in eutrophic freshwater systems.
- II. A chemical characterisation of The Lake, with notes on its suitability for blue-green algae.
- III. An investigation into the impacts of stormwater discharged into The Lake, with special note on the import of bioavailable phosphorus (PO_4^{3-}).
- IV. Determination of the relative phosphorus adsorption capacity of vlei sediments.
- V. An investigation into the accumulation of microcystin in sediments and fish.

1.3 Constraints of the Study

Due to the time constraints of the study, sampling could not be carried out on a seasonal basis. However, site visits, conducted from February 1998 to October 1998, and additional data available for the wetlands, allowed a comprehensive picture of the ecological status of the wetland systems of the Noordhoek Valley to be drawn.

1.4 Study Site Description

1.4.1 Location

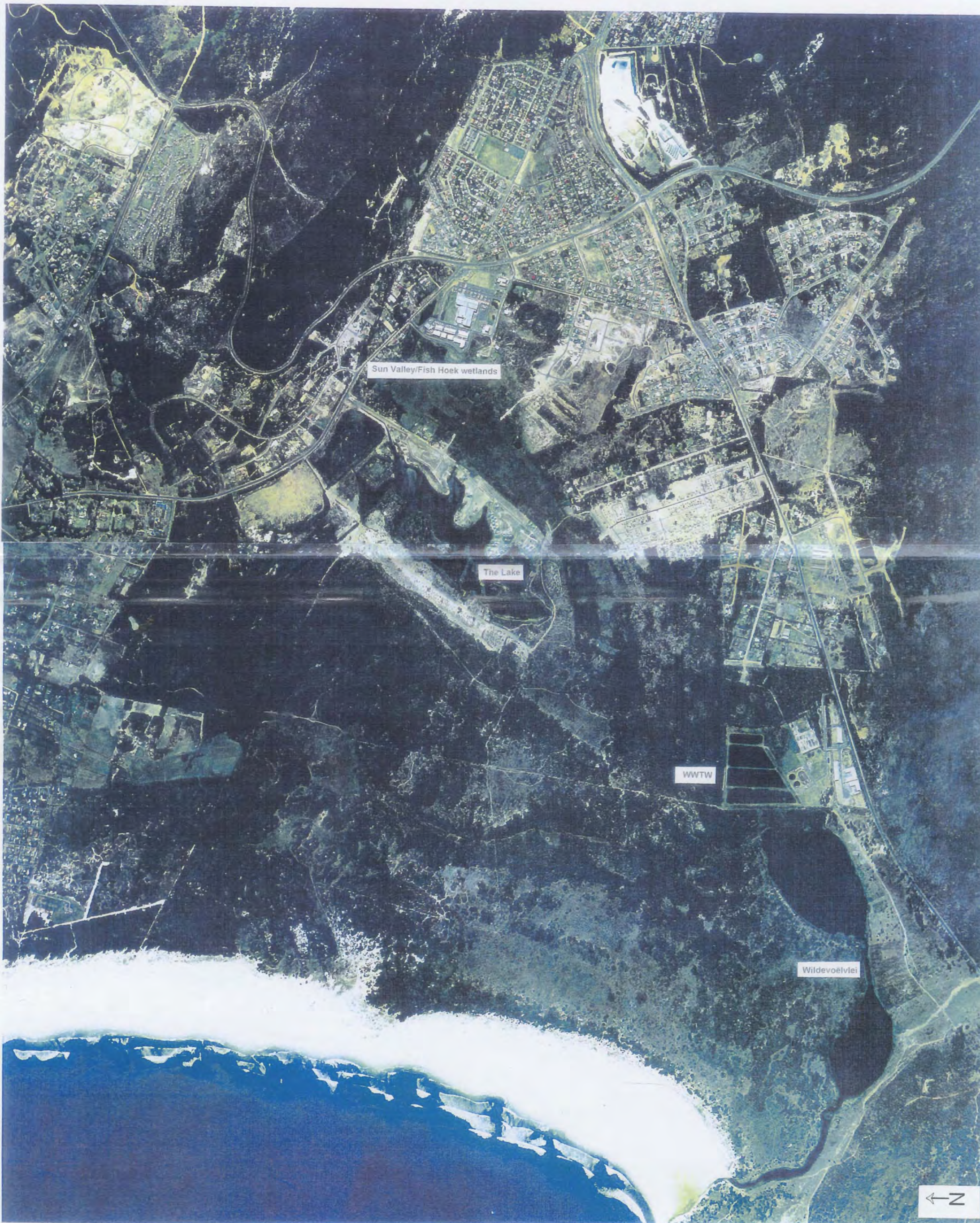
The Noordhoek Valley is located on the western shore of the Cape Peninsula, about 25 km south of the Central Business District of Cape Town, South Africa (34°07'S, 18°22'E). The area consists of a low-lying, flat-bottomed valley, flanked by mountains to the north and south, broken by a low sandy ridge to the east -the Fish Hoek Gap- and the Atlantic ocean to the west. The highest mountain is the Chapman's Peak to the north (590m). The central portion of the valley contains an extensive wetland area, featuring two coastal lakes and a number of seasonal vleis (Figure 1.2).

1.4.2 Geology and Soils

During the Late Pleistocene, some 125 000 years ago, the sea level was approximately 6m higher than today, allowing the sea to penetrate much further inland. During the last Ice Age, some 20 000 years ago, sea level fell to -130m, and then recovered to +3m about 6 000 years ago in the Holocene climatic optimum (Reid *et al.*, 1998). The barrier dune ridge landwards of the present shoreline was created during that time within the Flandrian transgression (Van Heerden, 1985). As sea level dropped to its present stand, the coastal zone prograded seawards (Rodgers *personal communication*³), leaving an extensive marshland behind. The prevailing south-easterly summer winds favoured the deposition of silt and water in some of the low-lying areas. This led to the formation of two salt pans: The Noordhoek Salt Pan, which presently is referred to as The Lake, and Wildevoëllei, a double pan system linked by a narrow isthmus and seasonally connected to the sea through a long semi-estuarine opening. Estuarine bivalve deposits found in the sediments of The Lake suggest that both Wildevoëllei and The Lake were once incorporated into a single estuary.

The foundation of the valley floor is the Cambrian Cape Granite, characterised by coarse crystals of white, potassium feldspar while the mountains surrounding the valley belong to the Table Mountain Sandstone Group (TMS). Two formations are present: the oldest sediments of the TMS the Graafwater and the slightly younger Peninsula formation. The Graafwater Formation is characterised by thin, ferruginous mudstones and is fine-grained, while thick quartz arenite sequences are typical for the Peninsula Formation (Theron, 1983). Tropical conditions in the Tertiary had little effect on the supermature, quartz-dominant sandstones of the TMS, but were extremely effective in weathering the large feldspars of the granite and

Figure 1.2 Aerial photo of the Noordhoek Valley, showing the wetlands and study site (WWTW = Wildevoëlvlei Wastewater Treatment Works).



Sun Valley/Fish Hoek wetlands

The Lake

WWTW

Wildevöelwei

← N

gave rise to high quality kaolinite. The total yield of kaolinite underlying the northern flanks of the valley is estimated to be over 60 million tonnes (Reid *et al.*, 1998).

The floor of the Noordhoek basin is formed by weathered granite bedrock, covered by silica sand containing Tertiary and Quaternary peat horizons. The latter contains machia pollen typical of the local Fynbos vegetation of today, while the former is rich in tree pollen of both palm and *Podocarpus* (Yellowwood) species. The finding of extinct palm pollen suggests a subtropical climate at that time (Coetzee, 1978). The peaty sands belong to the Noordhoek member of the Pleistocene Springfontyn Formation. This formation is overlain by intertidal, often phosphatic sediments of the Witzand Formation containing rounded, polycyclic quartz grains, in turn overlain by littoral calcareous beach and dune sands of the Late Pleistocene Velddrif Formation. In places these sediments can be up to 95 m deep (Rodgers, 1980; Reid *et al.*, 1998).

The soils within the Noordhoek catchment are varied and can be grouped into eight main forms. Sandy soils typical of the quartzitic fold ranges, such as the Clovelly and Hutton forms, can be found on the drier south facing slopes on the Kommetjie side, while in the wetter north facing Noordhoek amphitheatre soils of the Lamotte and Fernwood forms are common. On the lower slopes the Escourt forms overlay the kaolinite. The coastal foreland soils have all been developed from recent drift sands. In the valley bottom the unweathered quartzite layers give rise to a perched water table and although the soils of the slopes appear to be well drained, Lamotte and Fernwood soils are subjected to various degrees of wetness. Some of the soils with a high interflow potential are the Mispah, Darling and Longlands series while the rest of the soils in the catchment are considered to have low interflow (Chapman and Kreutzweiser, 1997) (Table 1.1).

³ Dr John Rodgers: Senior lecturer, Department for Marine Geoscience, University of Cape Town

Table 1.1: Soils of the Noordhoek basin (Modified from Chapman and Kreutzweiser, 1997)

Terrain Morphological Units	1° Soil Series	2° Soil Series	3° Soil Series	4° Soil Series
CRESTS	Saldanha Fw32 (90%)	Rock 8%	Mispah Ms10 (2%)	
MIDDLESLOPE (NORTH FACING)	Saldanha Fw22 (60%)	Mispah Ms10 (15%)	Lamotte Lt12 (15%)	Waterridge Cf20 (10%)
MIDDLESLOPE (SOUTH FACING)	Darling Es42 (55%)	Sonneblom (Cv21 30%)	Chester Hu22 (10%)	Longlands Lo21 (5%)
VALLEY BOTTOM	Saldanha Fw22 (40%)	Lamotte Lt12 (30%)	Longlands Lo21 (15 %)	Darling Es42 (15 %)
DEPRESSION	Pans (80%)	Chester Hu22 (30%)		

1.4.3 Flora

The typical flora in the area is the characteristic Cape Fynbos. Fynbos is generally described as being confined to infertile, sandy soils derived from quartzites and sandstones of the Cape Supergroup, and leached colluvial and dune sands of the low-lands, while non-fynbos communities occur on less sandy and more fertile soils (Taylor, 1978; Kruger, 1979; Boucher and Moll, 1980).

The weakly acid, well-leached sandy soils (with a paucity of most of the major nutrients) in the centre of the Noordhoek basin support the sandplain proteoid fynbos: a heath-type vegetation with sclerophyllous overstory and understory (Cowling, 1991), while dune, restioid fynbos grows on the younger, coarse, calcareous marine deposits (Cowling and Golding, 1998). Herbaceous dune pioneer vegetation is restricted to the hammock dunes on

the edge of the wetland area. The margins of the vleis and other fire protected sites allow for the development of evergreen shrubs and tree thicket.

The Noordhoek wetland area is heavily invaded by alien terrestrial trees, predominantly *Acacia saligna* and *A. cyclops*. *Acacia* spp. have a significant impact on the hydrology of the area. Invasion results in an increase of plant biomass between 50 and 100 % (Versfeld and Van Wilgen, 1986), resulting in significantly increased water utilisation and a related decrease in runoff from catchment areas (Van Wilgen *et al.*, 1996).

Corresponding to the vegetation types two different drainage patterns can be observed: relatively rapid drainage through the restioid and proteoid fynbos in the higher areas of the wetland and a slow drainage through shrubs and trees close to the vleis and lower lying areas.

1.4.4 Rainfall and Climate

No recorded climatic data are available specifically for the Noordhoek basin. However, the climate can be considered as Mediterranean with hot, dry summers and cool, wet winters. Gasson (1984) reports the temperature to be normally between 20°C and 24°C with a low value of 6°C during colder winter months and a high value of 26°C to 30°C during the hot summer months. The Cape Peninsula experiences highest wind speeds (southerlies) during summer, and lowest speeds (and greatest incidence of periods of calm) during the winter (Fuggle, 1978). The Chapman's Peak coastline is one of the most dynamic in the Cape Peninsula; erosive capacity is high and the sands of the Fish Hoek dunes are moved by wind with a speed as low as 12 km per hour (Harmse, cited in Heinecken, 1985).

The rainfall over the basin is both cyclonic and orographic with a pronounced winter peak. The topography plays an important role in the distribution of rainfall which is highest on the south-facing mountain slopes. The average annual rainfall varies between 1 200 mm in the Noordhoek mountains to 600 mm in the coastal wetland area (Heinecken, 1985).

1.4.5 Hydrology

A characteristic feature of the basin is the absence of any well-defined natural watercourses besides the Goede Hoop River which drains the Noordhoek Amphitheatre. The runoff from the remainder of the catchment seeps down to the valley, where the porous sand substrate acts like a sponge. The entire catchment of the basin, measured from a 1:50 000 Topocadastral Sheet 3418 AB and AD, is 31 km². The valley bottom forms an extensive wetland which

includes three separate water bodies: Wildervoelvlei, The Lake and Papkuilsvlei. However, during winter the whole area becomes inundated and the catchment becomes interconnected via sub-surface seepage (Heinecken, 1985).

Two distinct aquifers can be found in the area: an upper (0-30m depth) unconfined and a lower (40-90 m depth) confined aquifer. The surface aquifer is associated with the unconsolidated sands of the Bredasdorp Formation. The water is salty (10-16‰) and is discharged into the aquifer via direct vertical surface flow, or laterally from the flanks of the valley. The lower aquifer comprises the interface between kaolin and fresh unweathered rock. It is mainly recharged by lateral leakage from the TMS. However, it is thought that a hydraulic continuity exists between the sea and the upper aquifer (Kantey and Templer, 1985).

1.4.6 The vleis

1.4.6.1 The Lake

As the study is mainly concerned with the two permanent water bodies in the wetland, The Lake and Wildevoelvlei, these vleis and their specific catchments are discussed in detail. For further information on the system as a whole the reader is referred to KFD Wilkinson (1999). According to a survey done in 1999 the catchment of The Lake consists of The Lake estate itself and the northern portion of Fish Hoek. The Lake, located in the central part of the wetland, was first mentioned by the Cape Bird Club in 1959 (Winterbottom, 1960). It was described as a seasonal salt pan, dry in summer, forming a shallow lake during the winter. A salt mining industry utilised the pan since the eighteenth century and operation ceased some time between 1920 and 1947. At least until 1947 the pan was used as a racetrack in summer.

From 1940 to sometime in 1970 the pan received treated effluent from the Fish Hook sewage works. The sewage works discharged the effluent into the so-called "Fish Hoek sewer vlei", which was the most easterly vlei in an extensive wetland system east of the Noordhoek wetlands located along the Fish Hoek Gap. From the "Fish Hoek sewer vlei" the water drained westwards towards The Lake via a linear wetland chain, referred to as the Sun Valley Wetlands. Although no records exist of the quality of the effluent discharged, it is evident that it affected the quality of the vleis, for Waher (1971) stated that the water in the Sun Valley Vleis "...is usually turbid, green and scummy, and dead carp were observed floating

on the surface...". There are no official data on the volume of effluent discharged but Waher gives a figure of $1600 \text{ m}^3 \cdot \text{d}^{-1}$ (*ca* $584\,000 \text{ m}^3 \cdot \text{y}^{-1}$). Impacts on the hydrological cycle of the pan are reported. Post-1960 the pan stayed full, irrespective of annual rainfall, in contrast to its normal cycle of only achieving capacity during particularly wet years (Waher, 1971).

In 1971 a marina-type development was proposed for the Salt Pan. Construction of the first phase of the development started in 1974, leading to excavation of the pan floor, substantial earthworks on the southern end of the pan and stabilisation of the banks by concrete embankments. The lake which was created had an average water depth from about 1.6 m in winter to 0.6 m in summer (Kantley and Templer, 1985). Day (1985) describes the system as brackish (average salinity = 10‰) and eutrophic (average pH = 9.7, $\text{PO}_4\text{-P} = 0.1 \text{ mgL}^{-1}$, TN = 0.5 mg/l).

Building operations commenced in 1990 and the development of the southern shore was completed by 1995. At the time of the study The Lake was subjected to earth-moving activities on the north-western bank. The northern and eastern edges of the Lake are still undeveloped. A survey done in September 1998 estimated the area of The Lake to be $220\,000 \text{ m}^2$. The bed level was measured to be 1.4 m and the water level 3.89 m above MSL, respectively.

At present, maximum water depth occurs during September/October at about 2.7 m and declines to about 1.5 m during March/April. The main sources of water are groundwater (80%) and winter rainfall. The winter input comprises of 70% stormwater runoff and 30% direct rainfall. The stormwater can further be divided into runoff from The Lake Estate itself (30%) and overflow from the Sun Valley Wetlands (40 %) (Vivian Jones, *in writing*⁴). The Sun Valley Wetlands are presently used as detention ponds for the northern portion of the Fish Hoek runoff (Albert Duffy⁵ *personal communication*). The overflow of the Sun Valley Wetlands enters The Lake after being diverted into reedbeds at the northeastern corner. Outflow from the lake can take place in two ways, either by infiltration into the surrounding ground or through a conduit to discharge onto lower ground. A 10-m wide earth channel, approximately 1km long is situated at the north west end of the lake. The channel has a bed

⁴ Vivian Jones: Civil Engineer, KFD Wilkinson

⁵ Albert Duffy: Civil Engineer, Gibb Africa

level of approximately 3.6 m AMSL. Outflow is controlled by a sill with a height of approximately 4.1 m AMSL.

The Lake is inhabited by a dense stand of the pondweed *Potamogeton pectinatus*. Currently the pondweed is controlled by a harvesting machine. According to local residents harvesting does not follow sound ecological procedures, leading to temporal impairment of the plants and accumulation of dead plant material in the water. During the present study a dense dinoflagellate bloom was observed in late summer (April). The bloom was succeeded in June by a small bloom of *Microcystis aeruginosa*, which died off during the winter.

1.4.6.2 Wildevoëlvlei

Wildevoëlvlei is located at the northern side of the wetland at the foothills of the Rooikrans mountain range. The surface area of the double Wildevoëlvlei system - literally translated as 'wild bird lake' - is approximately 25 ha, with an average water depth of about 1m. The water level of the previously seasonal - regulated by rain, runoff and spring tides - vlei has been artificially-regulated since 1979 when a wastewater treatment plant was constructed on the eastern shore. The vlei drains into the Atlantic Ocean via a narrow outlet channel that lies to the north of Noordhoek Beach (Figure 1.1). The system functions as an estuary, receiving saltwater from the southern backshore lagoon. However, during the winter of 1998 for the first time in the past six years saltwater intrusions into the vlei were recorded.

The Wildevoëlvlei catchment consists of Crofter's Valley, Sun Valley, Faerie Knowe, Sunnydale, Capri and Masiphumale. The stormwater from these areas is discharged via a series of outfalls into the Pick'n Pay reed beds which in turn discharge into Wildevoëlvlei. The industrial developments of Fish Eagle Park and Heron Park, the Wastewater Treatment Works, the residential development of Imhoff's Gift and a portion of the residential development of Ocean View discharge directly into Wildevoëlvlei. A large portion of the wetlands and higher grounds to the south of Papkuilsvlei drains into Wildevoëlvlei.

The Wildevoëlvlei Wastewater Treatment Works (WWTW) daily discharges between 6 and 8 ML of treated effluent into the vlei. The approximate daily nitrogen and phosphorus loads of 18 and 21 kg give rise to areal loading rates of 70 and 80 mg N and P m⁻² d⁻¹ respectively (Harding *et al.*, 1995). A survey of the eastern vlei late in 1997 classified the vlei as hypertrophic, but stabilised by the presence of dense stands of Sago pondweed, *Potamogeton*

pectinatus (Harding, 1997). For unknown reasons, the macrophyte population collapsed a month after this report and was almost immediately replaced by a toxic bloom of the cyanobacterium, *Microcystis aeruginosa*. The algae was eradicated in April 1998 (for details see Harding *et al.*, *in press*), but re-established itself in the following summer (November).

CHAPTER 2

THE PROLIFERATION AND CONSEQUENCES OF CYANOBACTERIA (BLUE-GREEN ALGAE) IN EUTROPHIC FRESHWATER SYSTEMS

2.1 Introduction

Aquatic systems in an urban environment are subjected to massive anthropogenic nutrient input in the form of either non-point (stormwater) sources or point sources (industry, sewage). Most of these water bodies progress from low productivity or oligotrophic settings to productive mesotrophic conditions to overenriched eutrophic or hypertrophic conditions. The response to the so-called “cultural” eutrophication is excessive production of undesirable algae and aquatic weeds and oxygen shortages caused by their senescence and decomposition. Freshwater algal blooms (*Anabena*, *Microcystis*, *Nodularia*, *Oscillatoria* etc) have become a serious water quality problem in Australia, South Africa and Europe. From a human perspective it is desirable to prevent or minimise such processes for both aesthetic and health reasons. Algal blooms lower drinking water quality and the toxins produced in many blue-green algae have caused health problems for wildlife, livestock, pets and humans in contact with contaminated water. Given the vast variety of uses of urban water bodies such as recreation, housing development, fish farming and nature reserves, management guidelines are needed to eliminate the risk of toxic blue-green algae blooms. The objectives of this review are to give a short introduction to freshwater blue-green algae and the key environmental factors which lead to their proliferation.

2.2 Planktonic cyanobacteria

2.2.1 Ecology

It is beyond the scope of this paper to give a detailed description of the biology and ecology of cyanobacteria and the reader is therefore referred to Carr and Whitton (1973) and Fay, (1983). Cyanobacteria, commonly known as blue-green algae, belong to the oldest group of organisms on earth. The group first appeared about three billion years ago and are thought to have played an important role in the formation of the earth's atmosphere. The name “blue-green algae” stems from their superficial resemblance to eukaryotic green algae. Although

the cyanobacteria contain chlorophyll a and possess the ability of photosynthesis they are structurally and physiologically like bacteria (Friedmann 1982). Blue-green algae are a common component of freshwater phytoplankton communities, occurring in four different forms: unicellular, multicellular, filamentous and "sheet-like" aggregates of unicellular and multicellular types. A characteristic of this group is their tendency to form dense planktonic populations or blooms in eutrophic waters. In temperate lakes there is a characteristic seasonal succession of the bloom-forming algal species, due apparently to their differing responses to the physical-chemical conditions created by thermal stratification and light penetration. Usually the filamentous forms, which are able to fix atmospheric nitrogen, (e.g. *Anabaena* ssp., *Aphanizomenon flos-aquae* and *Gloeotrichia echinulata*) develop first, soon after the onset of stratification in late spring or early summer, while the unicellular-colonial forms (like *Microcystis* ssp.) typically bloom in mid-summer or in autumn. While some species remain planktonic throughout the winter, others overwinter on the bottom of the lake as vegetative colonies where they can survive for up to several years without light or oxygen (Carr and Witton, 1973; Reynolds *et al.*, 1981). A feature, unique to the blue-greens and shown in almost all bloom forming species, is the development of gas vacuoles, which allows for buoyancy control (Walsby, 1974).

2.2.2 Formation of blooms

Under optimal growth conditions, blue-greens tend to form algal blooms which can cover the entire water surface. The presence of "pea-soup green" water, the accumulation of malodorous decaying algal cells and the build-up of sediment rich in organic matter lead to user avoidance with the associated problems and implications for water quality management (Bruwer 1979; Thornton and McMillan, 1989). The most obvious sign of an advanced blue-green algae bloom is the formation of green "scum". During calm periods, scum leads to rapid deterioration of lake waters, by increased deoxygenation of underlying waters, subsequent fish kills, foul odours and lowered aesthetic values of affected waters (Paerl and Ustach, 1982). They are also suspected to lead to an impoverished lake fauna (Lindholm *et al.*, 1989).

2.2.3 Toxins

It has long been known that blue-green algae can be poisonous to mammals, waterfowl, fish and man. A scientific magazine in 1878 published the world's first report of an algal bloom.

The report noted that a bloom of cyanobacteria was found in Lake Alexandrina, South Australia. This outbreak was reported to have killed a number of sheep and cattle. Since then more than twelve species belonging to nine genera of blue-green algae have been implicated in animal poisoning (Gorham and Carmichael, 1980). A number of excellent reviews on the biochemistry and toxicology of toxic cyanobacteria are available (Codd *et al.*, 1989; Carmichael, 1992; Kenneth *et al.*, 1993). On a global basis the genus *Microcystis*, and in South Africa the species *Microcystis aeruginosa*, was found to be the most common bloom former. The many toxins produced by the former are referred to as microcystins. Microcystins consist of a seven-membered peptide ring, which is made up of five non-protein amino acids and two protein amino acids. It is these two protein amino acids that distinguish microcystins from one another, while the other amino acids are more or less constant between variant microcystins. Using amino acid single letter code nomenclature, each microcystin is designated a name depending on the variable amino acids which complete their structure. The most common and potently toxic microcystin-LR, contains the amino acids Leucine (L) and Arginine (R) in these variable positions. Early research focused on acute toxicity in laboratory mammals and more recently bioaccumulation of the toxins has been investigated (Laurén-Määttä *et al.*, 1994; Eriksson *et al.*, 1998). Concentrations of microcystin appear to be present only in primary consumers (zooplankton, gastropods), but several studies report implications for reproduction in fish (Kotak *et al.*, 1996). For mammals, in addition to being the source of serious illness (hepatointeritis, asymptomatic pneumonia, and dermatitis) they are thought to be the strongest tumour promoters known to science (Nishiwaki-Matsushima *et al.*, 1992). The South African guideline limit in drinking water is 1 mg.L⁻¹ for short term and 0.01 mg.L⁻¹ for long term consumption (Harding *personal communication*¹). The health implications of drinking water treatment process performance in removing microcystins were recently reviewed (Lambert *et al.*, 1994).

2.2.4 Degradation of toxins

Cyanobacterial toxins are normally present inside cyanobacterial cells and enter the surrounding water after cell lysis. The persistence of dissolved toxins in the water column seems to be dependent on the composition of other microorganisms present, rather than cyanobacteria. A bacteria species of the genus *Spingomonas* has been reported to enzymatically break down microcystins (Anderson, 1995). However microcystins may

¹ Dr. William R. Harding: Head of Scientific Service, Cape Metropolitan Council

persist for 2-3 weeks before biodegradation commences (Jones *et al.*, 1995). Chemical degradation seems to be minor, but sun radiation accelerates detoxification of the water (Tsuji *et al.*, 1994). Blue-green algae scums accumulate on the shores of lakes, ponds and rivers, forming crusts when dried out. Jones *et al.* (1995) reported detectable toxin concentrations in five-month-old *Microcystis* crusts, suggesting that microcystin is protected from degradation when encapsulated within the crust. It was also shown that re-wetting leads to rapid release of the toxins into the surrounding water.

2.3 Nutrients and Primary Production in standing Freshwater systems

2.3.1 The concept of trophic states in lakes

In 1907 Weber introduced the terms oligotrophic (from the Greek: oligos = little, trochein = to feed), mesotrophic (from the Greek: mesos = middle) and eutrophic (from the Greek: eu = well, good) to describe soil fertility of peat bogs. Oligotrophic bogs were poor in nutrients, eutrophic bogs rich in nutrients and mesotrophic between the two extremes. Naumann (1919) applied this classification to lakes and related the nutrient status to its biological effects on the system. Oligotrophic lakes, mostly found in regions dominated by igneous rock, had little phytoplankton biomass, where eutrophic lakes contained more phytoplankton and were predominantly found in fertile lowland regions. In 1968, Vollenweider proposed the theory that nutrient loading controlled lake productivity or trophic state. The concept of trophic state stimulated much discussion and research and with respect to its precise definition still lacks universal acceptance (Rast and Thornton, 1996). The essential axioms are: 1) that the greater the supply of nutrients to a lake, the more eutrophic the lake will be and/or 2) the higher the productivity of the lake, the more eutrophic the lake (Carlsö, 1979). The trophic status of a water body can alter naturally with increasing siltation and subsequently "terrestrialisation" of a water body. This process has been termed "natural eutrophication" (Reynolds, 1979). However, during the present century the overall progress from oligotrophic to eutrophic systems has mainly been attributed to "cultural eutrophication". Cultural eutrophication is the rapid enrichment of water with nutrients derived from human activities (Warwick, 1980).

2.3.2 Phosphorus as a key factor limiting phytoplankton biomass

The basic concepts which underlie our understanding of primary production in aquatic ecosystems originate from earlier agricultural research. The most fundamental principle of plant growth is Liebig's Law of the Minimum (Liebig, 1855). The Law of the Minimum states that plant growth is limited by the essential nutrient that is most scarce in the environment. The ratio of P:N:C in plant tissues on unit weight basis is 1P:7N:40C. The amplifying effects on P and N on plant growth have been known for centuries and have been used in pond culture to trigger algal growth.

The first studies that showed that phosphorus could be the limiting factor for algae growth were conducted with cultivated algae in the laboratory (Beijerinck, 1890; Pringsheim, 1912; Chu 1942). The first more ecological, rather than physiological approach was undertaken by Rodhe in 1948, who investigated phosphorus-algae relationships to conditions that exist in the real world. The so called enrichment experiments, where the response of phytoplankton is observed by adding individual substances to lake water, added a great deal to today's understanding of aquatic ecosystems. The work of Milton Potash (Potash, 1956) was one of the first enrichment experiments. In a series of bioassays of lake waters from the Great Lakes region of the USA, algae numbers were found to respond most often to the addition of phosphate, rather than nitrogen (Maloney *et al.*, 1972). Mesocosm experiments in which 320 L of Minnesota or Oregon lake water were enclosed in clear plastic bags and then enriched with various nutrients, found that P was the primary controlling nutrient (Powers *et al.*, 1972). Similar results were found for Lake Michigan waters (Schelske and Stoermer, 1972). Probably one of the most influential studies in phytoplankton ecology was Schindler's experimental lake research in northwestern Ontario. Whole lakes were enriched with P for a period of years. He concluded that the maximum biomass of temperate lakes is ultimately limited by the phosphorus supply (Schindler, 1977; 1978).

2.3.3 Bioavailability of phosphorus

Phosphorus occurs in freshwater systems in numerous dissolved and particulate forms. Particulate phosphorus includes phosphorus in organisms, mineral phases of rocks and soil, and phosphorus adsorbed onto dead particulate matter. Dissolved phosphorus is composed of orthophosphate, polyphosphates, organic colloids and low-molecular-weight phosphate esters (Wetzel, 1983). Although empirical models that predict trophic status of lakes are based on the total phosphorus concentration, only a fraction of the total phosphorus pool is available

for algal consumption (OCED, 1982). The definition of bioavailability is based on the assumption that the principle form of phosphorus directly available to algae is dissolved orthophosphate phosphorus (Rigler, 1966; Boström *et al.*, 1988a). Availability of phosphorus for algal growth depends therefore on the amount that can be transformed into orthophosphate (H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}). Most studies on bioavailability of phosphorus are based on an algal culture bioassay with yield determination combined with a chemical extraction scheme. For more detailed reviews on biotests to determine bioavailable phosphorus the reader is referred to (Hegeman *et al.*, 1983; Dorich *et al.*, 1985; Boström *et al.*, 1988a). For particulate phosphorus, the NaOH-extractable phosphorus (assumed to correspond to aluminium- and iron bound phosphorus) was found to be the most algal-available phosphorus fraction. HCl-extractable P (assumed to estimate calcium-bound P) was shown to be negatively correlated to algal extractable phosphorus. Furthermore, particulate phosphorus, derived from apatite was found to be unavailable for algal growth (Hosomi *et al.*, 1981; Boers *et al.*, 1984; Young and De Pinto, 1984). Dissolved phosphorus (filterable through a $0.45\mu\text{m}$ membrane filter) can be analytically separated into two fractions: reactive phosphorus and unreactive phosphorus (Rigler, 1973). Reactive phosphorus is the fraction which responds to colorimetric tests without preliminary hydrolysis or oxidative digestion. Bioassays cannot be made on these fractions separately but are generally made on the complete dissolved phosphorus pool. It was found that the amount utilised by algae was lower than chemically determined dissolved reactive phosphorus (Rigler, 1966; Dillon and Reid, 1981). In a study on lake and river waters with a high content of inorganic seston, total reactive phosphorus (measured chemically on unfiltered samples) was found to be the available fraction of total phosphorus for algae (Blakar and Lovstad, 1990). Corresponding results were obtained for a phytoplankton population dominated by blue-green algae in Lake Arungen (Krogstad and Lovstad, 1990; 1991).

2.3.4 Factors controlling bioavailability of phosphorus

The concentration of orthophosphate in the water column and, therefore, the concentration of immediately available phosphorus for algal growth, depends on allothochneous P input, sedimentation rate and the ability of sediments to retain phosphorus. Most of the sediment phosphorus is inorganic, for example apatite, derived from the watershed, and phosphate adsorbed onto clays and ferric hydroxides. Additionally, phosphate co-precipitates with iron, manganese and carbonates. Phosphorus flux across the sediment–water interface depends on

hardness, hydrologic conditions, adsorption capacity of the sediments, redox potential, pH and ionic strength (Patrick and Khalid, 1974; Richardson and Davis, 1987; Mann, 1990).

2.3.4.1 Adsorption capacity

The adsorption capacity of a soil depends strongly on its clay and silt, iron, aluminium and calcium content. Sorption of phosphates on surfaces is well known, particularly onto sesquioxides and clay minerals (Stumm and Morgan, 1981). Adsorption of the phosphate anion involves ligand exchanges with aquo-, hydroxo-, or olgroups, with the reactivity decreasing from aquo to hydroxo to ol (Berkheiser *et al.*, 1980). In terms of adsorption per unit mass of solid the affinity of total reactive phosphorus was found to be increasing from quartz to calcite (montmorillonite or kaolinite) to illite to goethite to iron/aluminium oxyhydroxyds at pH 7 and ionic strength 0.1M (House *et al.*, 1998). Phosphates are adsorbed by chemical bonding of the anions to positive charged edges of the clays or substitution of phosphates for silicate in the clay structure (Sample *et al.*, 1980). Many laboratory studies have shown that phosphorus adsorption involves two stage of reactions. Rapid P adsorption is associated with surface reactions (Parfitt, 1978). Slow reactions, have been attributed to slow diffusion into Fe-oxide crystals (Barrow, 1983; Parfitt, 1989) or aggregates of crystals (Madrid and Arambarri, 1985; Roden and Edmonds, 1997) and precipitation reactions (House *et al.*, 1998).

2.3.4.2 Ionic strength

Increases in ionic strength generally lead to increasing sorption, because of the compression of the double layer and possible cation exchange reactions (House *et al.*, 1998). Calcium salts in solution also tend to increase the sorption on clays, because of co-operative adsorption or the effects of Ca adsorption on the thickness of the double layer (Bar-Yosef *et al.*, 1988). In contrast increased anion concentrations may lead to decrease in adsorption, through competition for sorption sites (Caraco *et al.*, 1990).

2.3.4.3 Organic matter

Organic coatings can modify the sorption properties of the underlying minerals, either decreasing adsorption by competing with phosphorus for adsorption sites or enhancing

adsorption by inhibiting the crystallisation of Fe and Al oxides (Borggaard *et al.*, 1990). Additionally, organic surfaces can also act as adsorption sites for phosphorus (Sposito, 1984).

2.3.4.4 pH

The dissociation of orthophosphoric acid in aqueous systems is a function of pH. The first ionisation state (H_2PO_4^-) is the predominant species that takes part in phosphate sorption. Therefore, P sorption is greatest between pH 3 and pH 5, which is equivalent to the first ionisation constant. In acid soils, phosphorus is fixed as aluminium or ferric phosphates: at low pH the metal oxides have a positive surface charge. In alkaline soils activities of calcium and magnesium govern the retention of phosphorus. Phosphate is thought to form a monolayer on the mineral surface, replacing water molecules, bicarbonate ions and hydroxyl ions (Berkheiser *et al.*, 1980; Sample *et al.*, 1980). Moreover, increasing pH leads to the formation of calcium carbonate, which coprecipitates phosphates with carbonates (Otsuki and Wetzel, 1972).

2.3.4.5 Redox potential

It is beyond the scope of this review to give a detailed discourse into wetland soils. The reader is referred to Brinkman and van Diepen (1990). Typical features of waterlogged wetland soils are the formation of different oxygenated zones in the soil column. The simplest model is a three-layer soil, with the surface layer being oxidised (aerobic) followed by an alternating oxidised and reduced zone and a permanently reduced (anaerobic) layer (Reddy and Patrick, 1984). The aerobic/anaerobic interfaces lead to a steep redox gradient from +700 to -300 mV (Reddy and D'Angelo, 1994). Under oxidised conditions Fe^{2+} which is oxidised to Fe^{3+} resulting in the precipitation of P because ferric phosphate and the adsorption to ferric hydroxides and CaCO_3 . Reducing conditions lead to the release of P because Fe^{2+} is more soluble than Fe^{3+} . Furthermore, sulphate (SO_4^{2-}) reduced to hydrogen sulphide (H_2S) competes with P for iron to form ferrous sulphides. During reduction of iron (III) hydroxide or oxides to Fe^{2+} , hydrogen ions are consumed and the pH tends to rise. An increase in pH results in an increase of OH^- ions, which will replace P on the adsorption sites (Bostroem *et al.*, 1988b).

2.4 Intraspecific Competition and Cyanobacterial Dominance

2.4.1 Phytoplankton succession

The taxonomic composition of phytoplankton communities, the abundance and the relative dominance of the different species and groups present, undergo seasonal change. This process of continuous community change is termed succession. Under undisturbed conditions most phytoplankton populations are of relatively short duration. Typically, the growth and decline cycle of one specific population lasts on average 4 to 8 weeks. Factors which influence species succession can be grouped into three categories: allogenic, autogenic and sequential. Allogenic factors include salinity, temperature, light, turbulence and anthropogenic substances, whilst autogenic factors include life cycles, nutrients, water quality, ectocrines and predation (Smayda, 1980). Sequential factors refer to environmental modification, and hydrological disturbance. In temperate lakes the main factors influencing community composition are light, temperature and nutrients.

The first elaboration of the correlation between chemical composition of natural waters and phytoplankton assemblage is attributed to Pearsall (1932). He found that the main nutrients determining the composition of algal communities are P, N, and Si. An excellent review on the role of limiting nutrients in phytoplankton community ecology was conducted by Tilman *et al.* (1982). Our understanding of intraspecific nutrient competition in algae is based largely on the work of Alfred Redfield (1958), who determined the elemental composition of marine algae. He discovered that under normal growth conditions C, N and P will occur with relatively defined atomic ratios. The so-called Redfield ratio of P, N, and C in phytoplankton tissues is 1P:16N:106C. Carbon is rarely limiting for phytoplankton and only the N:P ratio has to be considered. N:P ratios of less than 16 indicate nitrogen limitation, where ratios above 16 indicate phosphorus limitation. Diatoms are regarded as superior P-competitors, and dominate at high Si:P ratios (spring), whilst as N-competitors they are subordinate to cyanophyte algae which dominate at low N:P ratios. Green algae are the poorest N-competitors, whilst in P competition they dominate cyanophytes, but are subordinate to diatoms. Corresponding to the prevailing nutrient cycle in temperate, undisturbed lakes, the typical pattern of phytoplankton succession shows a spring maximum of diatoms, sometimes followed by a second maximum in the autumn, an early summer maximum of Chlorophyceae (green algae) and a late summer maximum of Cyanophyta (blue-green algae). This was termed the traditional “seasonal paradigm” of phytoplankton succession (Reynolds, 1983).

2.4.2 Factors leading to cyanobacterial dominance

With increasing nutrient supply, in particular phosphorus, the phytoplankton flora deviates from the traditional seasonal community pattern. Reynolds (1984) describes two types of responses: first (summer and autumn) seasonal peaks become relatively more enhanced while intermediate minima stay the same and, secondly, different algae become dominant. Schindler *et al.* (1972), observed that, while one can say with considerably certainty that a lake will respond to increased inputs of P and N by increasing algal biomass and production, and that the magnitude of this bloom can be controlled by controlling the input of P alone, there is no way of making reliable predictions of what species will respond, or the rapidity of the response. However, with an increase in total phosphorus phytoplankton communities tend to shift towards cyanobacterial dominance (Schindler *et al.*, 1972; Lund, 1972a,b; 1978; Herath, 1997). Increasing supplies of phosphorus lead to an increase of phytoplankton growth until other essential nutrients become limiting. The first nutrient to become limiting after P is usually nitrogen. While other algae become nitrogen limited, the ascendancy of nitrogen-fixing cyanobacteria is favoured.

While it appears to be true that cyanobacteria predominate at N:P ratios of less than 30, exceptions do occur (Harding, 1996). A possible explanation is that N:P ratios become less important when both nutrients are in sufficient supply, i.e. if their concentrations are high (Reynolds, 1993a). Under constant nutrient supply, physical factors (temperature, light) become the dominant selection mechanism. Large suspended stocks of phytoplankton reduce light penetration. Blue-greens developed mechanisms unique to algae that enable them to outcompete other species under light-limiting conditions: gas vacuoles to control buoyancy. When subjected to suboptimal conditions, they respond by increasing their buoyancy (regulated by rate of photosynthesis) and move nearer to the surface and hence to the light (Walsby, 1974).

Shapiro (1990) postulated that pH is a stronger factor determining algal composition than is the N:P ratio. Cyanobacteria are supposed to be more tolerant of high pH conditions than other algae. An additional selective advantage at times of high photosynthesis is their ability to utilise CO₂ as carbon source (Shapiro, 1990).

Cyanobacteria are also regarded as having low light requirements, which allows for optimal growth during reduced light conditions due to decreased sunlight (autumn/winter) and times

of high algal biomass (Reynolds, 1987; Spencer and King, 1987). Furthermore, some species of cyanobacteria are able to offset the effects of photoinhibiting UV radiation encountered by near-surface populations (Paerl, 1988). The resistance to photoinhibition is achieved by producing increased amounts of carotenoid pigments which act as “sun screens” (P. Ashton, CSIR, *personal communication*).

Once established, cyanobacteria are able to inhibit the growth of other algae. It has long been known that cyanobacteria are able to produce secondary metabolites which are toxic to species of other genera (Carr and Whitton, 1973). They further exhibit a selective advantage purely due to their relatively large size, which makes them inedible to grazing zooplankton (De Bernardi and Guiussani, 1990)

2.4.3 Control of cyanobacterial blooms

2.4.3.1 Biological and chemical control

Chemicals are widely used to prevent the growth of nuisance algae, the commonest is copper sulphate. Other algicides include phenolic compounds, amide derivatives, quaternary ammonium compounds and quinone derivatives. Dichloron-aphthoquinone is selectively toxic to blue-greens. However, the hazards of using such toxic chemicals indiscriminately in the natural environment are well-documented (Lam *et al.*, 1995; Sabater and Carrasco, 1997).

Biological control by zooplankton is in principle possible, though not always practical nor as effective. This is due to the low nutrient adequacy, toxicity and inconvenient size and shape of most blue-green algae (Brabrandt *et al.*, 1983; De Bernardi and Guiussani, 1990). The only zooplankton reported to successfully graze on blue greens are *Daphnia ssp.*; however *Daphnia* populations tend to decrease with increasing nutrient content of the water (Karabin, 1985; Epp, 1996).

Microorganisms (fungi, bacteria and viruses) also appear to play an important part in regulating growth of blue-greens in freshwaters. Certain chytrids (fungal pathogens) specifically infest akinetes, and other heterocysts. Bacterial pathogens belonging to the group of Myxobacterales can effect rapid lysis of a wide range of unicellular and filamentous blue-greens, although heterocysts and akinetes remain generally unaffected. Viral pathogens

belonging to the group of cyanophages exhibit some degree of host specificity (Desjardin and Olson, 1983; Philips *et al.*, 1990).

2.4.3.2 Control of phosphorus loads

The general consensus regarding the management of blue-green algal blooms is the management of excess nutrient loads into receiving water bodies (Young and de Pinto, 1984; Harding and Quick, 1992; Herath, 1997). The control of phosphorus loads has been demonstrated internationally as one of the most effective ways of dealing with cultural eutrophication and has been successfully applied in the USA, Europe, Scandinavia and Japan (Herath, 1997). Management options can be divided into two broad categories: catchment management (decrease of nutrient export) or lake management (decrease of internal nutrient supply). Catchment options are, for example, management of urban and agricultural runoff, biological and chemical treatment of wastewater, nutrient diversion and implementation of legislation. Lake management options are dredging, chemical sediment treatment, and biomanipulation (Harding and Quick, 1992).

2.4.3.3 What concentration of phosphorus is acceptable?

A great deal of scientific effort has been spent formulating models that predict primary production as a function of predicted total phosphorus concentration. Jones and Lee (1981) and Goltermann (1980) have intensively reviewed the topic. Based on a significant correlation between phosphorus and chlorophyll *a*, where the chlorophyll *a*:P ratio is consistently about 0.5 (Lund and Reynolds, 1982), Vollenweider developed one of the most practical models in 1968 based on comparative studies of European and North American lakes. In this model, the trophic status of a lake is a function of the rate of aerial nutrient supply ($\text{g.m}^{-2}.\text{yr}^{-1}$); basin form and flushing rate in the form of mean depth/hydraulic residence time. Since it is impossible in any practical sense to manipulate mean depth or hydraulic residence time, this model was used to predict the likely effects of altering the rate of nutrient supply on lake trophic status.

Correl (1998) states that there is also no widely accepted consensus on the acceptable phosphorus concentration in a lake; a concentration of $100 \mu\text{g total P.L}^{-1}$ is unacceptably high and concentrations of $20 \mu\text{g.L}^{-1}$ are often a problem. In South Africa, the authorities have

legislated (Government Gazette, 1984) phosphorus control by way of an effluent standard of 1 mg.L⁻¹ dissolved ortho-phosphate (P) for sensitive catchments.

2.5 Conclusions

Due to increasing cultural eutrophication of receiving water bodies toxic freshwater algae blooms have become a serious water quality problem world-wide. Algae blooms lower water quality from aesthetic, ecological and human health points of view. Toxins produced by various species of blue-green algae are lethal to wild and domestic animals and have severe health implications for humans in contact with contaminated water.

The primary factor limiting algae growth in freshwater systems is phosphorus concentrations. Although an increase in primary production is traditionally based on the total phosphorus concentration in the water, only dissolved orthophosphate leads directly to algae proliferation. The concentration of orthophosphate in the water column is dependent on the equilibrium between sediment, pore and bulk water. Phosphorus flux across the sediment-water interface depends on hardness, hydrologic conditions, adsorption capacity of the sediments, redox potential, pH and ionic strength.

In temperate, undisturbed lakes, blue-green algae form short-term blooms during spring/early summer and autumn/late summer. In eutrophic waters these blooms are not only enhanced, but also the phytoplankton community shifts towards long-term blue-green algae dominance. Their selective advantage is based on a number of chemical and physical factors. The most important ones are their unique physical characteristics to fix atmospheric nitrogen and to control their buoyancy in the water column.

It is evident that water bodies in the vicinity of an urban environment are subjected to high anthropogenic pollution. Given the scarcity and increasing demand of freshwater resources in South Africa it is not only important to understand the factors that lead to the development of toxic algal blooms and their implications for the environment, but to recognise early signs in individual systems to undertake preventative measurements. Important parameters which should be monitored in lakes are internal and external phosphorus loads, species composition of phytoplankton and physical conditions such as water depth, turbidity and temperature.

CHAPTER 3

WATER CHEMISTRY OF THE LAKE

3.1 Introduction

The Lake is an artificial impoundment that forms the centrepiece of the Noordhoek Wetlands. Its catchment is undergoing development and The Lake itself is an integral part of a suburban housing development. Due to stormwater engineering The Lake is exposed to a large hydraulic loading of urban stormwater runoff. As a semi-enclosed water body with an annual outflow of approximately 30 days duration, phytoplankton responses are strongly related to the chemical composition of the incoming water as well as geochemical alterations of the water within the lake basin. Important chemical processes are the buffering capacity of the water, rainfall and solubility of minerals and the mobility, and therefore availability, of nutrients, in particular phosphorus. An understanding of these chemical dynamics is essential if phytoplankton proliferation in The Lake is to be managed effectively.

The objective of this chapter is, therefore, to characterise the aqueous geochemistry of the system and to identify the different chemical processes that impact on the algal community of The Lake. The main part of the chapter focuses on an interpretation of the results obtained from water samples analysed as part of this study as well as seeing them in context with other data available on the system. The chapter includes a description of the sampling procedure and analytical techniques used.

3.2 Material and Methods

3.2.1 Sampling procedure

Water samples were taken during two separate sampling trips in 1998. The first survey was conducted on 31 May. A total of 9 surface water samples were taken from different locations in the Lake. The second sampling trip was carried out on 31 August. A total of 12 samples were taken (see map of sampling locations, Appendix F). Samples were taken from the surface using pre-rinsed plastic bottles, whereas bottom samples were taken from water trapped in the van Veen grab sampler (Section 4.2.1). Samples were taken along an east west

transect and from the inlet and outlet. On both sampling visits, samples were collected by boat using plastic bottles which were pre-rinsed at the sampling site. Samples were transported and stored at 4°C before analysis in the laboratory.

Interstitial water for soluble reactive phosphorus (SRP) analysis was obtained by pressure filtration from sediment collected on the August sampling trip. Water samples taken in May were analysed at the Scientific Services of the Cape Metropolitan Council, and samples collected in August were analysed at the Department of Geological Sciences at UCT.

3.2.2 Analytical methods

The following section describes the analytical methods utilised for analyses of the water samples collected on August 31. Apart from the analyses of chemical oxygen demand and total phosphorus concentration, analytical methods carried out at the Scientific Services of the Cape Metropolitan Council are the same as those described below and are not listed separately. For detailed information the reader is referred to Harding (1996).

3.2.2.1 *pH and electrical conductivity*

The pH of the water samples was measured using a Metrohm 691 pH meter with combined glass-calomel electrode. The pH meter was calibrated before use with buffer solutions 7.02 and 4.00. Measurements of electrical conductivity (EC) were taken using a Crison Micro CM 2201 meter, conductivity probe and automatic temperature compensator.

3.2.2.2 *Alkalinity*

Alkalinity was measured on unfiltered samples. For samples with a pH higher than 7 alkalinity was measured by end-point titration to pH 4.5, and for samples with a lower pH stepwise titration to determine the equivalence point was used (Gran, 1952). For both methods standard 0.01 M HCl and a Radiometer TTT85 auto titrator were used. The procedure involved determining the volume of HCl required to titrate 10 ml of each sample to the end point pH.

3.2.2.3 Major cations and anions

Water samples were analysed for major cation and anion concentrations by ion chromatography (IC) using Dionex equipment. Samples were first filtered through a 0.22 μm microporous membrane filter and diluted with MQ water to attain an EC below 10 mS.m^{-1} . Before injection, each sample was passed through a Dionex Ongaard-P polyvinylprollidone cartridge to remove organic materials. Cation concentrations were determined with an HPIC-CG12A guard column and an HPIC-CS12A separator column, using H_2SO_4 (11 mM) eluent at a flow rate of 1 mL.min^{-1} and a sample loop volume of 25 μL . Detection was by a Dionex CD20 electrical conductivity detector, using a CSRS-I cation self-regenerating suppressor to suppress eluent conductivity. The run time per sample was 15 minutes. Anion (Cl^- , Br^- , F^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-}) concentrations were obtained using a sample loop volume of 50 μL , an HPIC-AGAA guard column and an HPIC-AS4A separator column with a combined Na_2CO_3 (1.80 mM)/ NaHCO_3 (1.70mM) eluent at a flow rate of 2 mL.min^{-1} . The choice of eluent precluded the determination of carbonic species. To suppress eluent conductivity an Anion MicroMembrane suppressor (AMMS) was used. Running time was 8 minutes per sample. The instrument is calibrated against a set of standards on a daily basis. On that basis accuracy can be estimated to be better than $\pm 2\%$ for most ions except for K^+ , for which it is $\pm 4\%$. The lower limits of detection are in the order of 0.001 mg.L^{-1} .

3.2.2.4 Trace elements

Trace elements were determined using inductive coupled plasma mass spectrometry (ICP-MS). Analyses were done in the ICP-MS laboratory at the Department of Geological Sciences, UCT. The instrument used is a Perkin-Elmer, Sciex ELAN 6000 ICP-MS. Analyses were performed on filtered samples for Li, Al, Cr, Mn, Ni, Cu, Zn, As, Se, Rb, Sr, Cd, Cs, Ba, Nd, Pb, and U.

3.2.2.5 Dissolved organic carbon

Analysis of dissolved organic carbon (DOC) was performed according to the persulphate-ultraviolet oxidation method for the analysis of total organic carbon using an autoanalyser (Standard Methods, 1995, 5310 C). Samples were filtered prior to analysis and had been

stored at 4°C (for 3 days) to limit biological degradation of organic matter. The analyses were conducted at the analytical laboratories of The Cape Water Programme, CSIR, Stellenbosch.

3.2.2.6 Chemical oxygen demand

Chemical oxygen demand was determined using the open reflux method (Standard Methods, 1995; 5220-B). The method is based on the oxidation of organic matter by a mixture of chromic and sulphuric acid. The sample is refluxed in strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). After digestion, the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulphate to determine the amount of $K_2Cr_2O_7$ consumed and the oxidizable organic matter is calculated in terms of oxygen equivalent.

3.2.2.7 Phosphorus

Total phosphorus (TP) was determined by digestion of unfiltered samples with persulphate and subsequent colorimetric determination of soluble reactive phosphorus (SRP) (Standard Methods, 1995; 4500-P B5). SRP was measured using the heteropoly-blue method. The method is described in detail in Standard Methods (1995). The phosphorus detection is based on the development of a blue coloured phospho-molybdate complex in filtered samples. The reaction is triggered by incubating the sample with a combined potassium antimonyl tartrate, ammonium molybdate and ascorbic acid reagent. The intensity of the colour is determined by colorimetry. Absorbance was measured at 880 nm using a TURNER model 340 spectrophotometer. P concentration was calculated from a calibration curve set up using the absorbance of solutions of known P concentration. All glassware was acid washed prior to analysis in order to minimise contamination. Standards were analysed with every run.

3.2.2.8 Silicon

Silicon was determined by the molybdosilicate method (Standard Methods, 1995; 4500-SiD). The method is based on the formation of a yellow colour complex between silica in solution and ammonium molybdate. The intensity of the colour is determined by colorimetry. Absorbance was measured at 440 nm using a TURNER model 340 spectrophotometer. Si concentration was calculated from a calibration curve set up using the absorbance of solutions of known Si concentration.

3.2.2.9 *Total suspended solids*

Water samples were well mixed and filtered through a weighed standard glass-fiber filter. The filter was then dried to a constant weight at 105°C. The increase in weight on the filter represented the total suspended solids.

3.2.3 Additional data

Additional data were obtained from the HomeOwners Association of The Lake, who kindly provided data that were collected during a monitoring study commissioned by the Association. The data were collected by DH Environmental Consulting (1998). Data collected by Barbara Gale from Aqua Catch were also made available and used in the present study.

3.2.4 Analysis of data

Data were analysed using the geochemical model MINTEQA2. The model is based on equilibrium thermodynamics and the Debye-Hückel theory that describes the activity of aqueous species. MINTEQA2 allows the calculation of speciation and mineral solubilities of a specific water sample. For details of the model the reader is referred to Chapter 4.

The program STARS was used to obtain Maucha diagrams (Maucha, 1932). The program is written in FORTRAN 77 and can be run on Hewlett-Packard computers with the HP-UX operating system and on SUN Sparcstations. The program was developed by Willis in 1992. Details of the program are given in Willis and Hill (1992).

3.3 **Results and Discussion**

3.3.1 Chemical composition of The Lake

Results obtained from the analyses of water samples collected from The Lake in May 1998 are presented in Table 3.1.

Table 3. 1: Analytical results of water chemistry analyses of samples taken from The Lake in May, 1998.

SAMPLE SITES		1	2	3	4	5	6	7	8	9
FIELD DATA										
Temperature	°C	10.0	15.3	15.8	16.9	16.7	16.6	15.8	17.4	17.80
PH		6.81	7.36	8.00	8.30	8.57	7.30	7.60	8.09	7.62
Transparency (Secchi disc)	M	0.3	0.3	0.3	0.2	0.25	0.3	0.3	0.3	0.8
ANALYTICAL DATA										
PH		7.33	7.98	8.05	7.90	8.52	8.23	8.07	8.25	8.10
EC	(mS.m ⁻¹)	59	32	464	438	437	444	248	397	530
Total suspended solids (TSS)	(mg.L ⁻¹)	8	9	10	23	14	10	10	8	3
Total alkalinity	(mg CaCO ₃ .L ⁻¹)	114	46	210	228	192	202	188	146	228
COD	(mg.L ⁻¹)	65	73	99	114	93	101	92	97	99
Anions										
Chloride	(mmol _c .L ⁻¹)*	9.70	12.3	36.1	37.0	32.7	35.8	34.98	39.49	40.34
Bicarbonate	(mmol _c .L ⁻¹)	2.28	0.92	4.20	4.56	3.84	4.04	3.76	2.92	4.56
Nitrate	(mmol _c .L ⁻¹)	< 0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Sulphate	(mmol _c .L ⁻¹)	1.79	2.27	9.20	9.41	8.33	9.12	8.91	10.06	10.27
Phosphate	(mmol _c .L ⁻¹)	0.004	0.002	0.001	0.001	0.001	0.001	0.001	< 0.001	< 0.001
Cations										
Sodium	(mmol _c .L ⁻¹)	8.23	12.03	37.02	35.05	35.96	31.53	26.17	37.03	37.49
Ammonium	(mmol _c .L ⁻¹)	0.01	0.01	0.02	0.02	0.01	0.02	0.02	0.01	0.02
Potassium	(mmol _c .L ⁻¹)	0.48	0.39	1.07	1.02	1.04	0.85	0.96	1.07	1.09
Magnesium	(mmol _c .L ⁻¹)	2.94	4.41	10.25	9.73	10.07	8.31	9.84	10.54	10.90
Calcium	(mmol _c .L ⁻¹)	4.33	2.62	5.77	5.87	5.36	4.82	5.14	5.78	5.88

*mmol_c = millimole charge

3.3.1.1 pH and alkalinity

The pH in The Lake is neutral to alkaline, varying from 6.81 to 8.57. The lowest value was recorded for Site 1, which is situated in the inlet channel.

The pH of the water controls most of the chemical processes such as mineral solubility and speciation of chemical elements as well as microbial activity and phytoplankton growth. As an index of the hydrogen ion (H^+) concentration it is a measure of the intensity of acidity or alkalinity. Alkalinity in waters is defined as the quantity and kinds of compounds present, which collectively shift the pH to the alkaline side of neutrality. In most waters alkalinity is controlled by the carbonate system, but borate, silicate, phosphate and organic anions can also affect alkalinity (Wetzel, 1983). Because of the calcareous nature of the sediments (Section 4.3.6) alkalinity was assumed to be mainly carbonate alkalinity. Total alkalinity in The Lake was found to be high, with a mean concentration of $180 \text{ mg CaCO}_3 \cdot L^{-1}$. Given the neutral to alkaline pH of the vlel carbonate alkalinity is assumed to be mainly in the form of HCO_3^- . It is customary to describe lakes containing large concentrations of alkalinity as hard water lakes (Hutchinson, 1975).

The carbonate system refers to the equilibrium between CO_2 - HCO_3^- - CO_3^{2-} . Temperature and the partial pressure of dissolved CO_2 control the equilibrium between these inorganic carbon species. At a temperature of $25^\circ C$ pure water in equilibrium with atmospheric CO_2 will have a pH of 5.66 (Drever, 1997). The partial pressure of CO_2 in the water is mainly governed by photosynthesis and carbonate minerals. of bicarbonate and hydroxyl ions. The Photosynthesis (eq.3.1) utilises CO_2 , decreases the partial pressure of CO_2 and increases the concentration result is an increase in pH. Alternately, decomposition of organic matter (eq.3.2) produces CO_2 and results in a decrease in pH.



The partial pressure of CO₂ is further affected by the formation and solubility of carbonate minerals, the most important one being CaCO₃. The solubility product of calcium carbonate is defined as

$$K_{cal} = \alpha_{Ca^{2+}} \alpha_{CO_3^{2-}} \dots\dots\dots (3.3)$$

Solubility of calcium carbonate thus releases bicarbonate ions and increases the pH. Pure water in equilibrium with atmospheric CO₂ and calcite has, therefore, a pH of 8.26 (Drever, 1997). The presence of other carbonates increase the pH even further. Very high pH values of lakes are usually found in endorheic regions, where lake water contains very high concentrations of Na₂CO₃. In 1985, Day reported an average pH and salinity of 9.7 and 10 ‰, respectively, for The Lake.

3.3.1.2 *Electrical conductivity*

The electrical conductivity (EC) of a water is a measure of, and is normally proportional to, the total ionic concentration or salinity, particularly in lakes dominated by the bicarbonate anion (Juday and Birge, 1933; Rhode, 1949). Thus changes in concentrations of the major ions will be reflected in conductivity changes.

The EC of The Lake varies between 32 and 530 mS.m⁻¹ (Table 3.1). The total concentration of dissolved solids (TDS) was estimated by adding the concentrations (mg.L⁻¹) of the major ions Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, HCO₃⁻ and SO₄²⁻. The sum of the major constituents is probably an underestimation of the true amount of TDS in the water as it does not take dissolved organic and un-ionised compounds into account (Standard Methods, 1995). However, it does give information on the salinity and purity of the water, as well as providing information on the accuracy of the conductivity measurements.

A comparison between EC (m.S.m⁻¹) and calculated TDS (mg.L⁻¹) shows that they correlate very well for all stations except Site 7 (Figure 3.1). The low EC value at this station is assumed to be due to an analytical error. The EC increases from the east to the west, reflecting the intrusion of freshwater. Site 1 and 2, having the lowest concentration, are

located in the inlet channel of the lake. The low TDS/EC concentration confirms that the observed inflow is incoming stormwater and does not represent the bulk lake water. The low temperature of water from Site 1 supports this assumption. Sites 1 and 2 are therefore not included in the following discussion. The impact of stormwater on The Lake is discussed in detail in Section 3.3.2. The average conductivity of The Lake was calculated to be 423 mS.m^{-1} . According to the Talling and Talling (1965) system for African lakes, The Lake is classified as class II, saline ($60\text{-}600 \text{ mS.m}^{-1}$). The salinity of Class II lakes is thought to be due largely to Na, Cl and HCO_3 as a result of accumulation and evaporation in closed basins or by inflows rich in solutes.

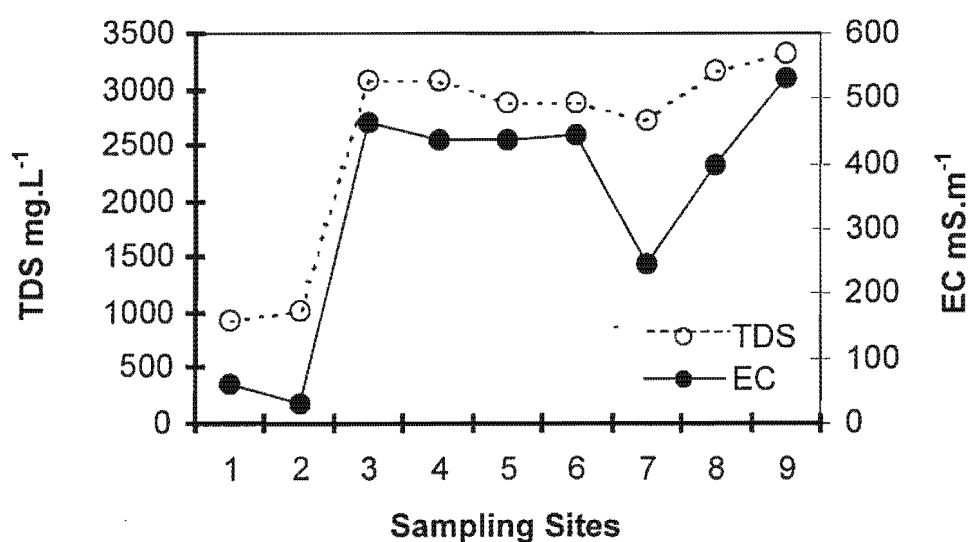


Figure 3.1: Electrical conductivity (EC) and total suspended solids (TDS) concentrations measured in surface waters of The Lake in May. TDS is calculated as the sum of the major ions in solution measured in mg.L^{-1} .

3.3.1.3 Ionic composition of major anion and cations

The ionic composition of the bulk water of The Lake is similar to that of diluted seawater.

The ionic dominance order is:

Cations: $\text{Na} > \text{Mg} > \text{Ca} > \text{K}$

Anions: $\text{Cl} > \text{SO}_4 > \text{HCO}_3$

Typical hardwater lakes are dominated by Ca and HCO_3 (Wetzel, 1983). The observed deviation from this rule can be explained by the chemical and physical processes that act upon water. According to Gibbs (1970) the three major mechanisms controlling the ionic composition of surface waters are rock dominance, atmospheric precipitation and evaporation-precipitation processes. Rock dominant waters are characterised by a dominance of Ca and HCO_3 , whereas waters strongly influenced by atmospheric precipitation are found to be Na and Cl dominant. Rainfall carries much of the atmospheric salt to lakes, and particularly in maritime regions accounts for a significant input of marine salts into fresh waters (Gibbs, 1970).

According to regional South African studies rivers and wetlands in the Western Cape were found to be almost without exception Na and Cl dominated (Silberbauer and King, 1991; Day and King, 1995). In The Lake the dominance of these two ions was to be expected considering its proximity to the sea, the lack of a natural freshwater inflow and its recharge by a saline, coastal aquifer.

The concentration of Ca and Mg in the water is predominantly governed by solution and precipitation processes. The solubility product of dolomite ($K=10^{-17.09}$) is much lower than of calcite ($K=10^{-8.43}$) (Drever, 1997). The first mineral to precipitate after only slight evaporation is therefore CaCO_3 , whereas MgCO_3 precipitates significantly only at very high pH values (>10). Due to high evaporation rates in summer Ca and HCO_3 concentrations decrease markedly as a result of precipitation of CaCO_3 (Wetzel, 1983). Decalcification is enhanced in HCO_3 rich waters under conditions of high primary production (Section 3.3.1.1).

3.3.1.4 *Organic matter*

Chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a water sample that is susceptible to oxidation by a strong chemical oxidant. COD measures between 95 and 100% of the total concentration of organic matter, both reactive and non-biodegradable (Drever, 1997). Pyridine and related compounds can resist oxidation and volatile organic compounds are oxidised only to the extent that they remain in contact with the oxidant (Standard Methods, 1995).

COD concentrations in the surface water samples of The Lake were found to be high ranging from 78 to 114 mg.L⁻¹. Organic matter in lakes can either be allochthonous (formed in soils of the terrestrial environment and transported into the lake) or autochthonous (humic substances formed within the aquatic environment). Average COD concentration in the bulk water of The Lake was higher than in the incoming stormwater. It is, therefore, assumed that a large proportion of the COD is produced within The Lake itself. In the aquatic environment dominant sources of organic matter are plankton and macrophytes. Stewart and Wetzel (1982) reported that dead macrophyte leaves are rapidly decomposed into humic substances. Considering the dominance of *Potamogeton pectinatus* in The Lake and the large amount of cut dead plant material present at the time of sampling, it is assumed that the pondweed is likely to be the major source of organic matter in The Lake. For several vleis in the Cape Peninsula, Gardiner (1988) discussed the importance of organic matter as a matrix for cation/phosphorus complexes.

3.3.1.5 Nutrients

Nitrogen and phosphorus concentrations measured in The Lake are summarised in Table 3.2.

Table 3.2: Nutrient concentrations and N:P ratios measured for water samples taken in May 1998.

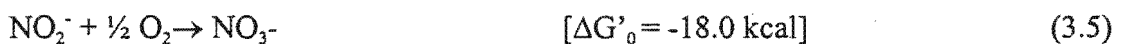
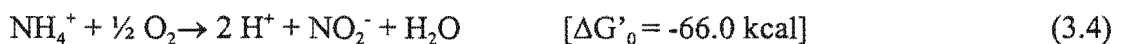
Site	1	2	3	4	5	6	7	8	9
Constituents mg.L ⁻¹									
NH_4^+	0.12	0.27	0.35	0.35	0.27	0.31	0.29	0.22	0.37
NO_3^-	0.02	0.05	0.05	0.05	0.05	0.05	0.06	0.05	0.07
Total P (TP)	0.42	0.23	0.19	0.25	0.20	0.15	0.19	0.09	0.10
Soluble reactive P (SRP)	0.39	0.21	0.13	0.10	0.07	0.08	0.09	0.02	0.02
$(NH_4^+ + NO_3^-) : SRP$	<1	1	3	4	4	4	4	14	24

Ammonia is the major nitrogenous end product of bacterial decomposition of organic matter, through a process referred to as ammonification. Because of their low stability intermediate nitrogen compounds formed in this process rarely accumulate (Wetzel, 1983). NH_4^+ is strongly sorbed to particulate and colloidal particles. Considering the high COD in The Lake it is, therefore, assumed that a large proportion of NH_4^+ is present in the form of particulate NH_4^+ . The measured dissolved NH_4^+ concentration is, therefore, likely an underestimation of the total NH_4^+ concentration in the water.

The concentration of NH_4^+ in the stormwater (Site 1) is lower than the NH_4^+ concentration of the bulk lake water. It is suggested that NH_4^+ in the lake could be produced internally rather than being introduced by external loading. Sources of NH_4^+ could be invertebrate faecal pellets and, probably more importantly, decomposing pondweed. Besides natural senescence, the current practice of pondweed harvesting at The Lake is likely to contribute significantly to the nitrogen concentration in the water (Section 1.2.4).

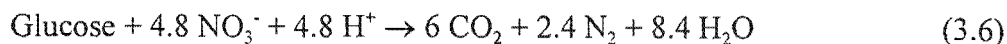
The main processes by which NH_4^+ is removed from the water are sedimentation, assimilation by plants and algae and transformation into NO_3^- by nitrification. An oxidised microzone is critical to the solubility and sorption properties of sediments. Without the oxidised layer the adsorptive capacity of sediments is reduced and a marked release of NH_4^+ from the sediments occurs (Wetzel, 1983, see also section 4.3.5).

Nitrification is a two step process that only occurs in the presence of oxygen. The first step is performed by chemolithotrophic bacteria of the genus *Nitrosomas*. These bacteria are mesophilic with a wide range of temperature tolerance (1-37°C), and grow optimally at a pH around 7 (Wetzel, 1983). Under the utilisation of energy and reduction of CO_2 ammonium is oxidised to NO_2^- (eq.3.4). During this process hydrogen ions are produced, resulting in a decrease in the pH. Oxidation of NO_2^- (nitrite) to NO_3^- is further conducted by *Nitrobacter*. This bacterial genus is less tolerant of low temperature and high pH.



Under oxidising conditions, NH_4^+ concentrations are generally low. However, nitrification is inhibited by low availability of NH_4^+ , low pH, high salinity and the presence of tannins in the water. As NH_4^+ was measured in excess over NO_3^- , NH_4^+ is not assumed to be a limiting factor. The prevailing salinity of The Lake could be inhibitory to nitrification, resulting in an accumulation of NH_4^+ in the water. Harris (1988) states that nitrification is in particular reduced by high chloride concentrations. Tannins, released from the adjacent Fynbos may also play a role.

NO_3^- assimilation by algae and denitrification are the main processes that reduce NO_3^- concentration in the water. Denitrification (eq 3.6) is the bacterial reduction of oxidised nitrogen anions. Denitrifying bacteria are biochemically and taxonomically very diverse, but restricted to anaerobic or microaerophilic (oxygen $< 4 \text{ mg.L}^{-1}$) environments (Dodds and Fey, 1995).



DH Environmental Consulting (1998) reported an average dissolved oxygen concentration in the water of 9.8 mg.L^{-1} . Although oxygen content is highly variable this is an indication that the water column of The Lake is on average well oxygenated. Its size and basin morphometry further are in favour of well-oxygenated surface water. In a relatively small water body such as The Lake, frictional stress of the wind at the water surface causes it to be driven directly in the direction of the wind, while friction at the bottom of the water column tends to retard the circulation. Strong winds, typical for the area, will also cause waves at the surface that will maintain high levels of dissolved oxygen in the water (Shillington, *in writing*¹). It is, therefore, inferred that the low NO_3^- to NH_4^+ ratio is caused by rapid assimilation of NO_3^- rather than denitrification of NO_3^- .

The concentration of total phosphorus (TP) and ortho-phosphate (SRP) in the incoming stormwater (Site 1) is higher than the average concentration in The Lake (Site 3-9). It is therefore concluded that incoming stormwater is a major source of P into The Lake. In The Lake itself the concentration of both TP and SRP decreases from the eastern to the western end.

The difference between TP and SRP reflects mainly the quantity of phosphate bound to organic substances and polyphosphate. These compounds do not react with the molybdate reagent. However, in the analyses of TP the sample is digested with persulphate prior to analyses which converts organic bound P and polyphosphates into SRP (Standard Methods, 1995).

¹ F.A. Shillington, PhD, Department of Oceanography, UCT

At Site 1 and 2 concentrations of SRP and TP are almost identical, indicating that most P entering The Lake is in form of SRP. Within The Lake the concentration of SRP is approximately half the concentration of TP, indicating that about 50% of the TP is bound organically. Organically bound P can either be P within plant material (detritus, algae) or P adsorbed onto dissolved organic carbon. Under high pH conditions organic surface functional groups are negatively charged and adsorption of P is low (Sposito, 1984). It is therefore concluded that the difference between TP and SRP is most likely due to uptake by algae. The reduction of TP and SRP to 50% from site 1 to site 2 is assumed to be due to dilution as the ratio between TP and SRP does not change.

The N:P ratio was found to be very low in the incoming water, as well as in the eastern half of The Lake. Dominance of urban-impacted waterbodies by blue-green algae is often linked to low prevailing N:P ratios (Shapiro, 1990). Zeekovlei, another alkaline coastal lake on the Cape Peninsula, has been known to be inhabited by blue-green algae since ca 1920. Since at least the last ten years the “pea-green” colour is associated with a continuous bloom of *Microcystis spp.* favoured by N:P ratios below 10 (Harding, 1996). N:P ratios of less than 16 indicate nitrogen limitation, where ratios above 16 indicate phosphorus limitation. The use of N:P ratios to predict phytoplankton composition can be problematic in cases of dense algae blooms. Some algae, especially blue greens, exhibit “luxury uptake” of P when it is available in the water. A dense bloom can, therefore, significantly increase the apparent (dissolved) N:P ratio (by taking up “excess” P, relative to N, P. Ashton, CSIR, *personal communication*).

The derivation of N:P ratios, from dissolved inorganic nitrogen and phosphorus is not as conclusive as the particulate and total N:P ratios as only the latter reflect the true cellular ratios. Nevertheless, even from the dissolved species it can be concluded that P is not limiting in The Lake and that further increase could lead to a shift in the phytoplankton community towards bluegreen algae dominance.

3.3.1.6 Trace metals

Water samples taken from The Lake in May 1998 were not analysed for trace elements, however data are available for samples taken in August. The Lake is characterised by neutral to alkaline pHs. As most heavy metals are relatively immobile at pHs higher than 6

(McBride, 1994) it is unlikely that the water column of The Lake contains high concentrations of heavy metals. Furthermore, the dominant residential and agricultural landuse in the catchment of the Lake is assumed not to contribute large amounts of heavy metals into The Lake. It is, therefore, anticipated that trace metal concentrations do not change significantly during the winter and that samples taken in August can be seen as representative of the heavy metal concentrations in The Lake. However, some variation is expected due to solubility of sedimentary minerals during winter. As expected trace metal concentrations in the bulk water are very low (Table 3.3). Nevertheless, Cr, Cd, Cs, Nd and U concentrations in sample M1 are approximately an order of magnitude higher than in other water samples. As no obvious source of possible contamination could be located this deviation could not be explained.

Table 3.3: Trace metal concentrations obtained by ICP - MS. Samples analysed were collected in August 1998.

SAMPLE SITES	M1	M2	M3	M4	M5	Inflow
PH	8.65	8.36	8.12	8.21		8.51
EC mS.m ⁻¹	97	78	79	117		87
Total elemental concentration ppb						
Lithium	3.21	2.12	2.12	3.23	1.78	1.81
Aluminium	n.d.*	n.d.*	2.65	1.44	n.d.*	n.d.*
Chromium	3.84	1.91	1.37	2.13	n.d.*	2.31
Manganese	12.6	4.69	12.2	4.24	0.97	3.46
Nickel	2.04	1.13	1.13	1.55	0.83	2.03
Copper	1.62	1.55	8.51	3.21	1.07	5.18
Zinc	12.2	10.3	10.8	11.9	6.65	11.6
Arsenic	1.45	0.73	0.81	1.10	0.61	0.93
Selenium	4.44	2.58	3.67	4.46	1.80	3.53
Rubidium	5.49	4.07	4.48	6.43	3.24	5.86
Strontium	465	359	343	557	310	486
Cadmium	0.45	0.025	n.d.*	0.019	0.013	0.013
Cesium	0.51	0.015	0.016	0.019	0.015	0.024
Barium	18.7	14.0	12.3	22.1	11.9	16.3
Lead	0.96	0.85	0.13	n.d.*	0.27	0.15
Uranium	0.60	0.11	0.23	0.19	0.12	0.11

• n.d. = not detected

Strontium concentrations are high. Strontium concentration is strongly related to the Ca concentration in the water. High concentrations have been reported in calcareous lakes, but

the ratio Sr:Ca falls systematically with increasing Ca (Hutchinson, 1975). As Sr is highly abundant in carbonates, Odum (1951) suggested that the Sr: Ca ratio depends strongly on the parent material. The ratio is very much higher in primary rock than in calcareous sediments, but the former material dissolves much less easily than the latter, leading to high Sr concentrations, but low Sr:Ca ratios in calcareous waters.

3.3.1.7 Speciation of metals using MINTEQA2

Speciation of metals was simulated using MINTEQA2. MINTEQA2 has a built in component to handle dissolved organic matter (DOM). DOM is characterised in terms of metal binding constants and binding site densities. These parameters can only be obtained by detailed information regarding the chemical nature of the humic substance. The model assumes a continuum of binding sites that can be described by a particular distribution. DOM is treated as complex material consisting of many monoprotic acid sites. The sites are assumed to be normally distributed with respect to their binding constants (logK values) for protons and metals (Nowicki, 1997). The MINTEQA2 database for DOM is based on values obtained for fulvic acids from the Suwannee River in Georgia, USA. Binding site concentrations (L) are estimated using the relationship:

$$L \text{ (moles of sites)} = (\text{DOC} \times 2) \times (5 \times 10^{-4}) \quad (3.7)$$

The computer simulation confirmed that under prevailing condition most of the metals would be complexed with other ions. Mg and Ca were predicted to be the main constituents governing metal availability. 90 % of Ni^{2+} , 89% of Zn^{2+} and 44% of Cu^{2+} was anticipated to be complexed with CO_3 . Förstner and Wittman (1979) investigated the co-precipitation of heavy metals with carbonates and suggested that it can be an important mechanism to remove heavy metals from solution. However, when overall heavy metal concentration is low, other metal sinks, such as highly reactive cations, can have a higher affinity for metals than CO_3 (Jenne, 1976, cited in Förstner and Wittman, 1979).

MINTEQA2 is programmed such that dissolved organic matter has a high affinity for metal cations. Under neutral to alkaline pHs deprotonation of the carboxylic and phenolic groups of DOM and DOC provide high affinity cation adsorption sites (Helling *et al*, 1964). Gardiner

(1988), who investigated the complexation behaviour of humic substances in several vleis in the Cape Peninsula, found that Fe was strongly complexed by the humic fraction. Assuming a DOC concentration of 50 mg.L⁻¹ MINTEQA2 predicted 92 % of Cu²⁺ to be bound in organic matter and only 2.4% complexed with CO₃. A similar pattern was anticipated for Zn²⁺: only 9% was calculated to be complexed with CO₃, whereas 90% was associated with DOC. Ni²⁺, however, was still more strongly affiliated with CO₃ (65%) than with DOC (35%). For all three metal cations the percentage bound to DOC increased with increasing DOC concentration. The model calculations suggests that under alkaline conditions as prevailing in The Lake metals in solution are likely to be complexed with dissolved organic matter. This would have the effect that metal would be more mobile and biological available for longer periods.

3.3.2 Temporal variation in water composition of the Lake

3.3.2.1 *Water sources of The Lake*

Harrison (1962) described two types of vlei systems in the Western Cape: acid vleis, fed by mountain streams, and alkaline vleis, which are not fed by any natural defined watercourse. The latter are referred to as vleis with a “local” catchment, as the only source of surface flow is runoff generated in the catchment. The Lake is an example of a vlei with a local catchment. As discussed in Chapter 2 the Noordhoek Valley falls within the South African winter rainfall region. Figure 3.2 illustrates annual rainfall and water table fluctuation of The Lake. The seasonal cycle of rainy winters and dry summers means that the water level of The Lake drops by about one meter in summer, and is then replenished by inflow of rainwater in the following winter. Most of the recharge takes place in the form of stormwater runoff, whereas only 30 % is accounted for by direct rainfall. Of the stormwater discharging into The Lake, 40% originated in the adjacent Fish Hoek catchment and was artificially routed into The Lake via the Sun Valley Wetlands.

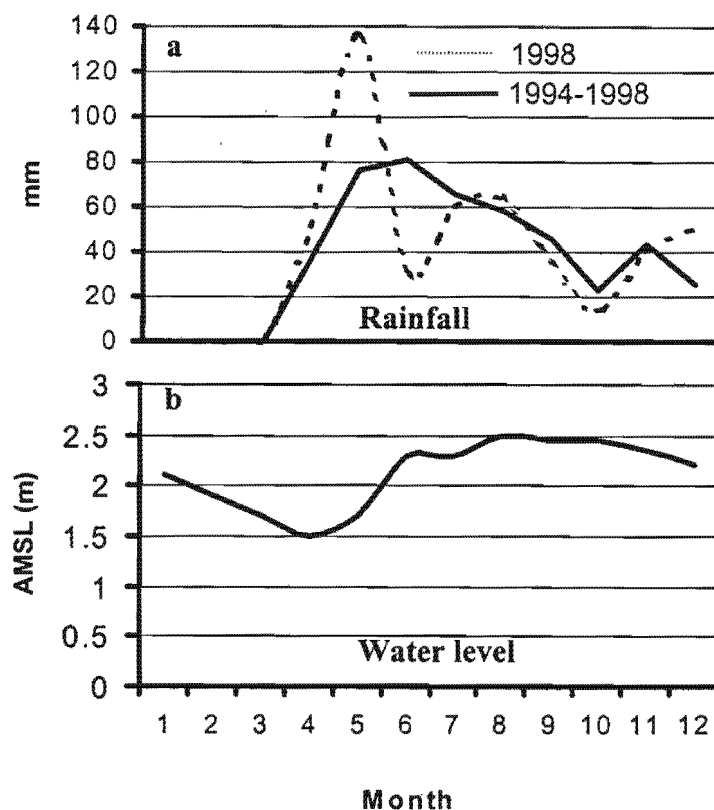


Figure 3.2: Physical data on rainfall and water level for The Lake. Rainfall, measured in mm per month are averages of daily readings from a local rainfall gauge. Rainfall data are presented as annual average for the last five years, as well as data for 1998 (a). Water level fluctuations are presented for 1998 (b).

During the summer the only source of water inflow to The Lake is groundwater. Data on the chemical composition of the groundwater were obtained in 1990 by the Division of Water Technology (CSIR) in Stellenbosch. The average composition of samples taken from five boreholes north-west of The Lake is presented in Table 3.4. The majority of the boreholes were inserted to a depth of 7.6 m. This depth coincides with the upper (0-30m depth) unconfined aquifer that forms the summer source of water to The Lake. Although the samples taken can only be seen as “spot samples” and are not representative for the whole aquifer, the data obtained gives some indication of the quality of the groundwater. The groundwater is moderately acidic (pH 5.8) and displays a typical maritime signature, resembling the

composition of dilute seawater (Maucha, 1932, see also Figure 3.3 a). Note that the analytical results from these boreholes show that the natural background salinity is fairly high with Cl between 9.7 mmol.L^{-1} and 11.4 mmol.L^{-1} (Table B.3, Appendix B). In addition, the survey obtained one sample of seepage water. This sample showed relatively high contamination in regards to K and DOC. According to the CSIR (1990) the sample is most likely to resemble pollution from the urban environment.

Table 3.4: Chemical composition of groundwater and seepage sampled in the vicinity of The Lake (CSIR, 1990). Chemical data for rainwater was obtained from Jonkershoek, Stellenbosch (Nowicki, 1997).

		Groundwater	Seepage	Rainwater
PH		5.8	6.5	4.9
EC	mSm^{-1}	140	70	no data
Total alkalinity	$(\text{mmol}_c \text{CaCO}_3 \text{L}^{-1})$	0.56	3.56	no data
DOC	(mg.L^{-1})	5.12	29	no data
CATIONS				
Sodium	$(\text{mmol}_c \text{L}^{-1})$	8.55	1.96	4.87
Ammonium	$(\text{mmol}_c \text{L}^{-1})$	<0.003	0.008	0.167
Potassium	$(\text{mmol}_c \text{L}^{-1})$	0.11	0.35	0.33
Magnesium	$(\text{mmol}_c \text{L}^{-1})$	2.91	2.02	1.98
Calcium	$(\text{mmol}_c \text{L}^{-1})$	1.05	2.75	1.90
ANIONS				
Chloride	$(\text{mmol}_c \text{L}^{-1})$	10.2	1.81	3.1
Nitrate	$(\text{mmol}_c \text{L}^{-1})$	0.005	<0.001	0.016
Sulphate	$(\text{mmol}_c \text{L}^{-1})$	1.9	1.58	1.46
Phosphate	$(\text{mmol}_c \text{L}^{-1})$	<0.002	<0.002	no data

Chemical data for rainfall in the Western Cape are limited. Data collected approximately 20 km from the coast near Stellenbosch show that the composition of rainfall is predominately influenced by the ocean (Table 3.4). Deposition of maritime salts result in the dominance of Na^+ and Cl^+ . Additionally, inputs of oceanic SO_4^{2-} lead to high sulphur concentrations in the rainwater. A comparison between the average concentrations of Na^+ and Cl^+ in The Lake at the end of summer (41 mmol.L^{-1} and 46 mmol.L^{-1} respectively (Appendix A) and in the

rainfall (3 mmol.L^{-1} and 5 mmol.L^{-1}) shows that concentrations in the rainfall are well below the normal range of Na^+ and Cl^+ levels present in the vle. It is therefore assumed that rainfall has a dilution effect on the water composition of The Lake. Note that although the rainwater is acidic (pH 4.9) the pH of the seepage sample is neutral. The increase in pH and the relative increase of Ca^{2+} concentration in the seepage indicate the leaching of calcium carbonate from the catchment. The soils of the Noordhoek catchment are described in Chapter 2. In general they can be described as skeletal quartzitic sandstone-derived soils or wind-blown regic sands. Of these regic sands, some are calcareous and others are acidic and decalcified. In combination with the ferruginous mudstones of the Graafwater Formation the acidic sands and the quartzitic sandstone derived soils have formed well leached podsols. As a result of the podsolisation the soils contain a diagnostic ferrihumic horizon and have suffered severe base cation depletion. The net results are soils of low pH. TMS-derived soils supporting montane fynbos communities show pH values between 3.2 and 4.5, while acidic sand supporting sandplain lowland fynbos communities have a pH around 5.2 (Wiskowski and Mitchell, 1987). In contrast the younger dune sands are not as well leached and lack the ferrihumic horizon. The sands are generally calcareous or associated with shell deposits, resulting in richer supply of base cations and anions and thus a higher soil alkalinity and pH. Aeolian sands supporting strandveld communities have yielded soil pH values of 6.6 to 7.5 (Wiskowski and Mitchell, 1987).

Analyses of water samples taken along the drainage route of the Fish Hoek stormwater shows that the composition of the samples were highly variable (Table 3.5). The flow direction of the water is from ST6 to ST1. As the samples were taken during a rainfall event it is thought that interflow and direct rainfall resulted in the dilution of the smaller water bodies (ST3 and ST4). Direct urban runoff (ST6) shows high contamination in respect to K^+ and NO_3^- , but low SRP concentrations. Low phosphorus concentrations were to be expected as the samples were taken in the middle of winter (Section 3.3.2). In general the water is alkaline, and higher in calcium and bicarbonate than water from The Lake.

Table 3.5: Analytical data for water samples taken from Fish Hoek Stormwater and Sun Valley Wetlands on August 31, 1998.

SAMPLE SITES		ST1	ST2	ST3	ST4	ST5	ST6
pH		8.62	8.05	8.18	8.4	8.33	8.11
EC *	($mS.m^{-1}$)						
Total alkalinity	($mmol$)	2.90	2.30	1.57	2.10	1.47	5.54
DOC	($CaCO_3.L^{-1}$)						
	($mg.L^{-1}$)	no data	34	8.4	no data	38.4	no data
Anions							
Chloride	($mmol_C.L^{-1}$)	2.15	3.28	1.95	1.68	5.58	5.44
Nitrate	($mmol_C.L^{-1}$)	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.08
Sulphate	($mmol_C.L^{-1}$)	0.31	0.52	0.35	0.63	1.49	0.87
Cations							
Sodium	($mmol_C.L^{-1}$)	1.70	2.65	1.51	1.80	4.69	4.51
Ammonium	($mmol_C.L^{-1}$)	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Potassium	($mmol_C.L^{-1}$)	0.09	0.13	0.09	0.08	0.26	0.29
Magnesium	($mmol_C.L^{-1}$)	0.83	1.33	0.69	1.04	2.51	1.94
Calcium	($mmol_C.L^{-1}$)	1.28	2.17	1.05	1.15	4.90	2.35
Total element concentration							
Lithium	ppb	0.29	0.55	0.28	0.35	1.75	0.70
Aluminium	ppb	42.2	7.35	10.7	45.2	5.82	7.61
Chromium	ppb	n.d.	1.6	0.99	1.14	2.65	0.71
Manganese	ppb	1.22	13.8	3.2	1.22	1.78	1.33
Nickel	ppb	0.91	1.51	1.22	0.74	2.2	1.77
Copper	ppb	5.58	3.43	5.82	0.71	4.2	10.30
Zinc	ppb	7.63	62.6	12.6	11.4	12.5	16.43
Arsenic	ppb	0.57	0.89	0.42	0.73	2.17	0.73
Selenium	ppb	1.31	1.31	n.d.	0.59	3.99	2.00
Rubidium	ppb	2.56	3.52	2.17	2.13	6.8	6.92
Strontium	ppb	204	333	162	218	348	423
Cadmium	ppb	0.02	0.22	0.02	n.d.	0.98	0.07
Cesium	ppb	n.d.	0.01	n.d.	0.02	1.14	0.12
Barium	ppb	6.07	9.75	5.14	4.54	8.9	7.15
Lead	ppb	1.08	1.42	n.d.	0.15	1.35	1.13
Uranium	ppb	0.041	0.05	0.11	0.43	1.85	0.52

• EC data are not presented, as data obtained were found to be unreliable, due to instrument malfunction

3.3.2.2 Variation in water composition

Maucha diagrams were used to illustrate the ionic composition of water samples (Figure 3.3). Strongly Na-Cl dominant waters can be described as “seagull shaped” (Figure 3.3a), whereas waters rich in HCO_3^- , Ca and Mg are described by “butterfly shaped” Maucha diagrams (Figure 3.3e). The latter is typical for the ionic composition of freshwaters, whereas the former is predominately a marine signature.

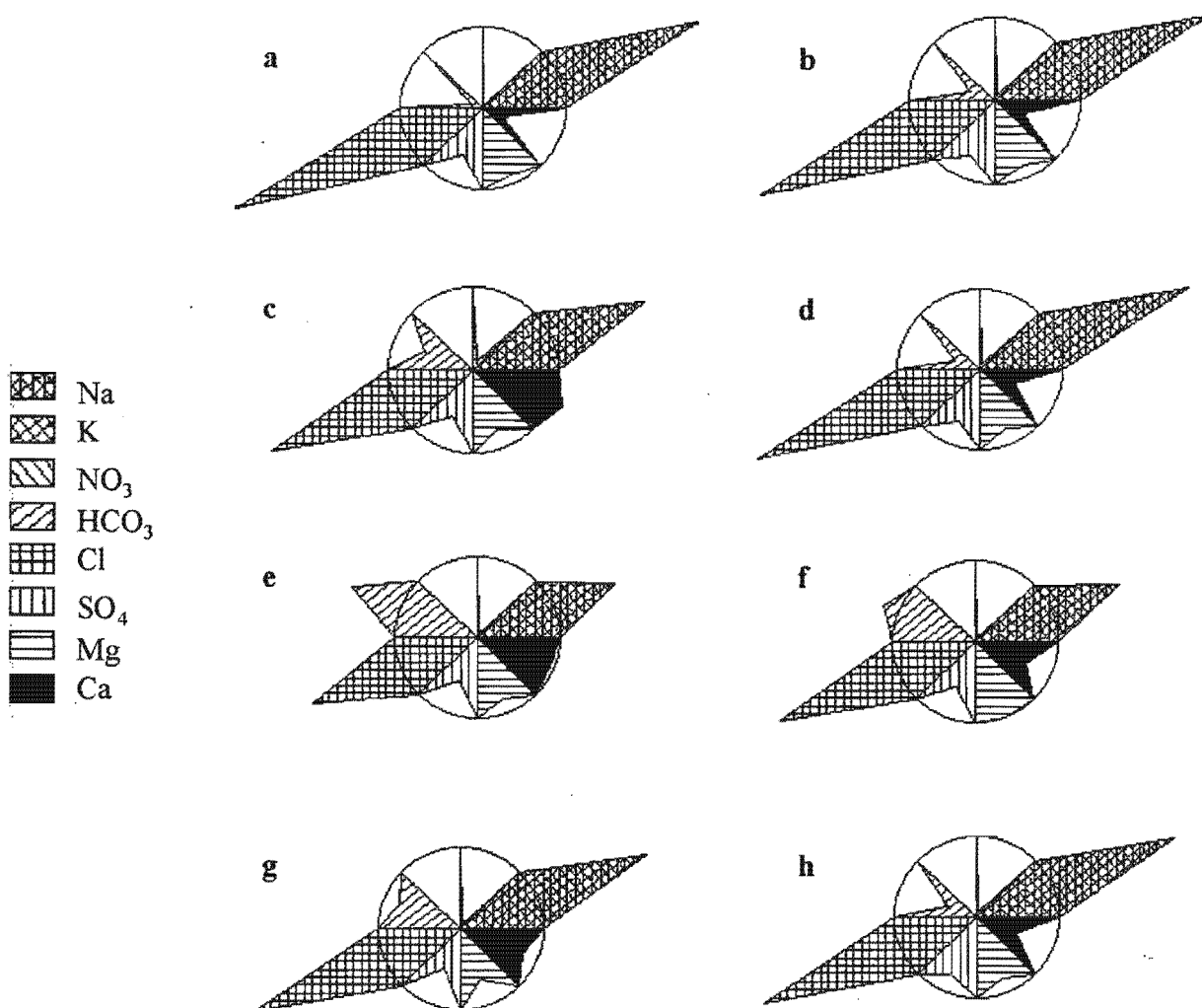


Figure 3.3: Maucha diagrams (Maucha, 1932) illustrating the relative concentration ($\text{mmol}_e\text{L}^{-1}$) of the major ions in stormwater runoff and groundwater in comparison to the ionic composition of surface waters of The Lake for different month. Areas of segments are proportional to the equivalent concentration of major anions and cations.

A comparison between the ionic composition of the average surface water of The Lake in April, May, August and October shows that the ionic composition is relatively consistent showing little seasonal fluctuation (Figure 3.3 b, d, f, h). Dominant ions are Na and Cl, reflecting the strong influence of marine precipitation during winter and the intrusion of saline

groundwater during summer (Figure 3.3a). Relative concentrations of Ca and HCO_3 increase during winter as result of freshwater inflow in the form of stormwater runoff. Note that with the exception of peak winter rainfall events (Figure 3.3e) the ionic composition of stormwater entering The Lake is strongly dominated by Na and Cl (Figure 3.3c, g). The ionic composition of surface water samples taken by the end of summer is very similar to the composition of samples taken by the end of winter. This indicates that although stormwater runoff appears to introduce fluctuations in the relative concentration of major ions in The Lake water, the overall effect on The Lake is negligible. The similarity of the water composition, despite the winter input of Ca and HCO_3 can be explained by the removal of these ions due to precipitation of calcium carbonate.

3.3.2.3 *Evaporation and precipitation*

The net effect of evaporation is to remove pure H_2O from solution, so that the concentration of all dissolved components tends to increase (Drever, 1997). The four data sets available for The Lake provide a good indication of the relationship between seasons and chemical composition of the water. The first sampling was done before the winter rainfall (April, Table B1, Appendix B) and provides a good baseline study of The Lake (D.H Consulting, 1998). The second sampling was conducted just after the first winter rainfall (May), the third in the middle of winter (August, Table B 3, Appendix B) and the last in October (Table B2, Appendix B) after most of the rainfall had taken place.

To investigate the effect of evaporation Cl (a conservative ion) is commonly used as a reference ion (Eugster, 1970, Jones et. al. 1977). With the exception of very concentrated solutions Cl is not removed significantly as a salt or by ion exchange processes or by plant uptake. A comparison between the Cl concentration at the end of winter to the concentration of Cl in the water at the end of summer, therefore, provides a good indication of the magnitude of evaporation. If the concentration of any other ion is plotted against the chloride concentration, the extent to which the concentration of that ion is controlled by evaporation becomes apparent and the degree to which other processes are influencing its concentration can be seen. On a log-log plot, progressive evaporation should cause points to lie on a line with a 1:1 slope, regardless of the initial ratio of the concentrations of the species being plotted (Drever, 1997).

As predicted the water of The Lake shows highest ionic concentrations at the end of summer (April) (Figure 3.4). The log-log plot of Na against Cl shows that all data points fall close to the 45° line (Figure 3.4a). This suggests that Na concentrations are predominantly governed by evaporation.

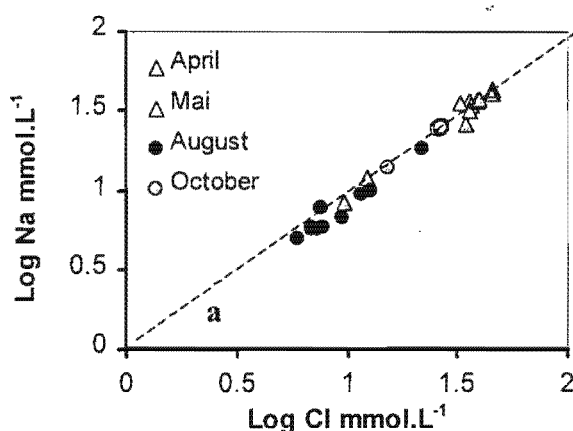


Figure 3.4a. Log-log plot of Na concentration versus Cl concentration for The Lake

SO₄ and K behave conservatively, too: for both ions all data points lie on a line parallel to the 45° line, but offset towards the negative end of the y-axis. The observed pattern suggests that both K and SO₄ are removed in a consistent manner from solution, independent of evaporation (Figure 3.5 a,b). K is most likely to be removed by adsorption onto clay particles, whereas SO₄ is thought to be removed by bacterial reduction into sulphur. If this assumption is correct the reduction would be independent of the SO₄ concentration and should, therefore, not be influenced by seasonal losses of water.

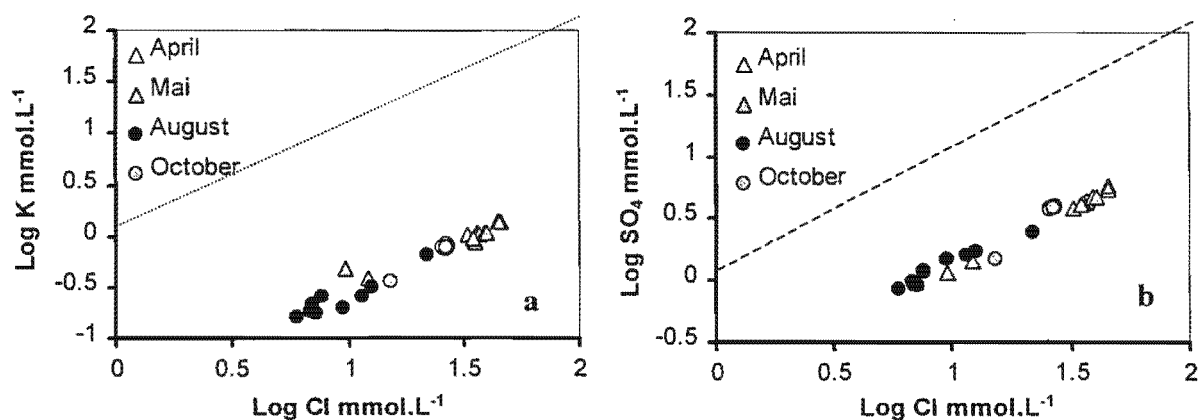


Figure 3.5a,b: Log-log plots of (a) K and (b) SO₄ concentrations versus Cl concentration for The Lake.

Relative to the Cl concentration, the concentrations of Mg, Ca and HCO_3^- decline more strongly in summer than in winter (Figure 3.6 a,b,c). It is suggested that during evaporation the water might become supersaturated in respect to these constituents leading to precipitation of carbonate minerals. In addition warm water conditions favour primary production and photosynthetic uptake of CO_2 (see Section 3.3.1.1). In comparison to Ca and HCO_3^- , the relative reduction of the Mg concentration is very small. Compounds of magnesium are much more soluble than those of calcium and are only precipitated under conditions of high evaporation. It is, therefore thought that the evaporation period is too short to lead to significant magnesium carbonate formation. The dominant minerals to precipitate are therefore thought to be low-magnesium carbonates such as calcite and aragonite (for a detailed discussion see Chapter 4). Gardiner (1988) reported rapid summer decalcification from Rondevlei. His results showed that the calcium concentration was negatively correlated with pH and primary production, confirming that photosynthetic uptake of CO_2 can cause decalcification (Section 3.3.1.1).

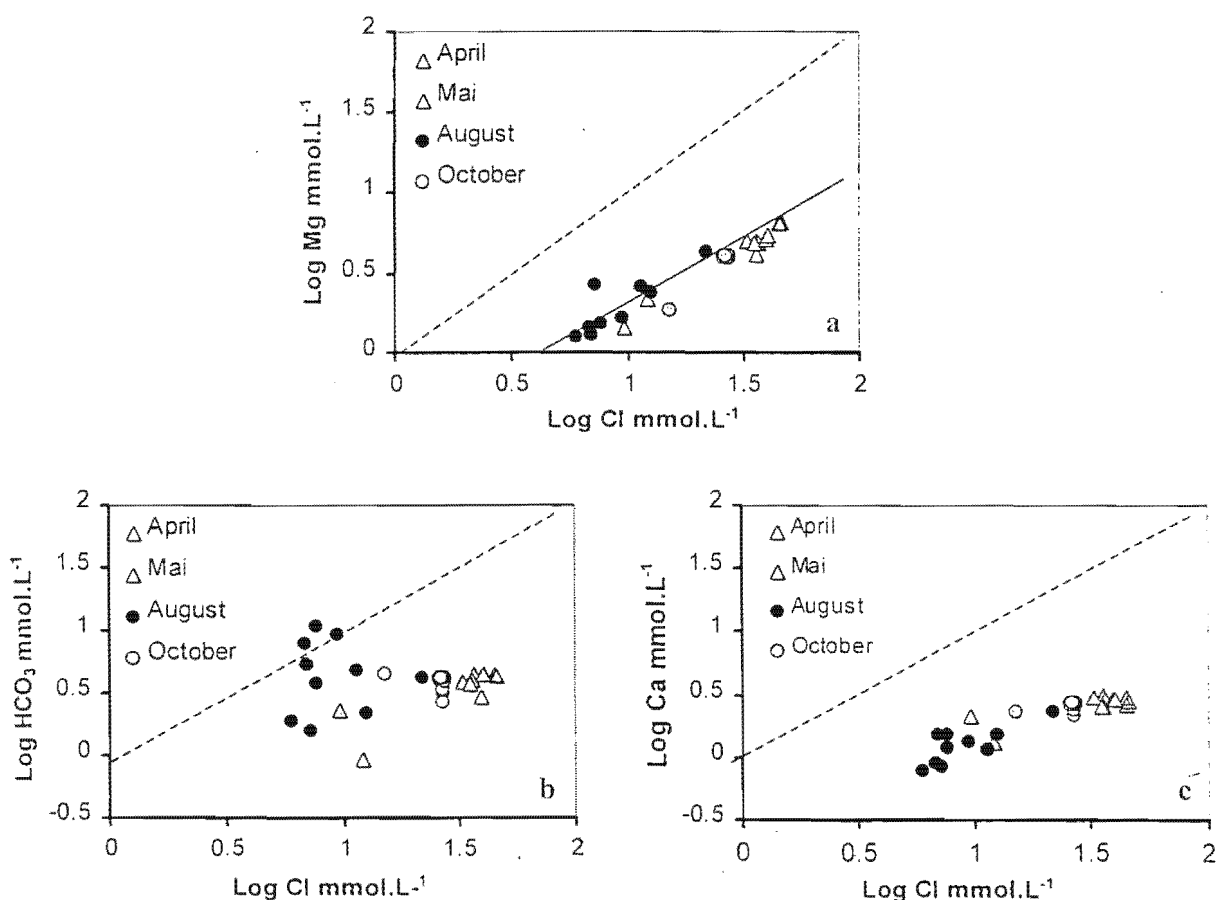


Figure 3.6: Log-log plots of (a) Mg, (b) HCO_3^- and (c) Ca concentrations versus Cl concentration for The Lake.

Similar to the interpretation of the N:P ratio, the ratio between monovalent and divalent ions (M:D) supplies information about the suitability of the prevailing chemical conditions in the water for different algae species (Goltermann and Kouwe, 1980). Pearsall (1932) suggested that diatoms are abundant only in calcareous waters with an M:D ratio below 1.5. For the different seasonal surveys the M:D ratios were 2.4 in April, 2.2 in May, 1.2 in August and 1.9 in October. With the exception of the mid winter sample (August) the ratio of M:D in The Lake is higher than 1.5, indicating that diatoms are not likely to dominate the phytoplankton community. This hypothesis is supported by D.H. Environmental Consulting (1998) who reported diatoms in the lake only during July and August.

3.3.3 Variations in phosphorus concentrations

A comparison between TP and ortho-P in incoming stormwater runoff and average bulk water of The Lake shows that the concentrations are higher in the runoff. This indicates that P generated in the catchment is imported into The Lake (Figure 3.7). The highest P concentration is found in the runoff following the first winter rainfall. This is due to the fact that P is strongly adsorbed onto particle surfaces, which accumulate during dry periods to be transported as suspended material during stormwater events. Although concentrations of suspended material are generally very variable, highest mineral concentrations are to be expected in the first winter runoff (usually May).

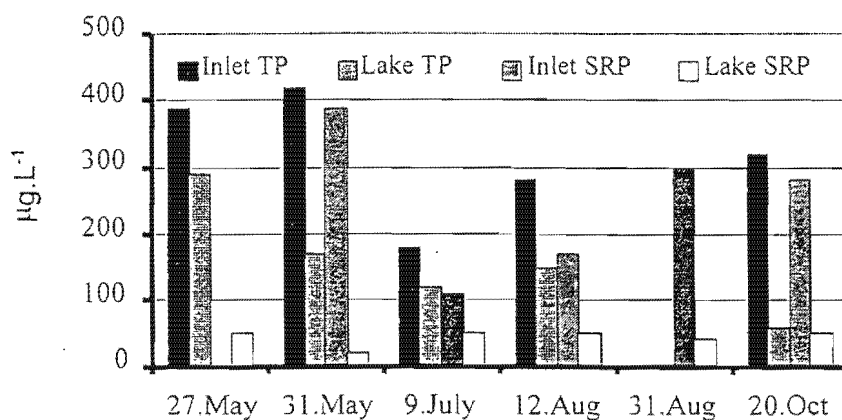


Figure 3.7: Concentration of total phosphorus (TP) and orthophosphate (SRP) measured in incoming water and The Lake.

Runoff as a source of pollution is problematic as the concentrations and total loads are highly variable and diffuse and, as such, generally difficult to trace and address. With increasing amounts of hardened surfaces, hydraulic loading from urbanised watersheds tends to be

characterised by large pulses of stormwater separated by intervals with relatively small volumes of baseflow (Leopold, 1968). Jones and Redfield (1984) postulated that N and P catchment exports increase greatly with development and that P tends to outpace N leading to a decline in N:P ratios as urbanisation proceeds. Table 3.5 illustrates the significance of urban stormwater runoff as a source of P.

Table 3.5. Hypothesised sources of total phosphorus in surface runoff ($\text{kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$) based on impervious residential areas (after Waller and Novak, 1981).

Source	kg of TP per ha per year
Vehicles	0.003
Animals	0.3
Vegetation	5.94
Atmosphere	0.12
Less sweeping of streets	0.9
Less leaf removal from gardens	3.6

According to Jones and Redfield (1984) the effects of urban stormwater runoff on the phytoplankton are not only stimulating from a nutrition point of view, but may also be inhibitory. The inhibitory effect is claimed to be due to reducing light penetration and imported heavy metals. The latter is not considered of great relevance in The Lake, as heavy metal import is very low (section 3.3.1.6). Reduced light penetration might be inhibitory to most algae species, but not to those that have an active buoyancy control such as the typical bloom formers as the *Dinophyceae* and *Microcystis spp* (Reynolds, 1983). In fact high turbidity favours typical bloom formers, while having a detrimental effect on the submerged macrophyte population.

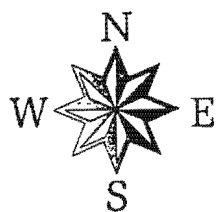
Despite continuous phosphorus input the TP-concentration in The Lake appears to be declining during the course of the winter. The high TP concentration at the beginning of winter indicates that TP concentrations in summer are higher than in winter. Similar results were reported for Rondevlei (Gardiner, 1988). Rondevlei is also subject to severe cultural eutrophication and showed decreasing SRP levels between July and August, with increasing concentrations during midsummer. As chlorophyll-a concentrations remained high during the entire period, Gardiner (1988) explains the decrease in SRP by rapid biological uptake.

According to the Organisation for Economic Cooperation and Development's classification (OECD, 1982), an annual mean TP concentration of $35\text{-}100 \mu\text{g} \cdot \text{L}^{-1}$ classifies a lake as

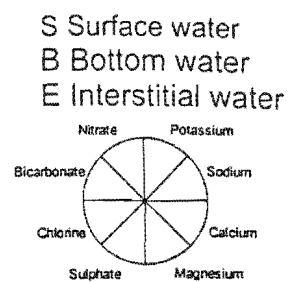
eutrophic. The classification is based on a combination of different factors that include transparency of the water and primary production. Apart from the P concentration the classification for eutrophic lakes stipulates that the mean and maximum chlorophyll-a levels have to be higher than, respectively, 8 and 25 $\mu\text{g.L}^{-1}$. Transparency, measured by Secchi-disk has to be lower than 1.5 m. Very low transparency values (<1 m) have been measured in The Lake and observed during the course of the winter, but no chlorophyll-a data were available. The OECD warns that to avoid arbitrariness the classification system should only be applied on total information and not only one or two parameters (OECD, 1982). However, the high P concentration in The Lake during the course of this study should be seen as a warning signal. The occurrence of two algal blooms, a dense dinoflagellate bloom in May and a smaller cyanobacterial bloom in July, support the assumption that this system is eutrophic.

3.3.4 Spatial variability

The Lake has been previously reported as a well-mixed system (DH Environmental Consultant, 1998). A comparison between water samples taken at various points in The Lake during winter (August) shows that although this might be true for vertical column mixing, it is not always true for horizontal water distribution (Figure 3.8). The main wind direction is the south-east /north- west axes. During winter north-westerly wind events are dominant. As illustrated in Figure 3.8 stormwater flowing into The Lake from the north-eastern corner is pushed towards the north. It is suggested that the stormwater does not mix with the entire water body, but instead is confined mainly to the north-eastern corner of The Lake. Under the assumption that the stormwater is the main source of phosphorus one can use the phosphorus concentration as an indicator of the stormwater movement. The interstitial SRP concentration are more than twice as high in the northern portion of The Lake than in the southern half. The P concentrations in the interstitial water reflect diffusion and mixing patterns and are proportional to the P concentration of the sediments (Boström *et al.*, 1988b). It is, therefore, suggested that the sediments in the northern part of The Lake are enriched with respect to phosphorus, leading to slower phosphate uptake rates in the sediments. The source of the phosphorus is thought to be incoming stormwater as well as runoff from residential gardens within The Lake Estate itself. Due to housing development the north eastern part of the Lake features blind ending, narrow channels which could provide shelter from the wind and “breeding grounds” for algae.



Key



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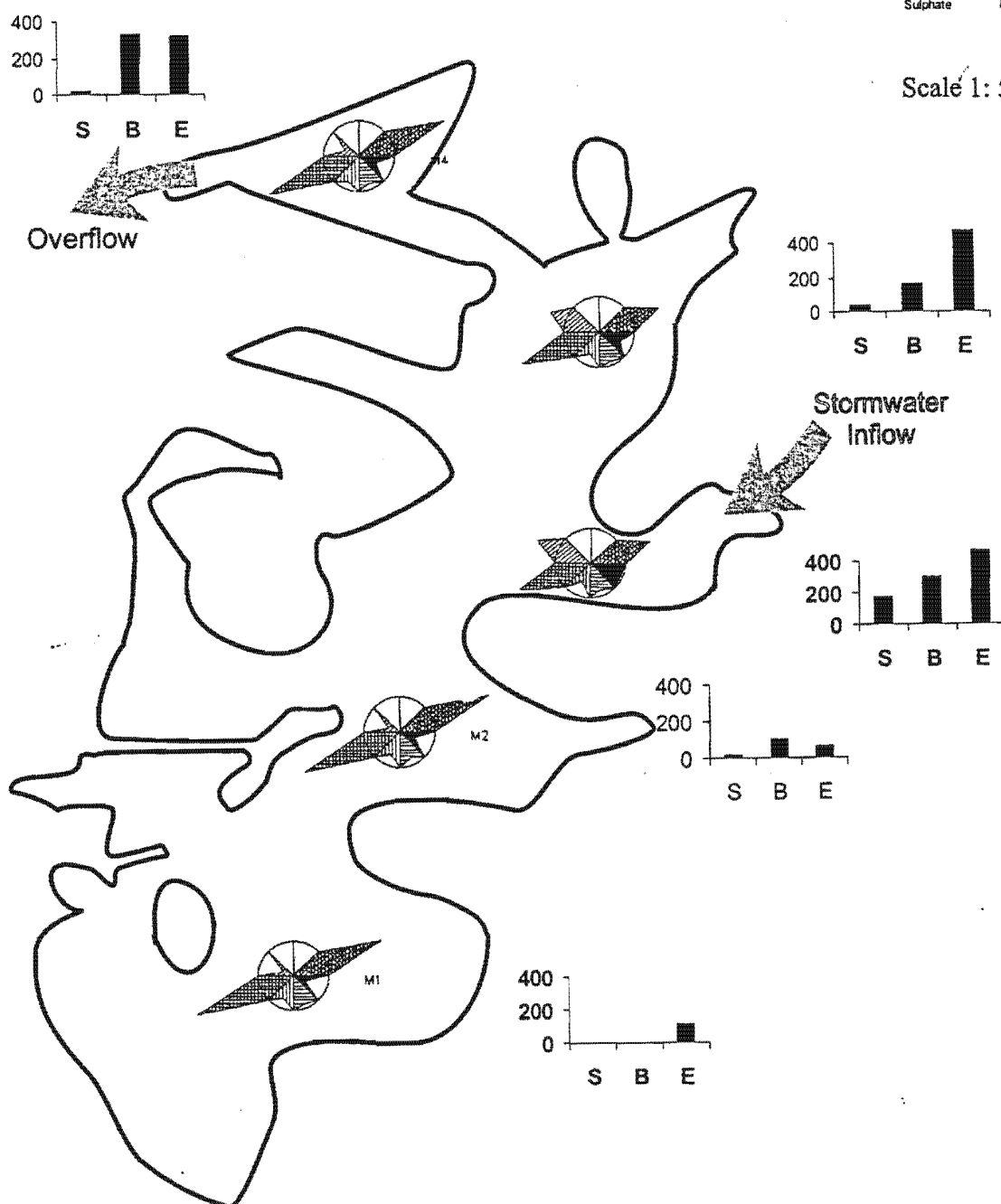


Figure 3.8: Distribution of ortho-P concentration ($\mu\text{g.L}^{-1}$) and ionic composition (mmol_c) in The Lake.

3.4 Summary

The former Noordhoek Saltpan today forms the centrepiece of a marina-type housing development. The semi-enclosed lake is characterised by a local catchment, making groundwater and winter rainfall its main sources of water. The seasonal cycle of rain in winter and dry summers results in seasonal water table fluctuations of approximately one metre.

The Lake is a Na-Cl dominant hardwater lake that undergoes seasonal decalcification. Due to freshwater import of Ca and HCO_3 rich waters during winter rainfall events, the overall water composition shows little seasonal variation. The shallow basin morphometry and the strong prevailing winds result in a well oxygenised water column. Observations of fish kills during periods of calm and warm days suggest local formation of stagnant water, resulting in the formation of H_2S and oxygen depletion. Heavy metal concentrations are low in the water, but nutrients, in particular phosphorus, are high.

The Lake hosts a dense population of the pondweed, *Potamogeton pectinatus*, which is characteristic of saline, eutrophic water conditions. High mineralisation rates, in particular, cause winter senescence of pondweed, result in autochthonous production of organic substances and inorganic nitrogen in the water. The major source of phosphorus into The Lake was identified to be urban stormwater runoff.

High nutrient loads combined with reduced light penetration results in the proliferation of bloom-forming algae. The occurrence of two algal blooms, a dense dinoflagellate bloom in May and a smaller cyanobacteria bloom in July, give rise to concern regarding the water quality of The Lake. The Lake has to be described as eutrophic, but algae blooms have been short-lived and, due to the presence of *Potamogeton pectinatus*, the system in its present condition is not expected to become dominated by algae.

CHAPTER 4

GEOCHEMICAL ASPECTS OF PHOSPHORUS RETENTION IN WETLAND SEDIMENTS

4.1 Introduction

As outlined in Chapter 2 the exchange of phosphorus between sediments and the overlying water is a major component of the phosphorus cycle in natural waters. Sediments can either act as a sink or a source of phosphorus, depending on their ability to retain phosphorus and the conditions of the overlying water (Wetzel, 1983). In order to understand and predict the biological response of the Noordhoek wetlands to increasing phosphorus input, information on the geochemical characteristics of the sediments is essential.

The main objective of this chapter is to gain an understanding of the capacity of wetland sediments in the Noordhoek Valley to retain phosphorus. Interpretation of the adsorption capacity is based on the analysis of sediments collected during the study. Due to time constraints it was not possible to cover the entire area of the wetland and sampling was, therefore, limited to the main water bodies in the wetland. Samples were taken from The Lake, the stormwater drainage system (Sun Valley/Fish Hoek wetland) feeding into the Lake and from Wildevoëlvlei. The chapter presents an outline of the sampling procedure and analytical techniques adopted in this study, together with an interpretation and discussion of the results. The discussion focuses on the consequences of the findings for future management of The Lake and Wildevoëlvlei.

4.2 Materials and Methods

4.2.1 Sampling procedure

A total of ten sediment samples were taken from different vleis within the study area. All samples were collected by boat. Two different sampling methods were applied. At the time of sampling Wildevoëlvlei sediments consisted mainly of a visually homogeneous mass of brown slurry. Sediments were collected by thrusting a bucket upside down into the sediment

until the increase in resistance indicated that a substantial amount of sediment had been collected.

Sediment samples from the other vleis were taken using a van Veen grab sampler that is a standard device for sampling sediments. The open grab was lowered under tension to the sediment surface. At the sediment surface, the tension was released causing a locking bar to disengage. Reapplying tension caused the arms of the grab to close and to trap the sediment. The grab and sediment were then lifted onto the boat where the grab was opened and the sediment slurry allowed to flow into a pre-washed bucket. The containers were labelled and pre-washed to avoid contamination, and covered to limit the effects of sunshine.

Grab sampling rather than core sampling was chosen in order to avoid contact with microcystin contaminated water. Furthermore, most P transfer reactions take place at the sediment/water interface and it was, therefore, considered that sampling the upper 20 cm of the sediments was sufficient for this project.

4.2.2 Sample preparation

According to Twitch (1987) air-drying of sediments alters their physical and chemical characteristics. In order to prevent alterations only wet sediments were used for the determination of the phosphorus isotherms as well as for clay mineralogy. To avoid changes in redox potential and to limit biological processes, samples were stored in sealed containers at 4 °C prior to all analyses.

The preparation of the sediment samples prior to X-ray fluorescence spectrometry (XRFS) analyses required them to be dried. Samples were spread onto plastic trays and air-dried. After drying samples were then gently ground, using an agate mortar and pestle until particles were small enough to pass through a 2 mm screen, and stored in plastic containers.

4.2.3 Analytical techniques

4.2.3.1 pH

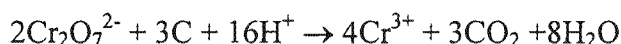
The pH was measured in wet sediments that had been sealed from exposure to the atmosphere. It was measured using a Crison micro pH 2001 pH meter with combined glass-calomel electrode. The pH meter was calibrated before use with buffer solutions, 7.02 and 4.00.

4.2.3.2 Particle size analyses

Particle size analyses were conducted at the Institute for Fruit Technology (Infruitec) in Stellenbosch according to standard methods (Van der Watt, 1966). Prior to analysis sediments were treated with hydrogen peroxide to remove organic matter. Amyl alcohol was added to make the sample foam free. Calgon was used as a dispersant.

4.2.3.3 Organic Carbon

The organic carbon content of the sediments was determined using the Walkley-Black method (Walkley, 1935). Organic matter in soil material may be oxidized by treatment with a hot mixture of $K_2Cr_2O_7$ and sulfuric acid, according to the equation:



After completion of this reaction, the excess dichromate is titrated with iron (II) ammonium sulfate hexahydrate. The amount of reduced dichromate solution is assumed to be equivalent to the organic C present in the sample, assuming that the organic matter has an average valence of zero.

Sediment samples ground for XRFS analyses using a carbon steel Siebtechnik swing mill were used for this analysis. Potassium dichromate solution, and thereafter sulphuric acid, was added to the ground samples and allowed to cool slowly. Ortho-phosphoric acid was added to facilitate the titration reaction. The excess dichromate was titrated with iron (II) ammonium sulphate solution to the ferroin indicator end-point.

4.2.3.4 Carbonate

The carbonate content of the sediment samples was determined by means of the “Karbonat-bombe” (Muller and Gastner, 1971), using the method of Birch (1981). Between 0.5 and 2 grams of ground sediment (depending on carbonate content) were reacted with 5 ml of concentrated HCl in the bombe. The reaction of calcium carbonate with HCl produces CO₂ gas. The volume of CO₂ gas is measured as a pressure change on a pressure gauge fitted to the bombe. The instrument was calibrated using known masses of pure CaCO₃.

4.2.3.5 Total element analyses by XRFS

Bulk element concentrations of major and trace elements in the sediments were determined by X-ray fluorescence spectrometry (XRFS) using a Philips PW X'Unique II X-ray spectrometer. Instrumental conditions are given by Willis (1995). Calibration was by means of international standard rock reference materials.

Powder briquettes and fusion discs were prepared from oven dried samples (105°C) which had been ground in a carbon-steel vessel for 2 minutes using a Siebtechnik swing mill to produce a fine powder ($\leq 70 \mu\text{m}$ particle size). Undiluted pressed powder briquettes were prepared for trace element analyses. Briquettes were pressed from 6 g of sample combined with 6 drops of Mowiol solution (2% Hoechst Mowiol N 70–80 in distilled water) as binding agent and boric acid as backing agent using a 30 mm diameter die under 7-10 tons of pressure.

For major element analyses, fusion discs were prepared. Approximately 3g of sample were dried at 105°C for 5 hours to determine any residual water. The sample was then roasted at 1050 °C overnight, so as to determine loss on ignition (LOI). Organic-rich samples were roasted in a stepwise procedure by spanning the temperature range from 105°C to 1050 °C. The roasted material was used to prepare fusion discs. Fusion discs were made by combining 0.7g of roasted sample with 6 g of Sigma 12:22 flux and 4 drops of wetting agent (2.9M LiBr.). Discs were produced in automatic mode by a Claisse Fluxy instrument, operating under program 8.

4.2.3.6 Clay fraction

The clay minerals were identified by X-ray diffractometry (XRD), after the clay size ($<2\ \mu\text{m}$) fraction had been separated from the remaining particle sizes. Isolation was achieved by dispersing the sample with Na_2CO_3 and flocculating with NaCl . The separated clay slurry was dialysed against distilled water, allowed to dry and ground to a fine powder using a mortar and pestle. The powder was pressed onto a metal slide. XRD scans were performed on dialysed Na-saturated clay using a Philips PW3890 diffractometer. The diffractometer was fitted with a Cu ray tube and operated at 40kV and 20mA. The scanning range used was 4 to $60^\circ 2\theta$ angle at steps of $0.05^\circ 2\theta$ and a counting time of 0.5. second/step.

4.2.4 Experimental determination of phosphorus isotherms

50ml centrifuge tubes were filled with 6g of fresh wet surface sediments (0-10 cm depth) to which 25 ml of 0.02M NaCl solution spiked with various amounts of PO_4 had been added. The experiment was carried out in two steps. In the first procedure initial P concentrations used ranged from 0 to $10\ \text{mg.L}^{-1}$, whereas in a second procedure initial P concentrations were increased using 0, 10, 20, 30, 40, 50, 60, 70, 80, 100 and $200\ \text{mg.L}^{-1}$. The centrifuge tubes were capped with rubber bungs covered with parafilm to prevent contamination, and shaken horizontally on a reciprocal shaker for 24 hours. After the incubation period the tubes were centrifuged at 6000 rpm for 5 minutes. The supernatant was filtered through a $0.45\ \mu\text{m}$ Whatman filter and stored for P determination by the Murphy and Riley (1962) technique. The sediment residue was dried (60°C) and weighed. Samples were then separated into sand and mud fraction by passing through a $60\ \mu\text{m}$ sieve. The sand fraction was weighed and the amount subtracted from the total weight to obtain the percentage of mud. The amount of P sorbed to the sediments was calculated from the change in P concentration during the incubation and recorded as mg P per kg of mud.

4.2.5 Extraction of bioavailable P

Bioavailable P present in Noordhoek wetland sediments was determined at the Institute for Fruit Technology (Infruitec). Two methods were used: firstly by Mehlich acid extraction, Mehlich (1978) and secondly by alkaline extraction using the method described by Olsen *et al.* (1954). The acid extraction 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^+ on the

extraction system. A stock solution (600 cm³ NHF and 200 cm³ concentrated HCl, diluted up to 20 dm³ with de-ionised water) is added to the sediment sample and shaken thoroughly, before filtering through Whatman No.2V filter paper. In the case of the alkaline extraction (Olsen *et al.*, 1954), phosphorus is extracted from the sediments with a 0.5M Na HCO₃ solution (pH =8.5). After both extraction methods P-free charcoal is added to the filtered suspension to remove interfering organic acids and to decolourise the extract. Total inorganic phosphates in the extracts are determined by automated colorimetric analysis by first converting condensed phosphates present to ortho-P by hydrolysis with sulphuric acid at 90°C. The total phosphate concentration is then determined following the ascorbic acid method described by Murphy and Riley (1962).

4.2.6 Geochemical modelling

Reaction path modelling was done using the geochemical models MINTEQA2 and PHREEQC. The models are mathematical representations of solution samples at chemical equilibrium. MINTEQA2 Version 3.11 was developed by the Centre for Exposure Assessment Modelling of the United States Environmental Protection Agency (USEPA). PHREEQC is derived from the Fortran program PHREEQE, but has been completely rewritten in C. PHREEQC essentially combines the capabilities of four earlier codes: PHREEQE, WATEQ4F, PHREEQ-M, and NETPATH, with some added capabilities and improvements. For the purpose of this study the most important feature of PHREEQE is its ability to use redox couples to distribute redox elements among their valence states in speciation calculations.

4.3 Results and Discussion

4.3.1 General characteristics

Sediment samples differed strongly on the basis of colour and consistency (Table 4.1). Shell fragments were found in samples from The Lake and in the Loch Venus sample. Benthic macrofauna was found to be very scarce in all samples with only two groups present. The ghost midge larva of the Dipteran family *Chironomidae* was present in samples of The Lake and Wildevoëlvlei, while Oligochaetes were only detected in the latter. Samples from both

vleis exhibited very strong odour of sewage, but whereas samples from The Lake had a characteristic “rotten egg” (H₂S) smell, Wildevoëlvlei samples had a typical sewage odour.

Table 4.1: Summary of in situ evaluation of sediments.

	Fish Hoek vlei	Loch Venus	The Lake	Wildevoëlvlei.
average pH	7.01	6.99	6.98	4.58
colour	white	Brown	black	brown
consistency	clayey	Sandy	semi-solid	slurry
odour	none	None	rotten egg	sewage smell
shell debris	none	Present	present	none
plant litter	none	None	present	present

The Wildevoëlvlei sediments were found to be acidic, varying from pH 4.2 to pH 4.7, whereas the sediments of the other vleis were neutral with very little variation (pH 6.98 – pH 7.01).

The red midge larvae, also referred to as “blood worm”, is commonly found in low oxygen conditions, such as lake bottoms or areas of high organic pollution. The red color is due to the presence of hemoglobin that stores oxygen. This allows them to live in sediments where oxygen is limited. Much of the earlier work on lake classification was based on the presence of different Diptera families, where the *Chironomidae* were indicative of eutrophic lakes (Thienemann, 1954). The absence of any other macrofauna in the sediments besides Oligocheates and Chironomidae further indicates eutrophic conditions (Wetzel, 1983).

Odour displayed by sediments is indicative of anaerobic decomposition of organic matter. The typical “sewage smell” is attributable mainly to volatile fatty acids, aromatic compounds and ammonia, while the “rotten egg” smell, typical of waterlogged sediments, results from the formation of reduced sulphur compounds, in particular H₂S. The “sewage smell” is a result of hydrolysis and fermentation of organic material by a heterogeneous group of facultative and obligate anaerobic bacteria, while the rotten egg smell is produced by strictly anaerobic sulphur reducing bacteria.

4.3.2 Particle size

The distribution of different grain sizes within the samples of the Noordhoek sediments is presented in Figure 4.1. Sand is the dominant fraction, contributing more than 60 % in all samples analysed. According to Wentworth soil texture classification scheme sediments from Wildevoëlvlei (W) are categorised as sand, whereas sediments from The Lake (M) are categorised as loamy sand and sandy loam. Sediments collected from the Sun Valley/Fish Hoek wetland, which serves as a stormwater drainage system for parts of the Fish Hoek stormwater as well as for overflow from the Serina kaolin mine can also be described as sandy loam for Loch Venus (LV), whereas the sediments of the Fish Hoek vlei are higher in clay content and qualify as sandy clay. Sample FV1 was taken from the edge of the vlei and is not seen as being representative for the vlei.

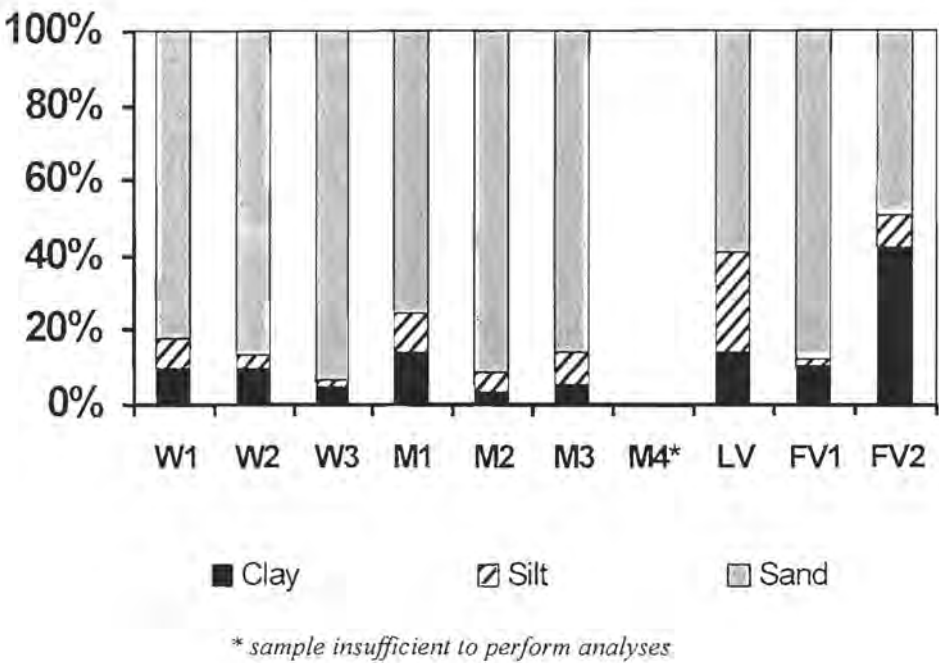


Figure 4.1: Distribution of grain size classes in analysed samples. The clay fraction refers to grains smaller than 0.002 mm, silt to 0.02-0.002 mm and sand to grains between 2.0 and 0.02 mm.

The sediments are representative of the geology of the area. Given the proximity to the beach, the high wind erosion and the geological origin of the vleis (Section 1.2.1) the high percentage of sand within the samples was to be expected.

During the separation of the clay fraction for XRD analyses, very little actual clay mineral material could be separated from the Wildevoëlvlei sediments. The scarcity of clay minerals can be explained by the location of Wildevoëlvlei at the foothills of the Rooikrans mountains. The Rooikrans mountain is characterised by sandy soils typical of the quartzitic fold range such as Lamotte and Fernwood soil forms (Table 1.1). The Lake is situated in the centre of the valley basin and is not only subjected to runoff from the northern mountain range, which are dominated by Clovelly and Hutton soil forms, but also, especially the eastern end, to runoff from the Serina kaolin mine areas.

The trend in Loch Venus and Fish Hoek vlei towards more clayey sediments can be explained by discharge of runoff from the rehabilitation area at the Brokkefeld Serina kaolin mine. Waher (1971) describes the sediments in The Lake (prior to construction of the Marina development) as very variable, predominantly consisting of fine sand, but in places very silty and clayey. Sediments in The Lake are up to 80 m deep, with deep layers of clay (John Rodgers, *personal communication*¹). It is, therefore, thought that dredging of the vlei in 1972 did not have a significant impact on the sedimentology of The Lake.

The grain size of sediments is the primary factor controlling sediment capacity for concentrating and retaining trace elements (Thorne and Nickless, 1981). It is well established that elemental concentrations show a general increase from coarse to fine grained fractions as the latter have a larger surface area (e.g. Förstner and Wittman, 1979).

4.3.3 Organic Carbon

The percentage of organic carbon is highly variable within and amongst the different vleis. The Lake varies from 2.7 % to 13.1 %, Wildevoëlvlei from 3.1 % to 26 %, while the organic carbon content in Loch Venus and Fish Hoek vlei was found to be 2.8 % and 0.9 %, respectively.

¹ Dr. John Rodgers: Senior lecturer at the Department of Geological Sciences, UCT

At the time of sampling The Lake hosted a dense stand of the pondweed, *Potamogeton pectinatus*. Depending on the density of the plants at different sampling points, a proportion of living plant material was collected with the sediment sample. It is, therefore, likely that the organic carbon results obtained overestimate the true organic matter content in the sediments. However, the dense population of the pondweed should result in a high organic detritus flux to the sediments and organic matter would be expected to be high in the sediments. In addition the presence of pyrite (Section 4.3.4), indicates that organic matter is abundant within sediments of The Lake. In comparison, the sediment sample collected from Loch Venus, taken from a macrophyte-free bottom had a much lower organic content (3 %). This is surprising as the vlei is only seasonally flooded and during summer hosts a dense community of sedges (*Ficinia spp*, *Scirpus spp.*) and grasses, predominantly couch grass (*Paspallum vaginatum*). Fish Hoek vlei did not display any plant growth. In addition riverine vegetation does not exist, which explains the very low organic matter content of the sediments.

In Wildevoël vlei the population of submerged macrophytes was negligible at the time of sampling. A high concentration of organic matter was to be expected due to the high organic content of the secondary treated effluent that is discharged into the vlei. However, concentrations were probably elevated due to the die-off of the macrophyte population prior to sampling (Section 4.3.1).

Lanz (1997) discussed the overestimation of organic carbon in reduced sediments using the Walkley Black Method. He argues that dichromate, used to oxidize the organic matter, can also oxidize ferrous iron present in minerals. Samples from the Lake are characterized by the presence of various highly unstable iron sulphides. As the organic carbon determination was carried out on dried sediment oxidation of the iron sulphides may have occurred, leading to the formation of unreactive ironoxides. Overestimation due to the oxidation of ferrous iron can, therefore, be excluded.

4.3.4 Clay mineralogy

The clay fraction, separated from 6 sediment samples representing different vleis in the wetland, was analysed by XRD. The analysis was purely qualitative and due to time and

material restraints no attempt was made to analyse any mineral in depth. Information on the mineralogy was mainly used to gain an understanding of the interaction between dissolved P and wetland sediments.

Diffraction patterns of the untreated Na-saturated clay fractions extracted from sediments samples are presented in Figure 4.2. In general the peak intensities for the clay minerals detected were affected by the powder mount used. Hand grinding is unlikely to yield particles much less than 40 μm . When packed as a powder, orientation of individual grains tends to be governed by juxtaposition of faces formed by preferential cleavages. Instead of random orientation, which will reflect the correct intensities of the minerals, particles are orientated in a plane parallel to the sample surface resulting in over emphasised intensities (Moore and Reynolds, 1997). Peaks between 7–20 $^{\circ}2\theta$ are most affected (L. Petrik, *personal communication*²). Deviation of the diffraction pattern from the baseline between 20 and 40 $^{\circ}2\theta$ indicates large quantities of amorphous material present in the sample .

² Leslie Petrik: Research Officer, Department of Geological Sciences, UCT

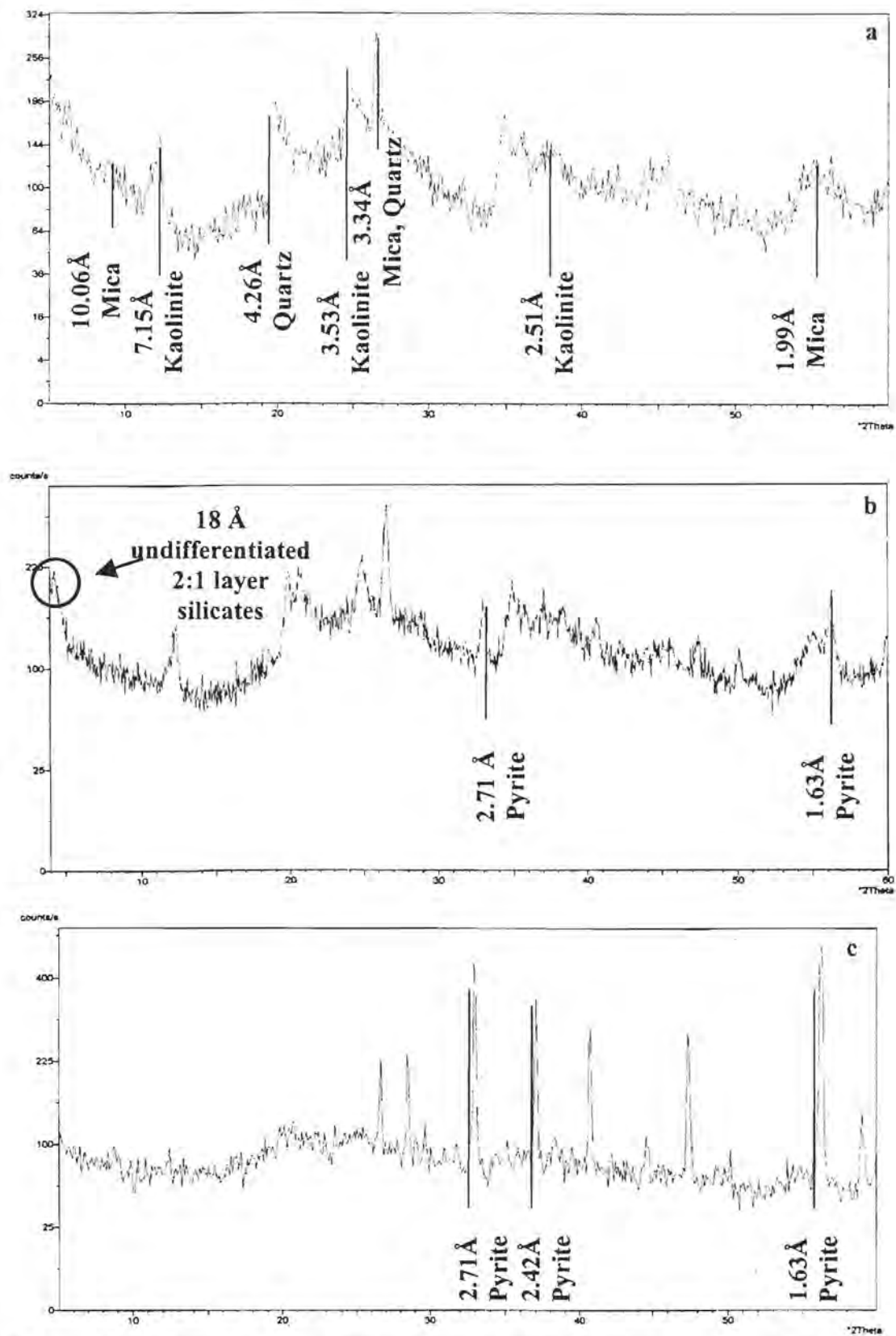


Figure 4.2: Diffractograms of Noordhoek Wetland sediments. Typical pattern for sediments from the Sun Valley/Fish Hoek Wetland (a) and the eastern (b) and western side (c) of The Lake.

Kaolinite was identified by three peaks at 7.15 and 3.58 Å with a smaller peak at 2.51 Å. Subdominant is mica, identified at 10.06, 3.34 and 1.99 Å. A very intense Quartz peak is seen at 3.34 with smaller peaks at 4.26. Considering the very small principal mica peak at 10.06 Å it is assumed that very little mica is present and that most of the peak at 3.34 Å is caused by quartz. Peaks between 15 and 18 Å indicate the presence of 2:1 mixed-layer silicates, e.g. smectite, vermiculite or chlorite. Differentiation of the expanded minerals was not carried out. Without heating of the clays or solvating with ethylene glycol it is impossible to distinguish between different 2:1 minerals. Non-clay minerals were detected as pyrite at 1.63, 2.71 and 3.13 Å, and quartz.

The minerals were not evenly distributed between the samples. Fish Hoek Vlei and Loch Venus sediments were dominated by kaolinite, mica and quartz, whilst no pyrite was detected (Figure 4.2a). The mica peaks show a very broad peak expansion, indicating the weathering of mica to Vermiculite. Pyrite is only detected in sediment samples from The Lake. Diffractograms of sediments from the eastern part of The Lake show clearly the presence of clay material, identified as kaolinite and mica, as well as pyrite (Figure.4.2b). Towards the west, however, pyrite becomes the dominant mineral and only very small amounts of kaolinite and mica were identified (Figure.4.2c). The difference in mineral composition between sediments in the western and the eastern part of The Lake is thought to be due to runoff from the catchment as well as the influence of stormwater from the Fish Hoek area. The eastern site is exposed to direct mountain runoff, whereas the western site is only fed by interflow.

Kaolinite is a weathering product of feldspars. In the Noordhoek Valley the aluminium hydroxide silicate originates from the potassium feldspar associated with the Cape Granite (see Chapter 1). Crude kaolinite is a mixture of three main minerals: kaolinite, quartz and mica. In the mining process kaolin is extracted and the waste mica and quartz returned to the quarry for backfilling. Kaolinite, a 1:1 clay mineral, is characterised by low a surface area and low cation exchange capacity (McBride, 1994). In acid to neutral systems the clay may become positively charged, providing the basis for anion exchange sites.

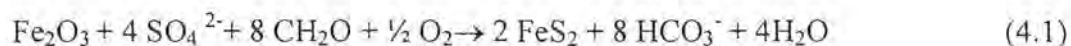
Mica refers to a group of 2:1 phyllosilicate minerals, which are characterised by relatively strong electrostatic forces between the negatively charged silicate layers and potassium as the

balancing cation between the interlayer spaces (Fanning *et al.*, 1989). Mica, occurring in flakes, is common in coarse-textured sediments close to igneous and metamorphic rock types (Fanning *et al.*, 1989). Although the kind of mica occurring in unconsolidated sediments depends upon the origin of the sediments the most common forms of mica are muscovite and biotite (Frye *et al.*, 1962). Muscovite is normally much more resistant to weathering than biotite. In the highly weathered environment of the Noordhoek Valley muscovite is, therefore, more likely to be the dominant form.

From the shape of the mica peaks it appears that in The Lake expandable 2:1 minerals are formed. Barshad (1948, cited in Fanning *et al.*, 1989), was the first to show that vermiculite could be formed from biotite. Since then the transformation of K-bearing micas to expandable 2:1 minerals by replacement of the K^+ ion with hydrated cations has received much attention (see review by Norrish, 1973). The replacement of K^+ with weakly hydrated cations such as Rb^+ and Cs^+ results in an increase of surface area and therefore in an increase of the cation exchange capacity of the mineral (McBride, 1994).

The presence of quartz could be a result of inclusion of some silt into the clay fraction during clay separation or it could be present in the sediments as physically weathered quartz grains of less than 2 μm equivalent diameter.

Pyrite (FeS_2) is formed mainly under the combination of three conditions: a brackish or saline environment, an iron source and a high organic matter content (especially if sulphate-rich). The main chemical reaction of formation is (Drever, 1997):



Under reducing conditions the first iron sulphide minerals to form are amorphous FeS , which undergoes diagenetic conversion to pyrite. A phase diagram illustrating the relationship between redox potential and the activities of different FeS minerals is shown in Figure 4.3. Monosulphides represent the first reaction product between sulphide and ferrous iron. This includes amorphous (FeS_1), mackinawite (FeS_{1-x}) and greigite (Fe_3S_4). Although greigite is not strictly monosulphuric, it is often included in this group because it is, like the others, very unstable (Rabenhorst and James, 1992). The group (referred to as acid volatile sulphides - AVS) is responsible for the characteristic black colour of the sediment and is often

accompanied by an odour of H_2S (Doner and Lynn, 1989). They are rarely identified in X-ray diffraction techniques, due to their instability in the presence of oxygen. However, for tidal marshes in South Carolina, Rabenhorst and James (1992) report the fraction of the AVS to be approximately one tenth of that of pyrite.

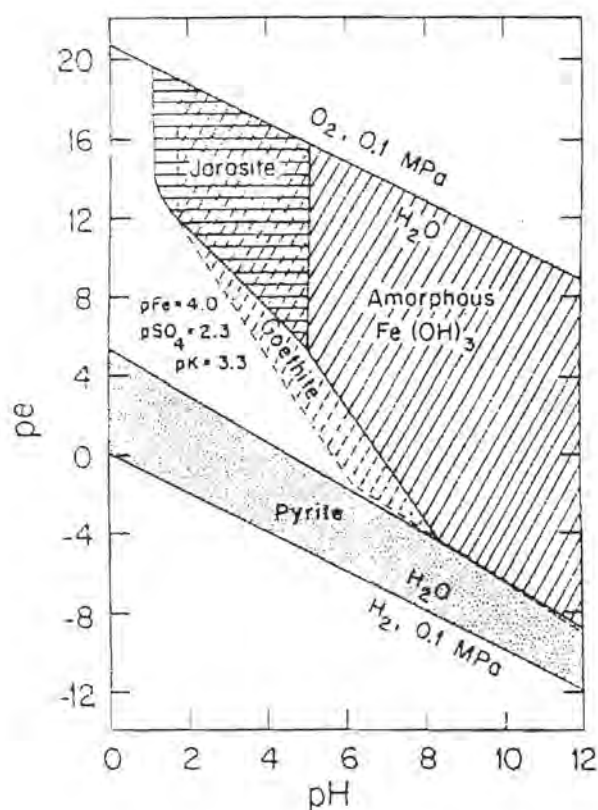


Figure 4.3: A pH-pe diagram of pyrite, jarosite, amorphous $\text{Fe}(\text{OH})_3$, goethite, and soluble components at 0.1 MPa total pressure and 25°C. The activities of solution species are $(\text{Fe}^{2+}) + (\text{Fe}^{3+}) = 10^{-4}$, $(\text{SO}_4^{2-}) = 5 \cdot 10^{-3}$, $(\text{K}^+) = 5 \cdot 10^{-4}$. Shaded areas represent solid phases (Diagram redrawn from Doner and Lynn, 1989).

4.3.5 Redox status

Although no attempt was made to measure the redox status of the sediments, there is strong evidence of reducing conditions in most of the samples. Firstly, all samples with exception of sample F1 displayed a change in colour after exposure to air. Samples from the Lake changed from a dark black to grey while samples from Wildevoëlvlei and Loch Venus changed to a light brown. Secondly, the strong odour displayed by the sediments is indicative of strongly reducing conditions.

Under anaerobic conditions the catabolism of organic matter by microorganism can be achieved either by fermentation or by anaerobic respiration (Lovely and Phillips, 1989; Cho, 1982). The formal definition of fermentation is that organic substrates act both as electron donors and, as acceptors, and may concern large polymers such as starch and cellulose. The organic substrata play the role of an internal electron donor and one of the metabolites produced acts as an electron donor. The organic substrate is not fully oxidised to CO₂ in fermentative processes which accounts for build-up of partially reduced compounds (alcohol, fatty acids) (Schlesinger, 1991).

The metabolism of organic substrates by anaerobic respiration involves inorganic electron acceptors, such as nitrate, sulphate and CO₂. Such metabolism generally uses small molecules produced by fermentative metabolism or by aerobic biodegradation that takes place in the nearby oxic environment (Ottow, 1971). The products of fermentation, organic acids and alcohol, are converted to acetic acid by acetogenic bacteria .

The build up of amino and fatty acids ("sewage smell") in sediments of Wildevoëlvlei could be caused by two mechanisms. Firstly, the supply of organic material is higher than the bacterial breakdown and secondly the oxygen content of the sediments is not low enough for the strictly anaerobic acetogenic bacteria. Both The Lake and Wildevoëlvlei are subjected to strong winds. The oxygen content of the microzone is influenced primarily by the intensity of microbial and respiratory metabolism. High organic input leads to rapid depletion of the oxygen, hence to reducing conditions. In Wildevoëlvlei these winds result in frequent perturbation of sediments, whereas in The Lake the dense stock of pondweed stabilises the sediments and prevents strong perturbation. Re-oxygenation of sediments may, therefore, occur in Wildevoëlvlei, but not in The Lake, resulting in lower (more negative) redox potential in the latter.

Phosphorus retention and release is strongly redox-dependent (Reddy and D'Angelo, 1994). The sediment-water interface separates two different environments. The sediments are characterised by slow molecular diffusion processes, whereas in the water particles move at much higher and more variable rates (Wetzel, 1983). In terms of exchange processes the most important property of the sediment-water boundary is the oxygen content of the upper few millimetres. This zone is referred to as oxidised microzone. The presence of an oxidised

microzone will result in an upward-diffusion of Fe^{2+} , Mn^{3+} and subsequent formation of Fe^{3+} and Mn^{2+} oxides. This surficial oxide layer exhibits a high adsorption capacity for phosphate and promotes the removal of P from the water. By contrast, under very reducing conditions such as those prevailing in The Lake, sulphur scavenges free Fe^{2+} to form monosulphides and pyrite. Fe^{2+} is no longer available for P adsorption, resulting in an overall decrease of the adsorption capacity of the sediments (Roden and Edmonds, 1997).

4.3.6 Chemical composition

The concentrations of major and trace elements determined by means of XRFS for the sediments analysed are summarised in Table 4.2 a and b. The sum of the weight percentages of the major elements fell within the range of 97–102 %, indicating acceptable analytical accuracy for the purpose of the study.

Table 4.2a: Analytical results of major element concentrations in sediments. Values are given in mass percent of the relevant oxides. Sulphur and iron are reported as reduced species.

Sample Sites	W1	W2	W3	M1	M2	M3	M4	LV	FV1
Major elements									
SiO_2	58.3	68.4	81.4	13.8	77.5	65.5	20.2	57.4	91.5
TiO_2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.2	0.2
Al_2O_3	4.9	2.6	2.1	1.5	2.2	1.9	6.4	4.4	3.6
FeO	1.3	1.6	1.3	4.2	3.1	2.1	7.9	2.0	1.3
MgO	0.6	0.4	0.3	1.7	0.8	0.6	1.6	0.9	0.1
CaO	4.2	4.4	1.1	26.1	4.3	12.6	12.4	11.8	0.6
Na_2O	0.1	0.0	0.1	0.2	0.1	0.2	0.3	0.1	n.d
K_2O	0.4	0.2	0.3	0.1	0.2	0.2	0.4	0.3	0.2
P_2O_5	1.7	2.2	0.3	0.2	0.1	0.2	0.8	0.2	0.0
S	1.9	1.1	0.8	4.3	2.2	1.5	5.8	1.5	0.1
H_2O	4.1	2.9	1.8	2.9	1.0	0.9	4.7	2.0	0.4
LOI	23.6	17.7	12.9	39.4	10.4	15.4	37.3	18.8	3.0
Total	100	101	102	98	101	101	97	100	101

Table 4.2b: Analytical results of trace element concentrations in sediments. Values are reported as mg.kg⁻¹.

Sample Sites	W1	W2	W3	M1	M2	M3	M4	LV	FV1
Trace elements									
Barium	109	71	47	98	60	55	149	131	55
Scandium	5.4	3.5	2.4	2.2	3.3	5.0	5.0	7.0	2.3
Zinc	92	44	12	14	5.5	6.9	243	22	13
Copper	29	19	11	5.0	5.5	9.3	7.9	11	8.7
Nickel	10	16	14	6.8	10	16	7.9	15	12
Cobalt	2.8	3.2	3.2	4.0	5.0	4.2	7.2	5.7	1.8
Manganese	193	258	111	553	343	200	600	355	75
Chromium	24	52.4	45.8	17	30	49	16	50	40
Vanadium	19	19.0	17.5	12	14	16	24	26	21
Molybdenum	0.9	5.7	4.9	4.0	4.6	6.1	8.4	5.1	3.7
Niobium	5.7	3.6	3.1	1.7	2.9	1.8	2.4	6.0	4.6
Zirconium	161	158	116	46	86	76	46	180	153
Yttrium	13	7.8	7.3	6	10	12	59	17	8.0
Strontium	186	182	55	1000	205	666	605	579	37
Uranium	2.2	2.6	1.0	2.4	1.2	2.4	3.7	2.0	2.2
Rubidium	26	16	14	7.7	11	12	23	22	18
Thorium	6.7	4.1	3.9	3.2	2.3	3.6	5.3	5.0	4.0
Lead	40	22	17	8.9	6.7	5.1	18	12	15

It is common procedure to discuss sediments on the base of four major components: resistate minerals, carbonate minerals, clay minerals and organic fraction, where SiO₂ is interpreted as representing the quartz distribution, CaO the carbonate mineral distribution, FeO the oxide distribution and Al₂O₃ the mud/clay fraction (Degens, 1965). In the strongly reducing environment of the Noordhoek sediments FeO was considered to be representative iron sulphide minerals (Section 4.3.5).

No significant correlation (at the 95% confidence level) was found between the clay size fraction and weight percentage of AlO₂. This can be explained by the similar quantity of mica and kaolinite in the sediments, as most of the mica flakes occur in the coarse-grained size fraction. AlO₂ was found to be significant correlated to TiO₂, K₂O, V, Y, Rb, Th, Ba and Zn. K is most likely to occur as adsorbed K⁺ ions in the inter-layer spaces of micaceous clay minerals, whereas it becomes replaced by Rb in the transformation process towards expandable 2:1 layer silicates (Figure 4.4a, c). In the presence of organic matter V is found as VO²⁺ in reducing environments and substituted into the structure of layer silicates (McBride, 1994). Titanium is found in biotite and hornblende, both are associated with igneous rocks such as granite (Milnes and Fitzpatrick, 1989). Ba and Zn are strong chemisorbents and adsorb onto clay surfaces. However, the strength of the correlation is weak (Figure 4.4 b),

which could indicate a different distribution of the elements between the vleis. Wildevoëlvlei sediments are characterised by a very high organic matter content and low pH. Curtis (1966) proposed that various trace metals form complexes with organic matter. The low pH leads to reduced cation exchange capacity of clay minerals, but dissociation of the carboxyl groups in organic matter (McBride, 1994). Under these conditions organic matter has, therefore a higher affinity for trace elements than clay minerals. It is, therefore, suggested that most of the trace elements in Wildevoëlvlei are associated with the organic matter, rather than with the clay fraction. Sediments of The Lake are alkaline and more clayey and clay minerals are expected to dominate the cation exchange capacity.

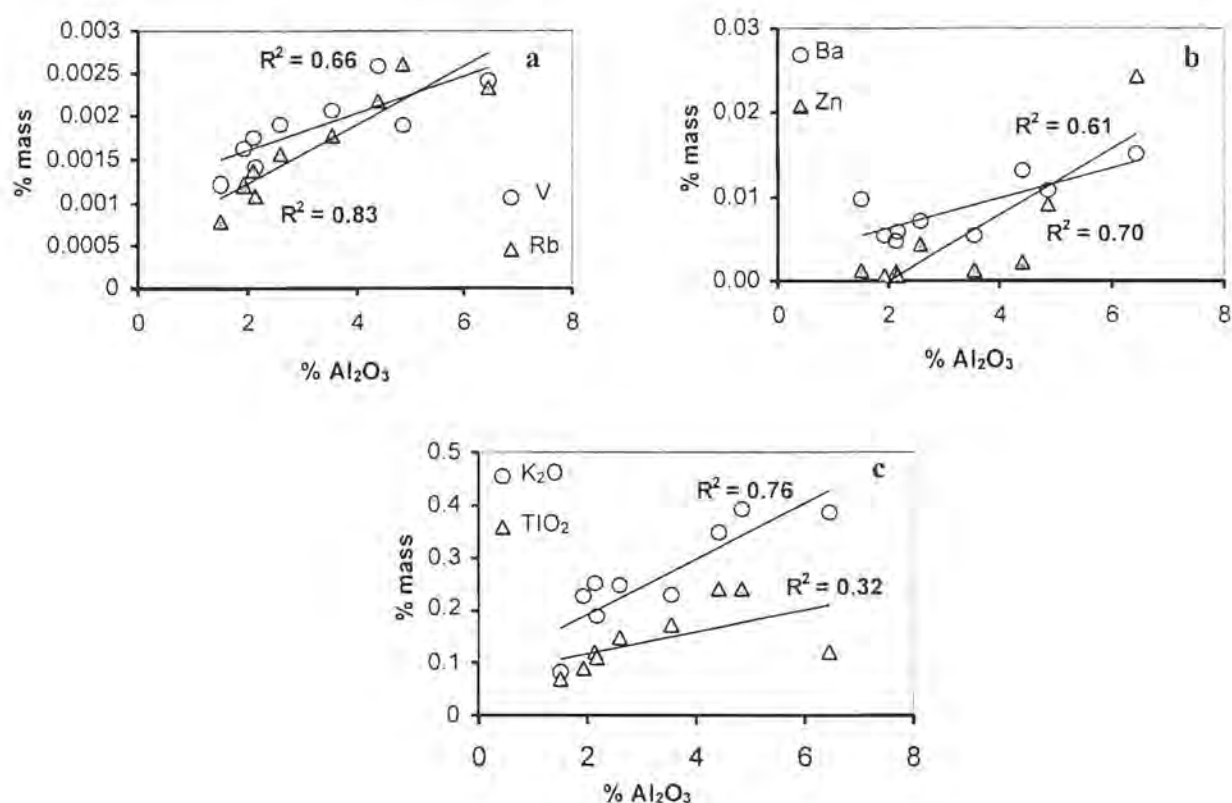


Figure 4.4: Correlation between the percentage weight fraction of, V, Rb (a), Ba, Zn (b) and TiO_2 , K_2O (c) and the clay fraction in Noordhoek wetland sediments. The clay fraction is represented by the percentage weight fraction Al_2O_3 . The correlation is significant at the 95% confidence level.

There is no significant correlation between SiO_2 and the sand size fraction. The clay mineral analyses shows that a significant amount of quartz occurs within the fine fraction. SiO_2 in

form of quartz is, therefore, distribution within all grain sizes and a strong correlation with the sand size fraction should not occur.

As discussed Noordhoek wetland sediments are presumed to be strongly reducing. Fe determined by XRFS is taken to represent various ironsulphide minerals. In oxidised sediments Fe forms various polyhydroxy species of polycations, hydroxides, oxyhydroxides and oxides, which are often associated with clay surfaces (Oades, 1984). The lack of correlation between the percentage weight fraction of Al_2O_3 and FeO confirms that very little Fe is present in form of oxide clay coatings, indicating that most of the Fe is present as Fe^{2+} . FeO is positively correlated with S, Zn, Co, U, MgO and LOI. FeO and Mn are both strongly correlated to S indicating the presence of manganous sulphides and, as discussed earlier, ironsulphides (Section 5.34). Under reducing conditions Co is complexed with S, forming strong insoluble sulphides. Zn is a chalcophile and tends to occur as the extreme insoluble sulphide mineral, sphalerite (ZnS). In oxidised environments it chemisorbs on oxides and would be associated with Fe (McBride, 1994).

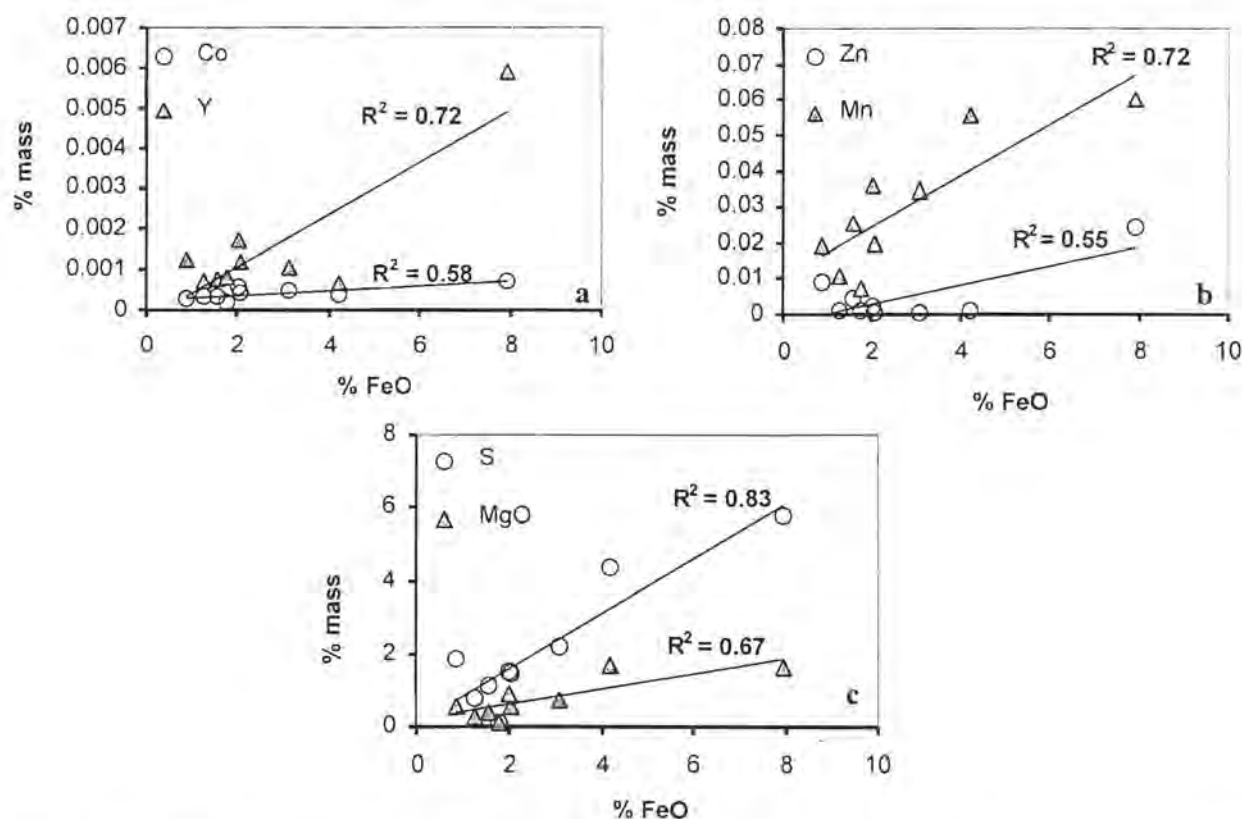


Figure 4.5: Correlation of the percentage weight fractions of Co and Y (a), Zn and Mn (b) and MgO and S (c) with the percentage weight fraction of FeO in Noordhoek wetland sediments. The correlation is significant at the 95% confidence level.

There is a very strong correlation between Sr and percentage weight of CaO. This was to be expected as Sr replaces Ca in carbonates due to isomorphous substitution (Wehmiller, 1972) (Figure 4.6). Mg was also found to be significantly correlated to that fraction, however the correlation is not very strong. According to Berner (cited in Drever, 1997) high Mg-calcite is less stable than low Mg-calcite and it was discussed in Chapter 3 that high magnesium calcite is unlikely to form within the Noordhoek wetlands. The weak correlation between Ca and Mg confirms that assumption.

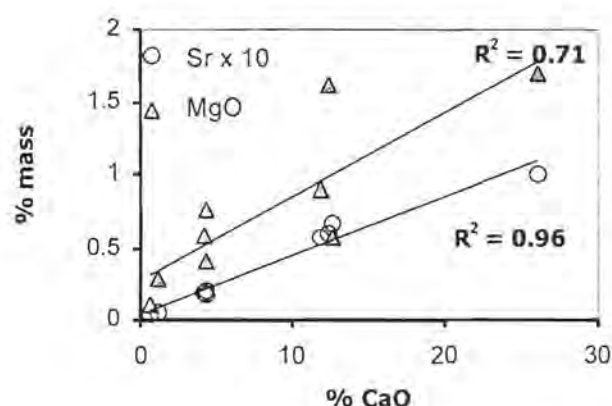


Figure 4.6: Correlation between the percentage weight fractions of MgO, Sr and CaO, in sediments of the Noordhoek wetland. The correlation is significant at the 95% confidence level.

A better insight into the carbonates present is obtained by comparing the weight percent of CaO to the percentage weight of CO₂ that evolves from the sample upon oxidation (Karbonate bombe). If all CaO were present in the form of CaCO₃ the ratio of CaO/CO₂ would be close to 1.27. Table 4.3 shows CaO/CO₂ ratio obtained for the Noordhoek sediments. For all sediments evolving CO₂ the ratio greater than 1.27, indicating that all CO₂ is present in the form of CaCO₃.

Table 4.3: The CaO/CO₂ ratio for the samples analysed.

Sample	WV1	WV2	WV3	M1	M2	M3	M4	LV	FV1
CaO/CO ₂	no CO ₂	No CO ₂	no CO ₂	1.49	3.12	2.88	1.45	3.15	no CO ₂

Phosphorus was found to be significantly correlated with Cu, Pb and organic carbon. The strong correlation of phosphorus with Cu and Pb, is a reflection of the contamination of Wildevoëlvlei sediments in respect to these heavy metals (see Section 4.4).

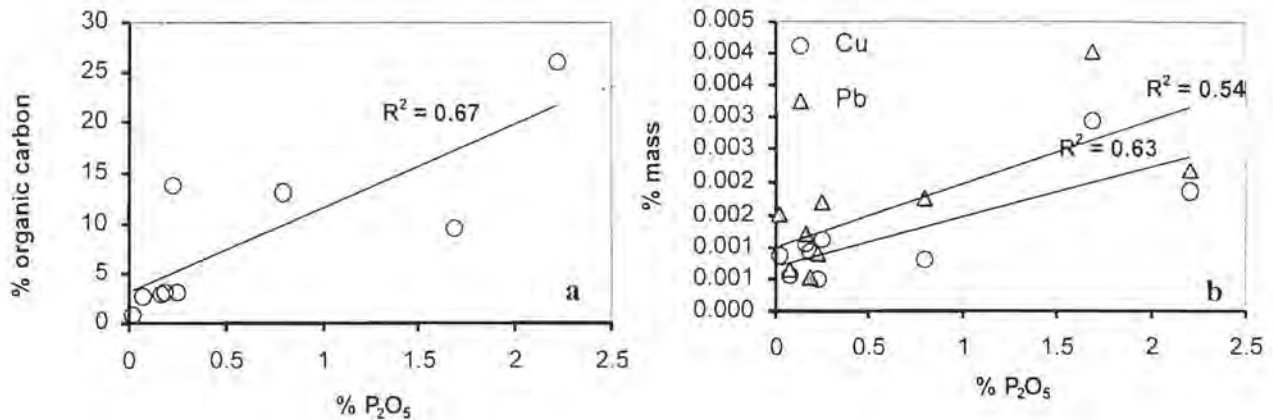


Figure 4.7: Correlation between organic carbon (a), Cu, Pb and (b) percentage weight fraction of P_2O_5 in sediments of the Noordhoek wetland. The correlation is significant at the 95% confidence level.

Loss on ignition (LOI) is mainly associated with organic matter and volatile compounds. In the Noordhoek sediments it is very strongly correlated with S, and CO_2 (Figure 4.8). No significant correlation was found between organic carbon and LOI.

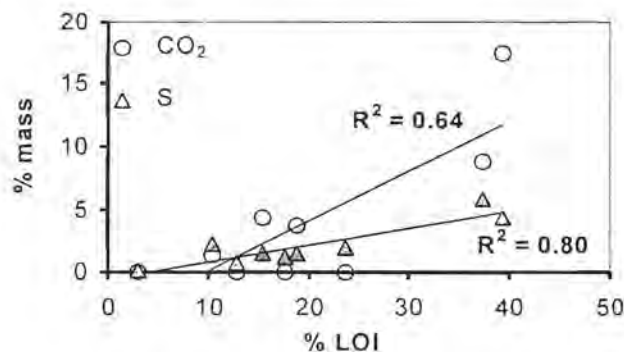


Figure 4.8: Correlation between percentage weight fractions of S and CO_2 and loss on ignition (LOI). The correlation is significant at the 95% confidence level.

4.3.7 Heavy metals

Although the pollution status of the Noordhoek wetlands with respect to heavy metals is not related to phosphorus contamination, it was seen as an important assessment in order to understand the complexity of the wetland. Knowledge of metal contamination is important for two reasons: firstly the presence of heavy metals has been considered to trigger the production of hepatotoxins by bluegreen algae (William Harding, *personal communication*³) and secondly it has important implications for the management of the wetlands.

To assess the pollution status of the Noordhoek wetlands with respect to heavy metals, results obtained from the XRFS analyses were compared to results obtained for other coastal wetlands in the Greater Cape Metropolitan area (Willis, unpublished data). It is well established that trace element concentration is strongly dependent on grain size, showing a general increase of elemental concentration from coarse to fine grained fractions (Förstner and Wittman, 1979). In the Bot River estuary Willis (1985) found highest concentrations of trace elements in the mud fraction. He attributed this phenomenon to the association of the trace elements with clay minerals or organic matter in the mud fraction.

To compare heavy metal concentrations between the different vleis the data were, therefore, normalised by dividing the concentration of the different metals by the sum of the concentration of Al and Fe. In order to suppress the overwhelming heavy metal concentration in Zeekoevlei, Rondevlei and Princess vlei sediments values obtained for the Noordhoek sediments have been multiplied by ten. It can be seen from Figure 4.9 that the relative heavy metal concentrations in the Noordhoek wetland sediments are approximately an order of magnitude lower than in the other three Cape Peninsula vleis. It is therefore concluded that the Noordhoek Wetland is relatively unpolluted with regard to heavy metals. This result can be explained with the predominantly residential landuse in the Noordhoek Valley area, whereas, Princessvlei, Rondevlei and Zeekoevlei are exposed to a fair amount of industrial effluent. Light industry is only located adjacent to Wildevöelvlei.

³ Dr William R. Harding: Head of Scientific Services, Cape Metropolitan Council

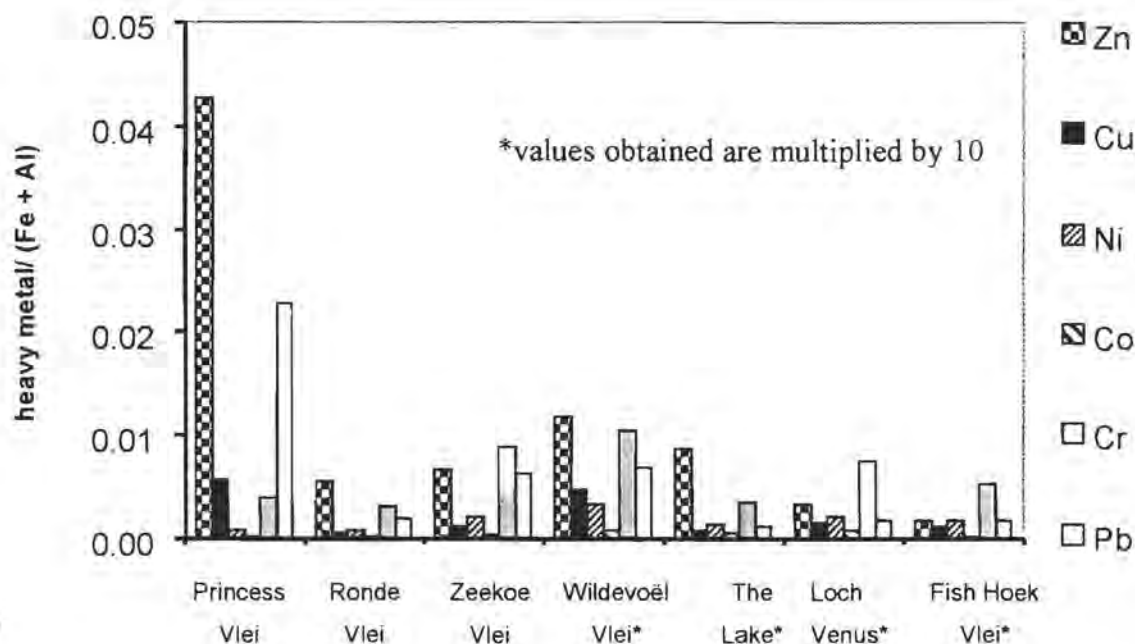


Figure 4.9: Concentrations of heavy metals in Noordhoek wetland sediments in comparison to concentrations reported for Princess-, Ronde-, and Zeekoevlei. The data are normalised by dividing the concentration of the different metals by the sum of the concentration of Al and Fe.

A comparison of heavy metal concentrations between the sample sites within the Noordhoek wetland revealed that Wildevoëlvlei has higher Cu and Pb concentrations than the other vleis (Figure 4.10a, b). Sample WV1 was collected upstream of the sewage outlet. As all three Wildevoëlvlei samples show the same trend it is therefore unlikely that the source of the metals is the WWTW. According to local residents polluted water reaches the vlei from a nearby industrial site, Heron Park. The stormwater outlet pipe draining the industrial area is situated approximately 20 m from sampling site WV1. In November 1998 local residents noticed that chemically polluted water was discharged into the stormwater drainage system. The outlet has been marked as a potential hazard to the vlei and a proposal was made to divert some of the stormwater into the WWTW (KFD Wilkinson, 1999).

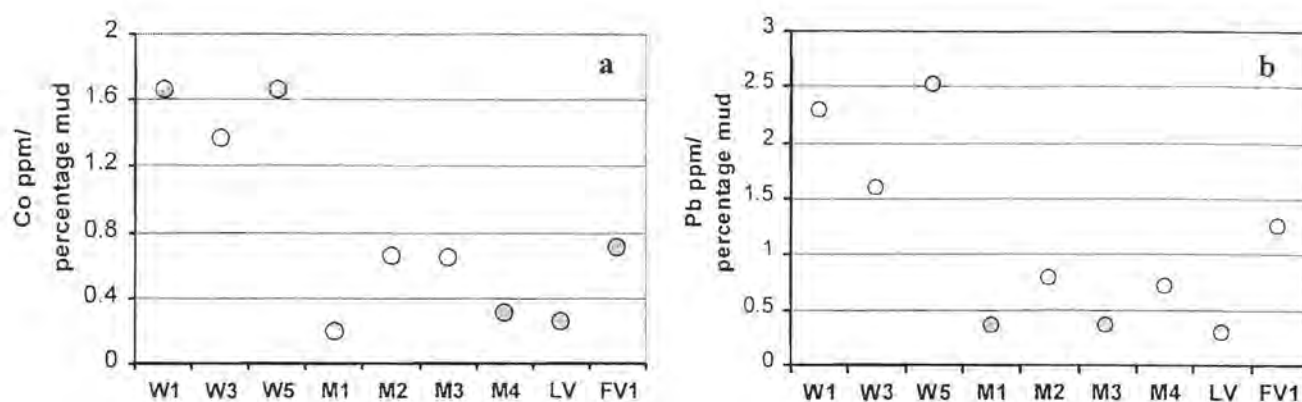


Figure 4.10: Distribution of Co (a) and Pb (b) in the mud fraction of Noordhoek wetland sediments.

Comparing the distribution of the Zn concentration within the Noordhoek sediments it is apparent that sample M4 has an elevated Zn concentration (Figure 4.11). Statistically, the concentration was marked as an outlier (defined as being larger than mean + 1.96 Standard Deviation). The high concentrations could be an indication of anthropogenic pollution or alternatively be an artefact of the small sample size analysed. Adjacent to the site is an old municipal waste site, which could leach contaminant into the aquatic environment. However, the sample does not show elevated concentrations for any of the other elements. It is therefore unlikely that a seepage plume from the waste site is the source. During site visits to The Lake a number of old iron drums were located at various sites in and around the vlei. The elevated Zn concentration at site M4 may reflect the influence of some metal waste around the site.

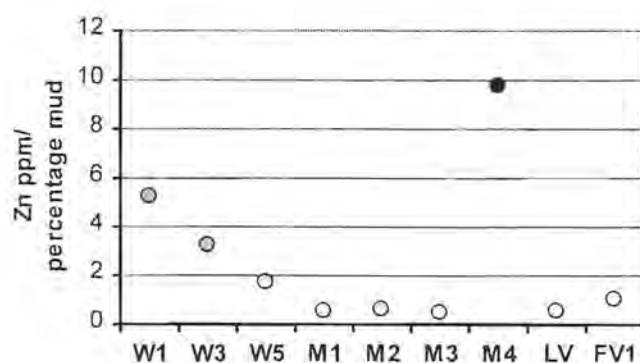


Figure 4.11: Distribution of Zn in the mud fraction of Noordhoek wetland sediments. Solid marker indicates polluted site.

4.3.8 Phosphorus

4.3.8.1 Available soil phosphate

Indices of available phosphate are usually designed for agricultural purposes. The basic idea is to classify soils on the base of crop responsiveness to phosphate. As discussed in chapter two only a limited fraction of the total phosphorus pool in the soil is available for plant growth. Using a standard chemical extraction process the amount of phosphate obtained from the soil represents an index of its availability to plants. Based on field experiments every method establishes the probable critical level below which phosphate fertiliser should be added. The determination of a suitable method is strongly dependent on soil properties as well as the crop of interest.

Acid concentrations used in the Mehlich test method are normally low, resulting in extracting solution pH values generally below 2. All three inorganic P forms are dissolved to some extent by acid, where $\text{Ca-P} > \text{al-P} > \text{Fe-P}$ describes the decreasing order of solubility (Mehlich, 1978). The Olsen method makes use of bicarbonate, which precipitates soluble Ca as CaCO_3 , causing release of Ca-P. The presence of carbonates in soils has often been viewed as a problem for strong acid extractants, as CaCO_3 has a tendency to neutralise the acid, resulting in a reduced extraction potential and therefore lower phosphorus yield. Though it is generally accepted that acid extractions are more appropriate for acid soils and bicarbonate containing reagents are more suitable for calcareous soils, there is evidence that the Olsen extraction performs reasonably well on acid soils (Farina and Channon, 1979 cited in Fixen and Grove, 1990). Results obtained from the Olsen and the Mehlich extraction are presented in Table 4.4.

Table 4.4: Bioavailable P determined for Noordhoek Wetland sediment using Olsen and Mehlich methods for extraction.

Sample	Available P (mg.kg^{-1})	
	Olsen	Mehlich
W1	331	116
W2	436	275
W3	107	325
M1	56	10
M2	1	1
M3	28	40
M4	60	6
LV	32	36
FV1	4	11

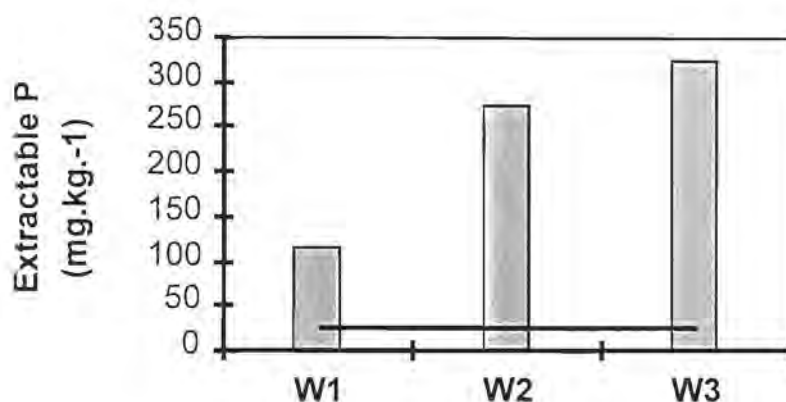


Figure 4.12b: Phosphorus concentration yield from acid extraction (Mehlich method). The solid line indicates the deficiency threshold as defined for the Mehlich extraction (Martin Fey, *personal communication*).

It has to be stressed that the indices do not allow for conclusions to be drawn on the total phosphorus content of the sediments. The indices are purely tools that allow the comparison of a group of sediments to experimentally derived deficiency threshold limits. Comparing results from the XRFS analyses it is clearly seen that the total pool of phosphorus in the sediments is much larger than the readily available fraction (Table 4.5).

Table 4.5: Comparison between extracted P (mg.kg⁻¹) and total P (mg.kg⁻¹) in Noordhoek sediments.

Sample site	W1	W2	W3	M1	M2	M3	M4	LV	FV1
Available P	116	275	325	55.9	0.9	28.3	60	32.2	14.1
Total P	4744	4647	525	481	160	389	1667	344	40

A comparison of the percentage weights of P₂O₅ relative to the mud fraction between the different samples shows that W1 and W2 have a higher concentration than the other sediments (Figure 4.13). Both samples were collected downstream from the sewage outlet pipe of the WWTW (Appendix F, Figure F.1). W2 is located in the middle of Wildevoëllei,

about 5 m in front of the outlet pipe, whereas W1 was collected near the isthmus that connects the upper and lower Wildevoëlsvlei basin. The mean concentration of P in the final effluent (1991-1996) is 5.4 mg L^{-1} (Kevin Fawcett, *in writing*)⁵. During a dye experiment in March 1998, where fluorescent dye was mixed with the effluent and discharged, it was shown that under calm wind conditions the effluent does not disperse rapidly, but remains located in the direct vicinity of the outlet pipe. The high concentration at W2 of P in sediment is, therefore, seen to reflect the direct exposure of the sediments to the effluent.

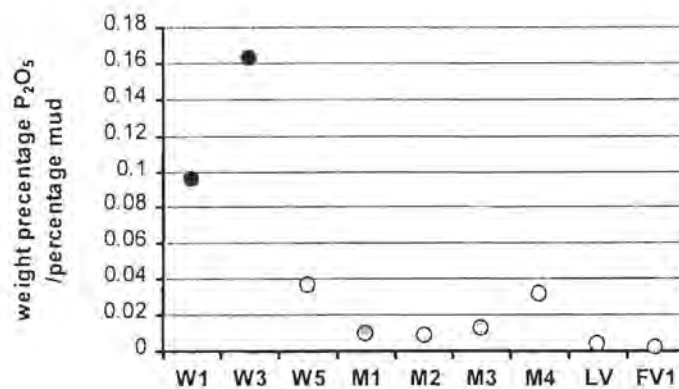


Figure 4.13: Distribution of P₂O₅/mud ratio in the Noordhoek wetland sediments Solid marker indicates polluted site.

4.3.8.2 Phosphorus adsorption isotherms

Amount of phosphorus sorbed was calculated using:

$$\frac{C_i - C_e}{M} V = C_s \quad (4.2)$$

Where C_i is the initial P concentration in the sediment solution, C_e the final P concentration in the sediment solution after 24 hours, M and V the mass of soil and the volume of solution used and C_s is the amount of P sorbed to the sediments (mg. kg^{-1}). Adsorption isotherms were obtained by plotting the amount of P sorbed against the equilibrium P concentration in solution. Apart from the Wildevoëlsvlei samples, sediments showed an approximation of the

⁵ Kevin Fawcett : Head of the Water and Waste Division of the Cape Metropolitan Council

L-curve isotherm (Sposito, 1989) (Figure 4.14). The data fitted the the Freundlich equation (Figure C.1, Appendix C):

$$C_s = K_F * C_e^b \quad (4.3)$$

Where K_F is the adsorption coefficient, b the intensity factor and C_e the final P (mg L^{-1}) concentration at equilibrium. K_F and b were obtained by fitting Eq.4.3 directly to the experimental data (least squares).

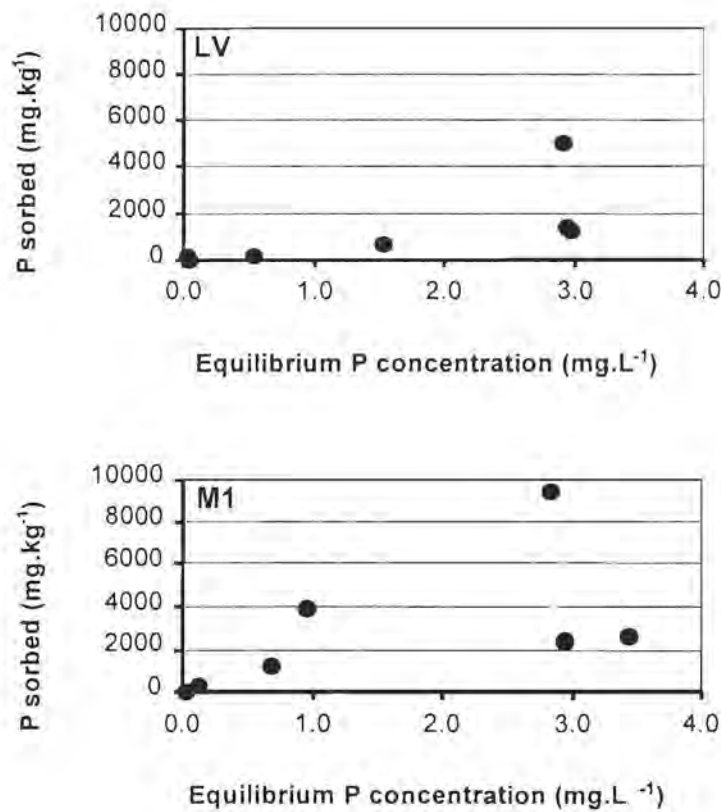


Figure 4.14: Adsorption isotherms obtained for different wetland sediment samples in the Noordhoek Valley. For sediments of The Lake and Sun Valley (M1, M2, M3, M4, LV) isotherms were obtained using initial P concentrations from 0 mg.L^{-1} to 200 mg.L^{-1} , whereas for Wildevoëlvlei (WV) and Fish Hoek (FV) vlei P concentrations from 0 mg.L^{-1} to 10 mg.L^{-1} were used. (Figure continues on next page.)

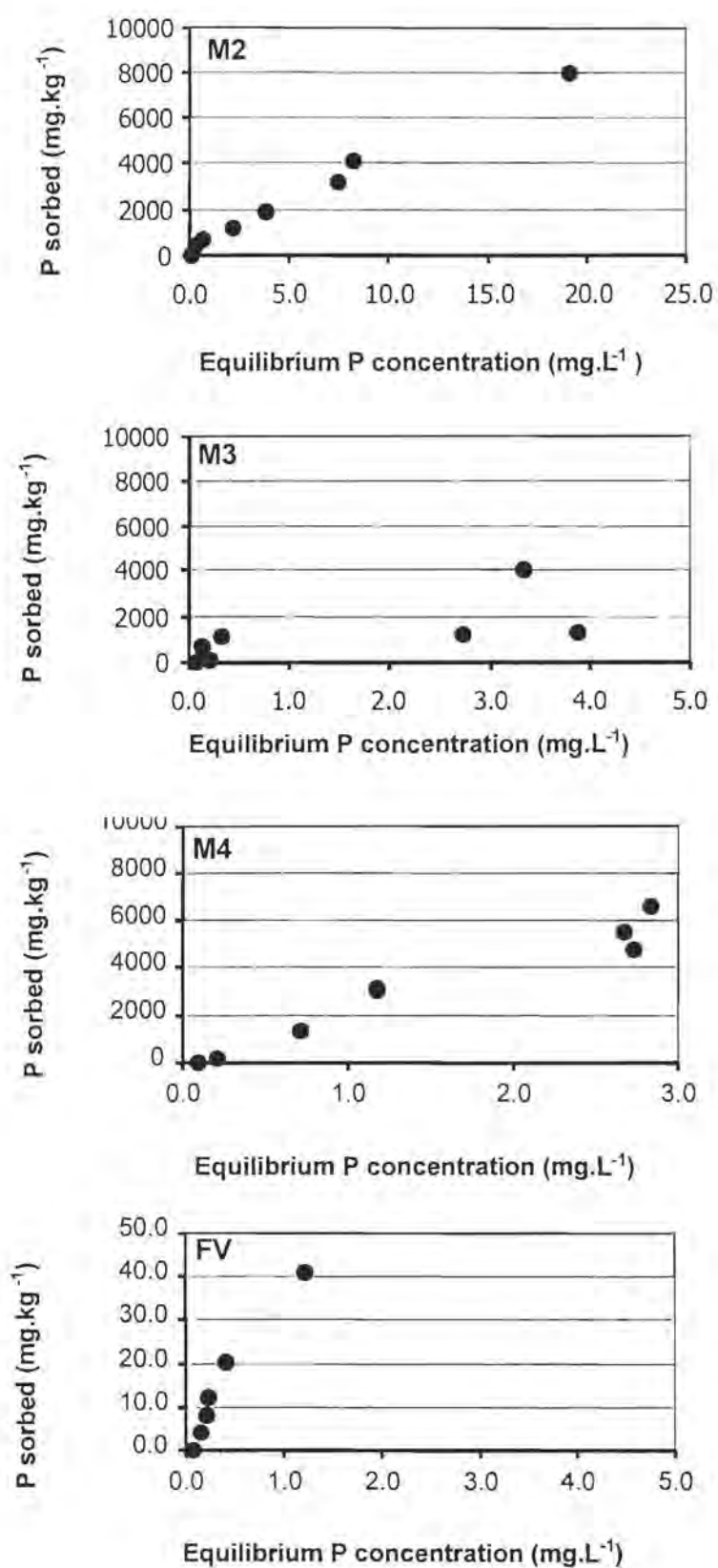


Figure 4.14 : Adsorption isotherms obtained for different wetland sediment samples in the Noordhoek Valley. (Figure continues from previous page).

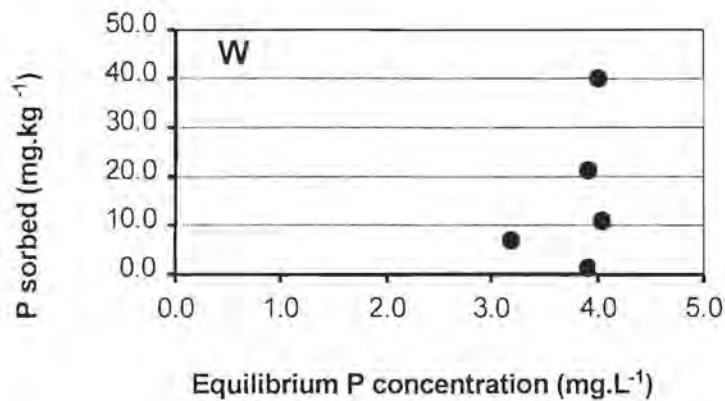


Figure 4.14: Adsorption isotherms obtained for different wetland sediment samples in the Noordhoek Valley. (Figure continues from previous page).

The following discussion does not include Wildevoëlsvlei sediments, which are discussed separately as they differ from the other sediments with respect to P adsorption. The sorption capacity of sediments is controlled by the degree of saturation of limited numbers of sorption sites, which is reflected in a characteristic concave shaped adsorption isotherm, as the sediments approach the saturation limit for adsorption (McBride, 1994). With the exception of sample M2 all isotherms obtained show a deviation from the typical L-shape curve for equilibrium concentrations obtained for samples incubated with an initial P concentration of 200 mg.L⁻¹. It is well documented that P adsorption is comprised of both fast and slow reactions. Fast reactions involve ion exchange reactions and follow first-order kinetics, while slow reactions involve chemisorption and precipitation under formation of surface complexes with crystalline structures (Sposito, 1989). At low P concentrations sorption processes are thought to be dominant, whereas precipitation becomes more important at higher concentrations (Holtan *et al.*, 1988). The Freundlich equation implies that the energy of adsorption decreases exponentially with increasing saturation of the surface (Bache and Williams, 1971). Inconsistency with respect to the L-shape curve typical for P-adsorption isotherms, suggests a change in the chemical reaction removing P from solution (Sposito,

1989). Roden and Edmonds (1997) found deviations from the L-shape isotherm in reduced iron-rich sediments and suggested that precipitation of Fe-phosphates resulted in the observed pattern. Sample M2, the only sample that did not show deviations from the L-shape curve is characterised by a significantly lower Ca concentration than the other samples, while having a similar Fe concentration. It is, therefore, suggested that the formation of Ca-phosphates leads to the observed deviation from the typical L-shape isotherm in calcareous Noordhoek wetland sediments. The formation of Ca-phosphates could be linked to an increase in solution pH during the incubation of the sediments with P. Following first order kinetics P readily displaces hydroxyl ions from sorbing surfaces, resulting in an increase of pH in the sediment solution (Mott, 1988). Lanyon (1996) reported an increase in pH from 5.46 to 7.03 for a Shortland soil that was incubated with a phosphorus concentration of 200 mg.L⁻¹. Given the neutral pH and the high concentration of Ca in the sediments of The Lake, release of OH⁻ could increase the pH and favour the formation of Ca-phosphates. However, as no measurements of the pHs of the equilibrium concentration were taken, this hypothesis can only be proven in a more detailed study.

The adsorption coefficient (K_F) is an indication of the capacity of sediments to adsorb P. Sediment surface reactivities are largely the result of the reactions of P with Al, Ca, and Fe cations that are themselves part of, or strongly sorbed to, colloid surfaces (Fixen and Grove, 1990). Calculated values for K_F and b for the different sediments are presented in Table 4.5.

Table 4.6. Comparison of the calculated values for the adsorption coefficient (K_F) and the intensity factor (b) for different Noordhoek wetland samples, using the Freundlich equation.

	M1	M2	M3	M4	LV	FV
K_F	1660	437	329	8709	234	1.1
b	1.0	0.9	0.8	1.5	0.7	34.0

With the exception of sample FV the sediments have very high adsorption coefficients. The low coefficient for sample FV is not surprising considering its high sand content (93%). In terms of adsorption per unit mass of solid the affinity of total reactive phosphorus increases from quartz to calcite to kaolinite to illite to goethite to iron/aluminium oxihydroxyds at pH 7 and low ionic strength (House *et al.*, 1998). The dominant clay mineral found in the

Noordhoek sediments was kaolinite. Kaolinite has historically been recognised for its reactivity with phosphorus. Its anion exchange capacity is restricted to edge surfaces, where positive charge can be developed at low pHs by protonation of O and OH ions at broken bonds (Dixon, 1989). Considering the neutral to alkaline conditions in the Noordhoek sediments kaolinite and mica are not considered to play an important role for P adsorption.

Given the sandy nature of the sediments it is hypothesised that the very high P adsorption capacity of the Noordhoek wetland sediments is an artefact of the analytical method that was used to determine the P adsorption isotherms. Due to the nature of the method applied, the number of adsorption sites was artificial increased, by a) aerating (oxidising) the sediments and b) increasing the specific surface area by dispersing the sediments.

Oxidation of the sediments will result in the oxidation of ironsulphides and formation of Fe-oxides. The hydroxyl groups on Fe and Al oxides provide high affinity adsorption sites for P. As suspension pH rises, P adsorption is less favoured by the greater negative charge at the oxide surface and the reduced polarisation of the metal-oxygen bond (Fixen and Grove, 1990). However, the strong affinity of Fe oxides for phosphate is mainly a function of the high specific surface area of submicroscopic particles, such that they usually dominate the behaviour of the soils in which they occur (Schwertmann and Taylor, 1989).

To compare the capacity of different sediments one has to compare the K_d values at a specific equilibrium concentration (Bache and Williams, 1971). A P concentration of $40 \mu\text{g L}^{-1}$ represents the equilibrium concentration at which vleis in the Cape Peninsula are classified as eutrophic (Bill Harding *personal communication*), $100 \mu\text{g L}^{-1}$ the upper limit that classifies a system as hypertrophic. From the isotherm obtained (Figure 4.14) it was assumed that the adsorption behaviour of the sediments for an equilibrium concentration below $100 \mu\text{g L}^{-1}$ is approximately linear. The adsorption coefficient (K_d) was, therefore calculated using:

$$K_d = C_s / C_e \quad (4.4)$$

(Slomp *et al.*, 1998). K_d was found to be positively correlated to FeO and Ca, where the correlation with FeO is stronger than with Ca (Figure 4.15a, b). The different distribution of these elements in the sediment can explain the recorded differences in adsorption capacity.

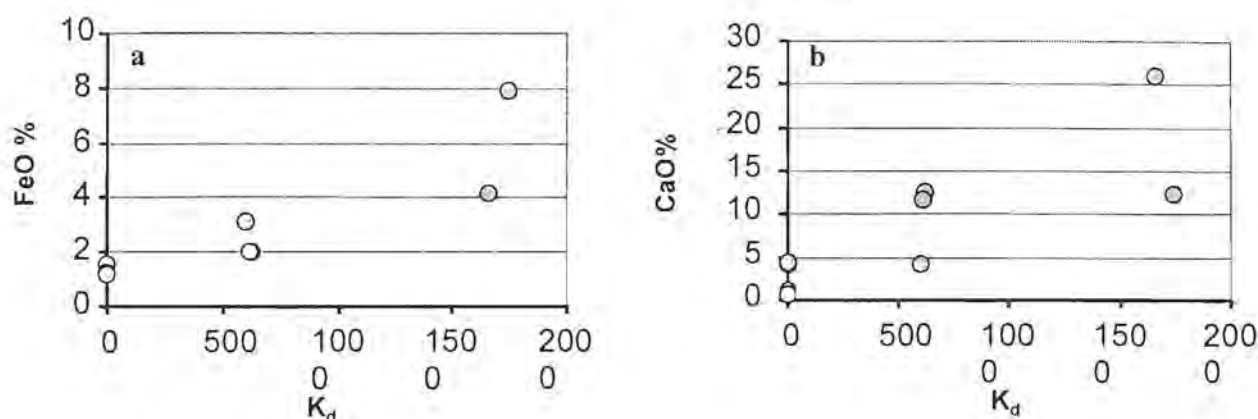


Figure 4.15: Plot of K_d at an equilibrium P concentration of $40 \mu\text{g.L}^{-1}$ versus the percentage weight fraction CaO (a) and FeO (b) determined by XRD.

The strong correlation to FeO and Ca suggests that P adsorption is controlled by oxidised acid volatile sulphides (Section 4.3.4) and Ca-phosphates. In the light of the discussion on the redox status of the vleis P adsorption onto Fe oxides is assumed to be only temporal, whereas sorption onto Ca-phosphates such as apatite and francolite is independent of the redox potential and therefore likely to be permanent. The importance of Ca phosphates as the controlling mechanism of P adsorption in The Lake and Loch Venus is discussed in more detail in Section 4.4.4

If one assumes the average water depth in The Lake to be 2.5 m (Section 1.4.6) the total volume of water in the basin is calculated to be 550 ML. Assuming an average P concentration of $200 \mu\text{g L}^{-1}$, the total P load is approximately 110 kg. Based on the data obtained from the isotherm study sediments of The Lake adsorbed between 2 g and 6 g of P per kg, when exposed to a P concentration of $200 \mu\text{g L}^{-1}$. According to the experiment between 20000 and 60000 kg of wet sediment should therefore be sufficient to remove P from the water column. However, as discussed earlier results obtained are strongly influenced by chemical alterations of the sediments that took place in the course of the adsorption experiment. The influence of oxygen in particular is discussed in detail in section 4.4.4.

Apart from chemical alterations of the sediments the most important difference between the steady state situation between lake sediments and bulk water in situ and sediments in a test tube is the amount of reactive surface. In the natural environment the particles are layered in the soil column. According to the “tipping bucket model” one can visualise the soil column as a stack of empty “buckets”, where each bucket symbolises the sorption capacity of one soil layer. As phosphate is applied to the surface layer, the top bucket must be filled (all sorption sites occupied) before phosphate can “spill” into the soil layer immediately below (McBride, 1994). Adsorption sites on particles that are not in direct contact with the overlying water are therefore not readily available. P adsorption onto these particles takes only place by slow diffusion processes. In reality, adsorption of phosphate onto sediments takes therefore much longer than simulated in the adsorption experiment. The implication of this are: firstly, that fast moving water (stormwater) does not have enough time to equilibrate with wetland sediments and secondly that in standing water phosphorus is available longer for phytoplankton utilisation.

Unfortunately, isotherm data for Wildevoëlvlei sediments were only obtained for sediments incubated with low P concentrations. Due to time constraints the experiment could not be repeated. From the data available it is not predictable if the data follow an L-shape isotherm curve or not. However, it is important to note that even if incubated with very low P concentrations (0 to 10 mg L⁻¹) P adsorption is very low, resulting in a consistent equilibrium concentration between 3 and 4 mg.L⁻¹ of phosphorus. Bache and Williams (1971), explain a shift of the P adsorption isotherm along the x-axis with high initial sediment phosphate concentration.

Total P in Wildevoëlvlei sediments as analysed by XRFS was found to be 4-10 times higher than in sediments of The Lake. In the last year (October 1997- May 1998) the WWTW discharges up to 6 Ml final effluent per day, containing average TP and ortho-P concentrations of 6.3 mg.L⁻¹ and 6.1 mg.L⁻¹, respectively (Davies and Gassner (1999). Davies and Gassner (1999) evaluated the water quality of Wildevoëlvlei. They reported only minor differences between TP and ortho-P concentrations measured in water samples taken directly at the sewage outlet and samples taken along the drainage route towards the sea. Davies and Gassner (1999) suggested that this was due a saturation of the vlei sediments with respect to P. The very low P adsorption and the consistent equilibrium concentration between 3 and 4 mg.L⁻¹ of phosphorus obtained from the P adsorption study appear to confirm this assumption. These findings have important implications for the management of

the vlei: Firstly, uptake of P by Wildevölvlei sediments is unlikely to occur. Secondly, under changing environmental conditions, such as reduced P input from the WWTW the sediments could become a source of P.

4.3.9 Geochemical modelling of phosphate dynamics in The Lake

To investigate the mechanisms that govern the phosphorus concentration in The Lake as well as to deduce the operative geochemical reactions that led to the observed phosphorus isotherms for sediments of The Lake, geochemical modelling was applied to the available water chemistry data. Because of the complexity of redox conditions between the bulk water and sediments, the computer program PHREEQC (Parkhurst, 1995) was used. A first step in the modelling process was to evaluate the saturation status of the bulk water with respect to various minerals using the model MINTEQA2 (Allison *et al.*, 1991). The results obtained were used in the PHREEQC calculations to specify equilibrium concentrations with respect to minerals that were reasonable for simulating P retention mechanisms, MINTEQA2 was further used to investigate the role of organic matter for phosphorus retention, and PHREEQC calculations were used to evaluate the natural equilibrium between Ca, Fe and phosphorus in The Lake.

The models are based on equilibrium thermodynamics and the Debye-Hückel theory that describes the activity of aqueous species. Built in databases of equilibrium constants allow the calculation of chemical speciation and saturation indices (SI). Saturation indices provide information about whether the free energy of dissolution of the solid phase in a solution or natural water is positive, negative or zero. If the saturation index is zero, the solution is in equilibrium with the mineral. If the dissolution energy is negative ($SI < 0$) the mineral will dissolve, whereas if the energy is positive ($SI > 0$) it will precipitate (Stumm and Morgan, 1981). Saturation indices are calculated as:

$$SI = \log \frac{IAP}{K} \quad (4.5)$$

where IAP is the ion activity product of the species in solution and K the equilibrium constant for the dissolution or precipitation reaction.

In order to simulate the reaction path in waters of The Lake several assumptions were made. Firstly, it was assumed that the prevailing conditions reflect thermodynamic equilibrium, secondly, that kinetics do not have a significant impact on the reaction path, and thirdly that no biological uptake takes place. Input data are presented in Table 4.7. Solution pH and temperature measured in the laboratory were entered as the equilibrium pH and temperature. Activity coefficients for the species in solution were calculated using the Davies equation (Davies, 1962). Alkalinity was entered as HCO_3^- and other contributions to alkalinity were disregarded. In all simulations use was made of the built-in MINTEQA2 database.

Table 4.7: Input data used in MINTEQA2 and PHREEQC simulations.

Reading input data for simulation 1			
		MINTEQA2	PFREEQC
SOLUTION			
<i>Temperature</i>	°C	22.0	22.0
<i>PH</i>		8.2	8.2
<i>Alkalinity</i>	(mg.L ⁻¹)	262	262
<i>Aluminium</i>	(mg.L ⁻¹)	0.02	0.02
<i>Sodium</i>	(mg.L ⁻¹)	481	481
<i>Chloride</i>	(mg.L ⁻¹)	1299	1299
<i>Phosphate</i>	(mg.L ⁻¹)	0.07	0.07
<i>Sulphate</i>	(mg.L ⁻¹)	416	416
<i>Calcium</i>	(mg.L ⁻¹)	114	114
<i>Magnesium</i>	(mg.L ⁻¹)	119	119
<i>Silica (H₄SiO₄)</i>	(mg.L ⁻¹)	2	2
<i>Fluorine</i>	(mg.L ⁻¹)	0.03	0.03
EQUILIBRIUM PHASES			
<i>Pyrite</i>	(mg.L ⁻¹)	0	10
<i>FeS</i>	(mg.L ⁻¹)	0	10
<i>Calcite</i>	(mg.L ⁻¹)	0	10

4.3.9.1 Phosphate mineral saturation indices calculated using MINTEQA2

MINTEQA2 predicted that the water was saturated with respect to various calcite minerals (Table 4.8). The highest saturation index was calculated for $\text{CaMg}(\text{CO}_3)_2$. However, as discussed in Section 3.2.5, Mg is not likely to be removed from the solution by precipitation. The contradiction between model and reality can be explained by the underlying assumptions of the model. MINTEQA2 calculations are based purely on thermodynamic equilibrium and do not take kinetics into account. In reality, one step in the reaction is often much slower than all the others, thus limiting the rate of the overall reaction (Drever, 1997). Therefore, although thermodynamically predicted, an extremely slow reaction rate may prevent precipitation occurring within any reasonable time frame.

Table 4.8: Calculated saturation indices for selected calcite minerals in The Lake using MINTEQA2.

Mineral	Formula	Saturation Index
ARAGONITE	CaCO_3	0.948
BRUCITE	$\text{Mg}(\text{OH})_2$	-3.448
CALCITE	CaCO_3	1.102
DOLOMITE	$\text{CaMg}(\text{CO}_3)_2$	2.457
MAGNESITE	MgCO_3	0.857

Berner (cited in Drever, 1997) investigated the kinetics of the growth of aragonite and high-magnesium calcite in seawater. Berner found that Mg is adsorbed to CaCO_3 surface sites at Mg/Ca ratios in solution greater than about 1. This leads to the formation of high magnesium calcite ($\text{CaMg}(\text{CO}_3)_2$), which was thermodynamically less stable than low magnesium calcite. It was therefore more soluble and a higher degree of supersaturation, relative to pure CaCO_3 , was necessary to cause growth. It is, therefore, proposed that although MINTEQA2 calculated water of the Lake to be supersaturated in respect to high-magnesium calcite, the rate of Mg precipitation is reduced due to its kinetically slow formation. It is further suggested that Mg precipitation only plays an important role under conditions of high evaporation.

Based on the XRD analyses (Section 4.3.4) and the MINTEQA2 calculation, equilibrium with respect to calcite, pyrite and monosulphides was specified in the PHREEQC calculations.

PHREEQC predicted that FeS would dissolve leading to formation of vivianite. Other phosphates predicted to precipitate were carbonate apatite and hydroxyapatite (Table 4.9). Despite the high calculated saturation index for vivianite (SI = 6.83) only 0.2% of the total phosphorus was predicted to be complexed in Fe-phosphates, whereas 99.05 % was calculated to occur as Ca-phosphates, and 0.7 % free in solution. Changes in the initial P concentration had no influence on the results. From the distribution of P between the different phosphates it is evident that in respect to thermodynamics the minerals most likely to control P availability in The Lake are Ca-phosphates. Furthermore, sedimentation and therefore depletion of P from solution is most likely to occur via the formation of apatite.

Table 4.9: Predicted saturation indices for phosphate minerals for water of The Lake in equilibrium with calcite, monosulphides and pyrite.

Phase	Formula	SI	log IAP	log KT
FCO ₃ Apatite	CaNaMg(PO ₄)(CO ₃)F	6.50	-108.20	-114.69
Hydroxyapatite	Ca ₅ (PO ₄) ₃ OH	3.97	-40.23	-44.20
Strengite	FePO ₄ ·2H ₂ O	-6.67	-19.95	-13.28
Vivianite	Fe ₃ (PO ₄) ₂ ·8H ₂ O	6.83	-29.17	-36.00

4.3.9.2 Evaluation of the adsorption isotherm data using PHREEQC

To investigate the effects of exposure of the sediments to O₂ saturation indices (SI) for the different phosphates at different oxygen contents of the water were calculated using the PHREEQC model. Calculated SI values are presented in Table 4.10.

Table 4.10: Saturation indices for minerals with respect to different oxygen content in water of The Lake.

O ₂ content (mg.L ⁻¹)	Saturation indexes			
	0.1	1	5	10
FCO ₃ Apatite	6.89	6.67	6.39	2.85
Hydroxyapatite	4.00	3.86	3.56	1.66
Strengite	-4.33	-3.23	-2.58	-2.95
Vivianite	11.52	13.67	14.84	13.89

In equilibrium with oxygen the water is still supersaturated with respect to apatite and vivianite (Table 4.10). However, the formation of Ca-phosphates decreases by approximately 40%, whereas the formation of vivianite only increases by approximately 10%. Figure 4.16 illustrates the activity of Fe and Ca phosphates as a function of the oxygen content of the water as predicted by the PHREEQC calculations. The activity of calcium phosphates decreases with increasing oxygen content of the water, whereas the opposite is true for iron phosphates. Furthermore, under anaerobic conditions, the activity of free phosphate is higher than under aerobic conditions. It appears that the decrease of free P in solution is a function of the formation of FeHPO_4 . When more oxygen is brought into equilibrium with the water the more monosulphides are oxidised, leading to an increase in Fe^{3+} in solution. The high affinity between Fe^{3+} and PO_4^- not only results in an overall decrease of free PO_4^- in solution, but also competes with the divalent Ca and Mg ions, leading to a destabilisation of Ca – phosphates.

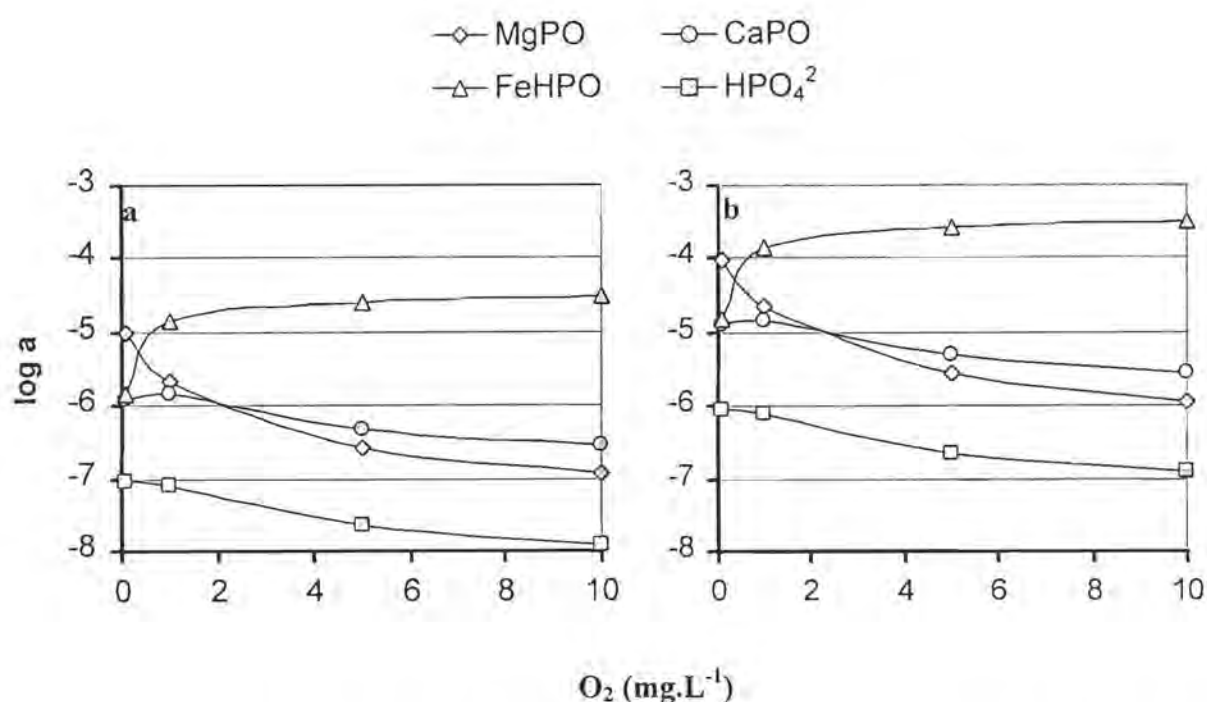


Figure 4.16: Calculated activities of selected phosphate complexes as a function of the oxygen content of the water using PHREEQC; a) high initial P concentration (10 mg.L⁻¹); b) low initial P concentration (0.5 mg.L⁻¹).

Based on the PHREEQC calculation it appears that oxidation of reduced sediments has a significant effect on the availability of Fe^{3+} in solution. It is, therefore, likely that during the

P adsorption experiment monosulphides became oxidised, resulting in a release of Fe^{3+} . Under alkaline, oxidising conditions most of the Fe will be in its insoluble Fe^{3+} form, generally as $\text{Fe}(\text{OH})_3$, which is known to have a very strong affinity for phosphate (Boström *et al.*, 1988b). It is suggested that the high phosphorus adsorption capacity of the sediments, observed in the laboratory, should be evaluated as a result of iron sulphide oxidation. Due to the lack of oxygen in the sediments formation of iron phosphates in situ is unlikely and is therefore assumed that the actual phosphorus adsorption capacity of the sediments is much lower than observed in the laboratory.

4.3.9.3 Conceptual model of P mobility and implication for the natural system

The two main processes removing P from solution, besides biological uptake, are mineralisation and adsorption onto sediment surfaces. Although a number of factors govern the mineralisation of P (see Chapter 2) it is generally accepted, that the most important parameters are the Fe and Ca concentrations in bulk and interstitial water (Goltermann and Kouwe; 1980, Holtan *et al.*, 1988). Roden and Edmonds (1997) stated that the importance of inorganic components in controlling availability depends on their relative abundance in the water. Although the Fe concentration of the water was not measured, the geology of the catchment suggests high Fe concentrations. In addition, the mineralogical analysis showed that pyrite and monosulphides are abundant in the sediments. Iron rich lakes are reported to have Fe concentrations around 0.5 mg.L^{-1} (Wetzel, 1983). Considering the calcareous nature of The Lake, the Ca concentration will be at least two orders of magnitude higher than the Fe concentration in the water. For Rondevlei, a vlei with a similar catchment and chemistry, Gardiner (1988) reported total dissolved iron concentrations to be nearly three orders of magnitude lower than concentrations of the major ions. It is therefore proposed that Fe plays a minor role in controlling P solubility in the water column of The Lake and that the parameter which is most likely to have the highest impact is the Ca/CO_3 system.

In hardwater lakes Ca controls phosphorus by sorption and precipitation processes. Ca^{2+} forms several insoluble phases with phosphate. The most thermodynamically stable form is apatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$ (Stumm and Morgan, 1981). The formation of apatite not only depends on the pH, but also strongly on the concentration of Ca^{2+} . According to Wetzel (1983), a Ca^{2+} concentration of 40 mg.L^{-1} at a neutral pH limits the solubility of P to approximately $10 \text{ } \mu\text{g.L}^{-1}$. Stumm and Morgan (1981) suggest that apatite can also form directly by conversion of

solid calcite. The co-precipitation of P with calcium carbonate causes further reduction (Otsuki and Wetzel, 1972; Murphy *et al.*, 1983). Co-precipitation of phosphorus with calcite is caused by the interaction between dissolved phosphate and the calcite surface during crystal growth, followed by incorporation of some of the surface phosphorus into the bulk structure as crystal growth proceeds. The calcium-phosphate ratio in the coprecipitation depends on the pH during the crystallisation process and on the concentration of calcium and phosphate in the solution (Danen-Louwerse *et al.*, 1995).

The adsorption capacity of the sediments itself is not only dependent on the type of substrate, but also on the number of adsorption sites. Traditional models ascribe P retention in the sediments as a function of the oxygen content and redox potential of surface sediments (Mortimer, 1941, Boström *et al.*, 1988b). Under reduced conditions most of the Fe^{3+} is converted into Fe^{2+} , resulting in a release of Fe^{2+} and ortho-P. More recent studies highlighted that not only reducing conditions are important, but more so the presence of S. It was suggested that competition between SO_4^{2-} and PO_4^{3-} for Fe (III) oxide surface binding sites reduces phosphorus retention in reduced sediments (Caraco *et al.*, 1990, 1991). Roden and Edmonds (1997) propose that iron-rich anaerobic sediments can immobilise substantial amounts of ortho-P under Fe (III) oxide-reducing conditions, but that extensive ortho-P release will take place if sediment Fe compounds are converted to iron-sulphides via bacterial sulphate reduction. The high S content, the presence of pyrite and the strongly reduced conditions of The Lake sediments suggest that most of the Fe is bound to S and therefore not available for P adsorption. In addition, ferric oxyhydroxides, which complexed P in the water column are likely to be reduced upon settling out on the bottom of the Lake, resulting in P release back into the water column.

4.4 Summary

Sediments of The Lake and Wildevoëlvelei reflect strongly the geology and the landuse of their catchments. Both vleis are very sandy although The Lake exhibits a greater fraction of clay and mud size grains than Wildevoëlvelei. The mineralogy of The Lake showed that the vlei is influenced by kaolin mining activity upstream as kaolinite and mica were found on the eastern site. Towards the Atlantic Ocean sediments become less clayey and highly crystalline pyrite reflects strong reducing conditions. From the visual appearance of the samples and the dense pondweed growth it is suggested that little disturbance of the sediments occur. An

oxidised microzone is therefore assumed to be non-existing. In contrast Wildevoëlvlei sediments were found to be very organic rich, sluggish and strongly influenced by the adjacent Wastewater Sewage Works. Clay minerals could not be separated from the sediments.

Given the predominant residential landuse in Noordhoek Valley, very little evidence of heavy metal pollution was found. In fact compared with other vleis in the Peninsula, the vleis have to be regarded as near pristine in terms of heavy metal pollution. However, phosphorus concentrations in some of the sediments and low benthic biodiversity indicate that both Wildevoëlvlei and The Lake are eutrophic, and therefore are subjected to anthropogenic pollution.

Experimentally determined isotherms were found to overestimate the phosphorus adsorption capacity of the sediments. Overestimation is thought to be due to alterations of the samples during the experiment such as oxidation and suspension. However, it is suggested that the results provide a base to compare different sites within the Noordhoek Wetland and help to explain the observed P concentrations in the water column. Based on phosphorus adsorption experiments it was found that, despite their sandy nature, sediments of The Lake have a very high phosphorus adsorption capacity. Samples from the Sun Valley/Fish Hoek wetlands which serve as a stormwater drainage route to The Lake were found to have a lower capacity and given the very kaolinite nature of the Fish Hoek vlei sediments, the adsorption surprisingly low. A different pattern was found for sediments of the upper Wildevoëlvlei basin. It was found that Wildevoëlvlei sediments have a very high yield of phosphorus, which results in a saturation of potential adsorption sites. For the ecological relevant P concentration range between $40\mu\text{g L}^{-1}$ and $100\mu\text{g L}^{-1}$ it was concluded that Wildevoëlvlei sediments have no P adsorption capacity at all, but instead could release phosphorus to the water column. The equilibrium concentration between Wildevoëlvlei sediments and water of low initial phosphorus concentration is estimated to be 40 times higher than the threshold for severe eutrophication.

CHAPTER 5

CONCLUSIONS AND FUTURE RECOMMENDATIONS

This chapter presents a summary of the assessment of the Noordhoek Wetlands and provides some general thoughts and recommendations about the management of the wetland. Detailed management strategies that were developed by Davies and Gassner (1999) are presented in Appendix E.

The World Conservation Strategy (IUCN, 1980) identified wetlands as the third most important life support system on this planet. South Africa is a signatory of the Ramsar Convention and, therefore, as all other signatories, is obliged to:

“...formulate and implement their planning so as to promote the conservation [...] and wise use of wetlands in their territory....” (Article 3.1).

The Noordhoek Wetlands have been fundamentally altered over the last thirty years, with the result that the ecological functioning of this magnificent piece of land has been profoundly altered. Within the Noordhoek wetlands the two main sources of P input are non-point source pollution in the form of stormwater runoff and point source pollution in the form of effluent from the Wildevoëlvlei Wastewater Treatment Works (WWTW). The combination of shallow basin morphology, high incident solar radiation (a long mean day length of 8 h) and a high nutrient load in the vleis, makes the Noordhoek wetland very prone to the invasion of bloom-forming algae species. It should be noted that visual degradation of the vleis in the form of algal blooms is a reflection of the ecological status of the wetland system as a whole

The Lake is characterised by Na-Cl dominant, alkaline, Ca-rich water. The Lake is subjected to a seasonal influx of P-rich stormwater runoff and undergoes seasonal decalcification. Geochemical modelling of the reaction path in the water suggests that Ca plays an important role in the removal of P from the water column. Investigation of sediment samples from The Lake showed that strongly reducing conditions prevail in the system. A combination of high organic matter content, lack of movement and high S concentrations appear to be the reason.

Suspension of sediments is thought to be prevented by a dense stock of the Sago pondweed, *Potamogeton pectinatus*. An assessment of the adsorption capacity of the sediments showed that sediments of The Lake have a high affinity for P. Nevertheless, the results obtained are suspected to overestimate the in situ adsorption capacity of the sediments. The occurrence of two algal blooms, a dense dinoflagellate bloom in May, 1998 and a smaller cyanobacteria bloom in July, 1998, as well as the dense population of *P. pectinatus* clearly illustrate the imbalance of the system. Being surrounded by an increasingly urbanised catchment it is likely that phosphorus concentrations will increase. In this respect the importance of *P. pectinatus* cannot be stressed enough. Phytoplankton production is known to be greatly reduced in portions of polluted lakes where sago pondweed is abundant (Aleem and Samaan 1969). The fact that the *Microcystis* bloom in Wildevoëlvlei was first reported after the crash of its pondweed population and the occurrence of *Microcystis* in The Lake at a time when the pondweed appeared to be in an unhealthy condition seems to confirm this.

Wildevoëlvlei is presently subjected to a daily load of 80 mg P per m². Total P concentrations in the sediments as analysed by XRFS were found to be 4 to 10 times higher than in sediments of The Lake. The high P background concentration in the sediments is assumed to have saturated most of the available adsorption sites within the sediments, and the sediments can no longer considered adsorb P in any significant concentration. The WWTW are presently being upgraded to cope with an average dry-season flow of 14 ML⁻¹, with a possibility of further extension to a total of to 22 ML⁻¹ once the catchment is “fully developed” (Stewart and Scott, 1996). Besides increasing its capacity, the WWTW will also upgrade its treatment processes in order to meet the legislated Special Standards for phosphorus concentration for sensitive catchments (1 mg of orthophosphate L⁻¹). The upgrading process incorporates two biological-phosphorus removal configurations (Johannesburg, Phoredoxsystem), with a potential to reduce the soluble orthophosphate load to a minimum of 1mg L⁻¹. However, it must be noted that this level of phosphorus concentration is more than two orders of magnitude higher than the ecologically sustainable limit for freshwater lakes on the Cape Peninsula (Davies and Gassner, 1999). Additionally, the South African Special Standard for phosphorus neither limits soluble polyphosphates nor the particulate phosphorus fraction (phosphorus bound to solids). Therefore the total orthophosphate concentration discharged can be well beyond 1 mg L⁻¹. Sediments incubated

with up to 10 P mg.L⁻¹ showed equilibrium solution concentrations between 3 and 4 mg.L⁻¹. It is, therefore, likely that once the external P load is reduced (through treating the effluent), the sediments will release inorganic P. Given the prevailing conditions in the vlei the formation of bluegreen algae is supported and their long-term proliferation is predicted.

As part of the study the fate of extracellular microcystins in Wildevoëlvlei was investigated. A detailed description of the work is presented in Appendix D. No detectable microcystin concentrations were found in sediments collected after the *Mycrocistis aeruginosa* bloom. Analyses of fish livers (*Liza richardsoni*) for microcystin concentrations were also negative. Incubation of Wildevoëlvlei sediments with standard microcystin-RR concentration showed that the sediments have a high affinity for the molecule. In summary it was concluded that the accumulation of microcystin in the sediments depends strongly on two factors: the extracellular microcystin concentration in the water and the presence of a competent degradative microflora. These two factors can have important implications for the management of future algal blooms. As the degradative ability of the microflora in Wildevoëlvlei has yet to be evaluated, the method for eradication of the algae should be chosen in such a way that it does not result in rapid release and exponential increase of toxins in the water.

According to Uttormark and Hutchins (1978) lake restoration techniques can be divided into three groups: reduction of nutrient inflow, disruption of internal nutrient cycles, and acceleration of nutrient outflow. The wetland as a whole is subjected to a high hydraulic load of P-rich stormwater. Management of stormwater runoff is problematic and adequate legislation in South Africa is not yet in place. It is, therefore, essential to strengthen the system by rehabilitating some of their fundamental properties and to mitigate the many impacts of urbanisation. This principle was adopted in developing the management recommendations presented in Appendix E.

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APPENDIX A ANALYTICAL APPRAISAL

A.1 PRECISION

A.2.1 Water samples

To test the precision of analyses some water samples were collected in duplicate and analysed. In addition the same samples were analysed two or more times. Repetitive samples were analysed on different days. Relative standard deviations (RSD) as calculated for the results obtained are presented in Table A.1 For the purpose of this study RSD calculations indicate levels of precision.

Table A.1: Relative standard deviations (RSD) as calculated for analytical results obtained for water samples.

Analyses	RSD (%)	
	Duplicate samples	Repetitions
EC	1.0-2.3	15-20
pH	0.0-0.5	0.0-0.7
Alkalinity	0.0-1.2	0.0-0.5
P	0.0-0.6	0.0-0.7
Si	0.1-0.9	0.1-2.3
HPIC analyses		
Na ⁺	0.2-2.2	3.5
NH ₄ ⁺	1.0-3.3	7.2
K ⁺	0.5-1.8	2.5
Mg ²⁺	0.3-2.0	5.5
Ca ²⁺	0.3-2.1	4.2
Cl ⁺	0.9-2.9	3.2
SO ₄ ²⁺	0.2-2.3	9.5
NO ₃	1.1-2.5	3.3

A.2.2 Sediment samples

To test the accuracy of sediment analyses, some samples were analysed twice. Repetitive analyses were carried out on the same day.

Table A.2: relative standard deviations (RSD) as calculated for analytical results obtained for sediments samples.

Analyses	RSD (%)	
	Repetitions	
pH	0.0-1.3	
% Organic C	8.5-9.1	
% Carbonate	8.7-15.4	

A.2 ACCURACY

A.2.3 HPIC Analyses

The cation-anion charge balance is an excellent test of the quality of major ion data for aqueous solutions since all aqueous systems must be electrically neutral (Standard Methods, 1995). A charge balance was calculated on all water samples using the equation:

$$\text{Charge balance} = \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}}$$

Charge balance for all water analyses considered in this study are presented in Appendix A.1.

A.2.4 ICPMS Analyses

Table A3: Accuracy of ICPMS Analyses.

	NIST-1640* Departmental ICP-MS	Published	NIST-1643d*	published Departmental ICP-MS
Li	53.64	50.7	16.96	16.50
Al	46.33	52.0	113.49	127.6
Cr	39.31	38.6	18.50	18.53
Mn	123.43	121.5	37.90	37.66
Ni	28.08	27.4	58.03	58.1
Cu	88.42	85.2	22.73	20.5
Zn	62.36	53.2	73.9	72.48
As	26.54	26.67	55.32	56.02
Se	22.33	21.96	10.77	11.43
Rb	1.96	2.00	11.72	13
Sr	123.05	124.2	293.45	194.8
Cd	22.94	22.79	6.4	6.47
Cs	0.13		4.68	
Ba	145.09	148.0	502.56	506.5
Nd	0.31		0.00	
Pb	28.53	27.89	18.36	18.15
U	0.79		0.02	

*international standards

APPENDIX B ADDITIONAL DATA

Table B.1: Water Chemistry of The Lake. Data collected on 27 of April 1998 by D H Environmental Consulting.

SAMPLE SITES		Inflow	1	2	3	4	5	6	7	8	9	10	11
ANALYTICAL DATA													
Temperature	(°C)	no data	17.7	18.0	17.3	17.3	17.4	17.7	17.8	18.2	17.5	17.6	18.1
PH		7.66	9.10	9.12	9.06	8.99	8.90	8.66	8.54	8.39	8.43	8.39	8.50
Salinity			3	3.5	3.5	3.5	3.5	3	3	3	3	3	2
EC	(mS.m ⁻¹)	204	572	593	584	584	572	577	566	560	574	592	569
Dissolved oxygen	(mg.L ⁻¹)		11.4	10.8	9.0	10.3	9.7	10.0	9.7	9.0	9.6	9.3	9.5
Turbidity	(NTU)	1	8	11	16	8	6	5	7	8	5	4	7
Transparency	(m)		0.30	0.30	0.30	0.32	0.46	0.60	0.35	0.30	0.65	0.70	0.35
Total alkalinity	(mg CaCO ₃ .L ⁻¹)		218						222				227
Total Phosphorus		0.39	0.24						0.29				0.38
Chlorophyll -a	(µg.L ⁻¹)		146						118				178
Anions													
Chloride	(mg.L ⁻¹)		1620						1600				1614
Nitrate plus nitrite as N	(mg.L ⁻¹)		<0.1						<0.1				<0.1
Sulphate	(mg.L ⁻¹)		550						514				514
Ortho-Phosphate	(mg.L ⁻¹)		<0.1						<0.1				<0.1
Cations													
Sodium	(mg.L ⁻¹)		985						930				936
Ammonium	(mg.L ⁻¹)		<0.1						<0.1				<0.1
Potassium	(mg.L ⁻¹)		53						54				53
Magnesium	(mg.L ⁻¹)		161						154				159
Calcium	(mg.L ⁻¹)		113						104				120
Charge Balance			0.4						-1.5				-0.2

Table B.2: Water Chemistry of The Lake. Data collected on the 20 of October 1998 by Aqua Catch.

SAMPLE SITES		Inflow	1	2	3	4	5	6	7	8	9	10
ANALYTICAL DATA												
PH		7.8	9.3	9.9	9.4	8.9	8.6	8.5	8.5	8.5	8.5	8.9
Saturation pH	(20°C)	7.3	7.5	7.6	7.5	7.4	7.3	7.3	7.3	7.3	7.3	7.3
EC	mS.m ⁻¹	226	380	382	382	381	381	381	376	386	382	383
TDS	mg.L ⁻¹	1446	2432	2445	2445	2438	2438	2438	2406	2470	2445	2451
Total alkalinity	(mg CaCO ₃ .L ⁻¹)	227	159	135	168	193	204	206	206	210	207	206
Hardness	(mg CaCO ₃ .L ⁻¹)	415	632	606	633	651	651	665	650	672	655	673
Total Phosphorus	(mg.L ⁻¹)	0.32	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Anions												
Chloride	(mg.L ⁻¹)	541	959	950	960	968	916	923	917	973	955	948
Nitrate plus nitrite as N	(mg.L ⁻¹)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sulphate	(mg.L ⁻¹)	141	381	380	369	375	351	365	355	365	372	364
Phosphate	(mg.L ⁻¹)	0.32	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cations												
Sodium	(mg.L ⁻¹)	316	579	578	571	564	562	558	553	565	557	571
Ammonium	(mg.L ⁻¹)	0.14	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Potassium	(mg.L ⁻¹)	14	31	32	30	30	30	29	30	30	29	30
Magnesium	(mg.L ⁻¹)	45	97	96	96	95	94	96	94	97	94	97
Calcium	(mg.L ⁻¹)	92	94	85	95	104	106	108	106	110	107	110
Charge Balance		4.9	1.5	1.2	1.1	0.7	3.1	2.5	2.4	1.3	0.8	2.6

Table B.3: Water Chemistry of The Lake. Data collected on 31 August 1998. Samples were taken from surface (S) and bottom (B).

Site		1S	1B	2S	2B	3S	3B	4S	4B	6S	6B
PH		8.65	8.62	8.36	8.2	8.12	8.14	8.21	8.04	8.51	8.02
EC	(mS.m ⁻¹)	97	111	78	130	79	78	117	205	87	85
DOC											
Total alkalinity	(mg CaCO ₃ .L ⁻¹)										
Cations											
<i>Sodium</i>	(mg.L ⁻¹)	152	179	131	214	114	129	226	420	134	134
<i>Ammonium</i>	(mg.L ⁻¹)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	5.2	<0.05	1.2
<i>Potassium</i>	(mg.L ⁻¹)	7.74	10.01	7.04	9.96	6.16	6.65	12.32	25.40	8.56	9.84
<i>Magnesium</i>	(mg.L ⁻¹)	41	3	34	62	30	64	57	102	32	36
<i>Calcium</i>	(mg.L ⁻¹)	52	47	35	45	31	33	60	90	61	61
Anions											
<i>Fluoride</i>	(mg.L ⁻¹)	0	0	0.04	0	0.035	0	0	0	0	0
<i>Chloride</i>	(mg.L ⁻¹)	339	273	244	410	214	259	452	784	248	274
<i>Bicarbonate</i>	(mg.L ⁻¹)	561	664	483	289	114	97	130	251	325	227
<i>Sulphate</i>	(mg.L ⁻¹)	142	110	93	155	81	87	165	231	88	117
<i>Bromide</i>	(mg.L ⁻¹)	0	0	0.77	0.00	0.67	0.00	1.19	1.96	0	0
<i>Phosphate</i>	(mg.L ⁻¹)	<0.01	<0.01	0.02	0.11	0.05	0.17	0.03	0.34	0.18	0.30
<i>Nitrate</i>	(mg.L ⁻¹)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Silicon	(mg.L ⁻¹)	1.5	0.4	3.4	4.4		3.3	8.7	6.0		13.3
Charge Balance		-20.7	-24.1	-21.2	-2.3	6.3	11.7	9.2	8.3	-0.3	5.2

Table B.4: Analytical results of Groundwater samples taken in the vicinity of The Lake (CSIR, 1990).

Site		1	2	3	4	5	6
Temperature (field)	°C	20.0	19.5	19.0	18.0	19.0	17.0
pH (field)		5.8	5.6	5.6	5.8	6.1	6.5
Saturation pH	(20°C)	9.2	9.1	9.2	9.0	8.3	7.6
EC	mS.m ⁻¹	128	129	139	142	160	70
TDS (calc)	mg.L ⁻¹	819	826	290	909	1024	448
TDS (sum)	mg.L ⁻¹	650	760	710	733	846	239
Total alkalinity	(mg CaCO ₃ .L ⁻¹)	19	22	17	24	57	178
Hardness	(mg.L ⁻¹ CaCO ₃)	146	184	181	187	292	239
DOC	(mg.L ⁻¹)	4.5	5.6	3.9	1.9	9.7	29
ABS 545 nm		0.002	0.001	0.002	0.005	0.002	0.021
ABS 275 nm		0.126	0.12	0.052	0.078	0.234	1.960
ABS 254 nm		0.168	0.16	0.068	0.098	0.311	2.506
Anions							
Chloride	(mg.L ⁻¹)	352	382	331	340	409	64
Nitrate	(mg.L ⁻¹)	<0.05	<0.05	0.14	<0.05	1.43	0.25
Sulphate	(mg.L ⁻¹)	46	93	113	112	93	76
Phosphate	(mg.L ⁻¹)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cations							
Sodium	(mg.L ⁻¹)	188	208	194	199	194	45
Ammonium	(mg.L ⁻¹)	0.07	<0.05	<0.05	<0.05	0.1	0.15
Potassium	(mg.L ⁻¹)	3.3	3.6	4.5	4.5	4.8	13.7
Magnesium	(mg.L ⁻¹)	26.8	35.2	34.7	34.4	45.8	24.5
Calcium	(mg.L ⁻¹)	14.2	15.6	15.6	18.2	41.2	55.3
Charge Balance		-2.2	-4.0	-2.1	-1.7	-0.3	11.8

APPENDIX C PHOSPHORUS ADSORPTION ISOTHERM

Linear expressions of the phosphorus adsorption isotherms obtained from the adsorption experiment were derived by plotting the log of the P equilibrium concentration vs. log P adsorbed (Figure B1). The adsorption capacity (K_F) and intensity factor (b) were calculated using:

$$\text{Log } C_s = \text{log } K_F + b * \text{log } C_e$$

Where C_s is the amount of P sorbed onto sediment surfaces and C_e the final P concentration in the soil solution after 24 hours.

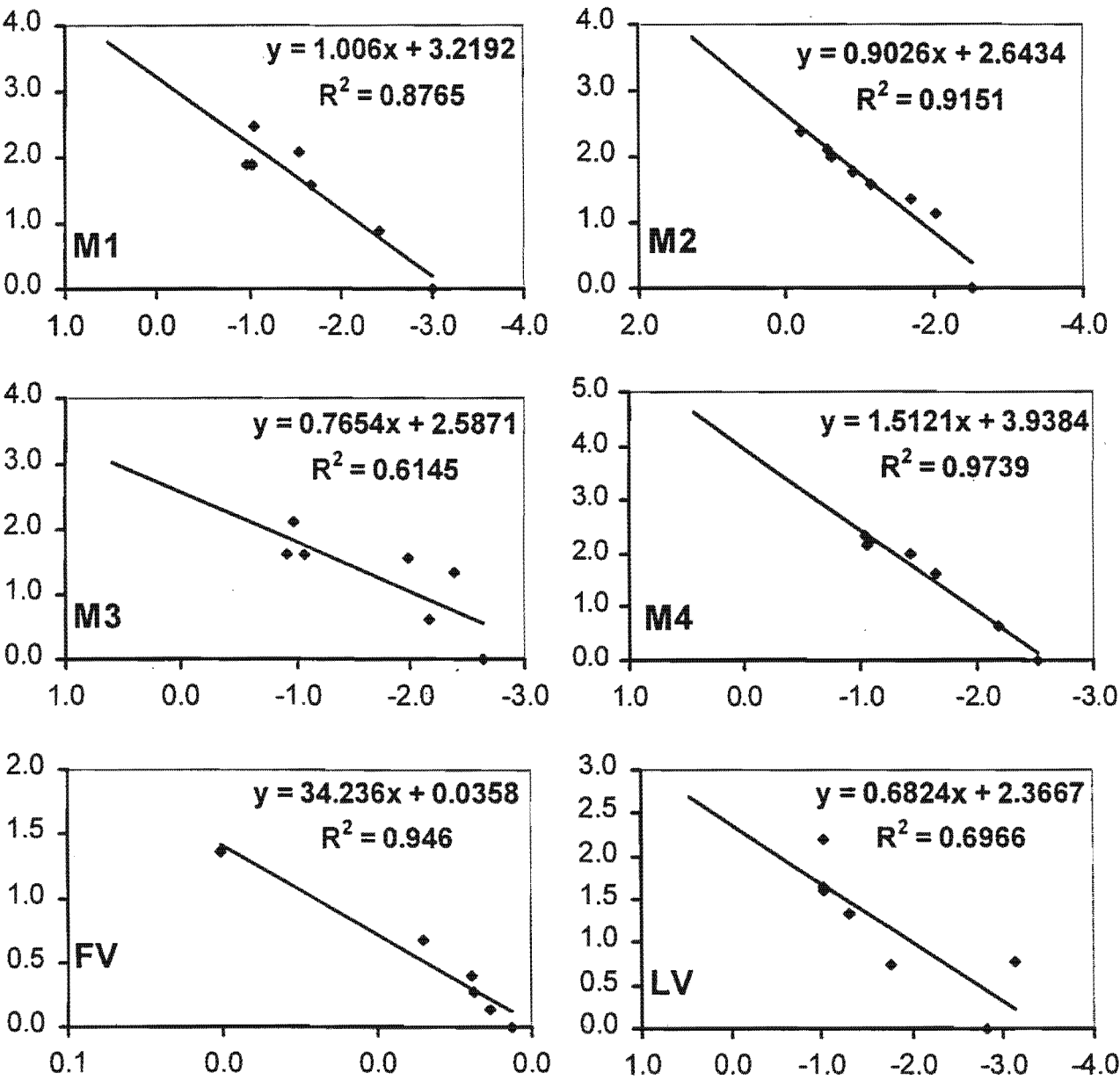


Figure C.1: Linear expressions of the P sorption data derived from Noordhoek Wetland soils according to the Freundlich equation, where $x = \text{log equilibrium P (mg.L}^{-1}\text{)}$ and $y = \text{log sorbed P (mg.kg}^{-1} \text{ mud)}$.

APPENDIX D

ACCUMULATION OF MICROCYSTINS IN FISH AND SEDIMENTS

D.1 Introduction

Analyses of the *Microcystis aeruginosa* bloom in Wildevoëlvlei during early 1998 indicated that toxins were being produced in the eastern vlei and, shortly thereafter, further investigations by the Directorate of Scientific Services of CMC showed very high concentrations of the toxins, 22 µg per g of freeze-dried tissue in the black mussel beds (*Choromytilis meridionalis*), situated just to the south of the Wildevoëlvlei outlet (Harding *et al.*, *in press*).

Initial screening of the cyanobacterial material from the vlei revealed the presence of two cyanobacterial hepatotoxins, microcystin-YR and LR. By mid-January the Department of Scientific Services quantified the combined concentrations to be 2700µg per gram of freeze-dried algal cells. Thereafter, and until the eradication of the algae, intracellular concentrations of microcystin varied between 200 and 1500 µg per gram of freeze-dried material. Extracellular microcystin concentrations in the water column were negligible.

On the 1st of April 1998 a management plan was implemented to eradicate the cyanobacterium from the Wildevoëlvlei system. The underlying principle of controlling the algae was a salinity enhancement of the vlei water. Within 7 days the salinity of the vlei water was artificially raised from below 1 ppt to 8 ppt (Harding *et al.*, *in press*). Concomitant with the first introduction of salt was the immediate decline in the chlorophyll-a concentration from 600 to 150 µl. The salinity-enhancement did not result in a “sudden death” event and no large pulse of microcystin was released into the water. Extracellular toxin concentrations remained for the entire period at the threshold of detection (100 ng.L⁻¹), whereas toxins in mussels and isolated algal scums were still detected as late as mid-April.

This report presents the results of an investigation into the fate of extracellular microcystin in the vlei environment.

D.2 Material and Methods

D.2.1 Sampling methods

D.2.1.1 Sediment sampling

A total of ten sediment samples were taken from different vleis within the study area. All samples were collected by boat. Two different sampling methods were applied. At the time of sampling Wildevoëlvlei sediments consisted mainly of a visually homogeneous mass of brown slurry. Sediments were collected by thrusting a bucket upside down into the sediment until the increase in resistance indicated that a substantial amount of sediment had been collected.

D.2.1.2 Collection of fish

A subsample of fish present in the vlei were collected using a trek net after the draw down of the vlei. Fish were separated into species, age classes, measured and frozen. After dissection in the laboratory liver tissues were processed for microcystin analysis. The tissue was quantitatively analysed using reverse-phase photodiode-array high-pressure liquid chromatography.

D.2.2 Analytical methods

D.2.2.1 Sample preparation

Fish livers and the upper 10 cm of the sediment core samples were freeze dried and resuspended in methanol containing 0.1 %TFA. After standing at room temperature for 30 min, the material was centrifuged at 12 000 x g in a microcentrifuge for 2 min and the supernatant decanted for analysis. Fish livers were freeze dried within 12 hours of dissection of the fish.

D.2.2.2 Measurement of microcystin-RR isotherm

The microcystin adsorption isotherm was determined by incubating Wildevoëlvlei sediments with known standard solution of microcystin-RR. 250ml sterile glass bottles were filled with 10g of wet surface sediments (0-10 cm depth) to which 50 ml of distilled water spiked with

various amounts of microcystin-RR had been added. Vials were incubated in the dark to prevent photochemical degradation. The microcystin-RR solutions were made up in a 0.02 NaCl matrix. Sediments were incubated for 2 and for 24 hours. Sediments incubated for 2 hrs were done in duplicate. Initial microcystin-RR concentrations used were 0, 100, 200, 500 and 1000 $\mu\text{g.L}^{-1}$. After incubation the suspension was transferred into centrifuge tubes. The tubes were centrifuged at 6000 rpm for 5 minutes. The supernatant was filtered through a 0.45 μm Whatman filter and frozen for subsequent microcystin-RR analysis. To monitor microcystin-RR degradation a 50 ml solution containing 200 $\mu\text{g.L}^{-1}$ microcystin-RR with no sediment added was used as control. The control was handled in the same manner as the other solutions.

D.2.2.3 Microcystin analyses

Toxin identification and quantification was done by photodiode-array highperformance liquid chromatography (PDA-HPLC), following the method developed by Lawton *et al.*, (1994). The instrument utilised was a Hewlett-Packard 1050-series pump, injector and diode-array detector (190-300nm, 2 nm resolution), coupled to a Hewlett-Packard 2-D Chemstation data analyses system. Component separation was achieved using a Hypersil-BDS column mounted in a 40 °C column oven and stepped-linear gradient of water: acetonitrile -each containing 0.05 % TFA. Methanol and acetonitrile (Rathburn Walkerburn, Scotland): trifluoroacetic acid (TFA, Fisons, Loughborough, England) and Milli-Q grade water (Millipore, Milford, Maryland, USA) was used throughout. All reagents were HPLC grade. The supernatant was concentrated, using a vacuum-elution manifold, and tri-functional, end capped C_{18} solid phase extraction (SPE) cartridges. Before usage the cartridges were conditioned with methanol, followed by HPLC-grade water. After toxin concentration the cartridge was sequentially washed with methanol and dried under vacuum. The concentrated compounds were then eluted with a mixture of methanolic trifluoroacetic acid, and blown down to dryness, under nitrogen, using a heating- block concentrator. The dry residue was then reconstituted in methanol and analysed using HPLC. Microcystin concentrations were obtained by comparison of peak areas (at 238 nm) of unknowns with pure microcystin (Calbiochem). For the analyses of collected vlel sediments and fish livers pure microcystin-LR and YR (Calbiochem) were used, whereas for determination of adsorption isotherm microcystin-RR standards were used. Identification of microcystins followed putative comparison of UV spectra with the microcystin standards (spectra acquired at 5nm intervals).

The limits of detection in water are typically of the order of 100ng per litre (William Harding, personal communication¹).

D.3 Results and Discussion

D.3.1 Detection of microcystin in fish

A total of 30 fish of the species *Liza richardsoni* were dissected and the obtained livers were analysed. All fish were sexual immature and ranged from 44 to 120 cm fork length. No detectable concentration of microcystin was found in the fish livers.

The dissected fish clearly showed that *Microcystis spp.* is an important contributor to the diet of *L. richardsoni*. Most laboratory studies on the effects of cyanobacterial hepatotoxins have been carried out on mammals (Falconer *et al.*, 1988). Interperitoneal injections of radiolabelled microcystin-LR into mammals revealed that most of the toxin accumulates in the liver (Brooks and Codd, 1987). Uptake of microcystin-LR by liver cells is via the bile acid transport system (Runnegar *et al.*, 1991). Studies on fish showed exposure to toxic cyanobacteria and extracellular microcystin resulted in extensive liver damage and death (Bury *et al.*, 1995). It is beyond the scope of this study to investigate possible physiological effects of the toxin for fish. What can be concluded from the results obtained here is that the toxin is not accumulating in the fish and that the fish are therefore likely to be fit for human consumption. However, *L. richardsoni* is known to be adapted to feed on toxic marine diatoms (Steve Lamberth, personal communication²). The lack of any detectable concentrations of microcystin in livers of *L. richardsoni* could be explained by the physiology of this fish species which allows the fish to feed on toxic bluegreen algae, without being negatively affected by it. It is, therefore, important to note that results obtained are only significant for this specific fish species and should not be seen as representative for all fish within Wildevogelvlei.

¹ Dr. William, R. Harding: Head of Department of Scientific Services, Cape Metropolitan Council

² Steve Lamberth: Linefish Researcher, Department of Sea Fisheries

D.3.2 Accumulation of Microcystin in sediments

No detectable concentrations of microcystin were found in sediments collected during the cyanobacterial bloom in Wildevoëlvlei in March 1998.

Previously, cyanobacterial toxins have been considered to be quite resistant to decomposition. Kiviranta *et al.* (1991) observed no biodegradation of microcystin-RR in 5 weeks when water from the river Vantaanjoki with natural populations of microorganisms was added to decaying *Oscillatoria agardhii* cultures. In a field study after algicide treatment of a hepatotoxic bloom of *M. aeruginosa*, Jones and Orr (1994) observed a bi-phasic degradation of microcystin-LR: after a lag phase of 9 d, 500 $\mu\text{g.L}^{-1}.\text{d}^{-1}$ of the toxin was lost in 3 d and this was followed by a slower degradation rate (10 $\mu\text{g.L}^{-1}.\text{d}^{-1}$). In 1993, Bourne found a bacterium of the genus *Sphingomonas* that enzymatically breaks down the cyclic structure of microcystins into a resulting linear chain of seven amino acids. In addition it was found that the breakdown products are a hundred times less toxic than the cyclic structure (Anderson, 1995).

As mentioned above, extracellular microcystin concentrations in Wildevoëlvlei were negligibly low during the entire time of the bloom. Sediments surfaces were, therefore, only exposed to the molecule after cell lyses. Considering the large quantities of secondary treated effluent discharged into Wildevoëlvlei it is assumed that the microbiological activity of the water is very high and degradation of organic molecules very rapid. It is, therefore, suggested that the concentration of microcystin in the water was never high enough to result in a significant concentration of microcystin in the sediments. The question arises if toxins would be exchanged between algal scum and sediments if the sediments were exposed to large quantities of scum. Jones *et al.* (1995) investigated the persistence in and release of toxins from dried crusts of *Microcystis aeruginosa* from Lake Mokoan in Australia. It was found that microcystin is protected from degradation while encapsulated within the dried *Microcystis* crusts. Leaching experiments demonstrated that re-wetting of the crust material leads to rapid release of microcystins. However, in the presence of competent degradative microflora biodegradation occurred within a few days.

In respect to future blooms the results obtained do not allow for further predictions. It appears that the accumulation of microcystin in sediments depends strongly on the

extracellular concentration in the water and the presence of competent degradative microorganisms. Rapala *et al.* (1994) showed that the degradation of cyclic hepatotoxins is related to the history of the lakes with respect to the occurrence of the blooms. Degradation was found to be faster for lake sediments that were exposed to blooms previously, than for lake sediments that have never been exposed to bluegreen algal blooms. It is, therefore, assumed that even if Wildevoëlsvlei sediments would be exposed to a higher extracellular concentration of microcystin, biological degradation is likely to prevent accumulation of the toxin in the sediments.

D.3.3 Adsorption of microcystin

Microcystins consist of a seven-membered peptide ring which is made up of five non-protein amino acids and two protein amino acids. In general microcystins contain five conserved aminoacids-residues, being D-alanine, methyldehydroalanine, D-isoglutamate, methyl-D-aspartate, the novel amino acid 3-amino-9-methoxy-2,8,8-trimethyl-10-phenyldeca-4,6-dienoate (ADDA) and two variable amino acid residues (Figure 7.2). It is these two protein amino acids that distinguish microcystins from each other, while the other amino acids are more or less constant between variant microcystins.

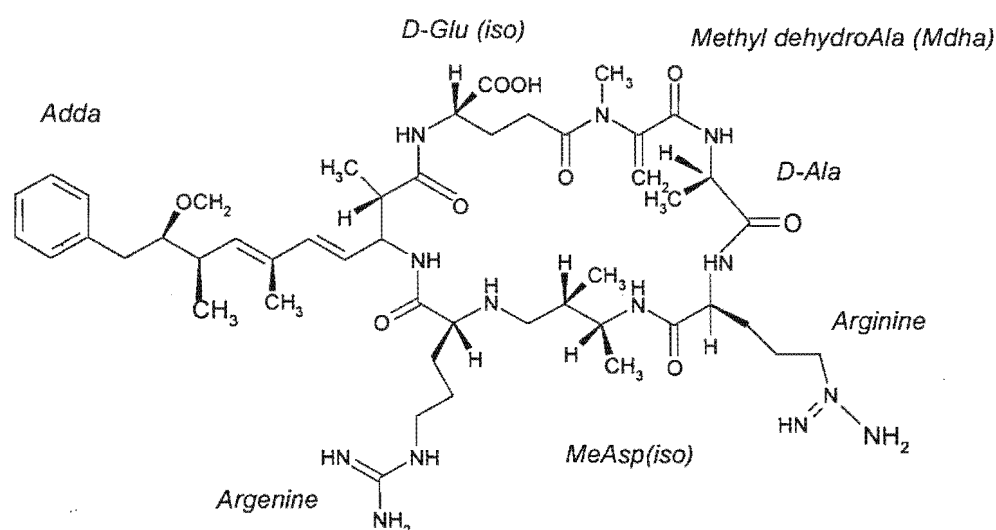


Figure D.1: Molecular structure of microcystin-RR.

During the experiment between $45 \mu\text{g.L}^{-1}$ and $76 \mu\text{g.L}^{-1}$ of microcystin was lost from the control vials, containing an initial microcystin-RR concentration of $200 \mu\text{g.L}^{-1}$. It is not likely that physical or chemical factors like light or pH caused the loss, since the vials were incubated in the dark. Biological degradation is also not considered to be important as the vials were sterile and solutions were made up in Milli-Q grade water. The loss was assumed to be linear. Equilibrium microcystin concentrations obtained after incubation of sediments were corrected for the microcystin loss during the experiment and data obtained are presented in Figure D.2.

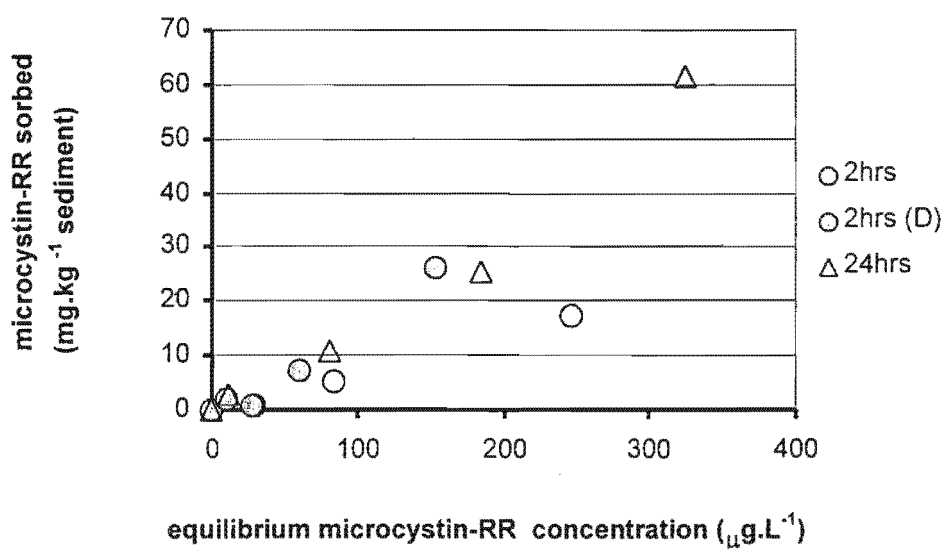


Figure D.2: Microcystin-RR adsorption isotherm obtained for Wildevoëlvlei sediments incubated for 2 and 24 hours.

Results obtained from the adsorption study showed a liner adsorption isotherm (Figure D.2). The term “isotherm” applies to a line joining points (on a map or a graph) at the same temperature. In studies of the properties of surface is applies to the graph showing the relationship between the amount of a molecule sorbed on to the sediment surface and the amount in the solution in contact with the surface. As seen in Figure D.2 adsorption behaviour for the different incubation periods were the same, indicating that adsorption occurs very rapid. The isotherms suggest a constant relative affinity of the sediment for the

microcystin-RR molecule. This type of adsorption behaviour is usually observed at the low range of adsorption and the results obtained do not allow for any further interpretation (Sposito, 1984). Considering the complexity of the molecule, interpretation of its adsorption behaviour is beyond the scope of this study. However, given the amphoteric character of the molecule depending on the pKa values of the different amino acids, the molecule can behave as a cation or an anion. In the context of the acidic Wildevoëlvlei sediments it is most likely to become positive charged (Arginine groups). It is, therefore assumed to have a high affinity for negative surfaces.

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APPENDIX E MANAGEMENT OPTIONS FOR THE LAKE AND WILDEVOËLVLEI (PREVIOUS PUBLICATION, DAVIES AND GASSNER, 1999)

E.1 MANAGEMENT OPTIONS FOR THE LAKE

E.2.1 Outflow from The Lake

The Lake is an important buffer for catchment runoff prior to discharge into lower lying areas such as Papkuilsvlei and the Atlantic Ocean. To utilize the full capacity of The Lake, the present overflow from The Lake (to the northwest) should be raised and used for emergency lake-level manipulations only. A second outlet should be located to the south-eastern end of the lake. These simple actions will redirect most of the low-quality, incoming storm water, along the *length* of the lake rather than, as at present, across its width. As such, the storm water will be retained for longer periods and the capacity and efficiency of the wetland to filter the storm water will be greatly enhanced. Furthermore, water movement from the east to the west, will improve water movement throughout the entire lake. It is understood that an old channel between The Lake and Wildevoëlvlei exists, which once directed water from the Salt Pan towards Wildevoëlvlei. To open The Lake into that channel would not only increase the water circulation within The Lake, but also contribute to the dilution of treated effluent at Wildevoëlvlei. In order to achieve the objectives some engineering of the system will be required for, at present, the reed beds near the Pick'n-Pay commercial development are higher than the current water levels of The Lake.

- **Recommendation:** Raise the present overflow from The Lake towards Papkuilsvlei and use it only for emergency lake-level manipulations. Locate a new overflow to the south-eastern end of The Lake for normal spillage into the channel that once connected The Lake to Wildevoëlvlei. Some engineering of the Pick'n-Pay reedbeds will be required in order to ensure correct water levels and directions of flow.

E.2.2 Lake water levels

Natural cycles of phytoplankton-macrophyte dominance are frequently related to water depth. In deeper wetlands, phytoplankton often have a competitive advantage, as light attenuation and wave action usually control the maximum depth of colonization and zonation of submerged macrophytes (Boltt *et al.*, 1969). In turbid waters light is scattered by suspended particles, and optimal growing depths for macrophytes are reduced. Thus, decreased water levels can overcome the effects of turbidity. As such, when the lake is generally the most turbid (in winter), water levels should not exceed 3m.

- **Recommendation:** Water levels in The Lake should be annually manipulated during winter not to exceed 3m, in order to favour the continuation of submerged plant growth.

E.2.3 Harvesting sago pond weed, *Potamogeton pectinatus*

Harvesting is a necessary management activity to control plant densities that would otherwise impede certain recreational activities on The Lake (e.g. canoeing). To minimize negative impacts on the biota, however, harvesting should not occur during breeding times of the fauna. To ensure nutrient removal from The Lake, cut plants should be removed from the

water column to a site away from The Lake. Harvesting should only control the pond weed and not eradicate it (see Stewart and Davies, 1986).

- **Recommendation:** Regular harvesting of *Potamogeton* will be a necessary management action; guidelines for harvesting should follow recommendations set out in Stewart and Davies (1986) and should not occur during major faunal breeding events.

E.2.4 Fringing vegetation and buffer zones

With the new regulations as laid out in the Urban-Edge Study, developments adjacent to wetlands are not allowed closer than 25m to any water body. Apparently, The Lake housing development does not fall under these new guidelines.

- **Recommendation:** We strongly recommend that further developments (if any) at The Lake be forced to provide an effective buffer zone (we suggest a minimum of 25m) between new properties and The Lake water body *per se*. Residents should be encouraged to plant aquatic vegetation such as reeds and sedges in order to rehabilitate the waterfront of The Lake. Public open spaces within The Lake development should be managed in such a way that it provides habitat and shelter for animals and plants, and simulates a natural lake environment.

E.2.5 Use of fertilizers and pesticides

Residents of The Lake should be actively discouraged from the use of commercial fertilizers and pesticides, as they contribute to the overall nutrient load in The Lake. For example the herbicide 'Glyphosate', also known by the trade name 'Roundup', comprises mainly phosphoric acids, thereby contributing to the overall phosphorus loads in the soil and ultimately in the lake, while recent evidence indicates that cyanobacteria may be able to metabolize phosphorus sources in Glyphosate (WR Harding, personal communication, 03 December, 1998). The use of such chemicals in proximity to an already destabilizing water body is, therefore, highly problematic. Although most of the products on the market have long been regarded as moderately biodegradable, their fate in aquatic environments is far from clear. Furthermore, residue products containing chlorine, for example, can be highly toxic to aquatic organisms, and recent vigorous debate has also ensued concerning their impacts on human health (section 7.5.5; Mendelson, 1998).

- **Recommendation:** A ban on the use of fertilizers and pesticides/herbicides in The Lake area should be implemented forthwith (see also section 7.5.5). Council should give serious consideration to the promulgation of suitable By-Laws to enforce such a ban.

E.2.6 Monitoring

The effects of recent building constructions and increasing storm-water loads require continuous monitoring. A monthly programme measuring variables such as total and biologically available phosphorus concentrations, *Potamogeton* health and densities, turbidity and TSS, water depth, α chlorophyll, and phytoplankton composition, should be implemented forthwith. This would provide a basis for rapid management of negative impacts.

- **Recommendation:** Active management of changing conditions in The Lake will be facilitated by the implementation of a monthly biological and water-quality monitoring programme.

E.2.7 Residents awareness

We recognize the difficulties inherent in the implementation of development restrictions for privately-owned land. However, developments that involve lakes and wetlands are nearly always insensitive to the very fragility of such environments: disturbances caused by urbanization almost always threaten wetland integrity and functioning and have major management and long-term cost implications for councils and for rate payers. We strongly urge that residents should be made aware that 'living with' lakes/wetlands, instead of 'against' them is in their best interests, as evidenced by the catastrophic degradation of Wildevoëlvlei earlier this year. We also urge the direct involvement of South Peninsula Municipality in the management of the system. It should be recognized that although The Lake does not fall under SPM's present jurisdiction, the system cannot be seen as an entity separated from other wetlands of the Valley. Any disturbance to it will have a 'knock-on' effect for the other wetlands. Pollution of The Lake will also effect the quality of the unconfined shallow aquifer that feeds the entire wetland area. Furthermore, algal cells and other nuisance organisms can be transferred by birds and carried to other water bodies in the area.

- **Recommendation:** In cooperation with the South Peninsula Municipality, the owner's association of The Lake, and the developer of the 'The Lake' housing development should formulate a management plan and code of conduct for the residents of The Lake. Within this document, the type and extent of The Lake housing estate should be properly formulated.

E.2 MANAGEMENT OPTIONS FOR WILDEVOËLVLEI

E.2.1 Reducing effluent discharge

E.2.1.1 *Marine outfall*

It is a given that Wildevoëlvlei has exceeded its assimilative capacity in regards to the discharge of effluent from the WWTW. The recent outbreaks of toxic *Microcystis aeruginosa* and the inability of the system further to modify nutrient inputs between the eastern outfall and the western seaward opening to the sea is testimony to this statement. One of the many options to resolve this situation has been the suggestion that the sewage effluent outfall to the vleis be engineered to bypass them by pipeline and to discharge treated effluent directly to the Atlantic Ocean in Chapman's Bay.

We urge that this is not an option for serious consideration for several reasons. The first is the sheer cost involved in its design and construction. The pipeline would have to pass overland for several kilometers, either to the north or to the south of the vlei, and then discharge well off the beach and below the marine euphotic zone, requiring an extremely lengthy structure. Furthermore, Chapman's Bay is an extremely high-energy shoreline with very strong wave action; the engineering would have to be massive in order to avoid storm damage such that this option is simply not economical.

Additionally, a marine outfall does not avoid or minimize pollution: it simply shifts it from one environmental medium to another and, as such, it is ecologically unacceptable. In this context, public sensitivity to such schemes and worldwide trends preclude any serious consideration of a marine outfall as a management option for this stretch of exceptionally scenic coastline in an area of high conservation and potential National Park and World Heritage status. From the point of view of water quality and human health, it is far more important actively to rehabilitate Wildevoëlvlei to a point where it can once again act as a biological filter.

- **Recommendation:** A marine sewage outfall to Chapman's Bay is NOT an option for further consideration.

E.2.1.2 Diversion of raw sewage

In order to reduce the volume of treated effluent discharged into Wildevoëlvlei we have considered the option of raw sewage diversion, prior to treatment at WWTW, to an alternative Wastewater Treatment Works; for instance, at Strandfontein. Our understanding is that Clovelly is presently linked to this system and, if this is the case, it should be a relatively simple matter to link the Noordhoek Valley system to this pipeline.

Apparently, this option was seriously considered prior to the construction of WWTW, but was rejected on the grounds of the costs involved in the construction of necessary infrastructure (Mr K Fawcett, Water and Waste Department, CMC, personal communication). Given the capacity and the location of the Strandfontein Wastewater Treatment Works, the potential is nonetheless there for it to serve as a regional treatment works. However, we urge caution when considering this suggestion, because the concentration of sewage effluent in large quantities in only one area could have tremendous ecological implications for the False Bay coastline and its inshore marine systems. False Bay is a low energy coast with a turn over of approximately 8-14 days; this makes the system sensitive to pollution (e.g. Brown *et al.*, 1991).

In this context, we note with alarm and no little incredulity that consultants, currently contracted to develop a strategic wastewater treatment strategy, are seriously considering the closure of the Simonstown Sewage Works and diverting the sewage from that area to Wildevoëlvlei (Mr M Obree, Catchment Management, CMC, personal communication). Whilst the former (closure) might be feasible, the latter (diversion to Wildevoëlvlei) is utterly inappropriate!

- **Recommendation:** We have been told repeatedly that to expect cessation of development in the Noordhoek Valley is 'unrealistic'. This may be so but, as professional ecologists, we would point out that unless a change in this mindset is effected both politically and managerially, the future development of the Noordhoek Valley, the associated increase in production of sewage and its discharge to Wildevoëlvlei, will further reduce the assimilative capacity of the vlei.
- **Recommendation:** If rezoning and development of Noordhoek Valley is not slowed or stopped, we recommend close re-examination of the option to divert sewage generated within the Valley, away from the Valley, for treatment at the Strandfontein Sewage Works.

- **Recommendation:** Given the destabilized condition of Wildevoëlvlei, diversion of sewage from other areas of the Cape Peninsula into WWTW is inappropriate.
- **Observation:** It is clear that unless management of Wildevoëlvlei is vigorous, taking steps to rehabilitate The Lake and to curb present pollution levels, then serious cyanobacterial outbreaks will regularly recur, with severe long-term cost implications and threats to human and stock health.

E.2.1.3 Recycling of treated effluent

The present saturation of Wildevoëlvlei by nutrients from the WWTW effluent (let alone future increases in quantities and, hence, in loads) dictates serious consideration of the use of a portion, or all, of the secondary-treated effluent for irrigation purposes. We must point out, however, that while such utilization of treated effluent will immediately reduce the present nutrient loads entering Wildevoëlvlei, in the medium- to long-term, the overall water-quality base for the catchment would probably be reduced, with elevation of nutrient and pollution levels in return flows and storm-water events. We also observe that although unquantified, the sewage reaching WWTW is at probably loaded with considerable amounts of a variety of heavy metals (K Fawcett, *personal communication*). Thus, before any decision is taken for or against this, at first sight reasonable option, close scrutiny and quantification of such loads (both heavy metals and toxins) must be carried out.

Potential sites for application could include Clovelly Golfcourse, and the Fish Hoek, Ocean View and the proposed Masiphumelele sportsfields, as well as schools sports fields throughout the Valley. Irrigation with effluent from WWTW is only recommended as long as a continuous monitoring programme is instituted (e.g. of soil pollution levels).

- **Recommendation:** The diversion of sewage effluent from WWTW for irrigation purposes on sports fields and golf courses is an option for consideration. This recommendation is made on condition that heavy metal and toxin levels of the effluent are first quantified, and that a soil-pollution monitoring programme is permanently instituted.
- **Recommendation:** We also recommend the enforced re-use of grey water generated in homes in the Valley (see General Recommendations, section 7.5.6 below).

E.2.2 Improving quality of effluent

E.2.1.4 Chemical phosphorus removal

In addition to the implementation of biological removal processes associated with the present upgrading of the WWTW, a chemical-phosphorus removal process should be implemented at the WWTW. Chemical precipitation of phosphorus can be achieved using iron salts added to the wastewater in the reactor. The Johannesburg biological phosphorus removal configuration provides for a “stripper” tank using ferric chloride. In the upgraded WWTW, chemical removal of phosphorus is proposed as an emergency procedure only, for use at times when the biological removal system fails to meet the requirements for phosphorus reduction. We urge that chemical removal be not simply an emergency procedure, but a continuous procedure, thereby enhancing phosphorus stripping from the effluents discharged to Wildevoëlvlei. Further, we suggest that a less environmentally harmful salt such as ferric sulphate be used instead of ferric chloride.

- **Recommendation:** Chemical stripping of phosphorus using ferric sulphate should become a routine at WWTW and not simply an emergency procedure.

E.2.1.5 Artificial wetlands

The most widely used constructed wetlands are, so-called, constructed reed beds, or root-zone treatment plants, which use a subsurface horizontal water flow (e.g. Brix, 1987). This design is mostly used for tertiary-water treatment processes and typically comprises a rectangular bed planted with macrophytes (e.g. *Phragmites* spp.; *Scirpus* spp), and lined with an impermeable membrane. Inlet and outlet constructions distribute and collect wastewater. The medium of the bed may be soil or gravel. Pretreated wastewater is simply led into one end of the bed and collected at the opposite end. During its passage through the reed bed, organic matter in the wastewater is supposed to be degraded aerobically; nitrogen is nitrified and subsequently denitrified, while phosphorus and heavy metals are adsorbed onto the soil particles. The role of the macrophytes in this treatment process is the provision of oxidizing microzones, due to oxygen release, and also provision of a large surface area for microbial growth (e.g. Armstrong and Armstrong, 1990). The growth of roots and rhizomes are thought to create macropores in the soil which increase and maintain the hydraulic conductivity of the soil (e.g. Kickuth, 1977).

If they are managed correctly, artificial wetlands can be very efficient at removing phosphorus. Reported filtration rates range between 50% and 90%. However, one has to keep in mind that the main process that removes phosphorus from water is its adsorption onto soil particles. Once all available adsorption sites are saturated, phosphorus will no longer be efficiently removed by the wetland. However, the adsorption capacity of an artificial wetland can be manipulated through size and soil management techniques.

Artificial wetlands are often considered as low-cost, and environmentally sound, alternatives to wastewater treatment. However, it is important to understand that a constructed wetland is part of a wastewater treatment configuration and is far from being a natural ecosystem.

- **Recommendation:** We recommend that the use of artificial wetlands for wastewater treatment be investigated further. Additional specialist input is required fully to evaluate the size of wetland necessary to cope with the loads emanating from WWTW.

E.2.1.6 Re-routing effluent through existing reed beds

Extensive reed beds already occur in the catchment to the north of WWTW. These beds, the so-called 'Pick'n-Pay' reed beds, comprise a dense stand of *Phragmites australis*, covering an area of about 41ha. They lie within a drainage line bordered by the developments of The Lake, Sunny Dale, Masiphumelele and industrial and commercial areas.

The question arises: can these existing reed beds be used to enhance the quality of WWTW effluent prior to discharge into Wildevoëlsvlei? The answer is 'possibly', but there are a number of problems to be overcome. Firstly, during winter the present reed beds receive large volumes of storm-water runoff from the catchment. It is likely, therefore, that an additional input of wastewater would exceed the present assimilative capacity of the system for pollutants. Secondly, for optimal utilization, the final effluent from WWTW would have to be

pumped against the topographic gradient to the top of the reed beds, allowing the effluent to gravity feed back through the beds towards Wildevoëlvlei. Thirdly, vegetated filter 'strips' will only be efficient under conditions in which wastewater passes over the area in uniform sheet flow; this allows optimal contact with reed-bed roots and the substrata that the reeds are growing in. In natural reed beds, flow is often not homogeneous, resulting in the formation of channels and inefficient filtration performance. To assess the filtration capacity of the Pick'n Pay reed beds it is, therefore, important to undertake a geochemical survey of the element composition (phosphorus, heavy metals) and a hydrological assessment of the flow pattern within the reed beds.

If the geochemical survey reveals a high contamination load in the sediments, topsoil should be removed.

If the hydrological assessment reveals that the waterflow is not homogeneous the beds would require the following engineering procedures:

- leveling of the ground in order to compensate for slope;
- devices, such as level spreaders, to ensure that water reaches the reed bed as a sheet flow (e.g. berms, placed at a perpendicular angle to the direction of flow through the reed bed);
- Additionally, should the option be adopted (hydrological leveling), subsequent maintenance will be considerable and will require regular mechanical removal or biomass hand-cutting, and/or burning, in order to maintain the system in an efficiently operational condition. Harvesting should be conducted in such a way as to encourage a mosaic of growth stages in order to maximize habitat diversity within the system.

Finally, the use of these reed beds would only be effective during low-flow conditions in the catchment.

- **Recommendation:** To make use of the present reed beds as a biological filter system, the present pollution load of the substrata and the hydrology of the system requires assessment. Under sub-optimal conditions (heterogeneous flow, high pollution load) reed-bed engineering is an option that would improve the condition of Wildevoëlvlei, but careful consideration of costs and long-term reed bed management implications are necessary before proceeding with this option. Discharge of treated effluent into the reed beds is only recommended during low-flow conditions in the catchment as the reed beds already receive a considerable quantity of polluted storm water. Should the option be implemented, maintenance will be considerable and will require regular mechanical removal or biomass, hand-cutting, and/or, burning, in order to maintain the system in an efficient operational condition. Harvesting should be conducted in such a way as to encourage a mosaic of growth stages in order to maximize habitat diversity within the system.

E.2.3 Reducing internal nutrient loads

E.2.1.7 Dredging

Wildevoëlvlei has been receiving daily treated sewage effluent for approximately 25 years. These effluents have saturated the lake to the point where it no longer can act as a biological

filter. The sediments of the lake are super-saturated with phosphorus (Gassner, 1999) and, even if effluent discharge were to immediately cease as we write, phosphorus is present in such large amounts, that suspension of sediments in the lake through wind action will inevitably encourage outbreaks of algal blooms for many years to come.

In this context, it is our considered view that the removal of sediments from Wildevoëlvlei is essential both in order to reduce the present internal phosphorus loading, and to rehabilitate the system. An additional consideration centres on the fact that Wildevoëlvlei sediments are likely also to have adsorbed high concentrations of heavy metals and organic pollutants (K Fawcett, personal communication) such that sediment removed from the lake will possibly require special treatment at an appropriate toxic-waste disposal site: e.g. Vissershoeck. This remark requires verification through research.

Complete removal of the sludge will drastically reduce the internal nutrient load, overall phytoplankton numbers, and improve water clarity. However, sludge-removal operations must be carefully timed to reduce the effects of nutrient and metal releases from disturbed sediments, as well as social impacts caused by odours. Accordingly, we suggest that sludge be removed using a suction pump and a bulk press, and that it take place during winter months and not during summer, although this is subject to unfolding events. It may well be necessary to implement sludge-removal procedures immediately, particularly bearing in mind the recent re-occurrence of toxic cyanobacteria (November, 1998).

- **Recommendation:** Sludge-removal using a suction pump system in conjunction with a bulk press should be considered as a priority operation. It should preferably occur during winter months in order to reduce the overall effects of nutrient- and toxic-metal releases, and social impacts, but this may not be possible in the light of the re-occurrence of toxic cyanobacteria in the vlei. Should investigations prove the sludge to be toxic, it should be removed and treated at an appropriate toxic-waste disposal site. If not, then the sludge could possibly be dumped to sea or to a land-fill site. Detailed research is required for an informed decision to be made.

E.2.1.8 Rehabilitation of the Sago pond weed; Potamogeton pectinatus

Subsequent to the collapse of the population of *Potamogeton pectinatus* in Wildevoëlvlei, there is still little sign of significant recovery of the pond weed in the eastern basin. Given the significance of the plant for water quality (section 5.2.3), and as a competitor for nutrients, a management priority must be the facilitation of recolonization of the vlei by this macrophyte. The most important environmental factors regulating the success of this plant are salinity, depth, and phytoplankton density. Brackish conditions (3‰ -11‰ NaCl; e.g. Howard-Williams and Davies, 1979) favour growth of the pond weed. However, if light conditions are poor and nutrient supplies are sufficiently high, such salinity levels may favour toxin-producing saltwater-tolerant algae, such as *Nodularia spumigena* (Harding *et al.*, 1998; WR Harding, *in litt.*, 13 October, 1998). Therefore, water depth, and hence, light penetration, are important variables to consider. Total or partial lowering of lake levels have proved to be highly successful for the recovery of pond weed elsewhere (e.g. Van der Valk and Davis, 1978).

- **Recommendation:** Whilst the maintenance of brackish-water conditions in Wildevoëlvlei will favour the re-establishment of pond weed in relation to freshwater cyanobacteria, given the present nutrient loads in the system, toxin-producing populations of salt-tolerant

algae may become problematic. We recommend, therefore, that intermittent lowering lake level take place by manipulating the mouth to the sea. This may assist the recolonization of the vlei by *Potamogeton*, through increasing light penetration for rooting seedlings. Such manipulation should occur only in close consultation with experts and should become part of a continuous management programme for the system.

E.2.4 Dilution and flushing of wastewater

E.2.1.9 Runoff

It has been suggested that the present and future discharges of treated effluents to Wildevoëlvlei could be diluted by concentrating runoff from the catchment towards one point in the vlei. Although such a plan might increase volumes of water entering the system, the low water quality of the runoff would only add to the present pollution loads.

- **Recommendation:** The 'dilution' of present or future effluent discharges to Wildevoëlvlei using storm-water runoff is NOT a sensible ecological management option simply because the low quality of such runoff will simply add to the present pollution problems of the system.

E.2.1.10 Water from the aquifer

An alternative approach to the dilution of effluent entering Wildevoëlvlei is the use of bore holes to local aquifers. However, in order to achieve sufficient dilution, a volume of between approximately five and six Mℓ d⁻¹ would be required. The removal of such a volume of water from either the confined, or unconfined, aquifers in the Noordhoek Valley would have very significant and detrimental implications for the water table and the wetlands as a whole.

- **Recommendation:** The use of groundwater to manage Wildevoëlvlei (dilution) is NOT an option for consideration because of the adverse effects its removal would have on the water table and the integrity of the wetlands of the Valley.

E.2.1.11 Seawater ingress and pulsed-effluent discharges

If effluent discharges to Wildevoëlvlei are to continue then management actions designed to enhance the rate at which effluent is run through the system should be implemented. Instead of a continuous and steady discharge of treated effluent, there is, in our opinion, little reason not to arrange discharges in a manner that enhance tidal pulses and which are timed according to the prevailing tides. If treated effluent were impounded and then discharged while tides were ebbing, unwanted effluent would probably move much more rapidly through the vleis. Conversely, reduced effluent discharges at times of high tide would enhance salt-water penetration of the system and encourage effluent mixing. This would not only re-establish the more natural semi-saline environment of the vleis, but would also inhibit the growth of nuisance freshwater cyanobacteria such as *Microcystis aeruginosa* (but see above, section 7.4.3.2). A pulsed discharge would be especially beneficial during summer, when the threat of blooms is highest and when the flow from the WWTW is relatively low.

- **Recommendation:** If effluents are not going to be diverted from WWTW (we urge that they *must*), then pulsed discharges of effluent from WWTW should be considered, particularly during summer months. Timing of discharges should be out of phase with ebb and flow tides in order to enhance flushing of effluent on the ebb tide and saline mixing on the flow tide.

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APPENDIX F MAPS OF SAMPLING LOCATIONS

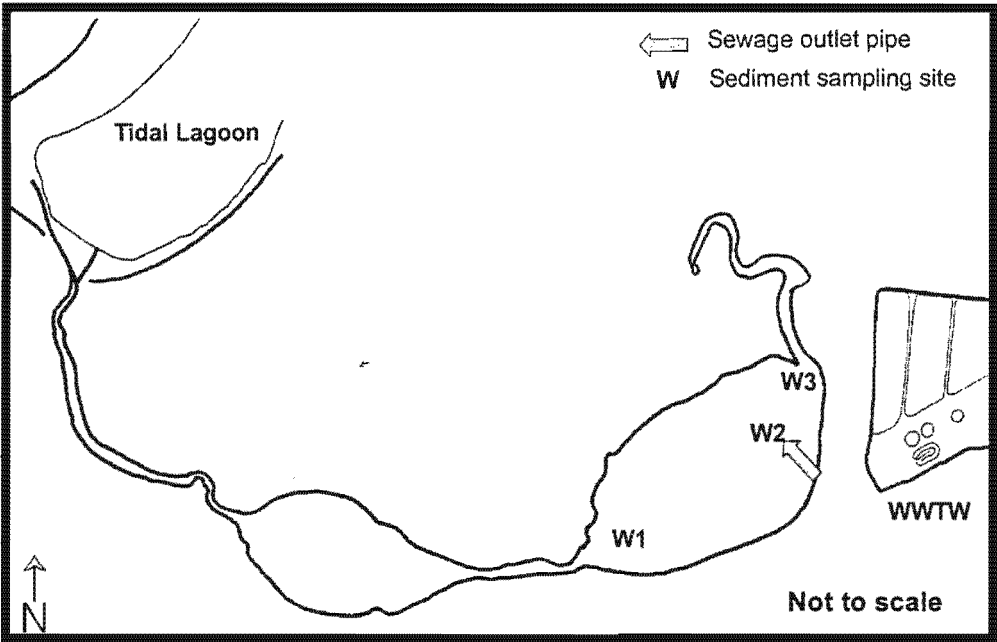


Figure F.1: Map of Wildevoëlsvlei showing sampling sites

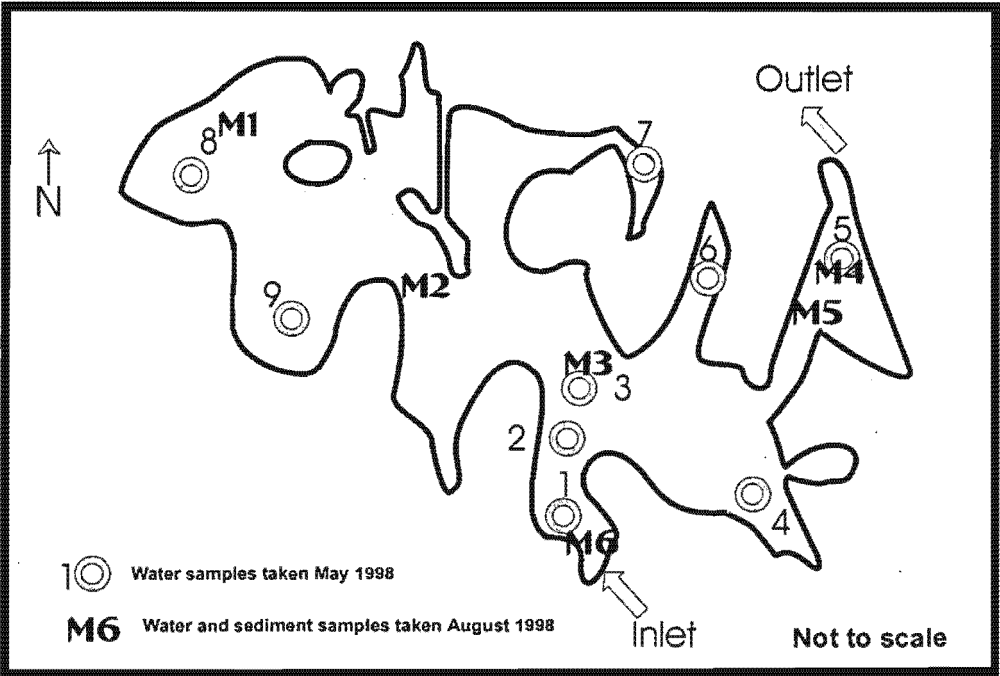


Figure F.2: Map of The Lake showing sampling sites.