A GEOCHEMICAL INVESTIGATION INTO THE OCCURRENCE AND FATE OF NITROGEN AND PHOSPHORUS IN THE LOWER OLIFANTS RIVER, WESTERN CAPE

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ABSTRACT

South Africa is a water stressed country and effective water quality management is critical if South Africa is to meet the sustainable development challenge. Knowledge of nutrient dynamics within aquatic ecosystems are of fundamental importance for water quality management, especially in cultivated areas where irrigation farming pose a salinization and eutrophication risk to water bodies. A range of water quality problems is associated with eutrophication, which is generally controlled by the nutrients nitrogen and phosphorus. The lower Olifants River is situated in an arid region with intensive irrigation agriculture. This study set out to investigate the loading and fate of nitrogen and phosphorus in the lower Olifants River. Two sampling runs were undertaken during the study. The first sampling run (water column samples only) took place during a reconnaissance site visit in June 2003, during which unfiltered water samples were collected. During the second sampling run in September 2003 filtered and unfiltered water samples were collected, as well as sediment samples (from which pore water samples were abstracted in the laboratory). Field measurements included pH, temperature, EC and dissolved oxygen. Water column and pore water samples were analyzed (in duplicate where sample volume allowed) for major ions, ammonium, nitrate and nitrite, dissolved reactive phosphorus, total dissolved phosphorus and total phosphorus and total dissolved nitrogen and total nitrogen. Dissolved organic carbon was furthermore determined for five selected water column samples taken during the second run. Sediment samples were analyzed for total carbon, organic carbon, total nitrogen, total phosphorus and particle size distributions. Large variations in salinity and nutrient content of the water column samples were found between the two sampling runs, with both major ion concentrations and nutrient levels (especially NO_3^-) being highest in the freshwater section of the river during low flow conditions. Agricultural return flows, which makes a more significant contribution to the river chemistry in low flow conditions than in high flow conditions, is deemed to play an important role in this phenomenon. The major pool of both nitrogen and phosphorus in the lower Olifants River is to be found in the sediments, and nutrient concentrations in the pore waters form a potential source of nutrients to the overlying water column. C:N ratios indicate that the organic matter present in the sediments upstream of the estuary is largely terrestrial in origin, whereas the more labile organic matter in the sediments of the estuary are largely

algal in origin. The salt marsh in the estuary was found to have a large influence on nutrient cycling in the lower Olifants River, with neither nitrogen nor phosphorus showing conservative behavior in the estuary. Results obtained during this study indicate that the estuary acts as a nitrogen sink and a phosphorus source to the ocean. Important processes effecting nitrogen cycling within the estuary include assimilatory nitrate reduction, denitrification, ammonification and dissimilatory nitrate reduction to ammonia. Phosphorus mineralization, adsorption to and desorption from iron oxyhydroxides are deemed to be controlling processes for phosphorus cycling in the estuary. Redox conditions control the nutrient cycling to a great extent, and the tidal influence of water high in ionic strength significantly effect various aspects of the nutrient dynamics in the estuary. N:P ratios suggest that the lower Olifants River upstream of the estuary is phosphorus limited, whereas the estuary experiences nitrogen limitation.

1. INTRODUCTION AND STUDY OBJECTIVES

1.1 Introduction

Water is one of South Africa's most important and limited resources. This is evident when considering that the average yearly rainfall in South Africa is 452 mm (Davies & Day, 1998), compared to the world average of 860mm (Cowan, 1995). The situation is made worse by inefficiencies in use and the growing demands of the economy. Effective water quality management is thus critical to South Africa, especially in the context of the sustainable development challenge.

The nutrients nitrogen and phosphorus play major roles in aquatic biogeochemistry, and have a large effect on water quality and aquatic ecosystems (Aston, 1980; Wetzel, 1983; Schlesinger, 1997; Flindt *et al*, 1999). Eutrophication of water bodies and the associated water quality problems due to nutrient loading from urbanized areas and diffuse runoff from cultivated land areas is a world-wide problem (Flindt *et al*, 1999). Drainage from irrigation farming has led to the eutrophication and salinization of the lower reaches of many rivers in South Africa (Lambrechts & Schloms, 1998), and South Africa has some of the most highly nutrient enriched surface waters in the world (Walmsley, 2000). Knowledge concerning inputs to and transformation of nitrogen and phosphorus within aquatic systems* are thus of fundamental importance to water quality management. Wetlands are sites that have a large influence on biogeochemical cycling, and are of special interest to the transformation of nutrients (Schlesinger, 1997).

The Olifants River catchment lies in the western, drier part of South Africa, and has a mean annual precipitation of 212 mm (van Veelen *et al*, 1998). Groundwater quality in the Olifants catchment is generally poor, with extremely high salt concentrations occurring in the north of the catchment. Due to the high salinity groundwater can only be used for irrigation purposes under ideal soil and crop conditions (van Veelen *et al*, 1998).

* = In the context of this literature review aquatic systems refer to both the water and the sediments in the system.

Humans have impacted on the lower part of the river through the building of dams and irrigation systems in the valley, and through the application of fertilizer associated with the intensive agriculture on the banks of the Olifants River. Further agricultural developments in the catchment are foreseen (van Veelen *et al*, 1998) and the potential of increased loading of nitrogen and phosphorus to the river is a reality. Marginal wetlands in the river and the Olifants Estuary, which is one of the most important estuaries on the west coast (Whitfield, 2000), have the potential to act as a filter for the added nutrients.

1.2 Study objectives

The main objectives of this study are to:

1. Determine the nitrogen and phosphorus loading in the lower Olifants River. For this purpose water column, pore water and sediment samples will be investigated.
2. To gain a basic understanding of the mobility and fate of nitrogen and phosphorus in the lower Olifants River. Nutrient speciation, the presence of reactive species and the potential for transformation reactions will be evaluated to address this objective.

2. LITERATURE REVIEW

2.1 Introduction

This literature review will touch upon eutrophication, the main concern of increased nutrient levels, and will then focus on the biogeochemistry of nitrogen and phosphorus in aquatic systems. Aspects that will be addressed under the latter will include the most important forms, sources, and transformations of nitrogen and phosphorus in aquatic systems, as well as the environmental conditions in wetlands that control these transformations.

2.2 Eutrophication

2.2.1 Definition

Eutrophication is defined as the process by which a water body becomes progressively enriched with plant nutrients over time (World Health Organisation, 1989; Walmsley, 2000). Although eutrophication is a natural process, it is often linked to anthropogenic inputs (Davies & Day, 1998). The environmental and social conditions as well as government policy in South Africa, has led to the fact that S.A has some of the most highly nutrient enriched surface waters in the world (Walmsley, 2000).

2.2.2 Degradation in water quality

The eutrophication of a water resource represents a serious degradation in water quality (WHO, 1989; Walmsley, 2000). These nutrients promote the development of both living and decaying biological material in the receiving systems and often shifts the main productivity from the benthic to the planktonic community (Flindt et al, 1999), which can ultimately pose a wide variety of water quality and user problems. Some of the most widely documented problems associated with eutrophication include toxic algal blooms and increased fish and invertebrate mortality (Walmsley, 2000), the disturbance of ecosystem structure and functioning (Lijklema, 1998), increased water treatment costs, and interference with irrigation agriculture via the clogging of irrigation equipment. A loss of biodiversity is also often found when nutrient levels increase in aquatic communities that own their specific species assemblages to low nutrient supply (Davidson & Cape, 2003).

2.2.3 Controlling nutrients

Algae and aquatic macrophytes require about 20 different nutrients (Walmsley, 2000). The rate and extent of aquatic plant growth is however dependent on the concentration and ratios of the nutrient that is present in the least quantity relative to the growth needs of the plant (following Leibig's law of the minimum). Because of nutrient supply and demand in nature, it has been observed that nitrogen and phosphorus are the most frequently the limiting nutrients in freshwater systems (Walmsley, 2000). Of these two elements, phosphate is generally the most important growth-limiting nutrient in freshwater aquatic environments (Boers *et al*, 1998; Walmsley, 2000).

2.3 Nitrogen and phosphorus in aquatic systems

2.3.1 Nitrogen

Nitrogen is found at a range of valance states that provide the potential for several oxidation-reduction reactions (Reddy *et al*, 2000). The result of this is that a wide array of biogeochemically convertible nitrogen compounds are found in the environment that make up the nitrogen cycle (Figure 1).

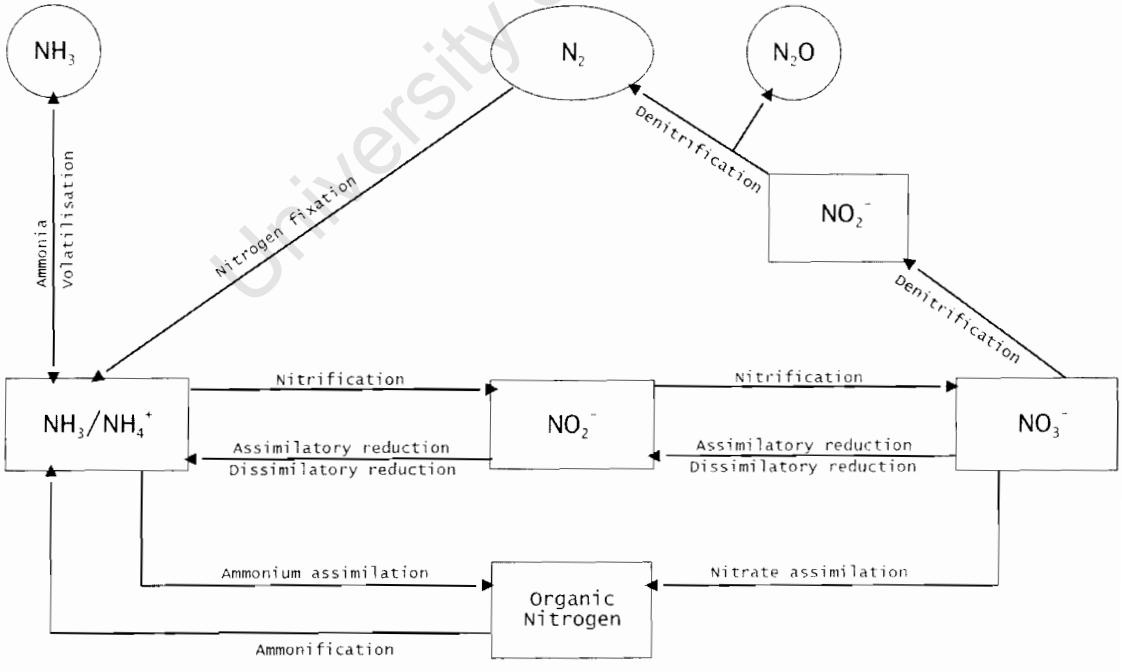

Figure 1: A simplified version of the nitrogen cycle.

The dominant forms of nitrogen in the aquatic environment are dissolved molecular nitrogen (N_2), nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_3), ammonium (NH_4^+), and a large number of organic-nitrogen compounds (Wetzel, 1983; Eaton *et al*, 1995).

Molecular nitrogen makes up about 78 % of the atmosphere (Brady & Weil, 1999). It is a very stable molecule, needing considerable energy to break its inter-atomic bonds (Sprent, 1987). Lighting, humans (through the Haber process), and nitrogen fixing microorganisms can produce the energy necessary to fix molecular nitrogen (Thompson, 1996). Nitrogen fixation is however less energy efficient then the assimilation of combined inorganic nitrogen, and in aquatic systems nitrogen fixing is quantitatively significant only in conditions where bioavailable nitrogen is severely depleted (Wetzel, 1983).

Nitrate is the most oxidized form of nitrogen (+5) and is naturally produced by the mineralization of organic matter. During this decomposing process organic nitrogen is converted to NH_3 / NH_4^+, followed by nitrification where the NH_4^+ is converted to NO_3^-. Nitrate has a high solubility in water and is electrostatically repelled by negatively charged soil colloids (Artiola, 1996), and is considered to be the most mobile form of nitrogen (Groffman, 2000). Nitrate is generally perceived to be the principal form in which nitrogen is taken up by plants in arable soils (Richards, 1987).

Nitrite is an intermediate product of both the reduction of nitrate to molecular nitrogen and nitrous oxide (N_2O), and the oxidation of ammonia/ammonium to nitrate (Eaton *et al*, 1995). Nitrite is generally found at very low concentrations in surface water (Harck, 1995). Ammonia and ammonium function as an acid-base pair. At a pH below 8, NH_3 is seldom present and the reduced inorganic nitrogen is mostly present in the pronated form NH_4^+ (Groffman, 2000).

The most common inorganic form of nitrogen is ammonia/ammonium (Groffman, 2000). Free ammonia/ammonium is the first inorganic nitrogen form released in the mineralisation process, and most fertilizers are furthermore NH_3 (or urea which rapidly degrades to NH_4) based (Groffman, 2000). Ammonium is relatively immobile as it is strongly sorbed to soil colloids (especially clays).

Organic nitrogen occurs in a large array of organic compounds such as amino acids, proteins, amines and nucleotides. The degradability of organic matter depends amongst others on the C/N ratio, where organic matter with a high C/N ratio is less biodegradable than organic matter with a low C/N ratio (Wetzel, 1986). Organic nitrogen mineralisation depends furthermore on extracellular enzyme (such as protease) activity, microbial biomass and the soil redox conditions (Reddy *et al*, 2000).

2.3.2 Phosphorus

All natural phosphorus occurs in the oxidised form of phosphates (PO_4^{3-}), where each phosphorus atom is surrounded by four oxygen atoms (Emsley, 2000). Due largely to its single valence state the phosphorus cycle (Figure 2) is much less complicated than the nitrogen cycle. The phosphorus cycle is further unique in that it has no significant gaseous component (Schlesinger, 1997).

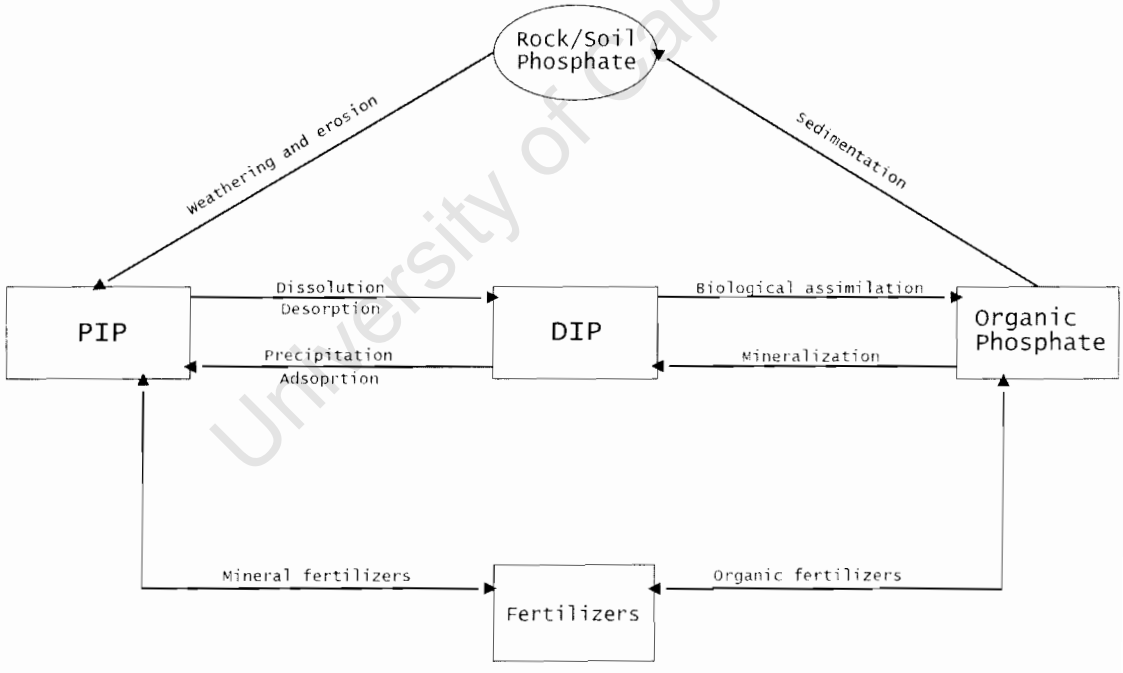

Figure 2: A simplified version of the phosphorus cycle.

Phosphates occur in the environment as dissolved inorganic (DIP) and organic (DOP) forms, as well as particulate inorganic (PIP) and organic (POP) forms. Organic forms of phosphates generally make up the bulk of phosphates in the aquatic environment (Wetzel, 1983). Phosphate is extremely reactive, especially under oxic conditions

where phosphate interacts with many cations (Wetzel, 1983). Under aerobic conditions PIP will thus form an important pool of phosphate. Phosphate is furthermore strongly sorbed by soil components and does not easily move through soil (Mengel & Rehm, 2000). The only inorganic form of phosphorus that organisms can utilize directly is orthophosphate (PO_4^{3-}), which is a DIP (Wetzel, 1983).

2.4 Sources of nitrogen and phosphorus to aquatic systems

Nitrogen and phosphate share many common sources, which include inputs from inflowing surface water and groundwater, surface runoff and erosion from agriculture, atmospheric deposition (ammonia and nitrate as N, and dust containing P), and animal excreta (Wetzel, 1983; Oenema & Roest, 1998). Generally the main contributors of nitrogen and phosphorus loading to aquatic systems are run-off from agriculture, sewage and effluent from treatment works (Lijklema, 1998). In estuaries, river flows are considered to be the major source of N and P (Tappin, 2002) in the absence of marked coastal upwelling and exchange of waters.

As a significant part of the nitrogen cycle takes place in the atmosphere, atmospheric deposition would be expected to play a more significant role towards nitrogen loading than to phosphorus loading (with the possible exception of dust deposition). Oxides of nitrogen (NO_x) are formed during combustion processes (Baumbach, 1996), which ultimately form NO_3^-. Atmospheric NO_3^- deposition has been found to range from 5 to more than 20 kg N ha^{-1} $year^{-1}$ (Johnson, 1992; Lovet, 1994; both *in* Groffman, 2000). Ammonia volatilization from animal waste can also contribute significantly to sources of atmospheric deposition. The Olifants river catchment has a low population density and little industrial development, and predominantly irrigated agriculture. Therefore atmospheric deposition is not expected to be a significant source in the Olifants River.

An additional nitrogen source compared to that of phosphorus includes nitrogen fixation both in the water and the sediments. As mentioned under section 2.3.1, nitrogen fixation is less energy efficient then the assimilation of combined inorganic nitrogen, and will only be significant where bioavailable nitrogen is severely depleted (Wetzel, 1983). The dominant natural source of phosphorus is the weathering of apatite minerals (Schlesinger, 1997).

Although global trends are evident, the relative contribution of sources to nitrogen and phosphorus loading will depend on the site-specific biophysical and chemical processes operating in the particular catchment. Important considerations then also include the connections (water flow/ hydrologic flow etc.) between sinks and sources within a catchment. Stable isotopes can be used as a method of identifying specific sources of nitrogen loading (Roadcap *et al*, 2001). Overlap between the variable isotopic compositions of potential sources and fractionation processes between source and sampling point can however cause limitations on the usefulness of the technique, and supporting hydrological data are necessary for data interpretation (Kellman & Hillaire-Marcel, 1997). Considering the constraints on this study stable isotopes are not deemed to be an appropriate method for source allocation. Agriculture is expected to be the largest source of both nitrogen and phosphorus in the lower Olifants River.

2.5 Mobility and transport of nitrogen and phosphorus in wetlands

Changes in environmental conditions can alter the behavior of elements by changing the forms in which they occur (e.g. the speciation). Important controlling factors in wetlands include hydrology, particle surfaces for adsorption, organic matter build-up, redox potential, pH, and the presence of reactive species such as complexing ligands (Ure & Davidson, 1995). The sediment-water interface is furthermore important to nutrient dynamics in wetlands.

2.5.1 Hydrology

The hydrological regime is crucial to wetland functioning (Zedler, 2000) and control processes such as water mixing, advective flux, residence time and the sedimentation of suspended nutrients. Wetlands are characterized by a slowing down of surface water flow, thus promoting the deposition of particulate forms of nitrogen and phosphorus.

2.5.2 Particle surfaces for adsorption

The slowing down of water associated with wetlands then also leads to the enhanced settlement of silt and clay particles. Clay particles are usually the most chemically reactive component in soils/sediments (due to their high surface charge to mass ratio) and sedimentation of clays therefore leads to wetland sediments having a relatively high ion exchange and specific adsorption capacity (McBride, 1994).

2.5.3 Organic matter

A characteristic feature of most wetlands is a build up of organic matter. This is due to the fact that rates of photosynthesis in wetlands are generally higher than in other ecosystems, while rates of decomposition are in turn generally lower when anaerobic conditions prevail (Reddy *et al*, 2000). As organic matter temporarily immobilizes nutrients, it reduces the potential threat of eutrophication of downstream waters. The build up of organic matter furthermore has a large influence on redox potential.

2.5.4 Redox potential

Redox potential regulates the speciation, mobility and bioavailability of chemicals in the environment, as well as plant and microbial respiration rates (Reddy *et al,* 2000). The redox potential is influenced directly by oxygen. Aerobic organisms use O_2 as their primary electron acceptor and aerobic respiration of organic matter rapidly consumes dissolved oxygen in water. O_2 diffusion through water is about 10^4 slower in water than in air (Reddy *et al*, 2000), and ambient conditions can change to anaerobic in a short space of time. Microbial activity generally changes to anaerobic when dissolved oxygen concentrations reach trace levels of 10^{-6} M (Mcbride, 1994).

Redox conditions of the system will depend on the inflow of electron acceptors (e.g. O_2, NO_3^-, Fe^{3+}, Mn^{3+}, SO_4^{2-}), the availability of organic and inorganic substrates and hydrologic conditions (Reddy *et al*, 2000). How much the reduction increases depends on the quantity of reactive electron acceptors compared with the quantity of electrons generated by organic matter oxidation. Mineralisation rates of organic nitrogen and phosphorus decreases as sediments become more reduced (McLatchey & Reddy, 1998).

Wetlands have anaerobic and aerobic interfaces, with redox gradients in the range of +700 to –300mV (Reddy & D'Angelo, 1997). Rooting macrophytes can have a marked effect on redox gradients by their ability to transport oxygen downward during photosynthesis (Lijklema, 1998). As plants produce O_2 in the day and respires during the night, redox gradients influenced by vegetation can have daily fluctuations. Redox conditions can furthermore have a significant effect on pH. Most reduction reactions consume H^+ (McBride, 1994; Drever, 1997). Metal ions made soluble by reduction can however precipitate as carbonates, hydroxides or sulfides (e.g. Mn^{2+} +

H_2CO_3 = $MnCO_3$ + 2H), generating protons in the process. Generally oxidation reactions generate hydrogen ions and lower the pH (e.g. pyrite oxidation and acid mine drainage).

2.5.5 pH

pH is a master variable in the aquatic environment and governs various processes (Langmuir, 1997). The pH of water is influenced by a wide array of organic and inorganic acids and bases. The $\sum CO_2$ system is the most important in regulating the buffer capacity of natural waters (Wetzel, 1983). One of the important influences of pH is its impact on the microbes that actively use and transform nitrogen. The optimum pH for the nitrification process is approximately 8.0. About 90 % of the optimum nitrification rate can take place at a pH between 7.5 and 8.5, and less then 50% of the optimum below a pH of 6.4 or higher than 9.6 (Viessman & Hamner, 1998). pH furthermore controls NH_3 volatilisation, with sediments having a pH >8 showing a high potential for NH_3 volatilisation (Groffman, 2000).

2.5.6 Reactive species

The redox potential and pH influence the availability of reactive species directly. Reactive species are especially important to the mobility of phosphate. Iron, aluminium and calcium can all adsorb to phosphorus in oxidized conditions, leading to the precipitation of the newly formed compound (Reddy & D'Angelo, 1997). Adsorption rates are controlled by redox condition and pH, adsorptive surface area (active aluminium and iron oxides or calcium carbonate) and temperature (Reddy & D'Angelo, 1997).

Many metalic compounds are reduced into more soluble (and bioavailable) forms under wetland anoxic conditions (Reddy *et al,* 2000). When ferric phosphate is reduced both the iron and the phosphate are mobilized. If the phosphate migrates to an oxic zone with available reactive species (e.g. ferric iron), the phosphate will adsorb to the iron and precipitate out again. Iron then often plays an essential role in the fixation of phosphates in sediments (Boers et al, 1998; Lijklema, 1998). The reduction capacity of oxidised iron compounds decreases with increasing crystallinity. Loveley (1987 in Reddy *et al*, 2000) found the following relationship, in order of most

reducible to least reducible: $FePO_4$> $Fe(OH)_3$> FeOOH > Fe_2O_3. In aquatic systems with a low pH, the availability of Fe and Al is enhanced, and in systems with a high pH the availability of Ca is enhanced. An intermediate pH thus probably leads to the highest precipitation of phosphorus.

When the availability of iron and aluminium is of concern one must also take organic matter into consideration, as both these metals form organic bonds. Metal-organic matter complexation is greater under wetland soil conditions, due to general high concentrations of dissolved organic compounds in the interstitial water. Due to complexation with organics significant amounts of Fe (II) can be present under aerobic conditions for several days (Reddy *et al*, 2000).

2.5.7 The sediment-water interface

Generally, the amount of nutrients accumulated in the top layer of the sediments is much higher than the amount of nutrients found in the overlying water. In the top 10 cm of sediments values of nutrients (per square meter) has been found that was more than three-hundred times the values of the 5m column of overlying water (Lijklema, 1998). The internal loading of nutrients are thus crucial to a system as they can be remobilized under the right conditions (e.g. phosphate under reducing conditions). Advective pore water inputs (e.g. from groundwater inputs potentially influenced by processes and human activities occurring away from the water body itself) may furthermore contribute significantly to nutrient inputs (Janke et al, 2003).

2.6 Nitrogen transformations in wetlands

Nitrogen in particulate form is generally removed by settling and burial in wetlands, while the removal of dissolved forms is regulated by plant and microbial uptake, and a range of biogeochemical reactions functioning in the sediment and water column (Reddy & D'Angelo, 1998; Reddy *et al*, 2000). Important biogeochemical reactions for nitrogen transformations that have not been discussed yet include nitrification, assimilatory reduction and dissimilatory reduction (including denitrification), and ammonia volatilization.

2.6.1 Nitrification

Nitrification is performed predominantly by chemoautotrophic bacteria and takes place in two phases. The first of these involve the oxidation of ammonia/ammonium to nitrite, the intermediate product. This first phase is the rate-limiting step that controls the overall reaction (Viessman & Hamner, 1998):

$$NH_4^+ + 1.5O_2 \xrightarrow{\textit{Nitrosomonas}} NO_2^- + 2H^+ + H_2O + \text{energy}$$

The step following on the above equation involves the oxidation of nitrite to nitrate, where:

$$NO_2^- + 0.5\,O_2 \xrightarrow{\textit{Nitrobacter}} NO_3^- + \text{energy}$$

At both stages of the nitrification process, the energy yields are low, and the nitrifiers (the *Nitrosomonas* and *Nitrobacter*) grow very slowly even under optimum conditions (Richards, 1987). In nature the oxidation of ammonium usually proceeds as far as nitrate, which is fortunate, as this does not allow nitrite to build up, which is toxic to microbes and plants.

The rate of nitrification follows zero-order kinetics, and is independent of the ammonia concentration (Viessman & Hamner, 1998). Important parameters of nitrification kinetics include dissolved oxygen concentration, pH and temperature.

There has been no detectable oxygen-related inhibition of the nitrification process at dissolved oxygen levels above 1.0mg/l (Viessman & Hamner, 1998). According to Reddy *et al* (2000) oxygen is the primary regulator of nitrification in wetland environments. The effect of pH on nitrification has been discussed earlier under (see section 2.4.5)

A temperature drop of 10°-12°C above 10°C results in a decrease of about one-half of the nitrification rate. Nitrification rates decrease even more rapidly at temperatures below 10°C (for example a temperature decrease from 10°C to 5°C halves the rate of

nitrification). The following equation has been suggested by Viessman & Hamner (1998), to express the effect of temperature on the maximum growth rate of *Nitrosomonas* over a temperature range of 5°C to 30°C:

(Viessman & Hamner, 1998), to express the effect of temperature on the maximum growth rate of *Nitrosomonas* over a temperature range of 5°C to 30°C:

$$\mu_N = 0.47e^{0.098\,(T-15)}$$

where:

μ_N = maximum specific growth rate of *Nitrosomonas*, (d^{-1})
e = base of Napierian logarithms, (2.718).
T = temperature, (°C).

Nitrification rates are thus expected to show both a strong seasonal and diurnal variation.

2.6.2 Assimilatory reduction

Assimilatory reduction involves the reduction of NO_3^- to NH_4^+ by microorganisms and plants with a subsequent incorporation of the nitrogen into their biomass as monomers (amino acids) and biopolymers (proteins) (Reddy *et al*, 2000). Assimilatory reduction thus leads to the temporary immobilization of the nitrogen compounds. Plants derive most of their nitrogen from soil pore water with only a small amount of nitrogen being directly utilized form the overlying water. Generally nitrogen assimilation by herbaceous vegetation is short term and cycled rapidly within the aquatic system (Reddy *et al*, 2000).

2.6.3 Dissimilatory reduction

Dissimilatory NO_3^- reduction is divided into two main pathways, namely denitrification (see reaction 1) and dissimilatory NO_3^- reduction to ammonium (reaction 2). In both cases, NO_3^- is used as an electron acceptor for energy generation by anaerobic bacteria (Reddy *et al*, 2000).

Reaction 1: $5C_6H_{12}O_6 + 24NO_3^- + 24\ H^+ \rightarrow 30CO_2 + 12N_2 + 42H_2O$

Reaction 2: $C_6H_{12}O_6 + 3NO_3^- + 6\ H^+ \rightarrow 6CO_2 + 3NH_4^+ + 3H_2O$

Dissimilatory reduction to ammonium occurs at very low redox potentials (<0 mV), whereas denitrification occurs at higher Eh levels (200-300 mV). Denitrification is typically the dominant pathway of NO_3^- removal in wetlands (Reddy et al, 2000), and ecosystems with high rates of denitrification (actual or potential) function as very effective sinks for NO_3^- (Groffman, 2000). Denitrification rates are generally limited in most wetlands by NO_3^- concentrations, and diffusion rates of NO_3^- from aerobic to anearobic sediments/waters (Martin and Reddy, 1997 in Reddy *et al*, 2000).

As denitrification is mediated by heterotrophic microorganisms, its rate may furthermore be regulated by organic C. As most wetlands are characterized high organic matter content, available carbon should not be limiting.

2.6.4 Ammonia volatilization

Ammonia volatilization has been touched upon before in this literature review (see section 2.4.5). It is an abiotic reaction influenced by the physicochemical characteristics of the wetland sediments and waters. Ammonia volatilization is regulated by NH_3 concentration, temperature, vegetation density, air movement above the water surface, mixing in the water column, algal activity and most importantly associated pH fluctuations (Reddy *et al*, 2000). The process of ammonia volatilization can be expressed by the following reactions:

$$NH_4^+ + OH^- = NH_{3(aq)} + H_2O$$

$$NH_{3(aq)} = NH_{3(g)} \quad (pH>8)$$

Ammonia volatilization can play a significant role in wetlands if the influent water contains high levels of NH_4^+, and if algal photosynthetic activity drives the pH above 8.5 (Reddy *et al*, 2000).

The biogeochemical processes described in this section generally leads to the effective processing of inorganic nitrogen. The release of dissolved organic N, most of which is resistant to decomposition during the breakdown of detrital tissue, can however result in the outflow of water with high levels of dissolved organic nitrogen. Wetlands usually function as sources of organic N, and as effective sinks for inorganic N. (Reddy *et al*, 2000; Mwanuzi *et al*, 2003).

2. 7 Phosphorus transformations

As there is no significant gaseous loss mechanism as in the nitrogen cycle, phosphorus tends to accumulate in wetlands. A recent study in lake Victoria (Mwanuzi *et al*, 2003) indicated wetland inorganic P retention of between 60-90%. Phosphorous retention within wetlands is regulated by physical (sedimentation and entrainment), biological mechanisms (uptake and release by vegetation, periphyton and microorganisms) and chemical mechanisms (adsorption and precipitation and exchange processes between the sediments and soil) (Reddy & D'Angelo, 1998; Reddy *et al*, 2000).

Phosphorus associated with particulate compounds (e.g. clays, hydroxides and carbonates) are removed from the water column through deposition brought on by the slowing down of surface water flow characteristic to wetlands. This build up of phosphorus in the sediments underlies the importance of the sediment-water interface in aquatic system nutrient dynamics.

Depending on the type of vegetation present in a wetland, vegetative uptake of phosphates can provide either a short or long term sink for phosphorus. Generally phosphorus in detrital plant/algal tissue is rapidly released to the water column (Reddy *et al*, 2000). Phosphorus uptake by plants will furthermore show a seasonal variation coupled to plant growth. Due to the high productivity in wetlands phosphorus may remain as part of organic matter buildup in wetland, which is relatively resistant to microbial breakdown under anearobic conditions (Reddy *et al,*

2000). The same anaerobic conditions will however lead to the mobilization of inorganic particulate phosphorus in the sediments (section 2.5.6).

The effectiveness of phosphorus uptake by periphyton plant communities are dependent on phosphorus loading, with periphyton communities being effective sinks in aquatic systems with low phosphorus loading, with their overall effect being low when nutrient loading is high (Reddy *et al* 2000). The adsorption and precipitation of phosphorus has been discussed under section 2.5.6.

3. SITE DESCRIPTION

3.1 Introduction

The site description provides the setting within which the results of the study can be interpreted. As the catchment forms an integrated unit in which hydrological processes interact, this section will focus on the description of catchment characteristics.

3.2 Location

The Olifants River catchment of concern (there are three Olifants Rivers in South Africa) is located in the south west of South Africa (Figure 3). Sampling was undertaken in the lower section of the river, from just upstream of the confluence of the Olifants River and the Doring River near Trawal, to the mouth of the river at the Olifants River Estuary. The estuary lies some 250km north north-west of Cape Town.

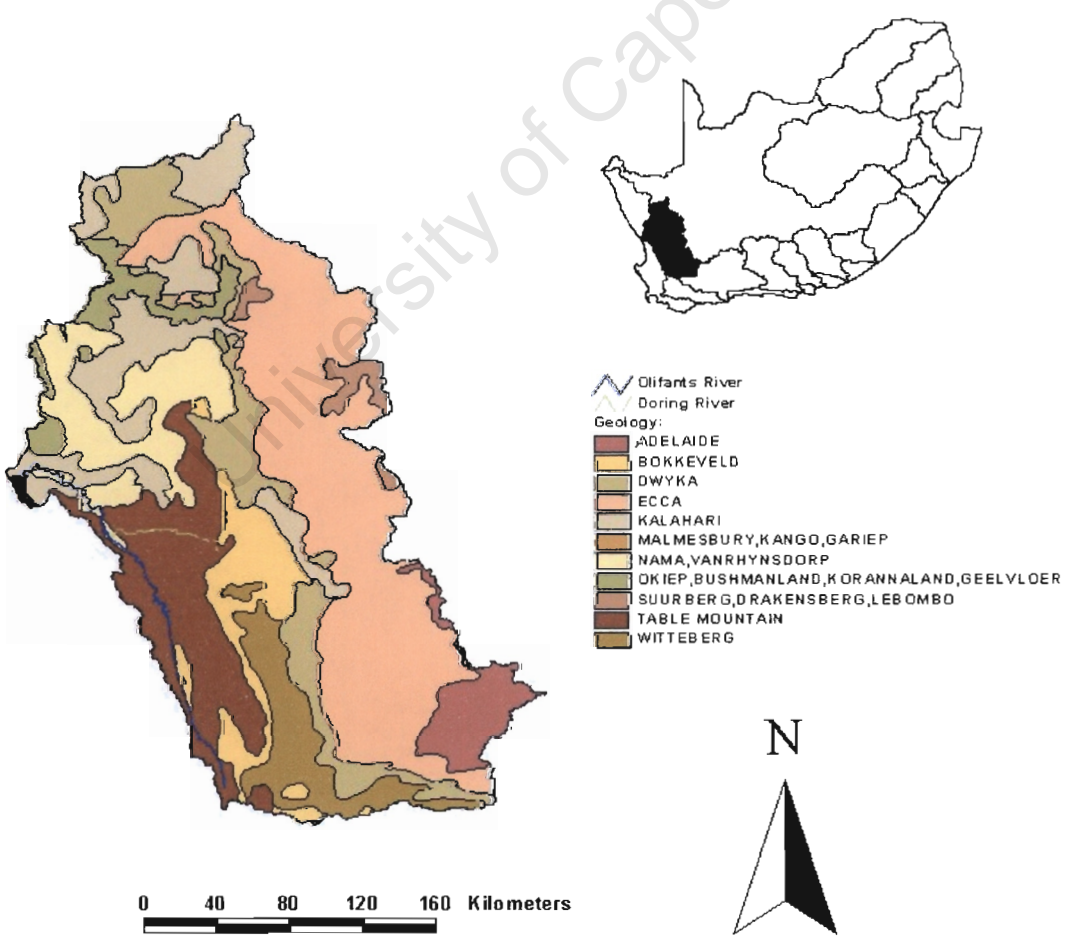

Figure 3: Location and geology of the Olifants River catchment (ENPAT, 2000).

3.3 Topography

The north-eastern region of the catchment has an undulating relief which is typical of the Western Karoo landscape. A steep topography is found in the south-western section of the catchment. Downstream of the confluence of the Olifants and Doring river the topography flattens out (Basson *et al*, 1998).

3.4 Geology

The catchment geology is depicted in Figure 3. The northern and eastern regions of the catchment are underlain by Karoo rocks, consisting mainly of the easily erodable Dwyka Formation tillites and shales, and the Ecca Group sandstones and shales (Morant, 1984). These stratigraphical units are part of the Karoo Supergroup, and are the main source of the clay rich sediments in the system.

The Doring River (of which only the lower section is depicted in Figure 3), an important tributary to the Olifants, drains mainly the eastern area of the Olifants catchment dominated by shales and mudstones of the Dwyka formation and the Ecca Group (van Veelen *et al*, 1998). The area in the western and extreme southern parts of Doring River catchment is underlain by sandstones and quartzites of the Table Mountain Group (TMG), Bokkeveld Group shales and Witteberg group shales and quartzites (Morant, 1984). These three stratigraphic series all form part of the Cape Supergroup.

The south-western region of the catchment is underlain by the TMG which consists mostly of quarzitic sandstones interlaced with shale horizons (Basson *et al*, 1998). The Olifants River itself drains mainly this area, and the usual low silt and salt loads of the Olifants up to the confluence with the Doring River, can be explained by the low weatherability of the quartzitic sandstones and quartzites (Morant, 1984). The north-western part of the Olifants Catchment is underlain by gneisses, schists and migmatites of the Namaqua Province (Morant, 1984).

The most striking attribute of the catchment geology in terms of this study, is the fact that the tributaries draining the relatively hard rock of the Cape Supergroup contribute clear and acidic water to the Olifants River, whereas those draining the easily-erodable rock of the Karoo Supergroup contribute turbid and saline water.

3.5 Soils

Soils in the catchment are dominantly moderate to deep sandy loam, with small areas of sand and clay (van Veelen, 1998). Soils of the agricultural areas surrounding the study site are mainly red-yellow apedal soils that are freely drained, have a high base status and depths deeper then 300mm (ENPAT, 2000).

3.6 Climate and hydrology

3.6.1 Precipitation and evaporation

The mean annual precipitation of the catchment is 212mm according to volume 4 of the Surface Water Resources of South Africa (1990). Mean annual precipitation values show a strong spatial variation in the catchment, varying from up to 1500mm at the source of the Olifants in the south west of the catchment, to less than 100mm in the northern parts of the catchment. (van Veelen *et al*, 1998). The Estuary lies in a dry region of the catchment, with a mean annual precipitation of between 100-200mm. Rainfall is strongly seasonal, with most of the Olifants River catchment receiving winter rainfall. Exceptions are the northern and eastern regions that receive limited summer rainfall (Langhout, 1998). Evaporation increases from the south-west to the north of the catchment, with values of about 1600 mm/annum to about 2400mm/annum respectively. In general, evaporation ranges from 1600mm/a to just over 1800mm/a over areas where irrigation is either occurring or where potential for irrigation exists (Langhout, 1998).

3.6.2 Run-off

Mean annual run-off (mar) for the Olifants River catchment is 1 008 million cubic meters (Surface Water Resources of South Africa, 1990). The catchment has rapid run-off due mainly to the impervious TMG sandstone and quartzite in the south western region of the catchment, and the sparse vegetation in the eastern and northern parts of the catchment (Morant, 1984). Mar varies from 500mm in the south -west to less then 2.5 mm in the west (van Veelen *et al*, 1998). Run –off patterns reflect the marked seasonality in the rainfall over the catchment, with little river flow occurring in the summer time and high flows occurring in the winter months from June to September. There is also an extreme variability in the peak flow of the Olifants River which ranges from one-tenth of the average monthly run-off, to as much as two and a half times as great as the monthly average (Morant, 1984).

Flooding in the lower parts of the Olifants River estuary is common in the winter months (Pennietjies van der Westhuizen, personal correspondence), which helps to maintain the connection of the river with the sea at the estuary.

3.6.3 Dams

Two important dams, the Clanwilliam and Bulshoek Dams, are situated in the Olifants River. The Clanwilliam Dam presently has a capacity of 124 million cubic meters (DWAF, 2003), whereas the Bulshoek dam, which was built as a control barrage for the low Olifants River Irrigation scheme, had a capacity of 7.5 million cubic meters in 1984 (Morant, 1984). During the first sampling run the Clanwilliam Dam was at a capacity of 13%, reflecting the fact that the first sampling was undertaken during an unusually dry season. During the second sampling run the Clanwilliam Dam was at a capacity of 85% after the area received good rainfall. Impacts of these dams include amongst others the regulation of flow (and the smoothing off of flow peaks), and the trapping of silt.

3.7 The estuary

The Olifants River Estuary is of national importance (Basson *et al*, 1998), due mainly to its pristine state and importance to avifauna. Sustenance fishermen from nearby Papandorp are furthermore reliant on the estuary for their daily living. A natural rocky obstruction upon which the low water bridge has been built at Lutzville, approximately 32 km form the sea, marks the head of the tidal effect in the Olifants River. The Estuary is permanently open to the sea (Morant, 1984). The Olifants River Estuary River inflow shows a strong seasonal variation, with the strongest flows occurring during the winter months. During the winter months water quality is determined by the river, whereas during summer months the seawater influences become stronger as river inflow decreases substantially (Taljaard, 1997). The Olifants River Estuary is shallow and generally well mixed (Morant, 1984).

Due mainly to irrigation development in the catchment, freshwater inflows into the estuary have been reduced by 34% from a natural scenario. Future developmental scenarios will involve a reduction of between 45% and 53%.(Basson *et al*, 1998) of the mean annual runoff entering the estuary.

The centre of the estuary basin is occupied by a large island called Die Eiland, which is approximately 0.5km wide and 1km long (Morant, 1984). The main channel runs along the northern side of Die Eiland, and in the southern side a narrower and much shallower channel exists with extensive salt marshes. Residence time of water is much longer in the southern channel. The two main channels join up again after Die Eiland and have a common mouth to the sea.

3.8 Vegetation

Three main Acocks (1988) veld types, with distributions largely following the same pattern as the topography and climate of the catchment, characterize the natural vegetation of the whole of the Olifants river catchment. Fynbos covers the south western part, while the False Karoo veldtype occurs in the far north and in parts of the eastern section of the catchment. Karoo and Karroid covers the remainder of the catchment, which includes the section sampled from just above Klawer to the Olifants Estuary (Langhout, 1998). Cultivated crops in the region include deciduous fruit (e.g. Koue Bokkeveld), citrus fruit (e.g. Citrusdal valley), table grapes (e.g. Trawal) and grapes used for winemaking that are cultivated along the Olifants between Klawer and Vredendal (Lambrechts & Schloms, 1998)

3.9 Land-use

Little urban development exists in the Olifants River catchment. No significant industrial development has occurred in the region, and only small scale industries have been established to support the requirements of the local farming communities. The main land use in the catchment is agriculture. Irrigation agriculture is well developed along most of the length of the Olifants River (Langhout, 1998). For information regarding the type of crops planted see section (vegetation).

Significant soil potential exists for increasing irrigation in the study areas, and the potential that has been identified to date is more than four times that which has been developed (Langhout, 1998). Water is the limiting factor in terms of future agricultural development, and the soil potential in terms of agriculture will most probably not be fully utilized in the near future.

4. METHODOLOGY

4.1 Sample protocol

4.1.1 Sample sites

Two sampling runs were undertaken during the study. The first sampling run (water column samples only) took place during a reconnaissance site visit in June 2003. Ten sampling sites were selected in what was an especially dry period for the catchment and the Western Cape as a whole. Samples were named WP 0 –WP 10 (**W**ater sample **P**reliminary run) in a downstream direction, with sample WP 0 taken in the surf zone just south of the estuary mouth (Figure 4 Figure 5).

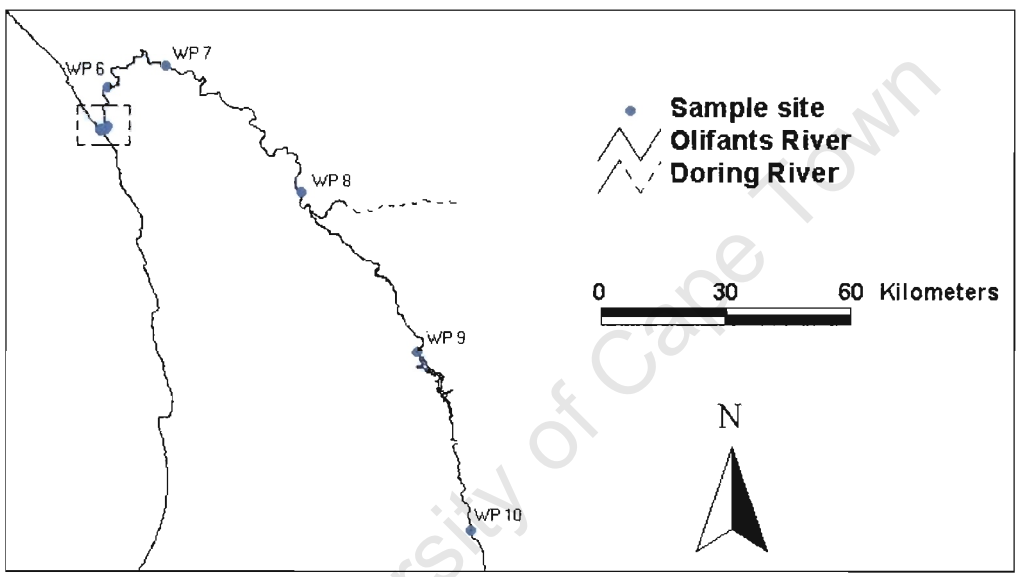

Figure 4: Sample sites of the first (June) sampling run.

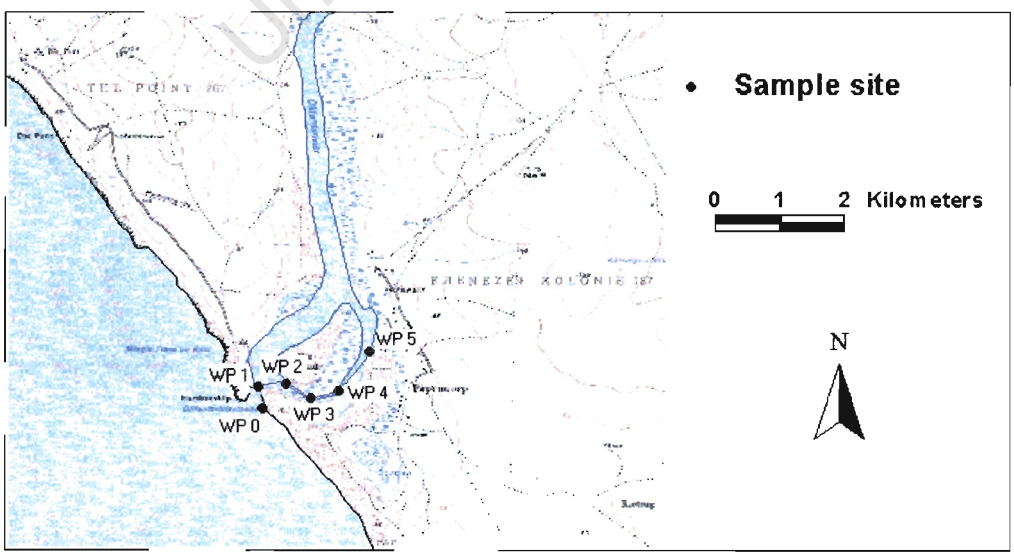

Figure 5: Sample sites of the first (June) sampling run.

The second, and in essence the main sampling run, was undertaken in September 2003 (after the rainy season). Water column as well as wet sediment samples (from which the pore water would be extracted once the samples reached the laboratory) were taken at each sampling point. Sampling sites were selected so as to be representative of the land use in the lower section of the catchment, and numbered W 10 (just upstream of the confluence with the Doring River) to W 1 (the estuary mouth). An eleventh sampling site (W 0) was taken in the surf zone on the beach at Strandfontein. Sampling locations of the second sampling run can be seen in Figure 6 and Figure 7.

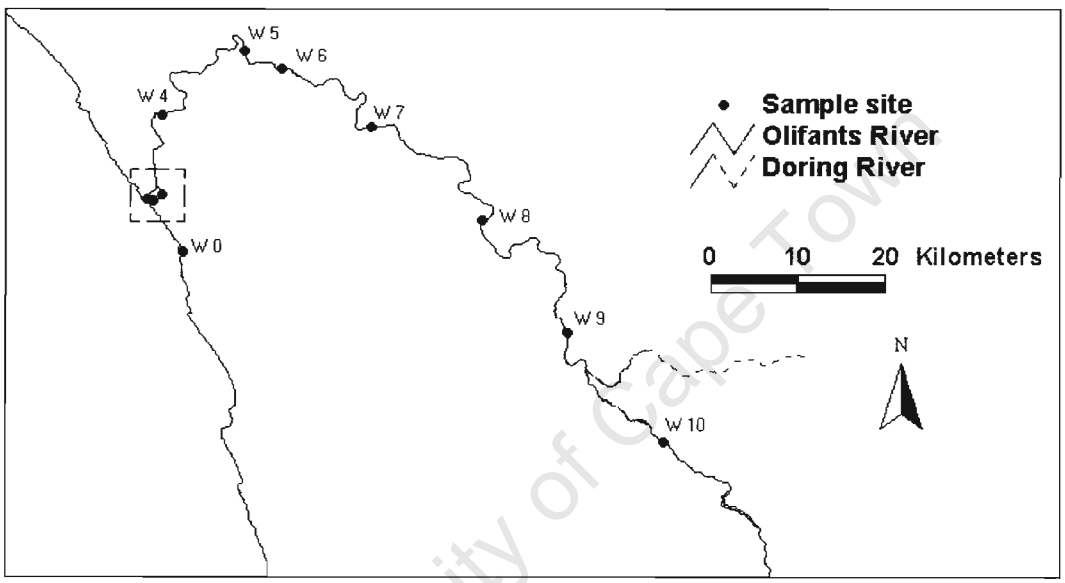

Figure 6: Sample site of the main (September) sampling run.

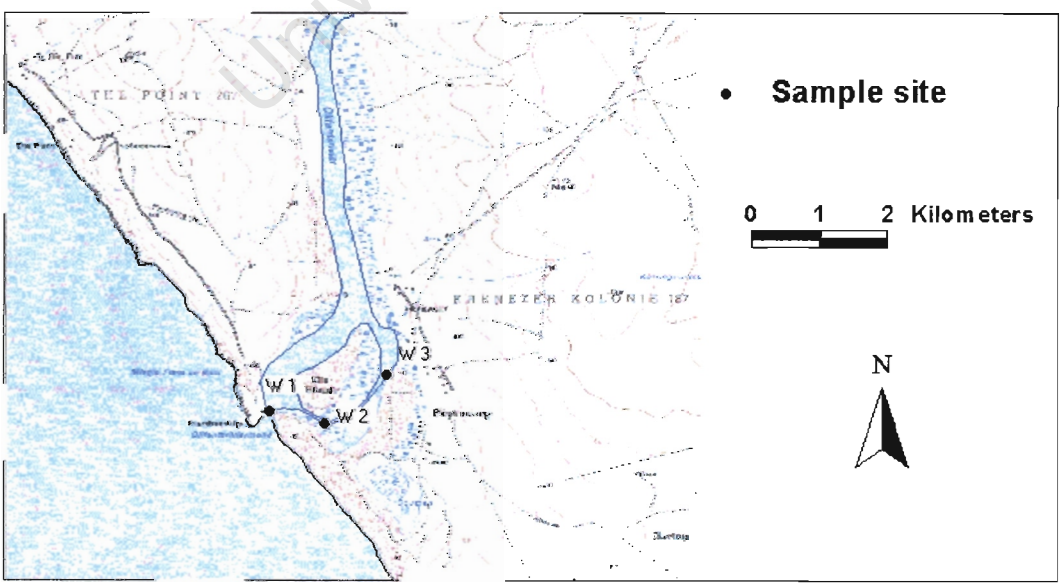

Figure 7: Sample site of the main (September) sampling run.

4.1.2 Sampling procedure

Water samples:

During the first sampling run unfiltered grab samples (one per site) were taken in 250 ml polyethelene bottles that had been rinsed with sample beforehand. Sample bottles were filled to the rim and capped tightly.

Six grab samples were taken at every sampling site during the second sample run. These comprised two 250 ml polyethelene bottles (for major ions and alkalinity titration's respectively), and four 100 ml glass bottles (for nutrient analysis). The polyethelene bottles were filled completely, and some air space was left in the glass bottles to prevent container breakage during freezing (see section 4.1.3). Acid (1:10 HCl) washed glass bottles were used for the nutrient samples as phosphates may adsorb onto the walls of plastic bottles (Eaton *et al*, 1995).

Two of the four glass bottles were used to store filtered samples. These samples were filtered immediately upon collection. 50ml syringes (rinsed three times with sample) and 0.45-μm-pore-diameter cellulose acetate filters (flushed with sample beforehand) were used for the filtering process. All unfiltered sample bottles were rinsed with unfiltered sample, and filtered samples with filtered sample immediately prior to sampling.

Throughout sampling grab samples were taken below the water surface. Once below the water/atmosphere interface, the sampling depth was unimportant as shallow lakes (> 5m) and shallow, flowing rivers fail to exhibit any sort of recognisable chemical stratification (Cowgill, 1996). Both filtered and unfiltered trip blanks (in glass bottles) were taken during the second sampling run.

Sediment and pore water samples:

Duplicate subaqueous sediment samples (S 1- S 10) were taken at each sampling site in the Olifants River (at the same locations as W 1-W 10). For this purpose a serrated PVC core was used, sampling the top 10cm of the sediment. Samples were double bagged directly after coring and subsequently placed into sealed polypropylene containers containing ice. The redox state of the containers were manipulated

depending on the perceived oxidation state of the sediments (a black colour and /or sulphurous smell was used to indicate anaerobic conditions). Where samples were adjudged to be anoxic, anaerobic pills (Merck Anaerocult® A) were added to the containers prior to the containers being sealed. Pore water was extracted from sediments (and named samples PW 1 – PW 10) by centrifuging at 4 000 rpm for 10 minutes. The resulting extraction was filtered immediately with 0.45-μm -pore-diameter nylon filters. Due to the sandy nature of the sediment no pore water could be extracted form the sample taken at W 1.

4.1.3 Sample preservation

Water and sediment samples are in a chemically dynamic state at the time of collection. At the moment the sample is removed, the chemical processes in the sample might deviate from what is occurring in situ for many reasons (Parr *et al*, 1996). Preservation techniques are especially important for nutrient concentrations, which are highly liable to change (Eaton *et al*, 1995). Due to the potential of interference with speciation determination, chemical (acid) additives were not considered as a preservation technique.

As most of the transformation reactions are biotically mediated, the preservation focussed on stunting microbial activity by temperature and light control. Nutrient water samples were placed on dry ice and frozen in the field. Major ion and alkalinity samples were placed on ice in cooler boxes (at a temperature of approximately 4°C). All the samples were kept in the dark during transport and storage. Nutrient samples were stored in a freezer and major ion samples in a fridge (4°C) once the samples reached the laboratory. Gardolinski *et al* (2001) compared different sample storage protocols for the determination of nutrients, and found that storing samples at 4^0C was efficient in maintaining original inorganic phosphorus and total oxidised nitrogen concentrations up to 8 days over a range of sample salinities. It was further demonstrated that freezing the same samples (at 20^0C) provided ideal storage conditions throughout the 247 day experiment.

The sediment sample containers (containing ice) were covered in black bags, and stored in a freezer within 48 hours of sampling.

4.2 Field analysis

During the first sampling run pH was measured with a Radiometer Meterlab PHM201, and EC and DO with a CIBRA Corning checkmate conductivity and dissolved oxygen probe. EC values above 2mS/cm (the upper limit of the Cibra probe) were measured in the lab using a WTW Multi 340i set. The pH, electrical conductivity (EC), dissolved oxygen (DO) and temperature of samples during the second sampling run was measured on site using a WTW Multi 340i set. The pH of samples WC5-WC10 was measured with a Radiometer Meterlab PHM201 after the pH probe on the WTW MULTI 340i starting showing drift problems. All field probes were calibrated on a daily basis, both before and after daily sampling (to evaluate possible probe drift). The above variables were measured immediately in a sample taken in a 500 ml glass flask during the main sampling run, and in situ for the first run. Due to the high variability found in natural systems, it was deemed judicious to include a short description of each sampling site (see Appendix A).

In order to determine the acid neutralizing capacity, i.e. the sum of all the titratable bases present in the sample, alkalinity of the water samples were determined within 12 hours of sampling. Alkalinity titration's were performed on 100ml unfiltered sample with a 0.02M HCl. Alkalinity was inferred from the titration as the molarity of acid needed to reduce the pH to 4.5 (Eaton *et al*, 1995).

4.3 Laboratory analysis

4.3.1 Water column and pore-water analysis

Major ions:

Major anions were measured using ion chromatography (IC). IC effectively distinguishes between the oxy-anions (e.g. SO_4^{2-}) and the halides (e.g. Cl^{-1}), and is the only method that provides a single instrumental technique for the rapid, sequential measurement of anions (Eaton *et al*, 1995). A Doinex ion exchange column was used for the anion analysis, and at least one duplicate per sample set was run. Prior to analysis samples were filtered through 0.45-µm-pore-diameter cellulose acetate filters and diluted to an EC value ranging from 100 to 150 µS/cm. In order to remove organic colloids that may interfere with the functioning of the exchange column, samples were filtered through 0.22-µm-pore-diameter Dionex Onguard II P filters

immediately prior to analysis. Due to the high salinities and hence the large dilutions of some of the samples (see Appendix B for dilution factors), various ions (e.g. NO_3^- and PO_4^{3-}) were diluted to below detection limits and only the most dominant anions were picked up in the IC analysis.

The cations Ca^{2+}, Mg^{2+}, K^+, and Na^+, were measured using Flame Atomic Absorption Spectrometry (FAAS). Samples were filtered through 0.45-µm-pore-diameter nylon filters prior to analysis, and run in duplicate.

Dissolved inorganic nutrients:

Dissolved (filtered through 0.45-µm-pore-diameter filters) inorganic nutrients were analysed on autoanalysers (Autoanalyzer II Technicon) using spectrophotometric methods. Analyses for the first sampling run were undertaken two months after sampling (with the samples frozen during storage), and analysis on the second sampling run was completed within two days of sampling. Standards were made up on a daily basis with analytical reagent grade chemicals and Milli-Q or artificial seawater (3.5% NaCl), depending on the salinity of the samples. Prior to analysis samples were brought to room temperature to avoid systematic volumetric errors. Blanks and standards run were run after a maximum of 20 samples to determine baseline or calibration drift.

Dissolved reactive phosphate:

Dissolved reactive phosphates (DRP) are the dissolved phosphates that respond (i.e. are reactive) to colorimetric tests without preliminary oxidative digestion or hydrolysis of the sample. Although DRP is largely a measure of orthophosphate (PO_4^{3-}), a small fraction of condensed phosphate present is usually hydrolysed in the procedure and is thus included in the DRP pool (Eaton *et al*, 1995). The ammonium molybdate ascorbic acid method used to determine DRP is based on the method proposed by Murphy & Riley (1962). The method used utilises Grasshoff's split reagent refinement (Grasshoff *et al*, 1983), solving the instability problem that is associated with Murphy & Riley's (1962) single mixed agent. The reduction of the antimony-phosphomolybdate complex (forming when ammonium molybdate and

potassium antimonyl tartrate reacts with orthophosphate) by ascorbic acid, was speeded up by heating the reaction coil to 70°C.

Ammonium-nitrogen:

The phenate method, where alkaline phenol and hypochlorite react with ammonia to form an indophenol blue colour proportional to the ammonia concentration, was used to determine total ammonia nitrogen, i.e NH_4^+-N and NH_3-N. The method is based on the method provided by (Grasshoff *et al*, 1983). The conjugate acid-base pair NH_4^+ - NH_3 has a pKa value of approximately 9.3, and ammonium is therefore the dominant species in waters with a pH of 8.2 or less, as is the case with the samples analysed. In order to improve stability, the reaction temperature has been lowered from 80°C to 65°C, and reaction combinations have been altered.

Oxidised (NO_3^-) nitrogen:

The cadmium reduction method, based on the method provided by Grasshoff *et al*, (1983), was used to determine oxidised nitrogen (NO_2^- + NO_3^-). The method involves the reduction of nitrate to nitrite by a cadmium reduction column. The resulting nitrite is incorporated into a diazo couple compound, with colour absorbance measured at 543 mm. Results are given as NO_3^--N as NO_2^- is generally found at very low concentrations in surface water (Harck, 1995, DWAF, 1996).

Total phosphorus and total nitrogen:

Total phosphorus:

Total phosphorus compounds were converted to dissolved orthophosphate by the persulfate digestion method (Eaton *et al*, 1995). Orthophosphate liberated from the organic fraction during the digestion was determined using the colrimetric method described in section 4.3.1.2. Standards and blanks used in the colrimetric method were also put through the digestion process. The digestions were performed on both filtered and unfiltered samples, and the results are given as total dissolved phosphorus (TDP) and total phosphorus (TP).

Total nitrogen:

The persulfate method (Eaton *et al*, 1995), an alkaline oxidation, was used to convert organic and inorganic nitrogen to nitrate for both filtered and unfiltered samples. The resulting nitrate was measured using the same spectrophotometric method described for nitrate analysis under section 4.3.1.2. Standards and blanks were also put through the digestion process.

Dissolved organic carbon:

A modified version of the Persulphate-Ultraviolet Oxidation method was used to determine dissolved organic carbon (DOC) levels for samples W 10, W 9, W 6, W 3 and W 2. The CO_2 produced by the persulphate oxidation in the presence of ultra violet light, was passed through a semi-permeable membrane into a solution of carbonate/bicarbonate and phenolphthalein. The resulting colour development in the solution was measured colorimetrically against potassium hydrogen phthalate standards.

4.3.2 Sediment analysis

Total nitrogen and total carbon:

Sediments were air dried at room temperature and subsequently homogenized by mortar and pestle. Total nitrogen and carbon was measured on a CHNS elemental analyser. It has been shown that acidification significantly effects concentrations of nitrogen (Ryba & Burgess, 2002), and untreated samples where thus used for the total nitrogen determination along with total carbon determination.

Organic carbon:

Since the temperature range in which organic carbon is combusted is not well separated from the range for the loss of other volatile species, mass loss upon ignition is not considered to provide reliable results for organic carbon determination (Wai Ting Tung & Tanner, 2003). Wet oxidation has been found to be unspecific, and the presence of reduced species in the sediment can further lead to an overestimation of organic carbon (Leong & Tanner, 1999). Direct acidification has been found to be the most accurate method of separating inorganic and organic carbon in sediments (Ryba & Burgess, 2002).

For each of the sediment samples, a known mass of sediments was pre treated with 5 cm^3 of 1M HCl in order to remove the inorganic carbon. Further HCl was added until it was established that effervescence had ceased upon further addition of acid. Subsequently, a total of 40 ml Milli-Q water was added to the acidified samples in two portions. The clear supernatant was removed after each step by decanting the liquid after settling. Upon this pre-treatment the extracted samples was dried, reweighed and subsequently analysed for residual organic carbon. The loss of soluble organic carbon was not taken into account in this determination.

Total phosphorus:

Two different methods were used to extract and measure the total phosphorus in the sediments: The first method extracted total phosphorus by acid (HF + HNO_3) dissolution. Amounts of air-dried sediment digested ranged between 0.2mg and 0.5mg for fine textured samples and for sand dominated samples respectively. The initial digestion step involved adding 5ml of a 4:1 concentrated HF and HNO_3 mixture to each sample, after which the samples were digested on a hot plate for 36 hours. Samples were subsequently allowed to dry. Following this step, 2.5 ml HNO_3 (min. 65%) were added to each sample, which were then dried on a hotplate. The last step was repeated once. The resulting digest was made up to a volume of 25ml with Milli-Q water, to which HNO_3 was added to insure a pH lower than 2 (in order to keep iron in solution) . Extracted phosphates were measured in the digest using the spectrophotometric method described in section 4.3.1.2. Iron precipitation was observed in the samples when the pH of the digest was raised with NaOH immediately prior to the spectrophotometric analysis (which is pH sensitive). This resulted in very low recoveries (20% on the standard), most probably due to phosphate scavenging by the precipitating iron oxyhydroxides.

A second method was used to overcome the iron precipitation problem. This technique involved progressively digesting 0.5 to 1.0 g of air dried sample with 5 ml concentrated HNO_3, 1 ml concentrated H_2O_2 and 1 ml concentrated $HCLO_4$ in a digestive microwave. The resulting digest was cooled overnight and made up 50 ml with acidified MilliQ water. The final volume was filtered and subsequently analysed on a JY Ultima Inductively Coupled Plasma Optical Emission Spectrometer. Total

phosphorus was quantified at a wavelength of 214.914 nm (with generator power at 1.2kW and plasma gas at 1.3 L/min).

Grain size analysis:

The soil samples underwent a rudimentary grain-size separation into sand size particles (2mm – 0.063mm), silt (0.063mm – 0.002mm), and a clay fraction (< 2μm).

10 or 20 grams of bulk sediment per sample (for fine textured samples and sand dominated samples respectively) were weighed out to two decimal places, and aggregates broken up. These sediment samples were sieved through a 63 μm sieve. After sieving the sediment left in the sieve was dried and weighed. The silt and clay fraction passing the 63 μm sieve were separated in terms of their settling velocity. The sample was dispersed with an ultrasonicator (Virsonic 475) and the settling time boundary between the silt and the clay fraction calculated by using Stokes law. The equation relating Stokes law with the settling time and grain size is given in Appendix B. After the settling of the silt fraction, the supernatant was decanted. The silt fraction was consequently dried and weighed. The clay fraction was determined by difference.

4.4 Data quality assessment

Bias (caused by systematic error) and precision (influenced by random error) are the principal indicators of data quality (Eaton *et al*, 1995). In order to assess the analytical precision of the methods involved duplicates of samples were analysed were the sample volume allowed. As the analytical precision of a method is not a constant and varies with concentration (Ramsey, 2000), relative standard deviations (standard deviation divided by the average concentration, also known as the coefficient of variation) are given in the tables found in the results section were duplicates were run. The duplicates ran for the carbon, nitrogen and phosphorus analysis on sediment samples were taken from different sub samples of the sediment, and thus provides an indication of both the analytical precision and the sample homogeneity. It must be noted that no measure of precision have been quantified for sampling uncertainty. In order to quantify bias internal standards were utilised for the major ion analysis (for both IC and AAS) and for the nutrient analysis in the water column and the pore water. The major elements in seawater are uniformly distributed as the residence time for the major ions are much longer then the mean residence time for water in the

oceans (Schlesinger, 1997), and the seawater major ion composition reported by Holland (1978) was used as an external standard against the samples taken in the sea (WP 0 and W 0). The method bias is reported as % recoveries (of the measured concentration of the standard compared to the "true" value) in the tables. A charge balance error (CBE) was done on the major elements (see Appendix B).

The detection limits of a particular analytical technique serve as a subsidiary data quality indicator. pH readings are taken to be accurate within 0.1 pH and weighing data values are accurate within 0.05g. IC and AAS have detection limits within sub ppm levels, and the spectrophotometric methods utilized for the nutrient determinations have detection limits within ppb levels. The detection limit for DOC is 1 mg/L. ICP-AES typically have ppm detection limits and the CHN elemental analyser used to determine the levels of nitrogen and carbon have detection limits of about 200 to 500 ppm.

5. RESULTS

5.1 Field measurements

The results of the field measurements taken during the first and the second sampling run are given in Table 1.

Table 1: Field measurements

First sampling run (June 2003)						Second sampling run (September 2003)					
Sample	D (km)	pH	T(°C)	EC (mS/cm)	DO (mg/l)	Sample	D (km)	pH	T (°C)	EC (mS/cm)	DO (mg/l)
WP 0	sea	7.9		54.5		W 0	sea	8.1	14	54.9	8.4-8.6
WP 1	0	7.8		54.5		W 1	0	7.5	16	36.1	8.26-8.46
WP 2	0.4	8.2		56.2		W 2	0.8	7.7	19	57.8	10.9-11.2
WP 3	0.7	8.0		81.5	10	W 3	2.0	8.0	21	41.5	6.47
WP 4	1.2	7.6		54.5	3.7	W 4	13.1	7.6	19	0.73	5.9-6.1
WP 5	2.0	8.0		48.5	5.3	W 5	32.8	7.0	17	0.452	7.1-7.3
WP 6	13.1	8.5	12	13.79	7.8	W 6	37.8	6.7	19	0.471	6.6
WP 7	37.8	8.3		3.27	8.7	W 7	55.1	6.7	20	0.385	6.13-6.4
WP 8	100.0	8.0	14.3	1.071	7.5	W 8	76.4	6.6	19	0.399	6.6-6.8
WP 9	154.3	6.6	12	0.163	4.8	W 9	100.0	6.7	19	0.24	7.4
WP 10	202.7	6.6	14.9	0.063	6.9	W 10	119.7	6.1	19	0.23	7.9-8.3

D = distance from river mouth (sea = sample taken in the sea)

The surface water in the higher reaches of the Olifants River during the first sampling run, and from sampling point W 10 to W 6 during the second sampling run, were slightly acidic. pH measurements indicate that the surface water in the coastal area (WP 0 and W 0) and the majority of the estuary were slightly alkaline at the time of sampling. Based on the dissolved oxygen (DO) measurements made, all the water column samples appeared to be well oxygenated.

Since the dissolution of ionic and ionizable solutes is favoured by ion-dipole bonds between ions and water (Stumn & Morgan, 1996), the majority of dissolved material in water is ionic. The electrical conductivity (EC) thus provides a convenient measure of salinity. Strong trends in EC are evident in both sampling runs, with EC increasing in a downstream direction. During both sampling runs an exception occurs to this trend, with the highest electrical conductivities being found in the southern channel of the estuary. Temporal trends in EC values can be evaluated by comparing samples of the two sampling runs that were collected at the same locations (Figure 8). The samples which locations correlate are: W 1 (WP 1), W 2 (WP 3), W 3 (WP 5), W 4 (WP 6), W 6 (WP 7) and W 9 (WP 8).

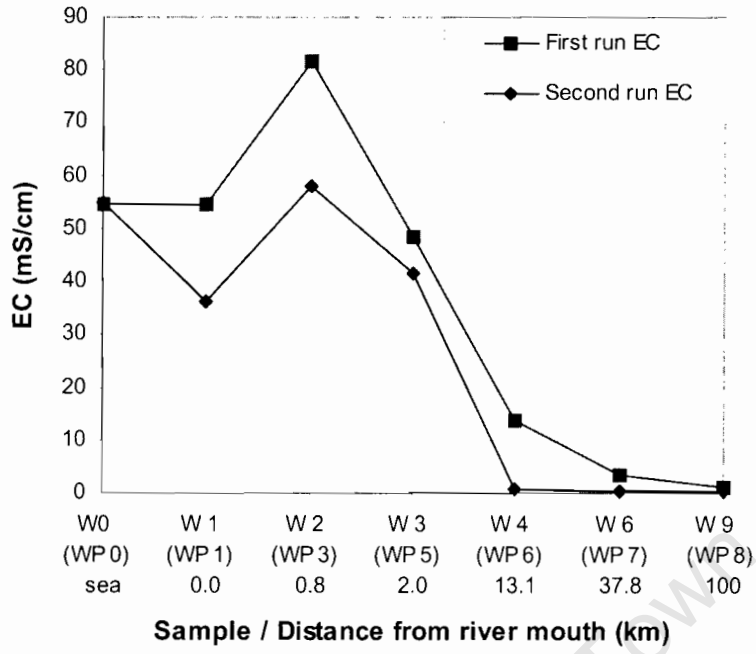

Figure 8: Comparative EC values between the two sampling runs.

The EC values (and hence salinities) of samples taken during the first run are higher than those of the second sampling run in both the estuary and the fresh water section of the river upstream of the estuary. EC values indicate a tidal effect up to the uppermost boundary of the estuary (the causeway at the low water bridge near Lutzville, approximately 37.8km from the river mouth) during the first sampling run. The influence of sea water (high ionic strength) is much smaller during the second sampling run where the estuarine effect seems to be between sample W 3 and W 4 (approximately 2 km and 13.1km from the river mouth).

5.2 Acid neutralizing capacity (ANC)

The ANC titration curves (Figure 9) indicate pH stability, which in most natural waters is provided mainly by the buffering effect of the carbonate system (Drever, 1988). The ANC of the water samples are strongly correlated with the salinity of the water, with samples W 10 – W 4 having much lower ANC's than samples W 3 – W 0.

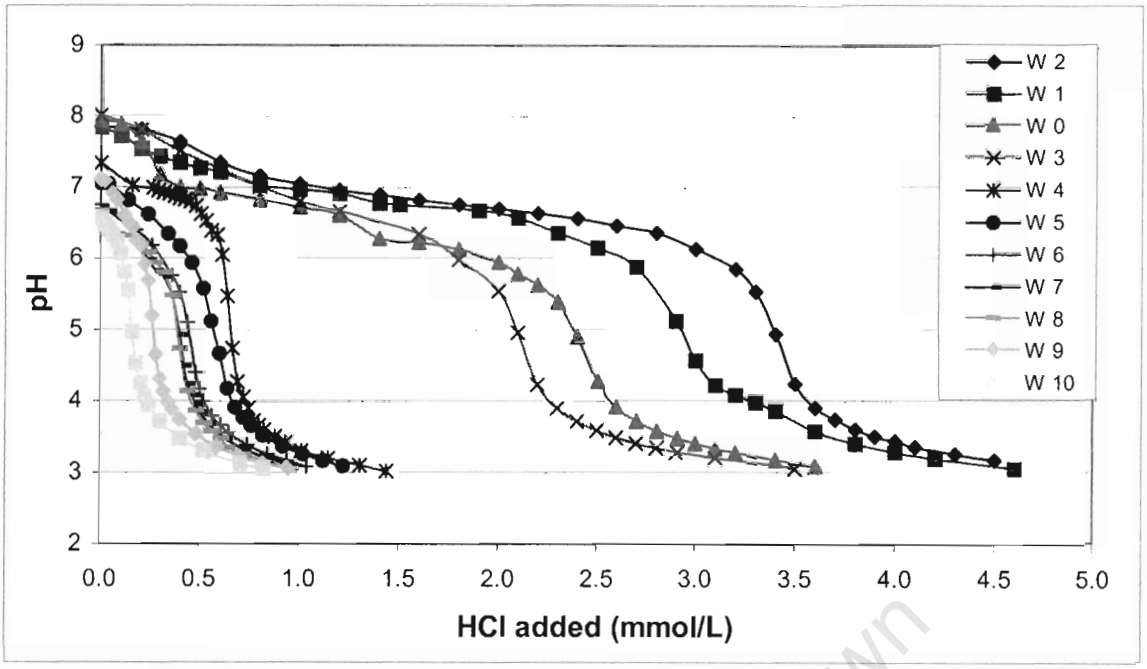

Figure 9: ANC titration curves.

The bicarbonate content of the water samples can be estimated from the ANC titrations by assuming that the ANC of the water is controlled mainly by the HCO_3^- / H_2CO_3 pair. With the bicarbonate endpoint at a pH of approximately 4.5 (Eaton *et al*, 1995) the HCO_3^- content can be inferred from the moles of acid needed to lower the pH of the sample to 4.5. The ANC of the samples, given in terms of HCO_3^- with an endpoint pH of 4.5, is given in Table 2.

Table 2: ANC of water column samples (as HCO_3^- in mmol/L)

Sample	W 0	W 1	W 2	W 3	W 4	W 5	W 6	W 7	W 8	W 9	W 10
ANC	2.56	2.56	3.46	2.16	0.68	0.60	0.45	0.42	0.42	0.29	0.18

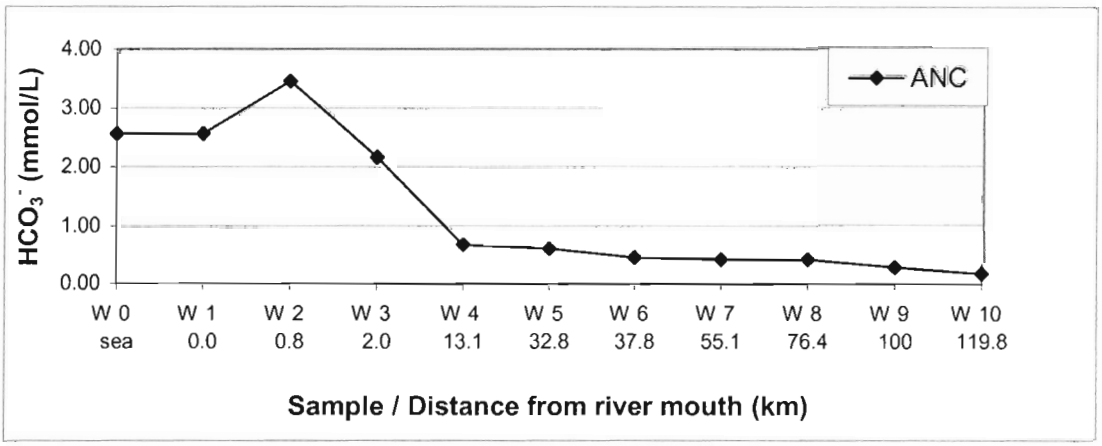

Figure 10: ANC of the water column samples.

5.3 Water column and pore water results

5.3.1 Major ions

The IC and AAS results of sampling run 1 are given in Table 3.

Table 3: Major ions in water column- sampling run 1 (mmol/L)

Sample	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}
WP 0	515	27.5	559	9.26	7.73	40.3
WP 1	541	26.4	460	2.10	9.43	39.5
WP 2	572	29.0	479	2.01	7.83	39.1
WP 3	876	41.1	731	2.97	10.3	113
WP 4	563	24.2	447	2.99	7.61	21.6
WP 5	499	23.1	400	1.91	7.06	36.4
WP 6	116	7.06	99.7			8.68
WP 7	19.7	2.98	21.6	0.24	1.49	3.04
WP 8	4.36	0.56	6.61	0.09	0.44	1.07
WP 9	0.89	0.03	0.92	0.03	0.07	2.06
WP 10	0.29	0.02	0.42	0.02	0.04	1.19
RSD[1] (%)	0.2-32*	0.1-6.7*	0.5 - 4.0	0.3 - 2.6	0.4 - 2.7	0.8 - 7.1
Recovery[2] (%)	90*	99*	95	98	97	97
Recovery[3] S.S. (%)	94	97	119	91	75	76

1 = relative standard deviation (n = 2)
2 = recovery on an internal standard
3 = recovery on a seawater standard (WP 0)
* = Reported data quality (Smith, unpublished data)

Due to the large range in concentrations of the major ions the above data can best be presented simultaneously by using a log normal plot (Figure 11).

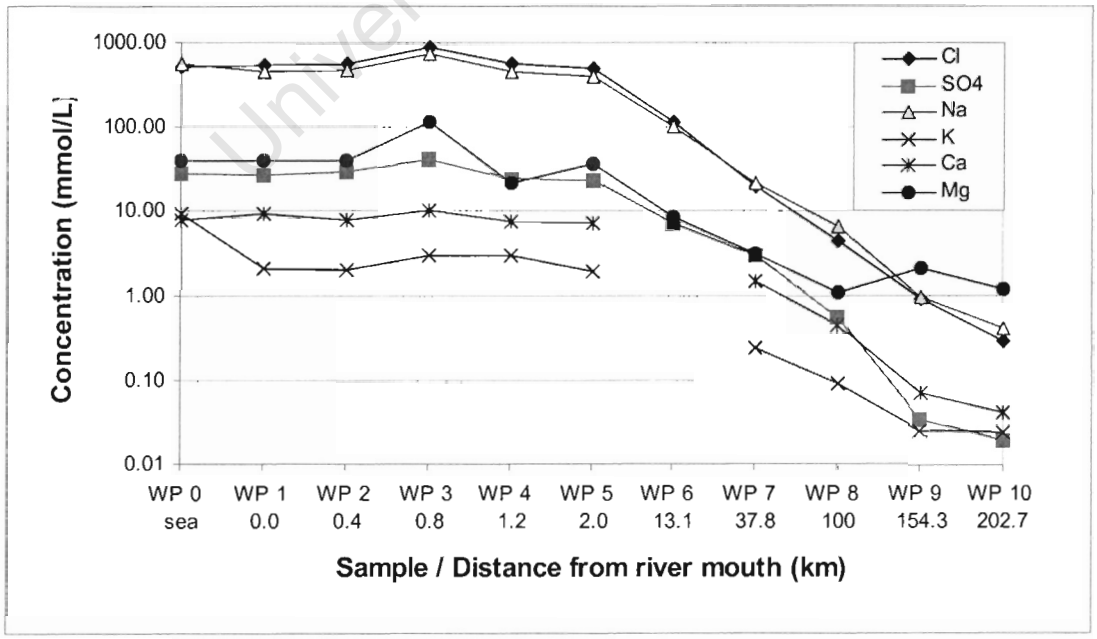

Figure 11: Major ions in the water column during sampling run 1.

Samples WP 10 and WP 9 have very low concentrations of SO_4^{2-}, and relatively high concentrations of Mg^{2+} (compared to WP 8). There is a general increase in concentrations of the major ions in a downstream direction, with concentrations being especially high in the estuary and seawater samples. Within the estuary the concentrations of Cl^-, SO_4^{2-}, Na^+, Ca^{2+} and Mg^{2+} are highest in the southern channel of the estuary (WP 4 – WP 2). The concentrations found in these samples are higher than those found in the seawater sample, pointing towards concentration upon evaporation processes being active in the southern channel. Na^+ and Cl^- are the dominant ions downstream from and including sample WP 8.

Table 4: Major ions in water column - sampling run 2 (mmol/L)

Sample	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}
W 0	517	19.7	428	9.34	7.09	56.8
W 1	197	7.54	245	5.45	4.52	33.8
W 2	524	27.4	469	9.51	7.34	59.1
W 3	366	12.3	318	6.98	3.67	42.2
W 4	3.68	0.29	4.13	0.10	0.41	0.65
W 5	1.91	0.26	2.56	0.06	0.40	0.41
W 6	1.36	0.17	2.43	0.05	0.37	0.38
W 7	0.96	0.10	2.13	0.05	0.24	0.35
W 8	1.11	0.15	2.26	0.05	0.24	0.35
W 9	0.29	0.07	1.82	0.03	0.15	0.24
W 10	1.72	0.14	2.47	0.03	0.09	0.23
T.B.	0.52	0.03	1.66	>0.01	0.01	>0.01
RSD[1] (%)	0.2-32*	0.1-6.7*	0.6 - 4.3	0.2 - 2.7	0.3 - 2.9	0.5 - 7.4
Recovery[2] (%)	90*	99*	96	99	99.8	97
Recovery[3] S.S (%)	95	70	92	91	69	107

[1] = relative standard deviation (n = 2)
[2] = recovery on an internal standard
[3] = recovery on a seawater standard (WP 0)
* = Reported data quality (Smith, unpublished data)

A similar pattern to that found during the first sampling run is evident in the second sampling run (Table 4; Figure 12), with concentrations of the major ions increasing in a downstream direction, and the highest concentrations of major ions (with the exception of K^+) being found in the southern channel of the estuary (W 3 and W 2). All the samples are sodium chloride dominated.

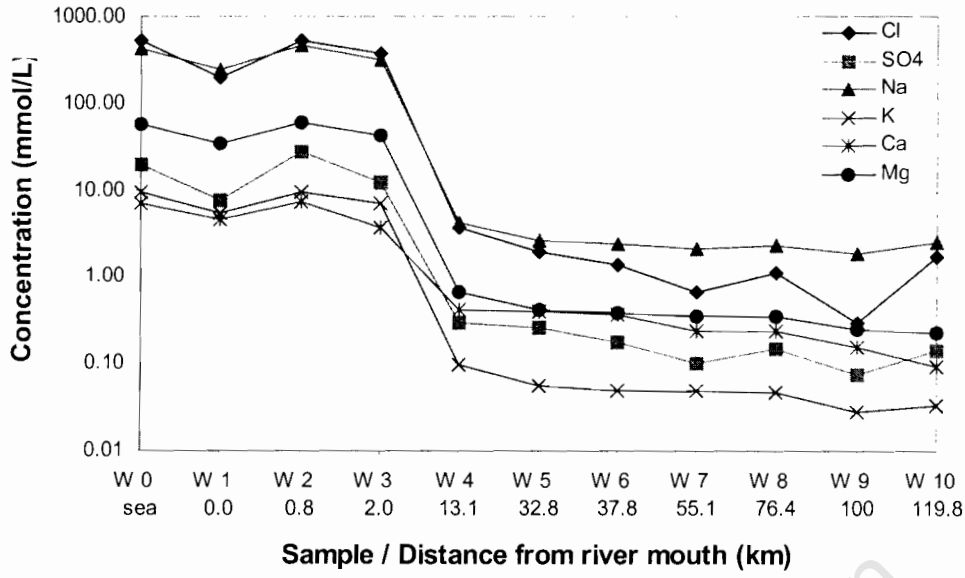

Figure 12: Major ions in the water column during sampling run 2.

The increase in major ion concentrations are much more gradual between samples W 10 – W 4 compared to the upstream portion of the first sample run. Major ion concentrations are furthermore much lower in comparative sampling locations in the freshwater section of the Olifants (upstream of the estuary) in samples taken during the second sampling run. A significant increase in major ion concentrations occurs between sample W 4 and W 3, where river water of low ionic strength mixes with seawater of high ionic strength.

The pore water samples, as is the case with the water column samples, are sodium chloride dominated (Table 5; Figure 13). Major ion concentrations increase in a downstream direction (with the notable exception of SO_4^{2-}), with concentrations being especially high in pore water samples PW 3 and PW 2. SO_4^{2-} concentrations are lowest in sample PW 6 – PW 4. Pore water to water column ratios of the major ions are generally larger than 1 for samples PW 10 to PW 4, and close to 1 for samples PW 2 and PW 3. SO_4^{2-} is the ion that exhibits PW:W < 1 most often (PW 2, 3 and 5).

Table 5: Major ions in pore water - sampling run 2 (mmol/L)						
Sample	**Cl^-**	**SO_4^{2-}**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**
PW 1	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
PW 2	469	15.4	484	11.5	6.69	51.2
PW 3	320	10.5	328	7.42	5.16	38.4
PW 4	9.57	0.43	20.4	0.45	1.14	2.23
PW 5	8.80	0.18	19.1	0.19	1.09	2.17
PW 6	5.16	0.18	12.6	0.19	1.21	2.32
PW 7	1.03	0.68	6.87	0.17	1.14	2.48
PW 8	3.56	0.64	7.57	0.10	0.87	1.13
PW 9	4.00	0.32	6.92	0.06	0.41	0.83
PW 10	1.38	0.18	4.13		0.17	0.29
RSD[1] (%)	0.2-32*	0.1-6.7*	0.5 - 3.8	0.2 - 3.6	0.2 - 2.2	0.2 - 3.4
Recovery[2] (%)	90*	99*	97.7	100.3	100.5 - 104.6	98.5

n.m. = not measured (no pore water available)
[1] = relative standard deviation (n = 2)
[2] = recovery on an internal standard
* = Reported data quality (Smith, unpublished data)

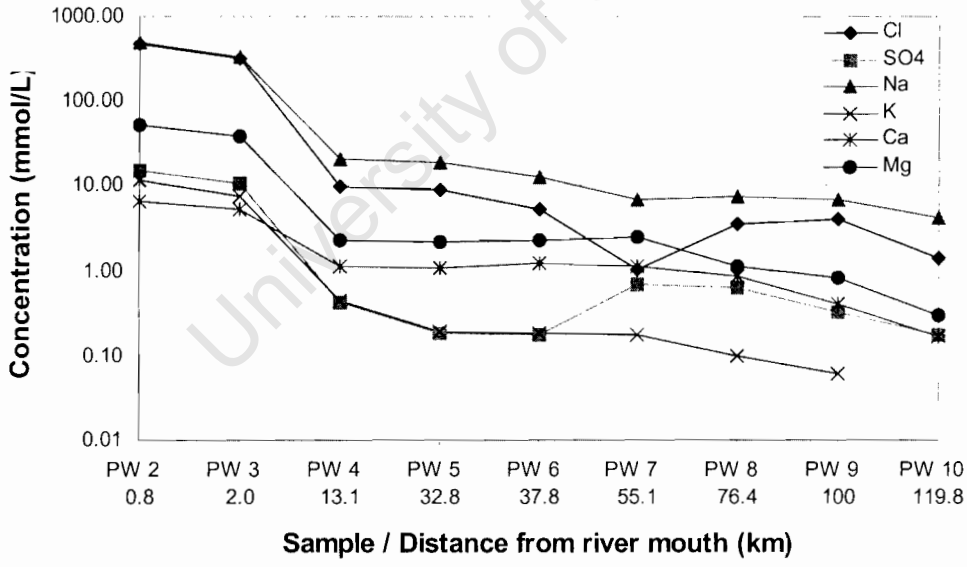

Figure 13: Major ions in the pore water during sampling run 2.

5.3.2 Inorganic and total nutrients

First sampling run:

Dissolved reactive phosphorus (DRP) and total phosphorus (TP) concentrations increase in a downstream direction, with both reaching a maximum at WP 3 (Table 6; Figure 14). From WP 10 up to WP 4 a large fraction of the phosphorus in the river is in the organic or acid hydrolysable form, and from WP 4 downstream the largest fraction of phosphorus is in the inorganic form. Concentrations of DRP and TP are higher at the estuary mouth (WP 1) than at both the freshwater inlet of the estuary (WP 7) and the seawater sample (WP 0). This indicates that the estuary acted as a source of phosphorus during the first sampling run. The level of DRP in sample WP 0 (3.4 µmol/L) falls in the upper range of concentrations reported in the literature (1 to 3.5 µmol/L) and well above the reported average of 1.5 ± 0.05 µmol/L for upwelled water on the west coast of South Africa (DWAF, 1996b).

Table 6: Nutrients in water column - sampling run 1 (µmol/L)

Sample	DRP	TP	NH_4^+-N	NO_3^--N	TIN	TN
WP 0	3.4	3.4	9.7	43	53	106
WP 1	4.0	4.2	11.5	37	49	94
WP 2	3.1	4.2	18.3	6.9	25	35
WP 3	4.9	5.8	5.7	1.5	7.2	186
WP 4	2.9	3.4	7.2	15	22	35
WP 5	1.3	4.7	7.2	3.6	11	32
WP 6	1.1	2.0	2.4	13	15	40
WP 7	1.1	2.6	6.3	41	47	107
WP 8	0.3	0.2	2.0	4.4	6.5	25
WP 9	0.1	0.7	6.4	17	24	58
WP 10	0.1	0.4	3.0	4.9	7.8	17
RSD (%)	0.6	0.7	1.4	1.2	n.a.	0.9
Recovery (%)	98	99	111	107	n.a.	98

DRP = Dissolved reactive phosphorus
TP = Total phosphorus
TIN = Total inorganic nitrogen
TN = Total nitrogen
n.a. = not applicable

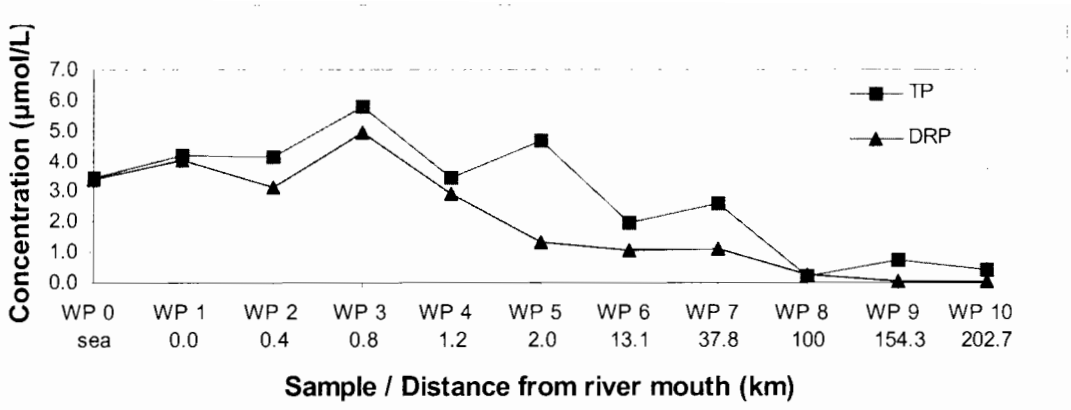

Figure 14: DRP and TP in the water column – sampling run 1.

The dominant form of inorganic nitrogen entering the estuary via the river during the first sampling run is NO_3^-, with a maximum concentration of 41 mmol/L (NO_3^--N), in sample WP 7 (Figure 15). In the estuary, NO_3^- concentrations drop significantly whilst NH_4^+ concentrations increase, reaching a maximum at WP 2. The results indicate that the estuary acts as a sink for NO_3^- and as a source of NH_4^+ to the sea. The NO_3^--N level in sample WP 0 (43 µmol/L) falls in the higher range of reported concentrations (0.1 to 45 µmol/L) for seawater, and above the reported average of 20 ± 4 µmol/L for west coast upwelled waters (DWAF, 1996b). The NH_4^+-N concentration found at WP 0 (9.7 µmol/L) is higher than the levels (5 µmol/L) normally found in well-oxygenated seawater (DWAF, 1996b).

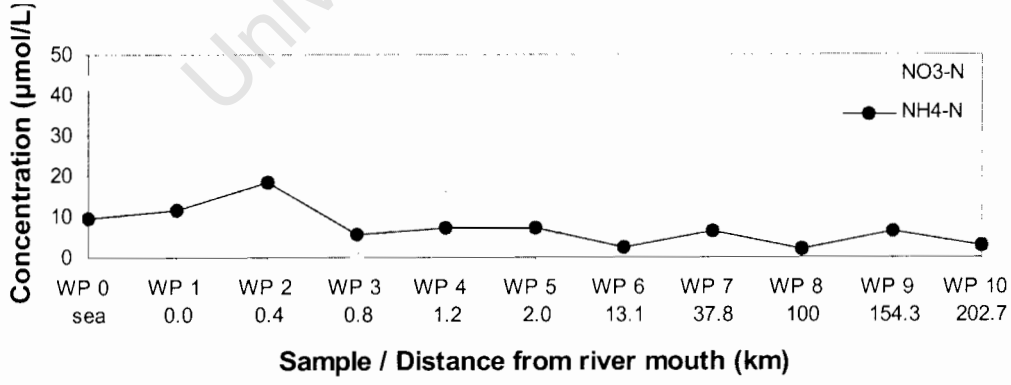

Figure 15: NH_4^+-N and NO_3^--N in the water column – sampling run 1.

Total inorganic nitrogen and total nitrogen levels generally show the same spatial trend (Figure 16). An exception is sample WP 3, where almost all the nitrogen is present in an organic form. The results indicate that the estuary acted as a total nitrogen sink during the first sampling run.

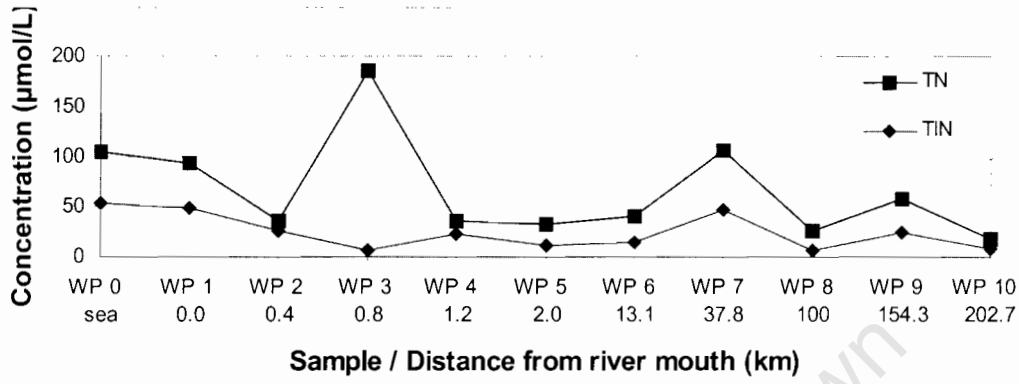

Figure 16: TIN and TN in the water column – sampling run 1.

Second sampling run:

A similar trend to the first sampling run is observed, with DRP and TP increasing in a downstream direction, reaching a maximum in the southern channel of the estuary (Table 7, Figure 17). Particulate organic phosphate levels peak in sample W 3. Overall the estuary seems to be a source of phosphorus to the ocean. The DRP concentration found in the seawater sample (1.25 µmol/L) is slightly lower than the reported average (1.52 ± 0.05 µmol/L) for upwelled water on the west coast (DWAF, 1996b).

Table 7: Nutrients in water column - sampling run 2 (µmol/L)								
Sample	**DRP**	**TDP**	**TP**	**NH_4^+-N**	**NO_3^--N**	**TIN**	**TDN**	**TN**
W 0	1.25	1.62	1.92	2.22	6.67	8.89	56.7	28.0
W 1	1.50	1.96	2.24	1.65	6.85	8.50	36.2	41.4
W 2	1.26	2.29	2.67	2.37	0.28	2.64	35.9	58.5
W 3	1.63	2.23	5.45	0.69	2.79	3.48	45.7	33.2
W 4	1.47	1.93	2.70	5.83	9.59	15.42	62.7	38.9
W 5	0.98	1.32	2.60	5.29	6.30	11.59	50.4	36.5
W 6	0.78	1.18	2.11	3.81	4.01	7.82	47.4	44.4
W 7	0.67	0.99	1.72	2.82	3.14	5.95	44.4	32.9
W 8	0.47	0.82	1.46	4.85	2.39	7.24	25.3	33.2
W 9	0.08	0.35	0.73	1.09	0.07	1.16	28.0	21.8
W 10	0.01	0.21	0.49	2.30	1.67	3.97	62.2	35.1
TB/LB*	0.01	0.07*	0.07*	1.92	0.60	2.51	4.6*	4.5*
RSD (%)	0.7	0.5	0.6	0.7	0.3	n.a.	0.8	0.9
Recovery (%)	103	99	99.0	101	105	n.a.	121	118

DRP = Dissolved reactive phosphorus
TP = Total phosphorus
TDP = Total dissolved phosphorus
TIN = Total inorganic nitrogen
TDN = Total dissolved nitrogen
TN = Total nitrogen
TB = Trip blank
LB = Lab blank
n.a. = not applicable

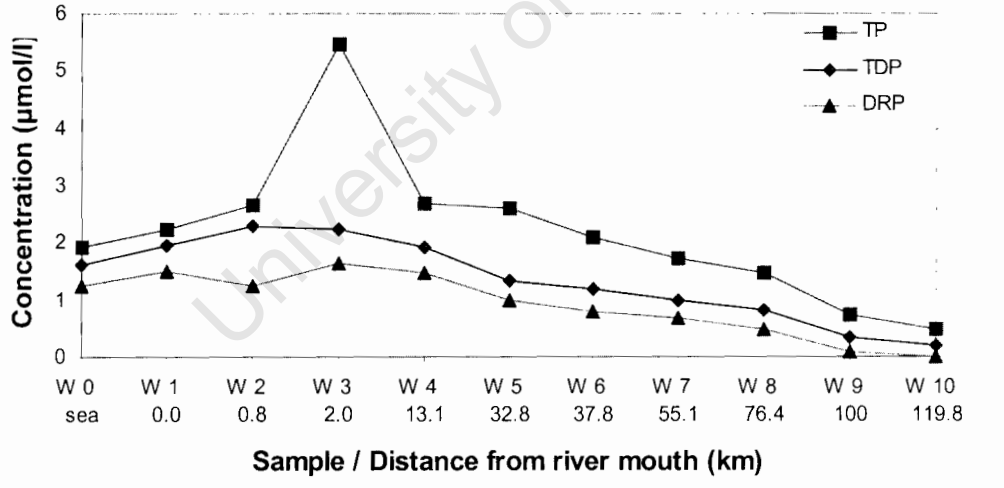

Figure 17: DRP and TP in the water column – sampling run 2.

NH_4^+ is the dominant form of inorganic nitrogen in the upper section of the study area (W 10 – W 8) during the second sampling run (Figure 18). At the freshwater inlet of the estuary (W 6) levels of NH_4^+-N and NO_3^--N are almost identical at 3.81 and 4.02 µmol/L, respectively. In the upper region of the estuary (W 5 to W 4) the concentrations of both increase, NO_3^- more so than NH_4^+. The levels of NO_3^- and

NH_4^+ decrease significantly in the southern channel of the estuary. The NH_4^+ concentration in W 0 is slightly lower than the seawater sample taken during the first run. The NO_3^- level in W 0 is significantly lower than that found during the first run, and the concentration of 6.67 µmol/L is well below the reported average of 20 ± 4 µmol/L for west coast upwelled waters (DWAF, 1996b).

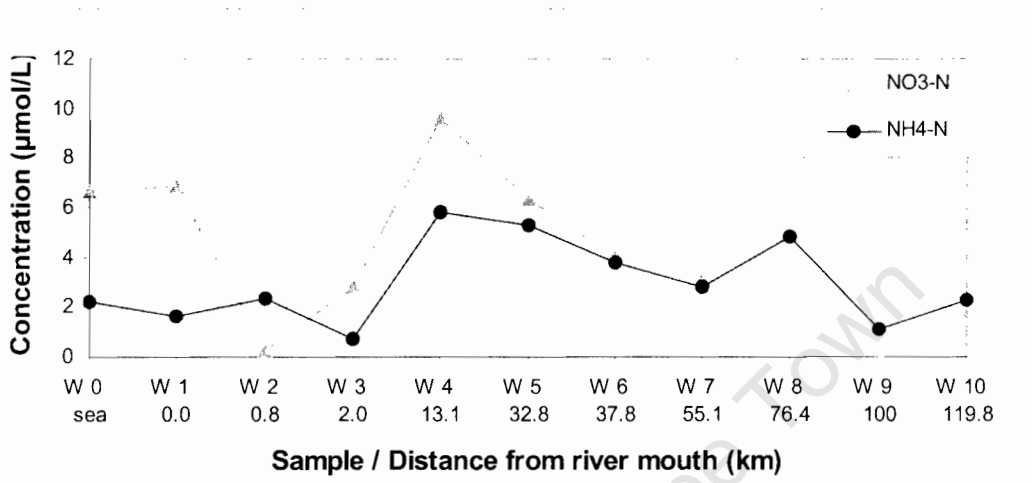

Figure 18: NO_3^--N and NH_4^+-N in the water column – sampling run 2.

The high nitrogen levels found in the lab blanks (Table 7), and the higher nitrogen concentrations found in filtered (TDN) compared to unfiltered samples (TN - Figure 19) indicate that significant nitrogen contamination took place during the total nitrogen digestions. Since all the water samples and pore water samples underwent the same digestion procedure, all total nitrogen results should be treated with the outmost caution. At most the total nitrogen results indicate that a substantial amount of nitrogen in the water is present in the organic form (since the observed difference between TDN/TN and TIN is significantly greater than the concentrations found in the lab blanks).

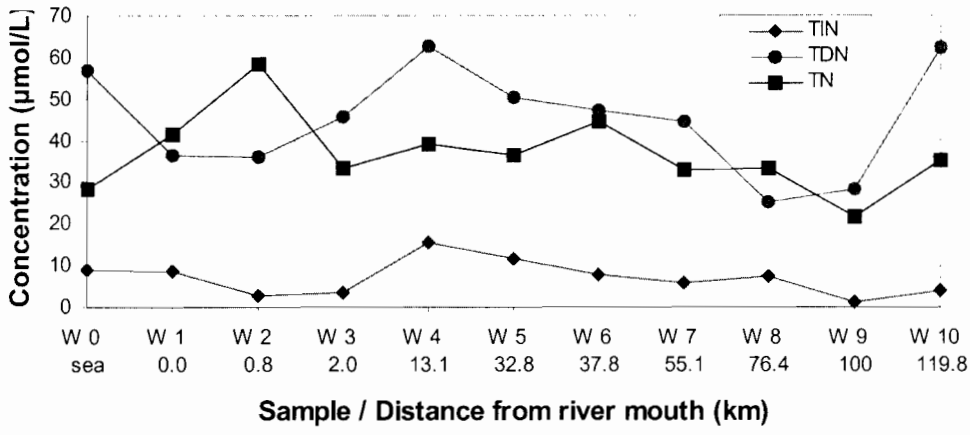

Figure 19: TIN and TN in the water column – sampling run 2.

Pore water:

Figure 20 indicates that both DRP and TP concentrations peak at sample W 7 and W 4. No clear trend in phosphate concentrations is evident. During the analysis it was observed that iron precipitation occurred in the sediments during storage and pore water extraction from the sediments. Dissolved phosphate was therefore most probably lost in the pore water through scavenging by iron oxyhydroxides. Results for the total phosphorus determinations on the sediment samples are expected to shine some light on the matter.

Table 8: Nutrients in pore water (µmol/L)						
Sample site	**DRP**	**TDP**	**NH_4^+-N**	**NO_3^--N**	**TIN**	**TDN**
PW 1	n.m.	n.m.	n.m.	n.m	n.m	n.m
PW 2	4.4	4.0	434	0.66	434	1068
PW 3	1.5	1.8	207	0.49	208	553
PW 4	5.8	6.2	59	0.65	59	133
PW 5	1.1	1.6	137	0.87	138	206
PW 6	1.1	2.5	73	0.76	74	262
PW 7	39	15.0	231	0.81	232	579
PW 8	1.6	2.8	31	27	58	123
PW 9	0.77	2.3	40	0.98	41	105
PW 10	1.8	2.8	38	0.32	38	207
LB	0.07	0.1	0.88	0.00		
RSD (%)	0.5	0.6	0.5	1.5	0.9	0.8
Recovery (%)	101	99	105	106	101	101

n.m. = not measured (no pore water available)
DRP = Dissolved reactive phosphorus
TDP = Total dissolved phosphorus
TIN = Total inorganic nitrogen
TDN = Total dissolved nitrogen
TB = Trip blank
LB = Lab blank

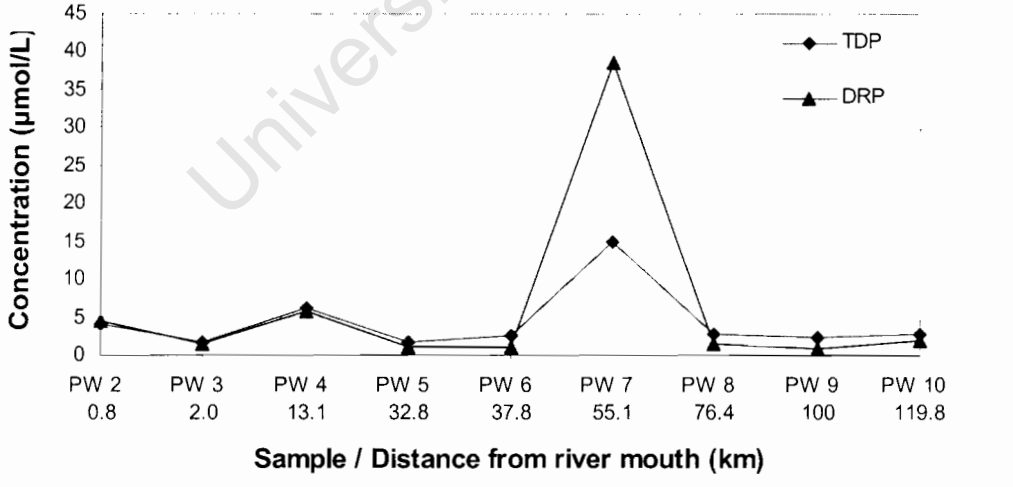

Figure 20: DRP and TP in the pore water – sampling run 2.

NH_4^+ is the dominant form of inorganic nitrogen in the pore water samples (Table 8). With the exception of sample PW 8, NH_4^+ is present at levels an order of magnitude higher than NO_3^-. As with the phosphorus concentrations, there is a peak of both inorganic and total nitrogen at PW 7. High concentrations of NH_4^+ are furthermore found in samples PW 2 and 3. A significant amount of dissolved nitrogen is present in the organic form in the pore water (Figure 21).

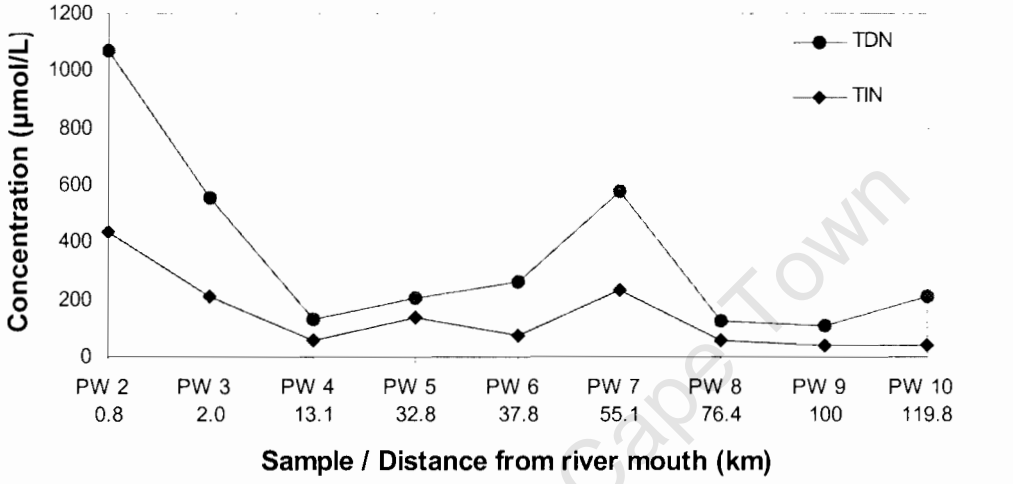

Figure 21: TIN and TN in the pore water – sampling run 2.

Nutrient concentrations (especially NH_4^+) are generally higher in the pore water than water column samples, (Table 9). Higher PW:W ratios occur for nutrients in the inorganic form (P and N) than for organically-bound nutrients.

Table 9: Pore water: water column nutrient ratios

Sample	DRP	TDP	NH_4^+	NO_3^-	TIN	TDN
W 2 / PW 2	3.5	1.7	183	2.4	164	30
W 3 / PW 3	0.9	0.8	300	0.17	60	12
W 4 / PW 4	3.9	3.2	10	0.07	3.8	2.1
W 5 / PW 5	1.1	1.2	26	0.14	12	4.1
W 6 / PW 6	1.4	2.1	19	0.19	9.4	5.5
W 7/ PW 7	58	15	82	0.26	39	13
W 8 / W 8	3.4	3.4	6.4	12	8.1	4.9
W 9 / W9	9.3	6.6	37	13	36	3.7
W 10 / W10	219	13	16	0.2	10	3.3

5.3.3 Dissolved organic carbon (DOC)

Significant levels of DOC were present in the samples taken in the section of the river with relatively low salinities. The low DOC concentrations found in the southern arm of the estuary (Table 10), might be due to analytical error, since chloride concentrations of 0.1% (W 2 and W 3 both have chloride concentrations of about 1 %) may inhibit the oxidation of organic matter (Eaton *et al*, 1995).

Table 10: Dissolved organic carbon (mmol/L)

Sample	W 2	W 3	W 6	W 9	W 10
DOC	0.09	>0.08	0.38	0.29	0.31

5.4 Sediments

5.4.1 Nitrogen, carbon and phosphorus content

The results of the nitrogen and carbon content determinations in the sediment samples are presented in Table 11.

Table 11: Sediment carbon, nitrogen and phosphorus content (mmol/kg)

Sample	TC	OC	TN	A-TN	TP	OC:TN
S 1	1166	38	6	4	7	6
S 2	1088	501	76	69	9	7
S 3	719	618	96	93	14	6
S 4[1]	**758**	**470**	**79**	**69**	**13**	6
S 5	554	461	71	69	12	6
S 6	275	167	33	31	10	5
S 7	777	425	40	24	3	11
S 8	291	264	32	26	5	8
S 9	92	221	12	14	3	18
S 10	9908	5231	505	256	5	10
RSD[2] (%)	**10**	**7**	**6**	**7**	**5**	

TC = Total carbon
OC = Organic carbon
TN = Total nitrogen in an untreated sample
A-TN = Total nitrogen in an acid treated sample
TP = Total phosphorus
[1] = average of S 4 (n = 2)
[2] = RSD of sample S 4 results (n=2)

As expected, sediment sample S 10 has by far the highest levels of carbon and nitrogen (the sediment sample taken in the riparian wetland consisted almost entirely of organic matter). In order to have a high resolution for the data being graphically illustrated for samples S 9 to S 1, the results from sample S 10 are not presented in Figure 23 and Figure 24.

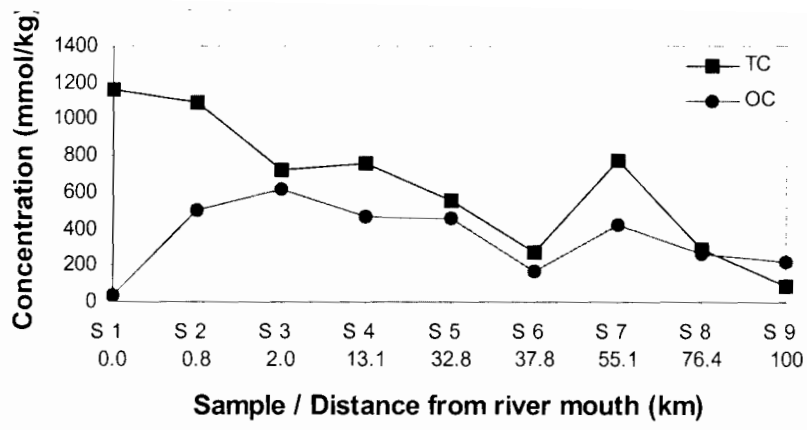

Figure 23: TC and OC in the sediments.

Both TC and OC levels show a peak at S 7 (Figure 23). From S 6 onwards TC increases in a downstream direction with the highest values being found at S 2 and S 1. The increasing levels of TC in the estuary correlates with the magnitude of effervesance observed during the removal of inorganic carbon with direct acidification. The highest levels of OC are found at sample S 5 – S 2, and the lowest levels at S 1.

The distribution of TN correlates strongly with that of OC ($R^2 = 0.98$), and is highest in the estuary (with the exception of the sample taken in the estuary mouth). The acid treated samples have lower TN levels than the untreated samples for nine out of the ten samples (Figure 24), pointing to a loss of nitrogen during the direct acidification process.

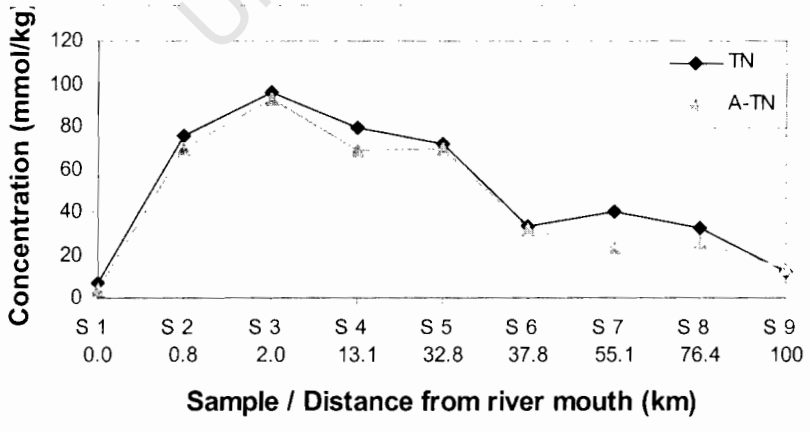

Figure 24: TN in untreated and TN in acidified samples.

Figure 25 illustrates that there is no correlation between TC and TN in the estuary (R^2 = 0.0141), whilst there is a strong correlation between OC and TN (R^2 = 0.97). The nitrogen in the sediments are thus associated with organic carbon, and hence with organic matter in the sediments.

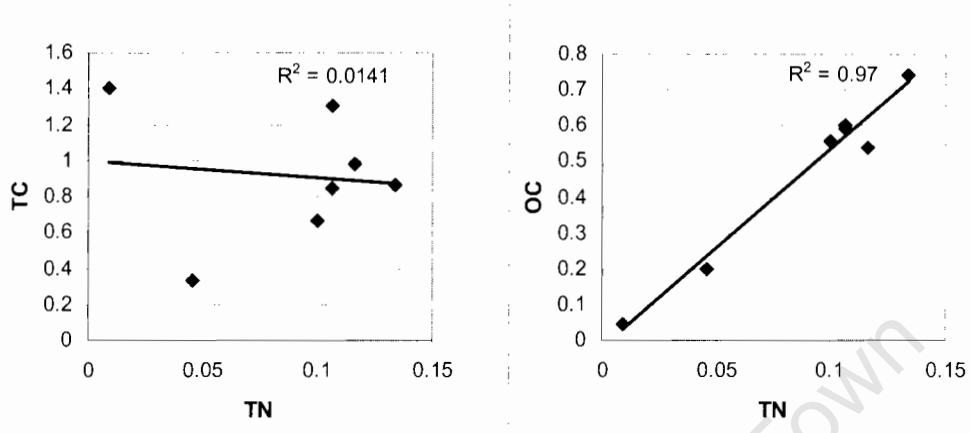

Figure 25: Correlations between TC, OC and TN in the estuary sediments.

The highest total phosphorus concentrations are found in the estuary sediment samples (Figure 26). TP levels show some correlation with organic carbon (R^2 = 0.64). The occurrence of phosphorus in the sediments shows a strong correlation with grain size. TP and the silt particle size have the strongest correlation with a R^2 of 0.82, whilst the sand sized fraction and TP has a negative correlation of 0.79.

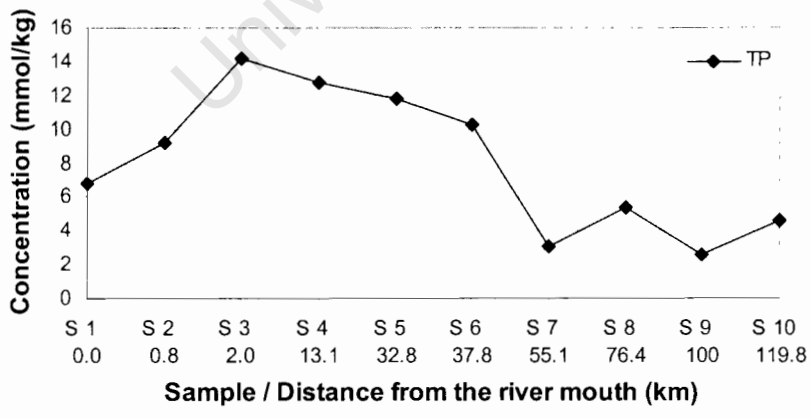

Figure 26: TP in the sediments.

5.4.2 Grain size analysis

The upstream samples consist predominantly of course grains, reflecting the parent material lithology of the catchment which is predominantly quart arenite. The finest grained sediments are found in the estuary (Samples S 6 – S 2). Sample S1 consists almost entirely of sand sized particles, indicating the marine (beach) origin of the sediment sample.

Table 12: Particle size distribution (weight %)

Sample	Sand (<63 µm)	Silt (2-63 µm)	Clay (<2 µm)
S 1	99	0.1	0.9
S 2	73	24	3
S 3	22	66	12
S 4	17	68	15
S 5	54	39	7
S 6	65	33	2
S 7	93	6	1
S 8	76	19	5
S 9	97.2	2.4	0.4
S 10	87	11	2

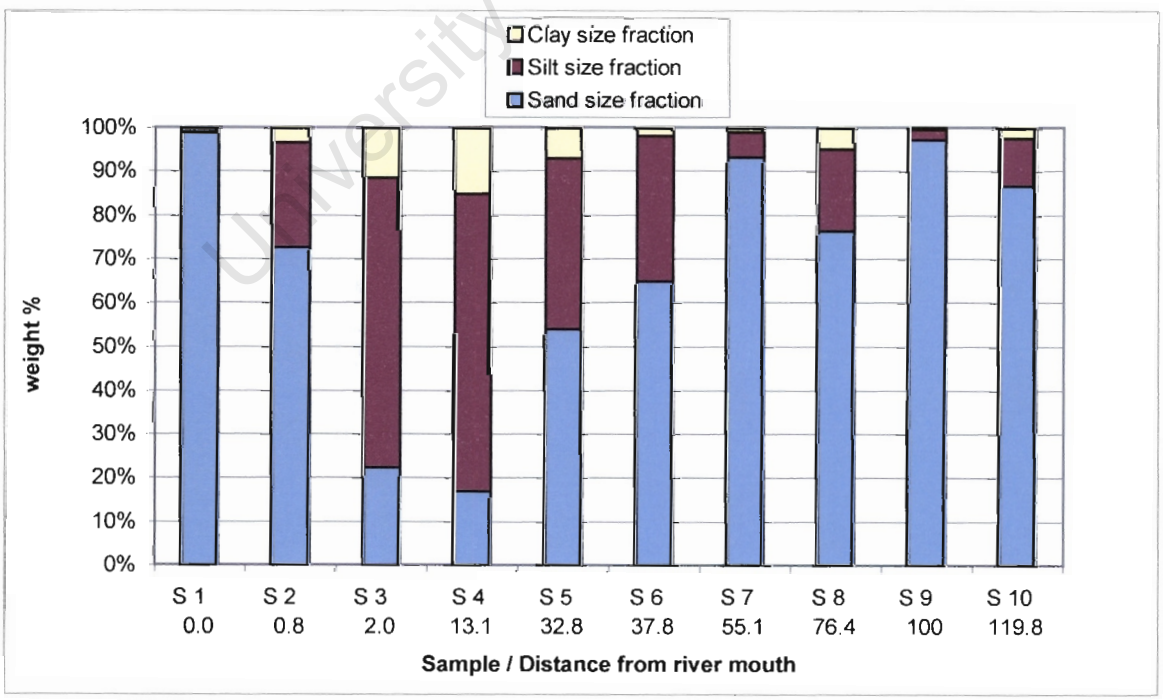

Figure 24: Sediment grain size distribution.

6. DISCUSSION

6.1 Salinity and major ion composition

All the water samples are sodium chloride dominated. This indicates that the major ion composition of the lower Olifants above the estuary is controlled mainly by atmospheric input of ions originating from the sea (Chester, 1990). In the estuary the major ion composition reflects mixing of river and sea water. The strong variability in salinity follows the trends reported by van Veelen et al (1998), where the surface waters of the lower Olifants River are more saline during the low flow conditions of the first sampling in June (late summer) than in the high flow conditions of the second sampling run in September (winter) (Figure 24). A similar relationship between concentrations for the two sampling runs exists for the other major ions (Tables 4 and 5).

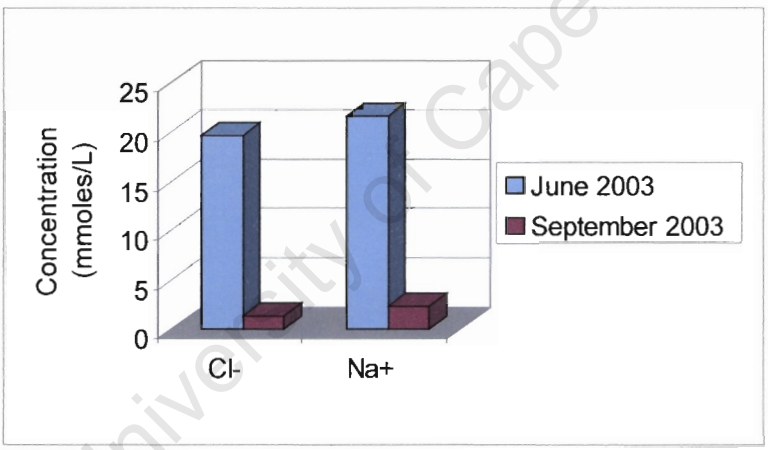

Figure 24: Na^+ and Cl^- concentrations between the late summer and winter just upstream of the estuary at sampling site W 6/WP 7.

Factors that most probably contributed to the higher salinities in the section of the Olifants River above the estuary during the first sampling run include evaporation far exceeding precipitation, with the Clanwilliam dam at 13 % capacity at the time of sampling, as well as the salinization effect of agricultural return flows which contributes significantly to the river flow during low flow periods. The lower salinities found during the second sampling run is due to the dilution effect of the high flow conditions caused by the winter rains. The salinity of the Olifants River is

strongly controlled by hydrological conditions, and shows a significant variation and rapid response to changing flow conditions.

In the estuary the salinity and ionic composition varied according to the strength of the freshwater inflow and the state of the tide. During the low river flow conditions of the first sampling run the tidal effect reached up to the low water bridge at Lutzville, whereas the tidal effect is between W 4 and W3 during the high river flow conditions of the second sampling run.

A process that occurs during the mixing of waters with different ionic strengths, and which has potential implications for nutrient dynamics, is flocculation. Suspensions that are stable in fresh water due to interparticle repulsive forces existing between electrically charged particles, can be destabilised in saline water by double layer compression and neutralization of charged particles by sea water ions (Duinker, 1980). This destabilisation process can then lead to the flocculation and settling out of fine grained particulate matter and humic substances transported in rivers during the early stage of estuarine mixing.

During both runs the highest major ion concentrations were found in the southern channel of the estuary. This observation most probably points to concentration upon evaporation (with major ion concentrations higher than those found in the seawater samples), and hence to a longer residence times of the waters in this section of the estuary. The fact that the pore water to water column ratios of the major ions are close to 1 for samples taken in the southern channel of the estuary, suggest that the pore water and water column have equilibrated in this section of the estuary. The low sulphate concentrations in the pore water samples in the estuary compared to that in the correlating water column samples most probably point to sulphate reduction taking place in the pore water. Estuarine sediments and salt marshes generally have high rates of sulphate reduction caused by anaerobic conditions, plentiful organic matter and high concentrations of sulphate in the overlying water (Schlesinger, 1997). Because oxidation of the pore water most probably occurred during extraction and analysis of the pore water samples, post sampling oxidation of sulphide probably contributed to the levels of sulphate measured in the samples. Loss of sulphide as H_2S (a sulphurous smell was observed during sampling) and/or the formation of sulphide

minerals (e.g. FeS) could explain the fact that the pore water sulphate levels were still lower, even after oxidation, than those found in the water column.

A fundamental principle in aqueous chemistry is that solutions are electrically neutral (Drever, 1997). A charge balance of the ions analysed in the samples should thus give a good indication of the quality and completeness of the data. Charge balance errors (CBE) of the water samples are given in Appendix B. Of these only the CBEs of the samples in the lower parts of the estuary (with high salinities) are acceptable. (< 5%). The high CBE errors (see Appendix B) in the rest of the samples point either to analytical error or that some ions with a significant total charge have been left out of the analysis. The large dilutions that were necessary for the major anion analysis by ion chromatography, could have resulted in some anions being diluted to below detection limits of the method, potentially contributing to the high CBE errors.

6.2 Nitrogen dynamics

6.2.1 Water column

Although the samples of the two different sampling runs were stored for different time periods, the storage protocols (see methodology section) are deemed to have been adequate to preserve the integrity of both sampling runs. Changes in concentrations of nutrients over time in samples have generally been found to be losses (Kotlash & Chessman, 1998), and if changes did occur in the samples of the first sampling run during storage, it would not have affected the qualitative comparison of the two sampling runs where the first run has higher measured concentrations than the second.

There is a marked difference in nitrogen concentrations in the lower Olifants River during low and high flow conditions in accordance with the observations reported by Morant (1984). Both NH_4^+ and NO_3^- concentrations were highest during the first sampling run (Figure 26). NO_3^- -N levels showed considerable variability at the freshwater inlet of the estuary (WP 7/ W 6), with concentrations of 41µmol/L and 4.01 µmol/L for sampling run one and two, respectively. NH_4^+ concentrations show less variability, with concentrations of 6.3µmol/L and 3.8 µmol/L being found for the two sampling runs at sampling point WP 7/ W 6. Total inorganic nitrogen levels measured during the first sampling run falls within the lower section of the

mesotrophic range (36-178 µmol/L), as set out by the Department of Water Affairs and Forestry (DWAF, 1996a).

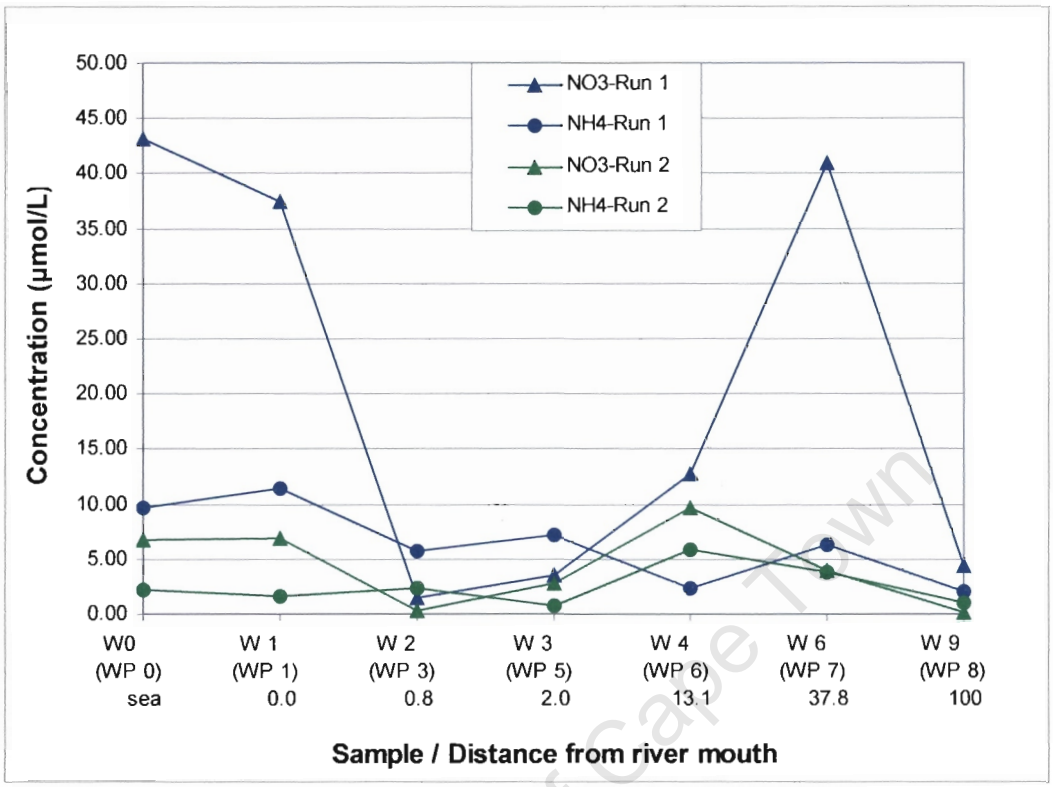

Figure 26 NO_3 and NH_4 during two sampling runs (comparative values).

During the low flow conditions of the first sampling run agricultural return flow would have contributed significantly to the base flow of the Olifants River. The higher mobility of nitrate in groundwater (due to its negative charge) than ammonium, and hence in subterranean agricultural return flow, could explain the observation that nitrate made up the dominant portion of total inorganic nitrogen (TIN) during the first sampling run. This line of reasoning would then suggest that the Olifants River was fed mainly by surface water run-off during the second sampling run, where absorption to negatively charged clays would have been minimal and ammonium concentrations would make up a larger proportion of the TIN pool compared to the first sampling run. According to DWAF (1996a), nitrate should make up > 80% of the TIN pool in un-impacted, well-oxygenated waters.

TIN, and especially nitrate concentrations are lowest in the southern channel of the estuary (Figure 26), and for most of the sampling points in the southern channel ammonia is present at higher concentrations than nitrate, which concurs with the literature where it has been found that the dominant form of nitrogen in salt marshes is generally ammonium (Schlesinger, 1997). Neither nitrate nor ammonium behaves conservatively in the estuary, and direct plant uptake, ammonia volatilisation and denitrification are probable processes responsible for the observed loss of TIN. Competition for nitrogen would be intense amongst the aquatic organisms during nitrogen limiting periods, and assimilatory reduction of ammonium and nitrate would be significant under the low N:P ratios seen in the low flow conditions and in the southern channel of the estuary. Although nitrogen fixation (which is likely to occur under nitrogen limiting conditions) would be locally important to cyanobacterial mats, the contribution of fixed nitrogen to the total nitrogen budget is small in the majority of shallow marine ecosystems (Herbert, 1999). Due to the alkaline influence of the seawater in the lower reaches of the estuary, and the added potential of algal photosynthetic activity to drive the pH above 8.5 (Reddy *et al*, 2000), ammonia volatilisation may contribute to the loss of nitrogen in the system. Denitrification has been shown to be very effective in removing fixed nitrogen from wetlands (Schlesinger, 1997; Groffman, 2000; Nilson and Janson, 2002), and probably plays an important role in the nitrogen cycling and the loss of nitrates in the southern channel, especially since the greater residence time of the water in this section of the estuary provides more opportunity for internal processes to influence the water quality. The DOC measurements indicate that there is sufficient organic carbon in the water column to support denitrification, and both the tidal influence and the river input provides nitrate for the denitrification process. From the data it seems that the estuary is a sink of nitrogen, especially in the southern channel of the estuary. South African estuaries often exhibit nitrogen limitation (Allanson & Winter, 1999), and nitrogen is often the limiting nutrient in estuaries and most marine coastal waters (Stumm & Morgan, 1996). The high concentrations of ammonium and nitrate in the sea water during the first sampling run is most probably due to an upwelling event, but could also have been influenced by the river as the seawater sample was taken at close proximity to the mouth (at low tide).

6.2.2 Pore water

The very high ammonium concentrations present in the pore water samples can be caused by the mineralization of organic matter (ammonification), with ammonium being the first inorganic nitrogen form released in the mineralization process (Groffman, 2000), and/or dissimilatory nitrate reduction to ammonia. The ammonium levels in the pore water have no correlation ($R^2 = 0.04$) with the total nitrogen (TN) in the sediments that is associated with organic matter. The rates of nitrogen mineralization however depends on both the quantity as well as the quality of the organic matter, i.e. whether the organic matter is highly refractory or labile (Herbert, 1999). C:N ratios have been used to infer the mineralization potential of organic matter, with lower C:N ratios generally rendering the organic matter more labile (Wetzel, 1983). There is no correlation ($R^2 = 0.07$) between the ammonium concentration in the pore waters and the C:N ratios of the organic matter present in the sediments, and it seems that mineralization of organic matter is not the main process governing the ammonium concentrations in the pore water. Dissimilatory nitrate reduction to ammonia has been shown to be favourable under anoxic conditions (Reddy et al, 2000). Studies by Herbert and Nedwell (1990), cited in Herbert (1999), illustrated that nitrate concentration plays a "key" role in determining whether nitrate is reduced to ammonium or gaseous products (by dentrification). It was demonstrated that nitrate ammonifying bacteria out competed denitrifiers at low nitrate concentrations, whilst the reverse was observed at high nitrate concentrations. Dissimilatory nitrate reduction may be an important process in the lower Olifants River considering the low nitrate concentrations found in all the pore water samples bar one. If sulphate reduction does take place as postulated, the low redox potentials (pe = 6.15 W) necessary for dissimilatory reduction will be attained, since sulphate reduction (pe = -3.75 W) takes place at even lower redox potentials (Stumm & Morgan, 1996). Dissimilatory nitrate reduction and/or dentrification in the pore waters are responsible for the low nitrate concentrations in the pore waters relative to the water column. In most wetlands denitrification rates are limited by NO_3^- concentrations, and diffusion rates of NO_3^- from aerobic to anearobic sediments/waters (Martin & Reddy, 1997 in Reddy *et al*, 2000).

It has been suggested that competition for cation exchange sites by ions in seawater, in conjunction with ion pairing of ammonium, play an important role in the flux of

ammonium for estuarine sediments to the water column (Gardner *et al*, 1991; Seitzinger *et al*, 1991). Pore waters with higher salinities have been shown to have higher ratios of dissolved ammonium to exchangeable ammonium than pore waters with low ionic strengths (Seitzinger *et al*, 1991), and saline conditions thus enhances the flux of ammonium to the water column relative to fresh water conditions. The high ammonium concentrations in the pore water form an important potential source of nitrogen to the water column, especially in the southern channel of the estuary where nitrogen is limiting in the water column. The thickness of an oxidized microzone is an important factor influencing ammonium diffusion to the water column. Rooted macrophytes link nutrients in the sediments with that of the overlying water column, with potentially important implications for nutrient cycling in aquatic ecosystems (Flindt et al, 1999). Soto-Jiminez *et al* (2003) found that the macrophyte community forms an important route of transfer of nitrogen and phosphorus out of the sediment to the water column. The macrophyte link in the nutrient transfer between the pore water and the water column is of special relevance considering that macrophytes such as *Zostera capensis*, *Potamogeton pectinatus* and *Phragmites australis* are common in the Olifants River Estuary (Adams & Bate, 1997).

6.2.3 Sediments

The sediments are the largest pool of nitrogen. A strong correlation exists between the total nitrogen (TN) and organic carbon (OC) content of the sediments, indicating that the nitrogen is associated with organic matter in the sediments. The accumulation of organic matter in wetland sediments is common (Fischer & Reddy, 2001), and forms a temporary sink for nitrogen.

In section 6.3.2 it was pointed out that there was no observed correlation between the ammonia concentrations in the pore waters and the C:N ratios of the organic matter in the sediments. C:N ratios can however also be used to infer the origin of organic matter. In general vascular land plants have a C:N ratios of 20 or greater, and fresh algal organic matter has C:N ratios ranging between 5 and 8 (Meyers, 1994). These differences in elemental composition are due to the high protein content of algal matter, the scarcity of cellulose in algae, and its abundance in the organic matter of vascular plants (Twichell *et al*, 2002). Based on this differentiation the organic matter

in samples S 10 to S 7 is predominately terrestrial, and estuary samples S 6 to S 1 are largely algal in origin (Figure 27).

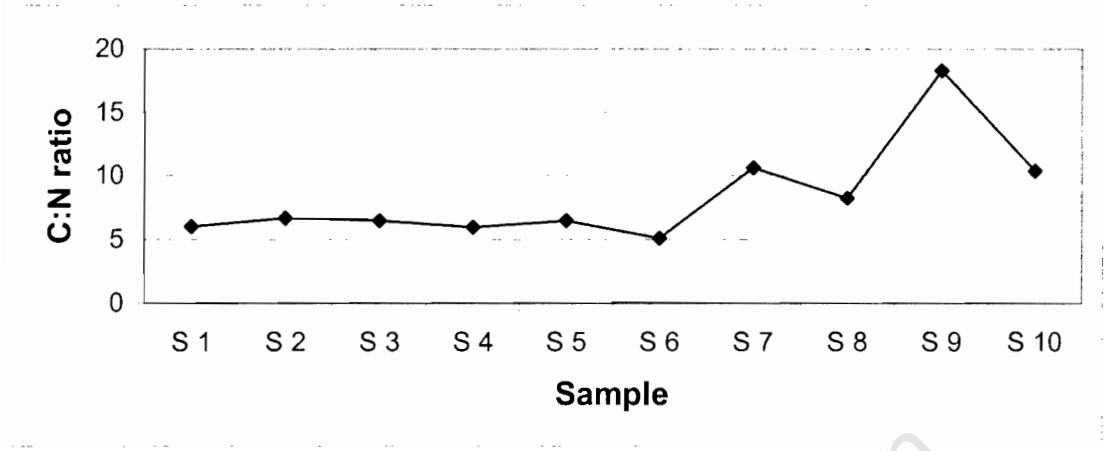

Figure 27: Organic matter carbon to nitrogen ratios of the sediments.

6.3 Phosphorus dynamics

6.3.1 Water column

In the section of the Olifants River above the estuary DRP concentrations were highest during the first sampling run, and both DRP and TDP levels were higher at the freshwater inlet of the estuary during the first run (Figure 25). This pattern where the highest dissolved inorganic phosphorus concentrations occurs in low flow conditions is similar to that in the Sundays and Great Fish rivers, where nutrient-rich agricultural return flows contribute significantly to the river base flow during the dry months (Adams & Bate, 1997). DRP concentrations found at the freshwater inlet above the estuary (1.1 and 0.78 µmol/L) were significantly higher than those reported for unpolluted rivers, which have average DRP concentrations ranging between 0.23-0.32 µmol/L. The observed concentrations in the lower Olifants River are however still much lower than those reported for polluted rivers which have DRP concentrations ranging from 3.23 – 22.6 µmol/L (Meybeck, 1982; 1993; Savenko & Zakharova, 1995; cited in Compton *et al* 1999). According to the freshwater quality guidelines as set out by the Department of Water Affairs and Forestry (DWAF, 1996a), the DRP values measured at the freshwater inlet of the estuary fall close to the lower eutrophic range (0.81-3.23 µmol/L).

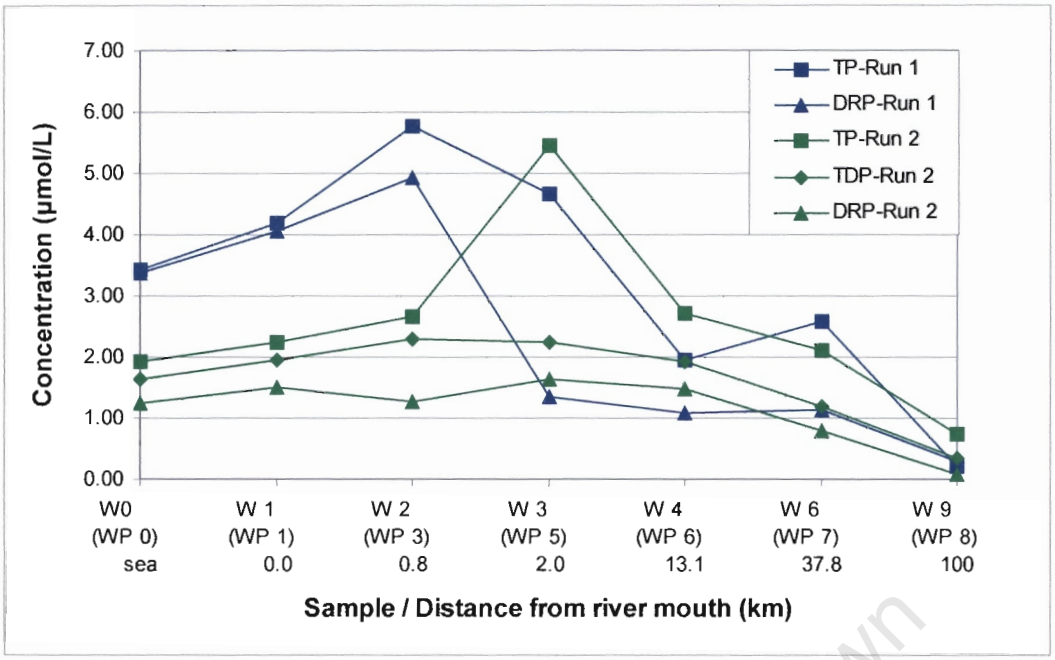

Figure 25 DRP and TP during two sampling runs (comparative values).

DRP and TDP concentrations of the two sampling runs are similar in the upper section of the estuary. In the lower section and the seawater samples, DRP and TDP concentrations were higher during the first sampling run. Upwelling events along the west coast that are typically associated with south-easterly winds occurring in summer, are probably responsible for the high nutrient concentrations found in the seawater sample taken during the first sampling run. Alternatively, the higher value could simply reflect the outgoing estuary tidal waters with the estuary providing a source of phosphorus to the coastal waters. The higher nutrient levels in the seawater coupled with the more pronounced tidal effect probable contribute, together with the riverine phosphorus input, to the significantly higher phosphorus concentrations in the lower estuary observed during sampling run one.

A comparison of DRP, TDP and TP to Cl ratios along the lower Olifants River indicates that phosphorus does not behave conservatively in either the river or the estuary. During both sampling runs phosphorus increases in a downstream direction along the river, with the highest phosphorus concentrations being found in the southern channel of the estuary. The data collected indicate that the estuary acts as a phosphorus source. Various processes could be responsible for this observation. The most likely causes include phosphate release through the mineralisation of organic matter, the desorption and diffusion of phosphate from the sediments (Nilson &

Janson 2002), desorption from iron-bound particlulate inorganic phosphorus (Compton *et al*, 1999) desorption of phosphates bound to humic acids during mixing in estuaries (Gardolinski *et al*, in press), and nitrogen limitation.

The mixing of waters with different ionic strengths in estuaries is of special relevance to phosphorus dynamics. DRP release from sediments and suspended load have been shown to increase with increasing salinities (Gardolinski *et al*, in press), and is caused by ion exchange or desorption associated with increases in ionic strength and pH. Increased ionic strengths (especially in terms of Cl^- and SO_4^{2-}) increases the competition for reactive sites on positively charged iron-oxides, and the alkaline conditions caused by the seawater influx can shift the charge from positive to negative on the iron-oxides present (Stumm & Morgan, 1985; McBride, 1994), reducing the phosphorus sorption capabilities of the particulate matter.

The estuary seems to be nitrogen limited (with N:P ratios below 10), especially during low flow conditions and in the southern channel of the estuary. Under such conditions directly available phosphorus (DRP) will not be taken up by aquatic organisms, as nitrogen is the growth limiting nutrient. The nitrogen limitation can explain the observation that a large fraction of the total phosphorus in the water column of the river is in the organic or acid hydrolysable form where phosphorus is limiting, whereas the largest fraction of total phosphorus is in the inorganic form where nitrogen is limiting. Nitrogen limitation thus probably contributes to the estuary acting as a phosphorus source.

6.3.2 Pore water

The concentrations of DRP and TDP are generally higher in the pore waters than in the overlying water column. The higher concentrations of phosphorus in the pore waters can be due to mineralization of organic matter in the sediments and/or phosphorus desorption in the sediments. The activities of the enzymes phosphatase and arylsulphatase have been shown to be the rate limiting step in phosphorus mineralization, and the activities of these enzymes are inhibited in anoxic conditions (Kang & Freeman, 1999). The factors pointing to the likely anaerobic conditions of many of the sediments samples (i.e. low sulphate concentrations, black colour, sulphurous smell), as well as the lack of correlation between pore water phosphorus

concentrations and organic matter content in the sediments, negates the role of organic matter mineralisation. If a substantial proportion of the phosphorus in the sediments is associated with iron and aluminium oxyhydroxides, desorption under anaerobic conditions would contribute significantly to the pore water phosphorus concentrations.

Visible oxidation (iron precipitation was evident on the sides of the sampling bags) of many of the sediment samples occurred during storage and pore water extraction. Ferrous iron is rapidly converted to ferric iron when sediment conditions change from anoxic to oxic. Under such conditions $Fe(OH)_3$ precipitates out of solution within seconds to minutes (Moore & Coale, 2000), scavenging orthophosphate and effectively removing phosphates from the aqueous phase. Fresh ferric hydroxides have immense phosphorus sorption capacities, and have been shown to reduce soluble phosphorus levels in pore water by orders of magnitude within minutes (Moore & Coale, 2000). The DRP levels measured in the pore waters are thus probably an underestimation of soluble phosphorus levels in most of the samples. The DRP concentration in sample PW 7 was extremely high, and it is postulated that the anaerobic storage method was most successful in keeping this sample in an anaerobic state, thus preventing phosphate scavenging by iron precipitation.

The pore water to water column ratios of DRP are close to one in pore water samples W 6, 5 and 3. In the other pore water samples this ratio is considerably higher than 1, indicating that the pore water can potentially be an important source of phosphorus to the water column through molecular diffusion and macrophyte uptake (especially if the measured pore water concentrations are in fact underestimated). The potential for molecular diffusion from the sediments depends largely on the redox conditions of both the sediment and the overlying water. Phosphate diffusing upwards from an anaerobic zone will be immobilised once it reaches an aerobic zone with available iron, manganese or aluminium oxyhydroxides in the sediments (Wetzel, 1983). An oxidised micro-zone probably occurs in the surface layer sediments sampled, considering the well-oxygenated state of the overlying water column. Bioturbation and the presence of macrophytes in the lower Olifants River, is expected to play an important part in mediating phosphorus transfer from the pore water to the water column.

6.3.3 Sediments

Generally, the majority of phosphorus transported from agricultural soils is in the particulate form (Oenema & Roest, 1998) and, as expected, the sediments form the major pool of phosphorus in the lower Olifants River. The TP levels in the lower Olifants River are the highest in the estuary. This is probably due to the deposition of particulate matter associated with the slowing down of water, the build up of organic matter in the sediments of the estuary, and the possible inflow of phosphate -rich waters associated with upwelling events. Total phosphorus in the sediments shows a strong correlation with grain size, with TP and the clay plus silt particle size fraction of the sediments having a R^2 of 0.79.

The total phosphorus (TP) levels in the estuary (6.8 – 14.1 mmol/kg) are much higher than the low TP values (which generally ranged between 3.23 – 6.46 mmol/kg) found in highly organic carbonate sediments in the north eastern Florida Bay oligotrophic estuary (Koch *et al*, 2001). The Olifants Estuary TP values are however still comparatively low to TP values found in estuaries reported in the literature, values of which have been reported by Andrieux & Aminot, (1997) The values reported range from 10 – 60 mmol/kg.

The TP levels of the sediments do not represent the reactive component of the phosphorus in the sediment, and often only a fraction of particulate phosphorus is bioavailable to aquatic organisms (Oenema & Roest, 1998). The bioavailability of the phosphorus depends on the fractionation of the phosphorus and the ambient water chemistry.

It has been shown that the measured distribution of phosphorus fractions in sediments is highly dependent on the fractionation method applied (Pardo *et al*, 1998), and results of these procedures are generally not comparable. Although no fractionation method was used to determine the fractionation of the phosphorus in the sediment, some observations were made in the field and laboratory that allow speculation on the phosphorus fractionation. Due to the iron precipitation observed in the sampling bags, the amount of iron-bound phosphorus is expected to be significant in most of the samples, especially in those taken upstream of the estuary and in the upper section of the estuary where ion exchange or desorption associated with increases in ionic

strength and pH (discussed in section 6.2.2) does not occur. The notion that iron-bounded phosphorus is significant in the study area is supported by the fact that the TP in the sediments shows a strong correlation with the clay and silt particle size, and iron/aluminium bound phosphorus and exchangeable phosphorus have been found to be associated with fine particles (Andrieux & Aminot, 1997). During the sediments digestions it was clear that significant amounts of total iron occurred in sediments S 9 to S 2, indicated by the iron precipitation in the samples when the pH of the digests was raised prior to spectrophotometric analysis, and the resulting low recoveries (20%) attained during the first digestion. It however remains an unanswered question how much of this iron was in the residual form and thus chemically inert before the digestion. The removal of dissolved iron (often bound to organic matter) by flocculation at low salinities in estuaries is commonly found (Chester, 1990; L'Her Roux *et al*, 1998), and will contribute to the particulate iron phase in the sediments. The significance of the contribution to the iron particulate phase by flocculation will depend on the ratio of the dissolved iron and particulate iron prior to mixing, which would be expected to be small under the redox and pH conditions normally found in natural waters (including the lower Olifants River).

Some of the TP found in the sediments is associated with organic matter, considering the correlation of TP with organic carbon (R^2 = 0.64) and TN (R^2 = 0.71) in the sediments. Unfortunately no data are available that provides information on the fraction of phosphorus that occurs in the residual fraction in the sediments.

The solubility of iron, which is controlled mainly by the redox potential (section 6.2.2) and pH of the water/sediments, is of importance when considering the availability of phosphates bound to iron in the sediments. Under aerobic conditions the pH needs to be below 2 for iron to go into solution. Such an event would be an unlikely occurrence, especially in the estuary where the ANC's of the waters is high. Further important processes that may affect the availability of TP in the sediments include the remobilisation of sediments rich in phosphorus and the associated release of dissolved phosphorus from the pore water by scouring of the river bed (House, 2003). This is anticipated to occur when the Olifants River is in flood (as well as by the tidal insurgence into the estuary), and underlies the importance of hydrodynamic conditions on nutrient cycling.

6.4 Catchment controls on nutrient dynamics

The strong seasonality in the rainfall, rapid run-off characteristics of the catchment, and extensive irrigation agriculture along the banks of the lower Olifants River contribute greatly to the observed seasonal variations in both major ion concentrations and nutrient levels. During low flow conditions agricultural return flow (fed by irrigation) contribute a proportionally larger fraction of water to the river flow than during high flow conditions. High flow conditions occurring in the rainy season, mediated by the rapid run-off observed in the catchment, serve to dilute the waters of the lower Olifants River. According to future agricultural development scenarios freshwater flow in the river will decrease, with freshwater inflows into the estuary expected to decrease by 45% - 53%. (Basson *et al*, 1998). Such a scenario would enhance the role of agricultural return flow in determining the chemistry of the lower Olifants River, leading to an increase in both major ion and nutrient levels.

Observed water column nutrient concentrations in the freshwater section of the river upstream of the estuary was not excessively high, even during low flow conditions. The moderate nutrient concentrations found are partly due to naturally low background levels (observed in the samples taken furthest upstream), and "obstructions" in the nutrient pathways that connect agricultural land to the river. The low background nutrient levels observed are due to the fact that the Olifants River drains mainly nutrient poor quartzitic sandstones of the TMG in the regions of highest rainfall. Upstream of the estuary dense riparian vegetation was observed along most of the length of the river. Riparian zones exert a disproportionately large influence on streamwater chemistry, can "significantly modify the chemistry of drainage waters for a range of parameters at a range of spatial scales" (Smart *et al*, 2001), and most probably modifies the nutrient signal of the catchment to the lower Olifants River.

The hydrodynamics of the lower Olifants River controls the transport and deposition of sediments, which form the major pool of both nitrogen and phosphorus in the system. A prime example is the deposition of fine particles (which shows a strong correlation with phosphorus) on the floodplain of the estuary. The hydrodynamics of the system further plays an important role in controlling the supply of electron donors (mainly organic matter) and electron acceptors within the different compartments (water column, pore water and sediment) of the lower Olifants River. The resulting

control of redox conditions has a large impact on nutrient cycling (as discussed in section 6.2 and 6.3). The longer retention time of water within the southern channel of the estuary and the resulting effects on the nutrient dynamics within the southern channel illustrates the important role of hydrodynamics within the system. The regular flooding of the Olifants River furthermore influences the nutrient state of the estuary by scouring sediment and keeping the estuary open to the ocean (Morant, 1984).

7. CONCLUSIONS

The lower Olifants River is characterised by a marked seasonal variation in salinity and nutrient concentrations. Major ions and nutrients (especially nitrate), occur at significantly higher concentrations in low flow conditions compared to high flow conditions in the freshwater section of the river upstream of the estuary. The salinity and nutrient levels of the Olifants River is strongly influenced by hydrological conditions, and shows a rapid response to changing flow conditions. Nitrogen and phosphorus concentrations were generally higher in the pore waters than the overlying water column, potentially forming an important nutrient source to the overlying water. The sediments form the major pool of both nitrogen and phosphorus in the lower Olifants River. C:N ratios indicate that the organic matter in the sediments of the lower Olifants River upstream of the estuary is of terrestrial origin, whereas the organic matter in the sediments of the estuary are largely algal in origin. The organic matter in the estuarine sediments are rendered more labile by the lower C:N ratios compared to the organic matter present upstream of the estuary.

The Olifants River Estuary, particularly the salt marsh section in the southern channel of the estuary, has a large effect on nutrient cycling. Neither nitrogen nor phosphorus behaves conservatively in the estuary, and the information obtained during this study suggests that the estuary acts as a nitrogen sink and a phosphorus source. Direct plant uptake, ammonia volatilisation and denitrification are probable processes responsible for the observed loss of nitrogen in the water column of the estuary. Ammonification and dissimilatory nitrate reduction to ammonia, coupled with the high ionic strength of the pore waters (effecting competition for cation exchange sites and ion pairing of ammonium) are responsible for the high ammonium concentrations in the pore water samples taken in the estuary. The main processes controlling phosphorus cycling in the Olifants River Estuary seem to be phosphorus mineralization, plant uptake, flocculation, and adsorption and desorption to iron and aluminium oxyhydroxides. Observations made in the southern channel of the estuary suggest that a significant fraction of the particulate phosphorus is iron-bound. No conclusive data however exist on the fractionisation of the particulate phosphorus, which is a matter that deserves further investigation.

A comparison of inorganic N:P ratios indicates that phosphorus is the limiting nutrient upstream of the estuary, whilst nitrogen is the limiting nutrient in the estuary. The nitrogen limitation in the estuary is probably partly responsible for the high DRP concentrations observed within the estuary, as nitrogen limitation will inhibit the biological uptake of phosphorus. Hydrodynamics controlling the supply of electron donors and acceptors play a vital role in nutrient cycling in the lower Olifants River, and the tidal influence of seawater (and hence alkaline waters of high ionic strengths) significantly affects the nutrient dynamics in the estuary.

8. REFERENCES

Acocks, J. P. H. (1988) *Veld Types of South Africa*. Botanical Research Institute. Pretoria.

Adams, J. B. & Bate, G. C. (1997) Preliminary assessment of the effects of altered freshwater flow on the flora of the Olifants River Estuary. In *Olifants / Doring River basin study. Synthesis of Environmental Studies*. Annexure B: Estuarine. DWAF report no. PE000/00/1298.

Allanson, B. & Winter, D. (1999) Chemistry. In *Estuaries of South Africa*. (eds. Allanson, B. & Baird, D.) Cambridge University Press. UK. pp. 53-90.

Andrieux. F. & Aminot, A. (1997) A two-year survey of phosphorus speciation in the sediments of the Bay of Seine (France). In *Continental Shelf Research*, Vol. 17 no. 10, 1229 -1245.

Artiola, J. F. (1996) Waste disposal. In *Pollution Science* (eds. Pepper, I.L., Gerba, C.P. & Brasseau, M.L). Academic Press. Canada. pp. 135-150.

Aston, S. R. (1980) Nutrients, Dissolved Gases, and General Biogeochemistry in Estuaries. In *Chemistry and Biogeochemistry of Estuaries* (eds. Olausson, E. & Cato, I.). John Wiley & Sons. Bath. pp. 233-262.

Basson, M. S. , Theron, T. P., Little, P. R. & Luger, M. (1998). *Olifants/Doring River Basin Study: Main Report*. Department of Water Affairs and Forestry, South Africa. DWAF report no. PE000/00/0198.

Baumbach, G. (1996) Air Quality Control: *Formation and Sources, Dispersion, Characteristics and Impact of Air pollutants – Measuring Methods, Techniques for Reduction of Emissions and Regulations of Air Quality Controll*. Springer-Verlag. Germany.

Boers, P. C. M., Van Raaphorst, W. & Van Der Molen, D. T. (1998) Phosphorus retention in sediments. In *Water Science and Technology*. Vol. 37 no. 3, 31-39.

Brady, N. C. & Weil, R. R. (1999) The Nature and Properties of Soils, 12th Edition. Prentice Hall. USA.

Chester, R. (1990) *Marine Geochemistry*. Chapman & Hall. Great Britain.

Compton, J., Mallinson, D., Glenn, C. R., Filippelli, G., Föllmi, K., Shields, G. & Zanin, Y. (1999) Variations in the Global Phosphorus Cycle. In *Marine Authigenesis: From Global to Microbial*, SEPM Special Publication no.66. 1-13.

Cowan, G. I. (1995) *Wetlands of South Africa: South Africa and the Ramsar convention. South Africa Wetlands conservation Programme.* Department of Environmental Affairs and Tourism. Pretoria.

Cowgill, U. M., (1996) Sampling Waters: The impact of Sample Variability on Planning and confidence Levels. In *Principles of Environmental Sampling* (ed. Keith, L. H.), 2nd edition., American Chemical Society, USA. pp. 317-336.

Davidson, A. W. & Cape, J. N. (2003) Atmospheric nitrogen compounds – issues related to agricultural systems. In *Environment International,* **29**, 181-187.

Davies, B. & Day, D. (1998) *Vanishing Waters.* University of Cape Town Press. South Africa.

Department of Water Affairs and Forestry (1996a) South African Water Quality Guidelines. 2nd edition volume 7 – Aquatic ecosystems. RSA.

Department of Water Affairs and Forestry (1996b) South African Water Quality Guidelines for Coastal Marine Waters. 2nd edition volume 1 – Natural Environments. RSA.

Department of Water Affairs and Forestry website, (2003) http://www.dwaf.gov.za/Hydrology/applets/weekly/weekly.asp?region=E

Drever, J.I. (1997) *The Geochemistry of Natural Waters: Surface and Groundwater Environments*. 3rd edition. Prentice Hall. USA.

Duinker, J. C. (1980) Suspended Matter in Estauries: Adsorption and Desorption Processes. In *Chemistry and Biogeochemistry of Estuaries*. (eds. Olausson, E. & Cato, I). John Wiley & Sons. Northern Ireland. pp. 121-152.

Eaton, A. D., Clesceri, L. S. & Greenberg, A. E. (eds) (1995) *Standard Methods for the Examination of Water and Wastewater.* 19th edition, American Public Health Association United Book Press. Washington, D.C.

Emsley, J. (2000) *The shocking history of phosphorus: A biography of the devil's element*. Pan Books. UK

Environmental Potential Atlas (ENPAT) (2000) Western Cape. Department of Environmental Affairs and Tourism, South Africa.

Fischer M. M. & Reddy, K. R. (2001) Phosphorus flux from Wetland soils Affected by Long-Term Nutrient Loading. In *Journal of Environmental Quality*, **30**, 261-271.

Flindt, M. R., Pardal, M. A., Lillebo, A. I. Martins, E. & Marques, J. C. (1999) Nutrient cycling and plant dynamics in estuaries: A brief review. In *Acta Oecologica,* **20** (4), 237-248.

Gardner, W. S., Seitzinger, S. P., & Malczyk, J. M. (1991) The effects of Sea Salts on the Forms of Nitrogen Released From Estuarine and Freshwater Sediments: Does Ion Pairing Affact Ammonium Flux? In *Estuaries*, Vol. 14, no. 2., 157-166.

Gardolinski, P. C. F. C., Hanrahan, G., Achterberg, E. P., Gledhill, M., Tappin, A. D., House, W.A. & Worsfold, P.J. (2001) Comparison of sample storage protocols for the determination of nutrients in natural water. In *Water Resources*, Vol. 35, no. 15, 3670 - 3678.

Gardolinski, P. C. F. C., Worsfold, P. J., & McKelvie, I. D. (article in press) Seawater induced release and transformation of organic and inorganic phosphorus from river sediments. – *Water Research* accepted 28 October 2003.

Grasshoff, K. Ehrhardt, M & Kremling, K. (eds) (1983) *Methods of seawater analysis*. 2nd, revised and extended edition. Verlag Chemie Gmb, D-6940. Weinheim.

Groffman, P. M. (2000) Nitrogen in the Environment. In *Handbook of Soil Science*. (ed. Sumner, M. E.) CRC Press. USA. pp. C190-C200.

Hark, T. R. (1995) A geochemical investigation of the aquatic sediments, groundwater and surface water of the Verlorenvlei coastal lake, with special reference to nitrate transformations. M.Sc. dissertation. UCT.

Herbert, R. A. (1999) Nitrogen cycling in coastal marine ecosystems. In *FEMS Microbiology Reviews*, **23**, 563 - 590.

Herbert, R. A. & Nedwell, D. B. (1990) Role of environmental factors in regulating nitrate respiration in intertidal sediments. In *Denitrification in Soil and Sediment* (eds. Revsbech, N. P. & Sorensen, J.). Plenum Press, New York. pp. 77 – 90.

Holland, H. D. (1978) *The Chemistry of the Atmosphere and Oceans*. Wiley, New York

House, W. A. (2003) Geochemical cycling of phosphorus in rivers. In *Applied Geochemistry*, **18**, 739-748.

Janke, R. A., Alexander, C. R. & Kosta, J. E. (2003) Advective pore water input of nutrients to the Satilla River Estuary, Georgia, USA. In *Estuarine Coastal and Shelf Science*, **56**, 641-653.

Johnson, D.W. (1992) Nitrogen retention in forest soils. In *Journal of Environmental Quality*. **21**, 1-12.

Jurtshuk, P. (Jr.) (1996) Bacterial Metabolism. In *Medical Microbiology*. (ed. Baron, S.). 4th Edition The University of Texas Medical Branch of Galveston. USA.

Kang, H. & Freeman, C. (1999) Phosphatase and arylsulphatase activities in wetland soils: annual variation and controlling factors. In *Soil Biology & Biochemistry*, **31**, 449-454.

Kellman, M. and Hillaire-Marcel , C. (1997) Evaluation of nitrogen isotopes as indicators of nitrate contamination sources in an agricultural watershed. WRRI. USA.

Koch, M. S., Benz, R. E. & Rudnick, D. T. (2001) Solid-phase Phosphorus Pools in Highly Organic Carbonate Sediments of Northeastern Florida Bay. In *Estuarine, coastal and Shelf Science*, **52**, 279 -291.

Kotlash, A. R. & Chessman, B. C. (1998) Effects of water sample preservation storage on nitrogen and phosphorus determinations: implications for the use of automated sampling equipment. In *Water Resources*, Vol. 32 no. 12, 3731-3737.

Lambrechts, J. J. N. & Schloms B. H. A. (1998) Soils and Irrigation Potential Investigation. In *Olifants/Doring River Basin Study*. Department of Water Affairs and Forestry, South Africa. DWAF report no. PE000/00/0498.

Langhout, C. (1998) Physical Characteristics and Land Use. In *Olifants/Doring River Basin Study*. Department of Water Affairs and Forestry, South Africa. DWAF report no. PE000/00/0298.

Langmuir, D., (1997) *Aqueous Environmental Geochemistry*. Prentice Hall, New Jersey, USA.

Leong, L. S. & Tanner, P. A. (1999) Comparison of methods for determination of organic carbon in marnine sediment. In *Marine Pollution Bulletin*, **38**, 875-879.

L'her Roux, L., Le roux, S. & Appriou, P. (1998) Behaviour and Speciation of Metallic Species, Cu, Cd, Mn and Fe During Estuarine Mixing. In *Marine Pollution Bulletin*, Vol. 26 no. 1, 56-64.

Lijklema, L. (1998) Dimensions and Scales. In *Water Science Technology*, **37**, 1-7.

Loveley, D. R. (1987) Organic matter mineralisation with the reduction of ferric iron: A Review. In *Geomicrobiol. J.* **5**, 375-399.

Lovett, G. M. (1994) Atmosperic deposition of nutrients and pollutants in North America. An Ecologicl Perspective. In *Ecol. Appl.* **4**, 629-650.

Martin, J. F. & Reddy, K. R. (1997) Interaction and spatial distribution of wetland nitrogen processes. In *Ecological Modeling*, **105**, 1-21.

Meybeck, M. (1982) Carbon, nitrogen and phosphorus transport by world rivers: In *America Journal of Science*, **282**, 401-450.

Meybeck, M. (1993) C, N, phosphorus and S in rivers: from sources to global inputs, In *Interactions of C, N, phosphorus and S Biochemical Cycles and Global Change* (eds. Wollast, R. Mackenzie, F. T. & Chou, L.): NATO ASO Series I, v 4, Berlin Springer-Verlag. pp. 163-193

McBride, M.B. (1994) *Environmental Chemistry of Soils.* Oxford University Press, New York.

McLatchey, G. P. & Reddy, K.R. (1998) Wetlands and Aquatic Processes: Regulation of Organic Matter Decomposition and Nutrient Release in a Wetland Soil. In *Journal for Environmental Quality*, **27**, 1268-1274.

Mengel, D. & Rehm, G. (2000) Fundamentals of Fertilizer Application. In *Handbook of Soil Science*. (ed. Sumner, M. E.). CRC Press. USA. pp. D155-D174.

Meyers, P. A. (1994) Preservation of elemental and isotopic source identification of sedimentary organic matter. In *Chemical Geology*, **144**, 289 -302.

Moore, P. & Coale, F. (2000) Phosphorus fractionation in Flooded Soils and Sediments. In *Methods of Phosphorus Analysis for Soils, Sediments, Residuals, and Waters*. (ed. Pierzynski, G. M.) Southern Cooperative Series Bulletin No.# 396. Sera-IEG 17. North Carolina State University. USA.

Morant, P. D. (1984) Estuaries of the Cape. Part II: Synopses of available information on individual systems. Report no. 26: Olifants (CW10). Associated Printing and Publushing Co (Pty) Ltd. Cape Town.

Murphy, J. & Riley, J.P. (1962) A modified single solution method for the natural determination of phosphate in natural water. In *Analytica Chimica Acta*, **27**, 31-36.

Mwanuzi, F., Aalderink, H. & Mdamo, L. (2003) Simulation of pollution buffering capacity of wetlands fringing Lake Victoria. In *Environment International,* 29, 95-103.

Nilson, R. & Janson, M. (2002) Hydrodynamic control of nitrogen and phosphorus turnover in an eutrophicated estuary in the Baltic. In *Water Research*, **36**, 4616 - 4626.

Oenema, O. & Roest, C. W .J. (1998) Nitrogen and phosphorus losses from agriculture into surface waters; the effectcs of polcies and measures in the Netherlands. In *Water Science and Technology*, **37** (2), 19-30.

Pardo, P., López-Sanchez, Rauret, G. (1998) Characterisation, validation and comparison of three methods for the extraction of phosphate from sediments. In *Analytica Chimica Acta*, **37**, 183-195.

Parr, J., Bollinger, M., Callaway, O., & Carlberg, K. 1996: Preservation Techniques for Organic and Inorganic Compounds in Water Samples, In *Principles of Environmental Sampling* (ed. Keith, L. H.) 2nd edition., American Chemical Society, USA. pp. 267-296.

Pennietjies van der Westhuizen, (2003) personal correspondence with farm manager at Big Bend, property bordering the river.

Presley, B. J. & Trefry, J. H. (1980) Sediment –water interactions and the geochemistry of interstitial water. In *Chemistry and Biogeochemistry of Estuaries*. (eds. Olausson, E. & Cato, I). John Wiley & Sons. Northern Ireland. pp. 187-232.

Ramsey, M. (2000) Environmental Sampling: Estimating the Uncertainty. A One Day Workshop on april 24th 2000, presented by Dr. Mike Ramsey, Centre for Environmental research, University of Sussex, UK.

Reddy, K. R., & D'Angelo, E. M. (1997) Biogeochemical indicators to evaluate pollutant removal efficiency in constructed wetlands. In *Water Science and Technology*, **35** (5), 1-10.

Reddy, K. R., D'Angelo, E. M., & Harris, W. G. (2000). *Biogeochemistry of Wetlands*. In Handbook of Soil Science (ed. Sumner, M. E.). CRC Press. USA. pp. G89-G121.

Richards, B. N. (1987). *The microbiology of Terrestrial Ecosystems*. Longman Scientific & Technical. U.K.

Roadcap, G. S., Hackley, K. C., Hwang, H., and Johnson, T. M. (2001) Application of Nitrogen and Oxygen Isotopes to Identify Sources of Nitrate. Paper presented at the Illinois Groundwater Consortium Conference. April 9, 2001.

Ryba, S. A. & Burgess, R. M. (2002) Effects of sample preservation on the measurement of organic carbon, hydrogen, nitrogen, sulfur, and oxygen concentrations in marine sediments. In *Chemosphere*, **48**, 139-147.

Schlesinger, W.H. (1997) *Biogeochemistry. An analysis of global change.* 2nd edition. Academic Press. USA.

Seitzinger, S. P., Gardner, W. S.& Spratt, A. K. (1991) The Effect of Salinity on Ammonium sorption in Aquatic Sediments: Implications for Benthic Nutrient Recycling. In *Estuaries*, Vol.14 no. 2, 167-174.

Smart R. P, Soulsby C, Cresser M. S, Wade A. J, Townend J, Billet M. F, Langan S (2001) Riperian zone influence on stream water chemistry at different spatial scales: a GIS-based modelling approach, an example for the Dee, NE Scotland. In *The Science of The Total Environment,* Volume 280, Issues 1-3, 173-193.

Smith, M. unpublished data: Results from quality control (n = 10) undertaken at University of Cape Town IC laboratory in May 2003.

Savenko, V. S. & Zakharova, E. A. (1995) Phosphorus in riverine runoff.In *Doklady Rossiiskoi Akademii Nauk*, **345**, 628-685.

Sprent, J.I. (1987) *The ecology of the nitrogen cycle. Cambridge studies in ecology.* Cambridge University Press. Great Britain.

Soto-Jimenez, M. F., Paez-Osuna, F. & Bojorquez-Leyva, H. (2003) Nutrient cycling at the sediment-water interface and in sediments at Chiricahueto marsh: a subtropical ecosystem associated with agricultural land uses. In *Water Research*, **37**, 719 - 728.

Stumm, W. & Morgan, J. J. (1996) *Aquatic chemistry: chemical equilibria and rates in natural waters*. 3rd edition. John Wiley & Sons, Inc. USA.

Sundareshwar, P. V. & Morris, J. T. (1999) Phosphorus sorption characteristics of intertidal marsh sediments along an estuarine salinity gradient. In *Limnology and Oceanography*, **44**, 1693 -1701.

Surface Water Resources of South Africa (1990), Volume 4. Drainage regions E, G, H, J, K, L, Western Cape Appendices. Water Research Commission. South Africa.

Taljaard, S. (1997) The effects of future changes in run-off on the Olifants Esturary. Phase 1. Water Quality Parameters. CSIR report: ENV/S-C 97127. Environmentek, CSIR. Stellenbosch.

Tappin, A. D. (2002) An Examination of the Fluxes of Nitrogen and Phosphorus in Temperate and Tropical Estuaries: Current Estimates and Uncertainties. In *Estuarine, Coastal and Shelf Science*, **55**, 885-901.

Thompson, T. L. (1996) Agricultural Fertilizers as a Source of Pollution. In *Pollution Science*. (eds. Pepper, I.L., Gerba, C.P. & Brasseau, M.L) Academic Press. Canada. pp. 211-224

Twichell, S. T., Meyers, P. A. & Diester-Haas, L. (2002) Significance of high C/N ratios in organic-carbon-rich Neogene sediments under the Benguela Current upwelling system. In *Organic Geochemistry*, Vol. 33, issue 7, 715 -722.

Ure, A.M. & Davidson, C. M. (1995) Introduction to speciation. In *Chemical Speciation in the Environment* (eds. Ure. A. M. & Davidson, C. M.). Blackie Academic and Professional, UK. pp. 1-6.

van Veelen, M., Baker, T. & Pieterse, H.S. (1998) Water Quality Assessment. Olifants / Doring River Basin Study. Department of Water Affairs and Forestry, South Africa. DWAF report no. PE000/00/0798.

Viessman, W. & Hamner, M. J. (1998). *Water supply and pollution control*. 6th edition. Addison Wesley Longmoan, Inc. California.

Wai Ting Tung, J. & Tanner, P.A. (2003) Instrumental determination of organic carbon in marine sediments. In *Marine Chemistry*, **80,** 161-170.

Walmsley, D. (2000) Perspectives on Eutrophication of Surface Waters: Policy/Research Needs in South Africa. Water Research Commission report no. KV129/00. South Africa

Wetzel, R.G. (1983) *Limnology,* 3rd edition. Saunders College Publishing. United States of America.

Whitfield, A. K. (2000) Available scientific information on individual South African estuarine systems. Water Research Commision report no. 577/3/00. South Africa.

World Health Organisation (1989) *Global Freshwater Quality: A First Assessment*, Blackwell Reference. London.

Zedler, J. B. (2000) Progress in wetland restoration ecology. In *Tree*, **15** (10), 402-407.

APPENDIX A

Sampling site descriptions

Table 13: Short description of sampling sites - run 1		
Sample	**Distance***	**Description**
WP 0	sea	Just south of mouth in wave zone.
WP 1	0	River mouth, low tide.
WP 2	0.4	Salt marsh, abundant algae.
WP 3	0.7	Stagnant water (pond) in salt marsh, abundant algae.
WP 4	1.2	Salt marsh, very few algae.
WP 5	2.0	Very shallow water in salt marsh.
WP 6	13.1	Reed bed along steep river banks.
WP 7	37.8	Medium water flow, abundant algae
WP 8	100.0	Very sandy just upstream of bridge.
WP 9	154.3	Small river rapid covered with dense vegetation downstream of the Clanwilliam dam
WP 10	202.7	Slow flowing water, filamentous algae present

* = distance from river mouth (sea = sample taken in the sea)

Table 14: Short description of sampling sites - run 2		
Sample	**Distance***	**Description**
W0	sea	Sea sample, wavezone with big swell.
W1	0	River mouth, leap low tide.
W2	0.8	Very slow flowing water and abundant macrophytes in salt marsh
W3	2.0	Tide coming in strongly in salt marsh, flamingos present
W4	13.1	Steep river banks, reeds present and tide coming in.
W5	32.8	Agricultural area with riparian wetland, strong river flow.
W6	37.8	Very strong river flow, turbid water.
W7	55.1	River surrounded by intensive agriculture (vineyards)
W8	76.4	Submerged trees in river, intensive agriculture (vineyards)
W9	100.0	Just upstream of bridge, very windy
W10	119.7	Large riparian wetland

* = distance from river mouth (sea = sample taken in the sea)

APPENDIX B

Analytical calculations

Gain size analysis:
Stokes law relating settling time with grain size is given in the following equation:

$$t = \frac{18\eta h}{g(d_p - d_1)D^2}$$

where: n ή = viscosity (1.002×10^{-2} g/cm/s @ 20°C)
h = height of water (cm)
g = gravity (cm/s^2)
$d_p - d_1$ = difference in density between particle (assumed to be 2.65 g/cm^3) and the liquid (1 g/cm^3)
D = particle diameter (cm).

Charge balance error (CBE):

$$mmol_c/L = \left(\frac{mg/L}{molecular\ weight} \right) \times \text{ionic charge}$$

$$\text{CBE (\% difference)} = \left[\frac{(\sum cations - \sum anions)}{(\sum cations + \sum anions)} \right] \times 100.$$

Table 15: Charge balance for sampling run 1 – water column samples ($mmol_c/L$)

Sample	Cl^-	SO_4^{2-}	DRP	NO_3^+	anions	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	cations	CBE
WP 0	515	55.0	0.003	0.043	570	558.7	9.3	15.5	80.3	0.010	664	7.6
WP 1	540	52.8	0.004	0.037	593	460.0	2.1	18.9	78.7	0.011	560	-2.9
WP 2	572	58.0	0.003	0.007	630	479.1	2.0	15.7	77.9	0.018	575	-4.6
WP 3	875	82.1	0.005	0.001	957	730.4	3.0	20.6	225.4	0.006	979	1.2
WP 4	562	48.4	0.003	0.015	610	447.0	3.0	15.3	43.0	0.007	508	-9.1
WP 5	499	46.2	0.001	0.004	545	399.8	1.9	14.2	72.5	0.007	488	-5.5
WP 6	115	14.1	0.001	0.013	130	99.7	0.0	0.0	17.3	0.002	117	-5.1
WP 7	19.7	6.0	0.001	0.041	25.7	21.61	0.24	2.99	6.07	0.006	30.9	9.2
WP 8	4.35	1.11	0.0003	0.004	5.47	6.61	0.09	0.89	2.13	0.002	9.72	28
WP 9	0.89	0.069	0.0001	0.017	0.98	0.92	0.03	0.14	4.10	0.006	5.19	68
WP 10	0.29	0.039	0.0001	0.005	0.33	0.42	0.02	0.08	2.38	0.003	2.90	79

Table 16: Charge balance for sampling run 2 – water column samples ($mmol_c/L$)													
Sample	**Cl^-**	**SO_4^{2-}**	**DRP**	**NO_3^+**	**HCO_3^-**	**anions**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**NH_4^+**	**cations**	**CBE**
W0	517	19.7	0.0012	0.007	2.56	539	428	9.34	7.09	56.8	0.002	501	-3.6
W1	197	7.54	0.0015	0.007	2.56	207	245	5.45	4.52	33.8	0.002	289	17
W2	524	27.4	0.0013	0.000	3.46	554	469	9.51	7.34	59.1	0.002	545	-0.9
W3	366	12.3	0.0016	0.003	2.16	381	318	6.98	3.67	42.2	0.001	371	-1.3
W4	3.68	0.29	0.0015	0.010	0.68	4.66	4.13	0.10	0.41	0.65	0.01	5.29	6.3
W5	1.91	0.26	0.0010	0.006	0.60	2.78	2.56	0.06	0.40	0.41	0.01	3.43	10
W6	1.36	0.17	0.0008	0.004	0.45	1.99	2.43	0.05	0.37	0.38	0.00	3.24	24
W7	0.68	0.10	0.0007	0.003	0.42	1.20	2.13	0.05	0.24	0.35	0.003	2.77	40
W8	1.11	0.15	0.0005	0.002	0.42	1.67	2.26	0.05	0.24	0.35	0.005	2.89	27
W9	0.29	0.07	0.0001	0.000	0.29	0.66	1.82	0.03	0.15	0.24	0.001	2.25	55
W10	1.72	0.14	0.00001	0.002	0.18	2.04	2.47	0.03	0.09	0.23	0.002	2.83	16

Table 17: Charge balance for sampling run 2 – pore water samples ($mmol_c/L$)													
Sample	**Cl^-**	**SO_4^{2-}**	**DRP**	**NO_3^+**	**$^*HCO_3^-$**	**anions**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**NH_4^+**	**cations**	**CBE**
PW 2	469	15.4	0.004	0.001	3.46	488	484	11.5	6.69	51.2	1.0	554	6.4
PW 3	320	10.5	0.001	0.0005	2.16	333	328	7.42	5.16	38.4	0.6	379	6.5
PW 4	9.57	0.43	0.006	0.001	0.68	11	20	0.45	1.14	2.23	0.1	24.3	39
PW 5	8.80	0.18	0.001	0.001	0.60	9.59	19	0.19	1.09	2.17	0.2	22.8	41
PW 6	5.16	0.18	0.001	0.001	0.45	5.79	13	0.19	1.21	2.32	0.1	16.4	48
PW 7	1.03	0.68	0.039	0.001	0.42	2.17	7	0.17	1.14	2.48	0.3	10.7	66
PW 8	3.56	0.64	0.002	0.027	0.42	4.64	8	0.1	0.87	1.13	0.0	9.7	35
PW 9	4.00	0.32	0.001	0.001	0.29	4.61	7	0.06	0.41	0.83	0.1	8.2	28
PW 10	1.38	0.18	0.002	0.000	0.18	1.74	4	0	0.17	0.29	0.0	4.6	45

*HCO_3 = bicarbonate concentrations assumed to be the same as the in the overlying water column