NUTRIENT DYNAMICS IN AND OFFSHORE OF TWO PERMANENTLY OPEN SOUTH AFRICAN ESTUARIES WITH CONTRASTING FRESH WATER INFLOW

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ABSTRACT

The nutrient dynamics in two contrasting estuaries and in the adjacent nearshore environment along the south-east coast of South Africa was investigated seasonally. Due to an inter-basin transfer of water from the Gariep Dam to the Great Fish River, the Great Fish estuary is a fresh water dominated, terrestrially driven system with an annual fresh water inflow of 250 – 650 x 10^6 m^3 per year. In contrast, the Kariega estuary is a fresh water deprived, marine dominated system with a fresh water inflow estimated at 2.5 – 35 x 10^6 m^3 per year. The reduced fresh water inflow into the estuary is attributed to regular impoundments along the Kariega River. Water samples were collected from surface and subsurface layers along the length of the estuaries as well as from a series of transects occupied in the nearshore environment. Samples were analysed for nitrate, nitrite, ammonium, phosphate and silicate. Temperature and salinity were recorded at each station. A Land-Ocean Interactions in the Coastal Zone (LOICZ) budget was constructed for each estuary to describe the role of ecosystem-level metabolism as either a sink or a source of phosphorus, nitrogen and carbon.

Seasonal variation in physico-chemical properties and nutrient concentrations in the Kariega estuary was minimal due to constant low inflow, while in the Great Fish estuary, concentrations varied in response to changes in flow rate. Nutrient concentrations were consistently higher in the Great Fish estuary than in the Kariega estuary, largely reflecting differences in fresh water inflow. During periods of high flow (32.92 $m^3.s^{-1}$ in the Great Fish River) dissolved inorganic nitrogen (DIN) concentrations in the Great Fish estuary were an order of magnitude higher than those recorded in the Kariega estuary. Results of the LOICZ budgeting procedures revealed that in spite of the contrasting hydrodynamic features, the estuaries behave in largely the same manner – both predominantly sources of nutrients with heterotrophic processes dominating over autotrophic actions and both were net denitrifyers during all surveys. This was, however, due to different sets of processes operating in the two estuaries, namely low nutrient concentrations resulting in microbial activity in the Kariega estuary, and riverine influx of nutrients and phytoplankton combined with a short residence time of the water in the Great Fish estuary.

In the marine nearshore environment, higher nutrient concentrations were recorded adjacent to the Great Fish estuary than offshore of the Kariega estuary. This was due to a surface plume of less saline water leaving the Great Fish estuary, which acted as an 'outweller' of nutrients. Offshore of the Kariega estuary, on the other hand, the nutrient concentrations were characteristic of marine waters due to a lack of fresh water outflow from the estuary. Nutrient concentrations in the marine environment adjacent to the Kariega estuary were, at times, higher than those recorded within the estuary. This observation supports previous statements which suggest that the Kariega estuary is not an 'outweller' of dissolved nutrients and particulate material, but rather an extension of the marine environment.

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DECLARATION

The following thesis has not been submitted to any university other than Rhodes University, Grahamstown, South Africa. The work presented here is that of the authors.

CHAPTER 1 – INTRODUCTION

1.1 GENERAL INTRODUCTION

1.1.1 The Estuarine Environment

Estuarine circulation revolves around the meeting of fresh water from terrestrial drainage systems and saline water from the sea. The fresh water entering at the head of the estuary will result in a seaward movement of water in the surface layer as a result of a barotropic slope in water surface. At depth, however, a baroclinic gradient due to saline water entering through the mouth will result in a landward movement of the dense bottom layer. In the middle reaches, saline water will be entrained into the surface layer through turbulence (Schumann *et al.*, 1999). Implicit in this circulation is an adequate supply of fresh water to maintain a buoyant surface layer and an open connection with the sea in order for saline water to intrude into the estuary through the mouth. An understanding of this estuarine circulation prompted Pritchard's (1967) definition of an estuary as "a semi-enclosed coastal body of water which has a free connection with the open sea and within which seawater is measurably diluted by fresh water derived from land drainage".

In South Africa, the range of potential factors controlling the morphology of estuaries is highly diverse as the sub-continent spans a number of climatic and morphological zones and is subject to a range of marine conditions (Cooper, 2001). Inconsistent factors such as climate, rainfall and coastal morphology mean that many of the 465 independent river outlets are too small to remain permanently open to the sea, often experiencing extended periods without any freshwater inflow, and hence do not meet the requirements of the definition proposed by Pritchard (Morant and Quinn, 1999). In order to incorporate the smaller South African estuaries, Day (1980) proposed a new definition of an estuary as "a partially enclosed coastal body of water which is either permanently or periodically open to the sea and within which there is a measurable variation of salinity due to the mixture of seawater with freshwater derived from land drainage." This definition was later further broadened to include the lagoon and river mouth phases under differing fluvial conditions,

reflecting the substantially different physical environments around South Africa in which estuaries exist.

Estuaries form an interface between the terrestrial drainage system and the sea and are thus susceptible to changes made inland to the parent rivers, anywhere from the source to along the length of the river to the estuary itself. In addition, estuaries can be viewed as landward extension of the marine ecosystem, and are thus also influenced by the sea (Harrison *et al.*, 2000). The tidally driven constant ebb and flow of sea water into and out of an estuary not only influences the distribution of materials within a system, but is also responsible for the export and import of enormous quantities of organic and inorganic matter (Winter and Baird, 1991). The quantity and quality of the materials exported or imported depends on a dominance of either river flow or tidal action. Estuaries which are characterised by reduced freshwater inflow, resulting from water abstraction from impoundments and a resultant decrease in flow rate, are more likely to import material from the sea through a dominance of tidal exchange over river flow e.g. in the Kariega estuary along the Eastern Cape coastline, tidal volume outweighs volume due to river flow by 106:1 (Bate *et al.*, 2002). In fresh water dominated estuaries, on the other hand, transport of dissolved and particulate material is generally seaward (export) due to the net flux of water (Dame and Allen, 1996). An extreme example of this is estuaries which are the beneficiaries of water from an inter-basin transfer, e.g. the Great Fish estuary along the Eastern Cape coastline, in which base flow is sustained even through periods of low rainfall.

It has long been recognised that shallow inshore regions (such as embayments, wetlands and estuaries) produce more material (e.g. inorganic nutrients, particulate carbon, dissolved organic carbon) than can be utilised or degraded within the system, and that excess material is exported to the coastal marine environment where it may contribute to coastal ocean productivity (Winter and Baird, 1991). In 1968 Odum termed this phenomenon the 'outwelling hypothesis'. Two basic approaches can be taken to test the 'outwelling hypothesis'. The first is a direct approach which involves the measurement of the fluxes of water and material across an inlet, and is data rich, labour intensive but when properly designed, provides statistically meaningful observations (Dame and Allen, 1996). The

second is a more indirect approach and is concerned with the compilation of production and consumption budgets for estuarine and marsh systems and imbalances in the budgets are ascribed to either import or export of material from adjacent systems (Baird and Winter, 1989). The mass balance approach's greatest weakness is its difficulty in providing statistically meaningful estimates of transport, but requires less time and expense than the direct approach (Dame and Allen, 1996).

Several previous studies conducted on the import-export function of entire estuarine systems have reported the export of particulate organic material and inorganic nutrients (Baird and Winter, 1989; Dame *et al.*, 1986). More recently, however, the studies of Taylor and Allanson (1995) and Baird and Winter (1992) amongst others have provided evidence that in many micro-tidal estuaries, such as those found along the length of the South African coastline, the 'outwelling hypothesis' does not hold true and material is imported from the coastal environment.

Material in estuaries, whether imported from the adjacent coast or in the process of being either exported or recycled internally, is exposed to a range of diverse conditions. Estuaries are the site of very active biological transformation and loading from catchments, and this combined with the mixing of fresh and salty water creates strong gradients in chemical and physical properties within estuaries (Allanson and Winter, 1999).

1.1.2 The Chemical Structure of Estuaries

The chemical structure of estuaries is determined by four main factors: (1) the quality of inflowing river water; (2) oceanographic events such as upwelling and coastal transport which influence the nutrient status of the tidal prism; (3) the interactions which occur between these two primary sources of nutrients both within the water column and (4) their further modification over the tidally inundated saltmarshes (Allanson and Read, 1995). River flow has been identified as the most critical factor influencing estuaries because of its role in sedimentary and hydrodynamic processes (Joint and Pomroy, 1981; Reddering, 1988; Jordan *et al.*, 1991; Whitfield, 1992; Mallin *et al.*, 1993; Grange and Allanson, 1995;

Bate *et al.*, 2002). Seasonal changes in discharge cause regular and substantial changes in estuarine circulation and water column structure (Allanson and Winter, 1999). The catchment in which a river drains also has an effect on the quality of water entering estuaries, and a strong linear relationship has been demonstrated between the concentrations of inorganic plant nutrients in stream water, particularly nitrogen and phosphorus, and the degree to which land has been cleared for agriculture (Snow *et al.*, 2000).

In a sedimentological context, estuaries are widely regarded as sinks (net accumulation zones) (Cooper, 2001) and receive sediment from three main sources: inflowing rivers, the sea and material generated inside the estuary itself (mainly organic material) (Allanson and Winter, 1999). Sediment moving seaward from rivers must pass through estuaries and vice versa (Cooper, 2001). One would thus expect a progressive shallowing of estuaries over time as tidal inflow and aeolian deposition combine with fluvial and anthropogenic input to fill estuarine channels. This is, however, in theory not the case as floods periodically scour estuarine channels. The frequency of these floods has in recent times, however, diminished as a result of impoundments and increased fresh water abstraction due to the ever pressing domestic, agricultural and industrial demands in South Africa (Grange *et al.*, 2000). The reduction in the frequency of floods as well as a reduction in the volume of water per flood (Whitfield, 1992) has ultimately lead to the following changes in large permanently open estuaries (Whitfield and Bruton, 1989): poor sediment scour, increased sand shoals in lower reaches, channels becoming shallower; reduced riverine input of organic material but possibly high concentrations of fertilizer nutrients from farmlands and the loss of salinity gradient with a tendency towards hypersaline conditions in the upper reaches during droughts. The lower and middle reaches of these estuaries have become marine rather than polyhaline; with a smaller tidal prism due to accumulation of inorganic sediments and reduced tidal exchange of nutrients and organic material between the estuary and the marine environment. On the other hand, inter-basin transfer schemes are used to redistribute water from areas of surplus supply to those where there is a shortage of water, resulting in the introduction of foreign aquatic organisms, changes in flow, alteration of

habitats and ecology and changes in water quality in the receiving rivers and estuaries (Friends of the Earth, 1997).

Biological processes and oceanographic events in the nearshore environment influence the content of water entering estuaries on the flood tide, thereby affecting the chemistry of estuaries. The South African coast is considered to be micro-tidal (spring tidal range between 1.8 and 2.0 m and neap tidal range between 0.6 and 0.8 m) and wave dominated (although a gradient exists from south diminishing up both east and west coasts) (Schumann *et al.*, 1999). The nearshore environment off the Eastern Cape coast is dominated by the oligotrophic south westward flowing warm Agulhas Current. Nutrients in the nearshore are therefore largely derived from drainage of adjacent land (via estuaries and wave action) and renewal within the nearshore environment. Nutrients in the photic zone are assimilated by phytoplankton until such time that the concentrations are insufficient to sustain the requirements of the multiplying phytoplankton. The dead plants then sink, taking with them assimilated nutrients. These are then regenerated by bacterial decomposition of dead cells and tissue in fecal matter below the photic zone. The dissolved nutrients then require a means of transport back to the sunlit photic zone for use by phytoplankton (Pinet, 2000). This occurs in the form of upwelling on the landward edge of the Agulhas Current, where colder nutrient-rich water is brought up onto the continental shelf (Lutjeharms, 2000). In the Eastern Cape, the persistence of upwelled water has been reported at Port Alfred (Lutjeharms *et al.*, 2000), as well as off prominent capes in response to prevailing winds and coastal bottom topography (Schumann *et al.*, 1999). In the absence of upwelling events, in the Eastern Cape where the continental shelf widens offshore, strongly flowing currents, often stormy waves and persistent winds result in a great deal of turbulence which results in a well mixed water column on the shelf. This allows nutrients from the sea bottom to rise to the surface and become available to plants (Pinet, 2000).

The interactions in the water column which occur when fresh water from the rivers meet with saline water from the sea, involve complicated mixing processes. As stated earlier, it is well known that the quality of inflowing freshwater has an important control on nutrient availability in estuaries. As part of the hydrological cycle, water in the form of rain falls on

the land and moves with the help of gravity down slope towards the sea. In South Africa, and particularly the Eastern Cape, many of the estuarine catchments have been impacted upon, whether by clearing and fertilizing for agriculture, direct grazing or other human industrial intervention. Water falling in these catchments moves over the fertilized surfaces, gradually collecting in streams and rivers, or as ground water moving beneath the surface. As a universal solvent and a fluid, water collects a diversity of dissolved and particulate materials. Upon reaching the coast, the inexorable flow of water and transport of materials towards the ocean becomes complicated by numerous physical and biological processes that come into play as estuaries interact with the sea (Dame and Allen, 1996). Here strong gradients in chemical and physical properties, such as salts and temperature are a result of complicated mixing processes. The salty water desorbs ions from particles previously suspended in low ionic strength river water, so that concentrations of certain dissolved ions increase (Valiela, 1980). The increased salinity fosters aggregation of organic and inorganic particulate matter, which act as nucleation centres for the precipitation of dissolved organic material (Hollibaugh and Wong, 1999). These mixing processes taking place in estuaries are the reason estuaries are such important sites for biotic and abiotic transformations of inorganic and organic matter. Many of these changes take place in saltmarshes.

Saltmarshes perform many important biogeochemical functions such as sediment stabilization and bank protection; nutrient removal, storage and release; and transformations of inorganic nutrients to organic forms (DeBusk, 1999). Tidal saltmarshes provide a significant amount of ecological stability to associated ecosystems, acting as giant filters by removing and transforming large quantities of particulate and dissolved materials from tidal waters and gradually releasing nutrients over time, generally decreasing bioavailability downstream (Dame and Allen, 1996). Plant biomass decays on saltmarsh surfaces and its energy enters the food chain as detritus. Saltmarshes are a sink for nutrients but only in the growing season, where they reduce eutrophication by absorbing nitrogen and phosphorus from polluted water, but re-release the nutrients during decomposition, with potentially adverse effects (Adams *et al.*, 1999). Here changes in water level and degree of tidal flushing become important in determining the quantity of

nutrients released. Saltmarshes are generally considered to depend on recycled nutrients rather than those carried in fresh water (Adams *et al.*, 1999). However, rivers deposit muddy sediment and silt in saltmarsh areas from where the nutrients are derived, once again highlighting the importance of fresh water flow into estuaries.

1.1.3 Estuarine and Nearshore Nutrients

Estuaries are a major source of nutrients to the coastal marine environment. Other sources include the adjoining ocean (through upwelling), the atmosphere (in the form of precipitation), local water-column production and sea bed recycling of biologically produced organic compounds (Tett *et al.*, 2003). Transport and transformation in these areas are very active involving use, release and re-use of nutrients already in the environment. Much of the regeneration of organically bound nutrients to mineral nutrients takes place in the marine and estuarine sediments, which are the site of substantial biological and chemical activity (Valiela, 1980; Allanson and Winter, 1999). Microbial communities in these shallow coastal sediments are important sites for the mineralization of organic matter (Herbert, 1999). The shallow depth of the coastal zone means sinking particles do not remain exposed to microbial and animal consumers for long in the water and most organic particles fall to the bottom and are mineralised there (Valiela, 1980). Transformations in the sediments are mediated principally by bacteria and the resulting gradients of nutrients result in their release to the overlying water column (regeneration) where they may be taken up by plants in primary production, or adsorption (burial) into deeper sediments (Herbert, 1999). These two processes, along with uptake by phytoplankton, are the most significant sink for dissolved nutrients (Tett *et al.*, 2003).

1.1.3.1 Nitrogen

Nitrogen is a key constituent of all living matter (Herbert, 1999). Its availability is essential for primary production in plants and is generally considered to be one of the major factors limiting eutrophication in estuarine and coastal waters (Herbert, 1999). Nitrogen can occur in a variety of oxidation states from +5 (nitrate) to -3 (ammonium). The conversion of

nitrogen through these various oxidation states is a biologically controlled process (Tett *et al.*, 2003). The concentration of nitrogen is determined principally by inputs from fluvial discharge and from exchange across the sediment-water interface. Increased nitrogen concentrations can arise from anthropogenic inputs into fresh and marine water, namely sewage discharge, addition of agricultural fertilizers and organic industrial wastes (DWAF, 1996). Irrespective of its origin, all living matter contains nitrogenous macromolecules (e.g. nucleic acids, proteins and polyamino sugars) and these become available upon death and sinking of cells to decomposer organisms. In the marine environment, concentrations are therefore controlled either through delivery from the adjacent land (principally via estuaries) or enrichment from below as surface waters are typically depleted by phytoplankton uptake in favourable light conditions.

The amount of nitrogen mineralised by benthic flux and the ratio of ammonium, nitrate, dissolve organic nitrogen and nitrous oxide/dinitrogen released from the sediment to the overlying water column is determined by the quality (N:C ratio), quantity, spatial distribution of degradable organic matter and the diffusibilty of the decomposition products. These are determined, in turn, by the presence of rooted macrophytes and infauna and the concentrations of oxygen, ammonium and nitrate already in the water column (Herbert, 1999). Phytoplankton are capable of taking up a wide range of nitrogen forms from solution, but generally require reduced nitrogen and are frequently considered to prefer ammonium to nitrate, which is driven passively by diffusion into the cell. The acquisition of nitrate, alternatively, is an energetically expensive two-step enzymatically driven process (Tett *et al.*, 2003). Some species of phytoplankton, in particular a specialised group of prokaryotes which possess the enzyme nirogenese (Herbert, 1999), are capable of fixing gaseous nitrogen (N_2), dissolved in water, into ammonia and hence into organic nitrogen. This process, called nitrogen fixation, is energy demanding due to the strength of the dinitrogen (N-N) bond, and is regulated by carbon availability and other physico-chemical factors. Rates of nitrogen fixation vary greatly, but are generally low. There is a tendency for richer waters to support higher rates of this process (Valiela, 1980).

Whilst nitrogen fixation fixes nitrogen from an external source, the other steps of the nitrogen cycle occur within the system, as nitrogen is converted from one form to another depending on various biotic and abiotic factors. The release of ammonium from nitrogenous matter is known as ammonification (Herbert, 1999). Depending on the structural complexity of the organic matter, this can be either a simple deamination reaction or a complex series of metabolic steps involving a number of hydrolytic enzymes during which nitrogen-containing polymers are broken down into their mono-metric sub-units (Herbert, 1999). Not all ammonium produced during deamination of organic nitrogen in sediments is available to primary producers. A portion, which varies depending on the physico-chemical characteristics of the sediments, may be oxidised to nitrate in the surficial oxic zone. This process of ammonium oxidation, known as nitrification, provides a link between the reduced and oxidised sides of the nitrogen cycle, and plays a pivotal role in generating a source of nitrate for denitrifying bacteria (Herbert, 1999). Nitrification is a two stage process. The first step, controlled by ammonia oxidising bacteria produces nitrite which in turn is oxidised to nitrate catalysed by nitrite oxidisers in the second step. The microorganisms that carry out these reactions do so to obtain energy stored in the reduced nitrogen atoms (Valiela, 1980). Whereas nitrification involves the oxidation of reduced nitrogen, denitrification is a reductive process, whereby heterotrophic bacteria utilise nitrate as a terminal electron acceptor and reduce it to either gaseous products (denitrification), or ammonium (nitrate ammonification). Denitrification is a key process in the sediment nitrogen cycle as it decreases the amount of nitrogen available to primary producers as the end products, nitrous oxide (N_2O) and dinitrogen (N_2) diffuse into the atmosphere (Herbert, 1999).

1.1.3.2 Phosphorus

Phosphorus is an essential macronutrient which, with nitrate, is considered to be the principal nutrient controlling the degree of eutrophication in aquatic systems. It is accumulated by a variety of living organisms where it forms part of DNA molecules, molecules that store energy (ATP and ADP) and fats of cell membranes (DWAF, 1996). Phosphorus carried in surface waters may be in either a dissolved or particulate (suspended

sediment) and may be either organic or inorganic (primarily in solution as orthophosphate, a nutrient to plants, or as phosphate containing minerals suspended in the water column) (DeBusk, 1999).

Natural sources of phosphorus include the weathering of rocks and subsequent leaching of phosphate salts into surface waters, in addition to the decomposition of organic matter. Elevated levels of phosphorus may result from point-source discharges such as domestic and industrial effluents, particularly waste products from manufacturing phosphoric acid for fertilizer production, and non-point sources such as atmospheric precipitation, urban run-off, and drainage from agricultural land, in particular land from to which fertilizers have been applied (DWAF, 1996). Phosphorus concentrations in the estuarine and marine environment are controlled by a number of biotic and abiotic factors. The sediments are, as with nitrogen, the site of active retention, cycling and release. Diffusion between the overlying water column and the soil solution (porewater) is determined by concentration gradients. Biological control of phosphorus concentrations takes place in the form of assimilation by bacteria and phytoplankton (under favourable light conditions) of orthophosphate taken up from the surface of organic detritus and suspended particles, which are then consumed by filter feeders and excreted as inorganic phosphorus (Sobehrad, 1997). Sedimentation, decomposition and burial occur at varying rates, during which time organic matter is broken down by micro-organisms to smaller organic molecules (particulate and dissolved) and finally to orthophosphates which are either used by plants and micro-organisms or diffuse back into the water. An inorganic buffering effect maintains a relatively constant level of phosphorus concentrations due to adsorption of phosphorus from the sediments (Sobehrad, 1997). Orthophosphate ions are adsorbed by clays and iron or aluminium oxides (chemisorption) in the soil, and precipitation of phosphate with either iron or aluminium oxides or dissolved calcium forms solid compounds in the soil or water column, which may represent relatively long term storage of phosphorus as regeneration is very slow due to the stability of the complexes formed (DeBusk, 1999). This continuous two-step process of release and adsorption by the factors mentioned maintains an equilibrium between the water column and the sediments (Winter and Baird, 1991). The flow regime is also a major factor in the mobility, availability and

spatial distribution of phosphate within an estuary, settling into the sediments and being readily taken up during periods of low fluvial discharge and elevated during rainfall and associated high flow events due to flushing and resuspension of the sediments (DWAF, 1996). Although no process exists whereby phosphorus is removed from the aquatic environment (such as nitrogen during denitrification), saltmarshes can potentially represent a significant temporary sink for phosphorus, slowly releasing it down stream to the lower reaches of estuaries and the marine nearshore environment over time (DeBusk, 1999). As with nitrogen, phosphorus is typically depleted in the euphotic zone in the marine environment, increasing in concentration with depth due to a steady down drift of organic debris and faecal pellets (containing assimilated phosphate), which subsequently require a means of transport back to the surface zone.

1.1.3.3 Silicate

Silicate is a bio-limiting nutrient and a major constituent of diatoms which use silicate to encase their cells in a wall impregnated with silica (silica shell) (DWAF, 1995). The processes involved in the silicon cycle are fewer than that of nitrogen or phosphorus, comprising essentially only river (through drainage of silicate-rich basins) and ocean inputs, removal of dissolved silicon by diatoms and then dissolution from these cell walls on the sea bed upon death and settling (a slow process) (Tett *et al.*, 2003).

These nutrients, essential to primary production in coastal waters, are derived principally by erosion of adjacent land, particularly where anthropogenic activities have increased nutrient availability, and delivered via estuaries to the nearshore. Here, the organic matter made and chemical elements harnessed by phytoplankton support a pelagic and benthic food web leading from herbivorous protozoa and small invertebrates to larger carnivorous invertebrates to fish, sea mammals and birds. The importance of the quality of water delivered by estuaries to the marine nearshore environment thus cannot be over-looked.

The purpose of this project, was therefore to investigate the effect of anthropogenic activities on estuaries, namely the decrease of fresh water inflow through impoundment and

abstraction of water and the increase of flow through additional fresh water input, and ascertain whether these activities affect the concentrations of nutrients within the estuaries as well as the delivery of nutrients to the marine nearshore environment.

1.2 AIMS

The study will attempt to establish the following:

1. The concentration levels and distribution of nutrients (nitrate, nitrite, ammonium, phosphate and silicate) as well as the physico-chemical water parameters temperature and salinity throughout the length of two permanently open South African estuaries, and how anthropogenic alterations to flow affect these estuarine parameters.
2. The degree of influence of the estuaries on the adjacent marine nearshore environment off the estuaries, including:
    a.) how similar the estuaries are to the marine nearshore environment?
    b.) the spatial distribution of this influence?
3. The nutrient status of the two estuaries using Land-Ocean Interactions in the Coastal Zone (LOICZ) biogeochemical models over the various seasons of the year and whether the nutrient levels are within acceptable range according to the South African Water Quality Guidelines (SAWQG).

1.3 STUDY SITE AND DESCRIPTION

The study was conducted in and offshore of two estuaries along the Eastern Cape coastline of contrasting flow characteristics, the Kariega and the Great Fish estuaries. Although both the Kariega (33^{o} 41' S; 26^{o} 42' E) and the Great Fish (33^{o} 30' S; 27^{o} 09' E) estuaries are permanently open, supra-tidal barred systems according to Harrison *et al.* (2000), the mean annual runoff of the two are 2.5 - 35 x 10^{6} m^{3} per year and 250 - 650 x 10^{6} m^{3} per year, respectively (Grange and Allanson, 1995). These values represent opposite ends of the fresh water flow scale in Eastern Cape estuaries, resulting in the Kariega being tidally dominated, and the Great Fish estuary river dominated (Harrison *et al.*, 2000). These

opposing patterns of river flow are determined not only by the size of the catchment but also the extent of river regulation.

1.3.1 Kariega Estuary and Marine Nearshore Environment

The Kariega River has a much smaller catchment than the Great Fish River, with a size of 688 km^2 (Grange *et al.*, 2000) (Figure 1.1). The Kariega estuary has been described as a homogeneous marine dominated system with generally low nutrient concentrations (oligotrophic), low turbidity and a well-mixed water column throughout the tidal cycle (Grange and Allanson, 1995; Froneman, 2000; Bate *et al.*, 2002). The estuary is 18 km long with a narrow upper channel (40 – 60 m), which widens to 100 m in the lower reaches where it is bordered by sandflats and saltmarshes. The importance of these saltmarshes on the exchange of carbon, nitrogen and phosphorus with the adjacent estuary has been discussed by Taylor (1987). The estuary is considered shallow, averaging less than 3.0 m deep (Bate *et al.*, 2002). The river has been severely impounded by three dams, the largest being Settlers Dam about 50 km from the mouth, and several farm weirs (Figure 1.1). The construction of the dams has resulted in little to no flow into the estuary, except in times of extreme flood. As a consequence, hypersaline conditions may develop in the upper reaches of the estuary. The mouth is, however, maintained permanently open by the scouring action of the tides, which outweigh the volume of inflowing river water by 106:1 (Bate *et al.*, 2002). The Kariega estuary enters the sea alongside the coastal resort town of Kenton-on-Sea. Residential development, mostly in the form of retirement and holiday housing, is primarily confined to the mouth and lower reaches of the system. No industry is located along the estuary but several storm water drains enter directly into the system, the largest located at the mouth. The estuary also services the Kariega Park private nature reserve in the upper reaches, as well as numerous farmers involved in either agriculture (mostly chicory, a dry crop) or livestock grazing (cattle farming takes place on both banks in the middle and upper reaches).

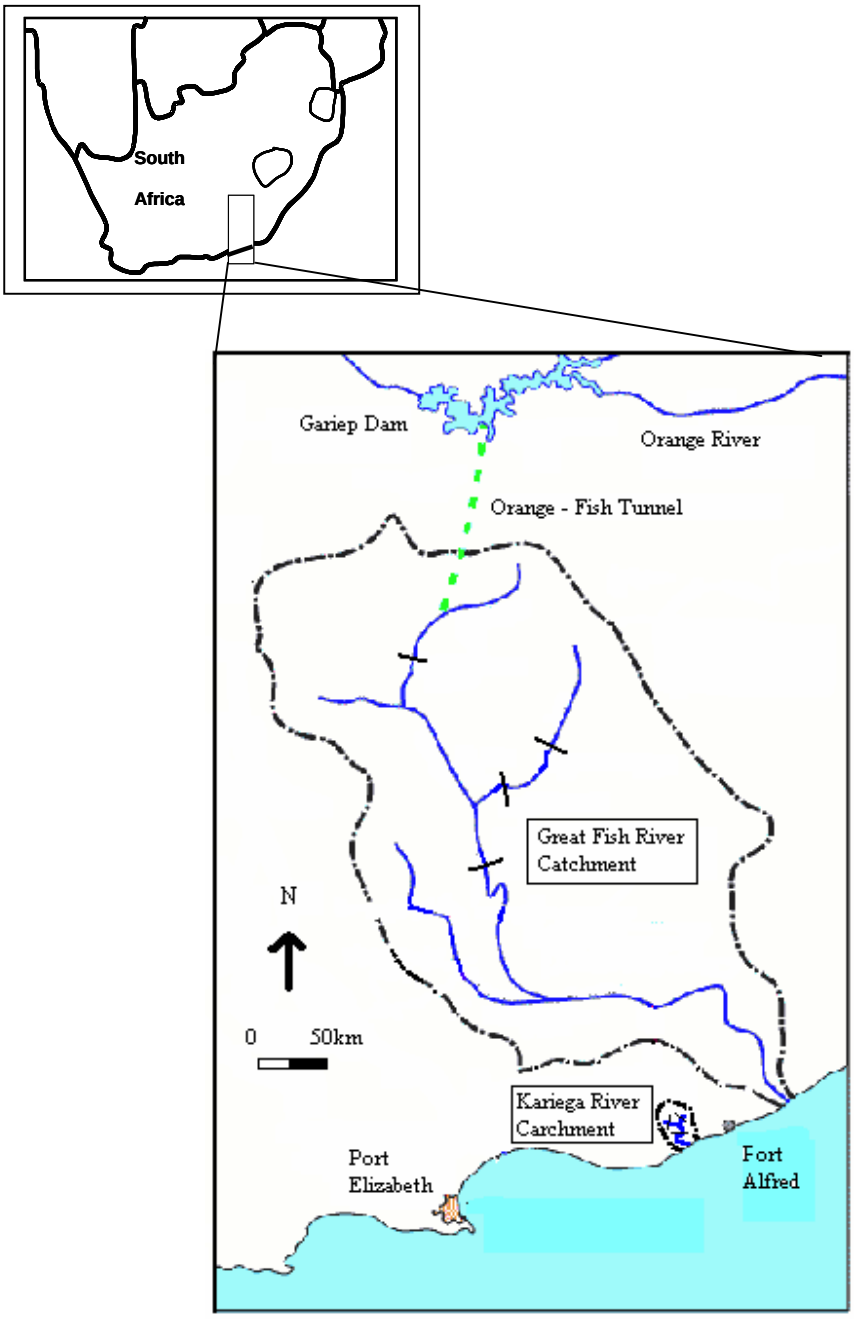


Figure 1.1 Map showing difference in catchment sizes of the Kariega and Great Fish Rivers, as well as regulation by dams, indicated as a bar across the river. There are three dams in the Kariega River catchment. The Orange – Fish Tunnel, linking the Gariep Dam to the Great Fish River, is shown.

Offshore of the Kariega estuary the bottom topography consists of broken reef, sandy gullies and pinnacles rising up to and sometimes, depending on tide and swell conditions, breaking the surface. 'East' and 'west rock', on the north-east and south-west of the mouth, rise from a depth of roughly 12 m and are exposed on the surface, with numerous other pinnacles around them lying at various depths below the water. Between these two areas and opposite the mouth, a section of broken sometimes sand covered reef can be found. The eastern bank of the mouth is rocky with mostly sandy beach stretching west to the rocky eastern bank of the Bushmans estuary, a permanently open system approximately 2.5 km south-west of the Kariega estuary.

1.3.2 Great Fish Estuary and Marine Nearshore Environment

The Great Fish River has a much larger catchment area of 30 427 km^2 (Allanson and Read, 1995) (Figure 1.1). The Great Fish estuary (situated approximately 50 km from the Kariega estuary) has been described as a stratified system (Grange and Allanson, 1999) with elevated turbidity and nutrient concentrations (Froneman, 2000). The estuary is approximately 8 km long and 30 m wide in the main channel of the mouth region, where it is restricted by the presence of extensive sand banks. It can, however, be up to 200 m wide following flood events. The lower to upper reaches can reach depths of 3-6 m, but the estuary is generally shallow, averaging between 1 and 2 m (Cowley and Danial, 2001). Prior to 1977, the natural flow regime of the river exhibited seasonal extremes including periods of zero flow, distinct pools and periods of mouth closure (Bate *et al.*, 2002). In 1977, however, an 82 km tunnel was opened between the then H.F. Verwoerd Dam (now the Gariep Dam) on the Orange River and the upper reaches of the Great Fish River system (Figure 1.1), designed to supply water, primarily for irrigation, to the Great Fish River valley. The mean annual runoff of the upper river has increased by between 500 and 800 per cent, but mainly because of abstractions for irrigation and transfer to the Sundays River via a canal below a regulating reservoir (Elandsdrift Dam), the mean annual discharge of the lower river into the estuary has changed little, although seasonal variations have been considerably reduced (O'Keefe and de Moor, 1988). In addition, the inflow of low salinity water from the Orange River has diluted the highly mineralized Great Fish River water.

The system is now terrestrially driven, with marine sediment only occurring close to the mouth (Grange *et al.*, 2000). Due to the sustained flow, the estuary has been described as meso-eutrophic (Grange and Allanson, 1995). The fresh water inflow is also responsible for the allochthonous import of detritus material increasing inorganic turbidity (Grange and Allanson, 1995), which plays a part in limiting phytoplankton production (Grange and Allanson, 1995; Mallin *et al.*, 1999; Froneman, 2000; Grange at al, 2000; Nozais *et al.*, 2001). Although no formal housing development has occurred along the banks of the estuary, it services a small subsistence fishery and associated 'shacks'. Farming activities consist mainly of livestock (cattle, sheep and goats) ranching, while some of the low-lying floodplain areas along the banks of the river and estuary have been cultivated (mostly maize). In addition, some of the arable lands in the high-lying coastal region are cultivated with pineapple crops. There is no industry along the banks of the estuary.

Offshore of the Great Fish estuary, the bottom topography consists of fewer pinnacles than offshore of the Kariega estuary, and more extensive sand banks, particularly opposite the mouth. The sand is, however, interspersed with broken reef, and an often exposed pinnacle can be found 250 m north east of the mouth 250 m offshore. The eastern bank of the estuary is bound by a rocky platform (referred to as 'bat cave' by the local fisherman), with a mixture of sand covered and exposed rocks found extending south-west to Rocky Point, and further to Little and Great Fish Points.

Due to the opposing nature of the river flow entering the Kariega and Great Fish estuaries, they have been compared in numerous studies in an attempt to better understand the influence of river flow on the productivity and biodiversity of South African estuaries. These studies (Allanson and Read, 1995; Grange and Allanson, 1995; Allanson and Winter, 1999; Froneman, 2000; Grange *et al.*, 2000; Bate *et al.*, 2002) have focused on a variety of biotic and abiotic factors. In addition, Land-Ocean Interactions in the Coastal Zone (LOICZ) budgets for both the Kariega (1984 data) and the Great Fish estuaries have previously been calculated (Dupra *et al.*, 2002). What is apparent from this Kariega estuary study, and others mentioned previously, is that in the past the Kariega River exhibited

periods of high flow in response to rainfall events, which was not the case for the duration of the present study (even after the occurrence of heavy rains).

The area of the Eastern Cape in which the Kariega and Great Fish estuaries are located occurs in the warm temperate climatological region (de Villiers *et al.*, 1999), the transition zone between summer thunderstorm rainfall (eastern) and winter frontal rainfall (western) regions. The area thus experiences irregular rainfall occurring at various seasons throughout the year, but long term records indicate a bimodal rainfall pattern with peaks in autumn (March) and spring (September) (Bruton and Gess, 1988). Due to anthropogenic alterations, however, the flow rate in both rivers is not determined by rainfall within the catchment. The relationship between monthly rainfall recorded in the Port Alfred region and mean monthly flow rates in the Kariega and Great Fish Rivers over a ten year period from June 1994 to May 2004 is shown in Figures 1.2 and 1.3, respectively. Using the Spearman correlation (r_s) coefficient categories as in Grange and Allanson (1995), r_s results of 0.31 for the Kariega River and 0.42 for the Great Fish River indicate a "possible relationship, but one which may not be significant" ($0.3<r_s<0.6$). The absence of significant relationships emphasises the anthropogenic impacts (impoundments and an inter-basin transfer of water) within the two river catchments.

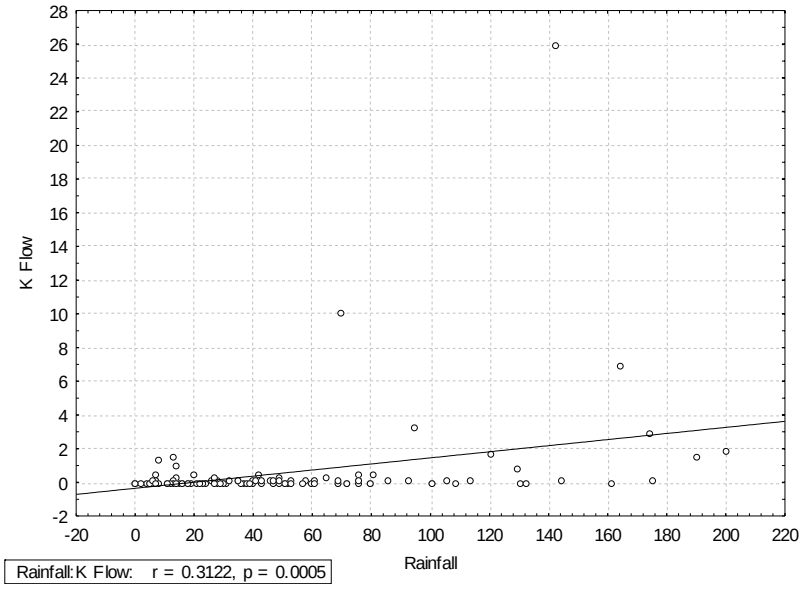


Figure 1.2 Graph displaying relationship of monthly rainfall (mm) at Port Alfred and mean monthly flow rate ($m^3.s^{-1}$) in the Kariega River form June 1994 to May 2004. The best fit line and Spearman's correlation co-efficient (*r*) are shown.

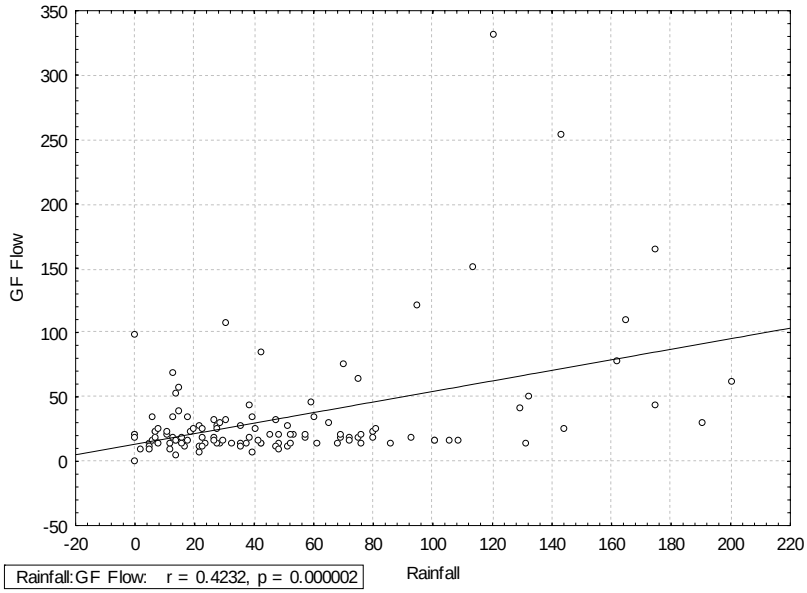


Figure 1.3 Graph displaying relationship of monthly rainfall (mm) at Port Alfred and mean monthly flow rate ($m^3.s^{-1}$) in the Great Fish River form June 1994 to May 2004. The best fit line and Spearman's correlation co-efficient (*r*) are shown.

1.4 LAND-OCEAN INTERACTIONS IN THE COASTAL ZONE (LOICZ)

The results of the seasonal surveys were used to construct LOICZ biogeochemical budgets. LOICZ budgets allow us to gain a better understanding of what changes are occurring to the key elements carbon, nitrogen and phosphorus in the coastal zone.

1.4.1 LOICZ Overview

The ultimate goals of LOICZ are to create regional and global syntheses and estimates on whether the coastal zone is accumulating organic matter. This is achieved by addressing carbon fluxes in an attempt to understand how the coastal zone affects material fluxes through biogeochemical processes, and characterize the relationship of those changes to environmental change, including human interaction (Dupra *et al.*, 2002). It has, however, proved more efficient to approach these estimates of carbon fluxes through fluxes of nitrogen and phosphorus, using the Redfield ratio. This involves the development of horizontal and, to a lesser extent, vertical material flux budgets and their dynamics ranging in scales from coastal systems such as estuaries and embayments, to regional seas and continental oceanic margins, based on the understanding of biogeochemical processes, data from coastal ecosystems and habitats and the human dimension (Dupra *et al.*, 2002). This is achieved by constructing many local budgets, following a budgeting procedure which is as internally consistent as possible within the limitations of available data. These budgets are then compared to seek patterns of similarity or difference in material fluxes. Accepted statistical procedures are then used to extrapolate the flux calculations from budgeted regions to unbudgeted regions, in order to improve our understanding of material fluxes to and from the coastal zone of the world's oceans (LOICZ, 2004). In doing so, material flux models are scaled up to evaluate coastal changes at spatial scales to global levels and eventually, across temporal scales to address global questions such as, is the coast a sink or a source for carbon dioxide, what are the mass balances of carbon, nitrogen and phosphorus in the coastal zone and how are humans altering these balances, with what consequences (LOICZ, 2004)?

1.4.2 LOICZ Model

The LOICZ method makes use of biogeochemical budget models that provide robust estimates of integrated system performance (Gordon *et al.*, 1996). A model is any simplified description or abstraction of a process. In science, models are tools that help us conceptualize, integrate and generalize knowledge. Natural systems such as ecosystems are usually very complex, and models vary greatly in the degree of simplification away from that complexity. 'Budget models' are simple mass balance calculations of specific variables (such as water, salt, sediment, C, N, P etc.) within defined geographic areas and over defined periods (LOICZ, 2004). The LOICZ Biogeographic Modelling Guidelines, devised by Gordon *et al.* (1996), state that a single general approach be used for building budgets to describe the coastal marine environment, in order to maximize comparability among budgets (David *et al.*, 2000). The model can be broken down into four parts:

Water budget – where fresh water inflow and evaporative outflow are balanced by a residual flow in order to maintain a constant volume;

Salt budget – salt must be conserved so salt flux not accounted for by salinity differences must be balanced by mixing;

Budgets of non-conservative materials – deviations of dissolved material concentrations from predictions based on water and salt budgets are quantitatively attributed to net non-conservative reactions of materials within the system; and

Stoichiometric relationships – used to link nutrient fluxes determined in the first three steps using the Redfield ratio.

A more detailed description of the methods used for calculating the budgets can be found in Chapter 2. One of the strengths of the models is that it has fairly simple data requirements:

- An accurate description of the system of interest, including location, average depth, area, catchment size of basin and seasonality,
- Data on the salinity of the system and adjacent ocean salinity,
- Volume of fresh water input and output (i.e. precipitation, evaporation, river flow, groundwater flow),

- Concentration of dissolved inorganic nitrogen and phosphorus for the system, the adjacent ocean, fresh water sources or other sinks or sources. (David *et al.*, 2000)

In addition, secondary data or data published in the literature can be employed to generate budgets. The key assumption used in compiling the budgets is that while carbon and nitrogen have gaseous phases and can be lost from the aquatic environment through diffusion, phosphorus does not, and is therefore conserved. This means the difference between the estimated fluxes of phosphorus into and out of a system is a measure of the net balance between production and respiration (Tett *et al.*, 2003). The system is ultimately described as either auto- or heterotrophic and a nitrogen fixer or denitrifyer and a sink or a source for dissolved inorganic phosphorus (DIP) and dissolved inorganic nitrogen (DIN).

1.4.3 LOICZ Community

The LOICZ project is a broad and diverse community of individuals who have an interest in the contribution that science can make to the sustainable management of the coastal zone. Whilst it is not the objective of LOICZ to undertake coastal zone management, a clear goal is to provide a sound scientific basis for the future sustainable use and integrated management of these environments under conditions of global change (LOICZ, 2004). LOICZ is a core project of the International Geosphere-Biosphere Program (IGBP): A Study of Global Change, of the International Council of Scientific Unions.

There is a large amount of existing and recorded data and work in progress around the world on coastal habitats at a variety of scales, and LOICZ has attempted to develop a scientific network of researchers to integrate the expertise and information in order to deliver scientific knowledge that addresses the overall goals (Dupra *et al.*, 2002). LOICZ encourage all researchers making use of the LOICZ biogeochemical modelling approach to publish their results. Over 1500 peer-reviewed publications have resulted from the LOICZ project, as well as a synthesis of work on global change in the coastal zone (LOICZ, 2004), in an ongoing attempt to answer the current working objective: “to asses, model and predict

the change in and resilience of the global coastal zone under multiple forcing and as an integral part of the Earth System, including the contribution of, and consequences for human use in the coastal zone".

CHAPTER 2 – MATERIALS AND METHODS

2.1 SAMPLING

Sampling was conducted seasonally (i.e. four times a year) to correspond with seasonal changes in rainfall and water temperatures. Surface and subsurface samples were collected from the two estuaries and their corresponding marine nearshore environments over three consecutive days on each of the sampling trips in an attempt to reduce time between the delivery of nutrients from the sampled estuary and dispersal in the nearshore environment. Sampling took place on an outgoing tide on each occasion in order to maximise the effect of the influence of the outflow on the nearshore environment.

Sampling took place on the following days

- June: 22nd – Great Fish marine environment
  23rd – Great Fish estuary and Kariega estuary
  24th – Kariega marine environment

- September: 21st – Great Fish marine environment
  22nd – Great Fish estuary and Kariega estuary
  23rd – Kariega marine environment

- December: 1st – Great Fish marine environment
  2nd – Great Fish estuary and Kariega estuary
  3rd – Kariega marine environment

- March: 8th – Great Fish marine environment
  9th – Kariega marine environment
  10th – Great Fish estuary and Kariega estuary

Note, the order of the March sampling was adjusted to avoid impending weather and sea conditions which would have made sampling difficult and resulted in a great deal of stations being lost due to wave action in the vicinity of the station positions.

Temperature and salinity were measured using a calibrated YSI 600XL Water Quality Monitor. At each station approximately 60 ml of water was collected in a plastic sample bottle from the surface using a bucket and from approximately 1 m off the bottom of the estuaries and from 5 and 10 m where possible in the marine nearshore environment using a messenger triggered 2.5 *l* General Oceanics Niskin water sampling bottle. A General Oceanics Niskin water sampling bottle consists of a PVC tube with a spring loaded cap on either end. A length of rope was attached to the bottle, which ran past the release mechanism for the spring loaded caps. A weight was attached to the bottle which was then lowered to approximately 5 m from the surface allowing for drift in the current. A brass weight or 'messenger' was then dropped down the line triggering the release mechanism causing the caps on either end of the bottle to close. The water sample was collected once the bottle had been returned to the surface, by being drained through a tap at the bottom of the bottle. The process was repeated for the 10 m sample.

Samples were taken along the length of the two estuaries. In the case of the Kariega estuary, the highest station was occupied below a causeway restricting the flow of the ebb and flood tides further up and back down the estuary. Ten stations were occupied along the length of the estuary positioned in the vicinity of prominent features such as stream inlets or saltmarshes. The last station occupied in was the mouth region. The river sample was taken above the causeway, feeding the estuary during times of elevated flow rates. Figure 2.1A shows the station positions in the Kariega estuary. In the case of the Great Fish estuary, samples were taken from the fresh water entering at the head on the surface and bottom, through fresh/salt water interface and down to a station occupied in the mouth region. Eight stations were occupied at approximately 1 km apart along the length of the estuary, with one additional sample taken in the fresh water approximately 2 km above station 1. Figure 2.1B shows the station positions in the Great Fish estuary. Stations denoted with ‘A’ in the results represent surface waters, while those labeled ‘B’ in the

results represent bottom waters. The bottom water was collected from approximately 50 cm from the bottom of the estuaries.

For the marine nearshore environment surveys, a grid was set up adjacent to each estuary prior to sampling using Garman GIS software. Figure 2.2 is a schematic representation of the grid occupied within the nearshore environment adjacent to the two estuaries. The grid consisted of five transects 500 m apart beginning 500 m north east of each mouth and ending 1500 m south-west of the respective mouths. Transects began in a line roughly parallel to the shoreline and contained four stations each, 200 m apart and beginning 250 m offshore. One additional station was placed between each transect 250 m offshore. A GPS was used to locate the station positions during each survey. Some stations had to be abandoned all together because of proximity to consistently breaking waves and rocks, while others were lost on any particular survey because of the rough and unpredictable nature of the sea in the nearshore environment. The majority of 10 m samples at the stations closer to the shore were not collected due to the shallow nature of the water. Stations denoted ‘A’, ‘B’ and ‘C’ in the results represent surface, 5 and 10 m station, respectively.

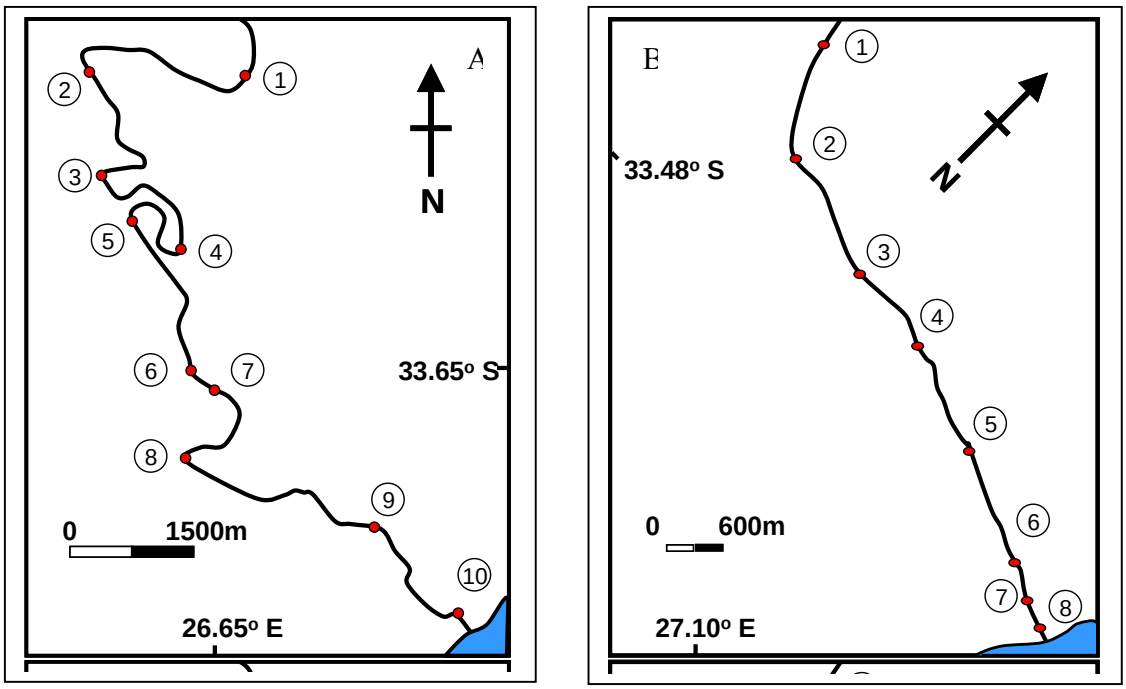


Figure 2.1 A. Station positions in the Kariega estuary. B. Station positions in the Great Fish estuary.

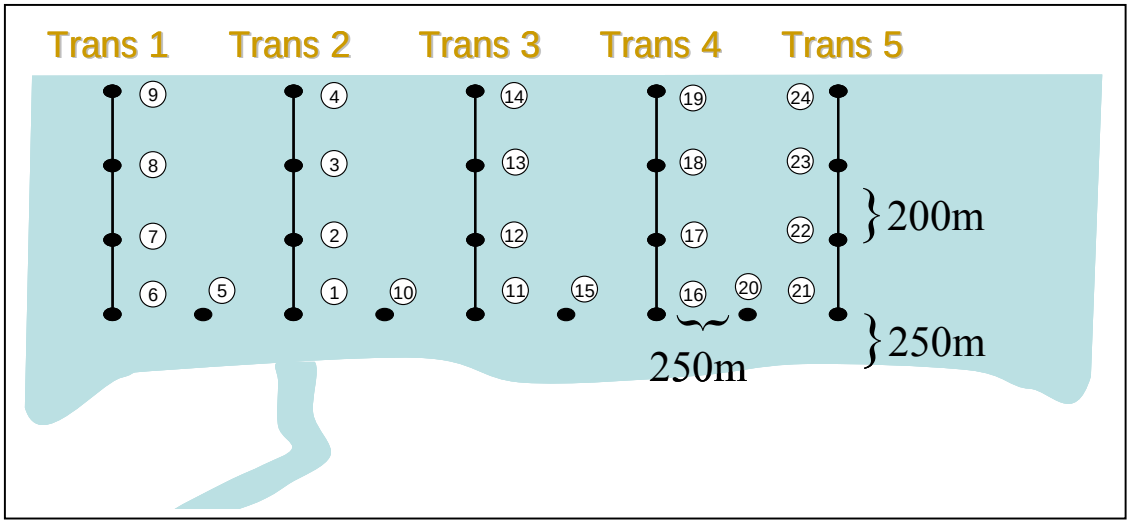


Figure 2.2 Station positions in the Kariega and Great Fish nearshore marine environments.

2.2 ANALYSIS

Samples were filtered on site using a syringe and 25 mm GF/C filters and kept chilled for analysis of phosphate, ammonium and silicate later the same day. Separate samples were frozen for analysis of nitrate and nitrite at a later stage. For the manual analysis of phosphate, ammonium and silicate, pseudo-replicates were used, while a single sample was used for the nitrate and nitrite determination.

2.2.1 Nitrate/Nitrite

Nitrate and nitrite were analysed colourmetrically using a Lachat Instruments QuickChem® continuous flow autoanalyzer. The method was calibrated using 6 known standards made up from sodium nitrate and deionized water. The pre-filtered samples were passed through a column containing granulated copper–cadmium to reduce the nitrate to nitrite. The nitrite was determined by diazotizing nitrite with sulfanilamide and coupling it with N-(1-napthyl)-ethylenediamine hydrochloride to form a highly coloured azo dye. This was measured colourmetrically at a wavelength of 540 nm. The process was then repeated without using the cadmium column to determine the original amount of nitrite in the sea water. The concentration of nitrate in the sample was then determined by the following equation,

nitrate = nitrite + nitrate (after reduction) – nitrite (before reduction)

2.2.2 Phosphate

Phosphate concentrations were determined manually. A 5 ml standard, 5 ml distilled water blank and three pre-filtered 5 ml samples from each depth at each station were pipetted with 0.5 ml of mixed reagent consisting of 10 ml ammonium molybdate solution, 25 ml diluted sulphuric acid solution, 10 ml ascorbic acid solution and 5 ml potassium antimonyl-tartrate solution, as described by Grasshoff *et al.* (1983). The samples were then vortexed, left for a minimum of 5 minutes and a maximum of 2 hours, in which time a colour developed which was proportional to the concentration of phosphate in the sample. This

colour was then read as absorbance in a Shimadzu UV-1201-VS spectrophotometer at 885 nm. The absorbance of the blank was subtracted from the absorbencies of the standard and the sample and the concentration calculated as:

(corrected sample absorbance/corrected standard absorbance) x 3 $mmol.m^{-3}$

2.2.3 Ammonium

Ammonium concentrations were determined manually. A 5 ml standard, 5 ml distilled water blank, 5 ml sea water blank and three pre-filtered 5 ml samples from each depth at each station were pipetted, according to the methods in Grasshoff *et al.* (1983) with 0.2 ml of citrate solution, 0.2 ml of phenol/nitroprusside solution, vortexed, pipetted with 0.2 ml of hypochlorite solution, again vortexed, covered with foil and left for approximately 24 hours for a colour to develop. This colour was then read as absorbance in a Shimadzu UV-1201-VS spectrophotometer at 630 nm. The absorbance of the sea water blank was subtracted from the absorbencies of the standard and the concentration calculated as:

(sample absorbance/corrected standard absorbance) x 4 $mmol.m^{-3}$

2.2.4 Silicate

Silicate concentrations were determined manually. A 5 ml standard, 5 ml distilled water blank, and three pre-filtered 5 ml samples from each depth at each station water pipetted with 0.2 ml of a mixed reagent consisting of 300 ml sulphuric acid and 300 ml ammonium molybdate solutions, vortexed, left for 5 – 10 minutes, pipetted with 0.2 ml of oxalic acid solution followed immediately by 0.2 ml of ascorbic acid solution and left for 30 – 60 minutes for a colour to develop, according to the methods in Grasshoff *et al.* (1983). This colour was then read as absorbance in a Shimadzu UV-1201-VS spectrophotometer at 810 nm. The absorbance of the blank was subtracted from the absorbencies of the standard and the sample and the concentration calculated as:

(corrected sample absorbance/corrected standard absorbance) x 100 $mmol.m^{-3}$

The calculated concentration was then multiplied by a salt error factor co-efficient corresponding to the salinity of the sample. Plastic test tubes were used for the silicate concentration determination.

2.3 THE SOUTH AFRICAN WATER QUALITY GUIDELINES (SAWQG)

The nutrient concentrations recorded in the estuaries as well as in the marine nearshore environments were compared to the concentrations recommended or stated as average in the South African Water Quality Guidelines (SAWQG). According to the SAWQG, the study site is situated on the south coast, which is defined as that section of coast extending from Cape Agulhas to East London and considered to be a transition zone between the cold temperate and warm subtropical regions. SAWQG for estuaries do not exist because they are such highly diverse and varied systems, so guidelines for both Aquatic Ecosystems (DWAF, 1996), which refer to the fresh water in streams and rivers, and the Natural Environment – Marine Coastal Waters (DWAF, 1995), which refer to the nearshore coastal zone, were used.

2.3.1 Nitrate

In South Africa, inorganic nitrogen concentrations (DIN, represented by nitrate + nitrite + ammonium) in unimpacted, aerobic fresh surface waters are usually below 35.7 $mmol.m^{-3}$ but may increase to above 357.1 $mmol.m^{-3}$ in highly enriched waters, resulting in eutrophic conditions if high concentrations persist and enough reactive phosphate is present. The south coast average concentration for marine coastal waters is 5.8 $mmol.m^{-3}$ and should not be exceeded in unimpacted surface waters.

2.3.2 Nitrite

Target values for DIN in unimpacted fresh surface waters have been stated above. In the marine environment, the average nitrite concentration for the south coast has been reported as 0.2 $mmol.m^{-3}$.

2.3.3 Ammonium

The target range for DIN in unimpacted fresh surface waters has been stated above. No average ammonium concentration for the marine waters along the south coast could be found, but concentrations in unpolluted sea water rarely exceed 5 $mmol.m^{-3}$.

2.3.4 Phosphate

Phosphorus is seldom present in high concentrations in unimpacted fresh water streams because it is actively taken up by plants. Concentrations of between 0.3 $mmol.m^{-3}$ and 1.6 $mmol.m^{-3}$ are commonly found, although concentrations as high as 6.5 $mmol.m^{-3}$ have been recorded. The average concentration in the sea on the south coast is 1.19 $mmol.m^{-3}$ and should not be exceeded in unimpacted waters.

2.3.5 Silicate

No acceptable average concentration for fresh water could be found but the average marine concentration for the south coast in the absence of upwelling is 5.2 $mmol.m^{-3}$, however concentrations as high as 100 $mmol.m^{-3}$ have been recorded in the coastal zone.

2.4 LOICZ BUDGET CALCULATIONS

A detailed description of the methodology of budget studies in coastal systems is described on the LOICZ website (http://www.loicz.org) and in Gordon *et al.* (1996). The equations expressed in this section were taken from these two sources, and the results checked against

the results of the Computer Assisted Budget Analysis for Research, Education and Training (CABARET) version V2001. For the Kariega estuary, a one-box model was used to calculate the nutrient fluxes, while for the Great Fish estuary, a one-box two-layer model was used to accommodate the stratification in salinity and nutrient concentrations.

Flow data was obtained from Department of Water Affairs and Forestry (http://www.dwaf.gov.za/hydrology). The nearest stations to the respective estuaries were used, Smithfield's station (P3H001, 33°33'08"S; 26°36'07"E) in the Kariega River and Matomela's station (Q9H018, 33°14'16"S; 26°29'42"E) in the Great Fish River. Rather than using the flow rate on the day of sampling or the mean flow rate of the month in which sampling took place, the mean flow rate for the thirty days prior to sampling was calculated and used as the flow rate (V_Q) in the budgeting procedure. Precipitation rate (V_P) was calculated using rainfall data from the Port Alfred region supplied by the South African Weather Service. The same value was used for both systems, differences in V_P arising from the different surface areas of the two estuaries. No evaporation data was available in the vicinity of the estuaries, therefore Hamon's (1961) equation was used to calculate the evaporation rate (V_E). Average daily temperatures from Port Alfred were used, supplied by the South African Weather Service. Evaporation rate on the day of sampling was calculated employing the equation,

$$E_t = 2.1\, H_t^2\ e_s / (T_t + 273.2) \qquad (1)$$

where E_t = evaporation rate on day t (mm.day^{-1}),

H_t = average number of daylight hours during month on which day t falls,

T_t = temperature on day t (°C), and

e_s = saturated vapour pressure of water in air at temperature T (kPa).

e_s was calculated as,

$$e_s(T_t) = 0.6108\ exp\ (17.27T_t / (237.3 + T_t)) \qquad (2)$$

2.4.1 One-box model

Water and salt have no internal inputs or outputs and behave conservatively within the system. This leads to the water balance equation (all values in $m^3.d^{-1}$),

$$V_Q + V_O + V_G + V_P - |V_E| + V_R = 0 \quad (3)$$

where V_Q (rate of river discharge), V_O (sewage discharge), V_G (groundwater discharge), V_P (precipitation falling directly onto the system) and V_E (evaporation from the system, always negative) are balanced by V_R (residual flow, either positive or negative) because the amount of fresh water flowing into the system must be the same as the amount of water flowing out to keep the volume constant.

There is an additional (potentially large) term to describe the in- and outflow of sea water from outside the system, V_X, the mixing flux. V_X is left out of the water balance because the water volume flowing in is deemed to be the same as the water volume flowing out for the sake of simplification.

For the salt budget, the water inputs and outputs are multiplied by the appropriate salinities. For most terms the water is regarded as fresh and the salinities are taken to be zero (S_Q, S_O, S_G, S_P, $S_E = 0$). This leaves S_R (the average salinity at the boundary) and S_X (the difference in salinity across the boundary between the system and the ocean). Salt must be conserved so the residual salt flux ($V_R.S_R$) is brought back into the system through the mixing salt flux ($V_X.S_X$) across the boundary via the tides, winds and general circulation patterns. Eliminating all the terms equal to zero, this leaves the salt budget as (in $m^3.psu.d^{-1}$),

$$V_R.S_R + V_X.S_{OCEAN} - V_X.S_{SYSTEM} = 0 \quad (4)$$

Re-arranging to solve for V_X (in $m^{-3}.d^{-1}$),

$$V_X = V_R.S_R / S_X \quad (5)$$

where $S_X = S_{SYSTEM} - S_{OCEAN}$ (6)

All dissolved inorganic nitrogen and dissolved inorganic phosphorus will be exchanged between the system and adjacent ocean according to the criteria established in the water and salt budgets. Deviations are attributed to net non-conservative reactions of nitrogen and phosphorus in the system. Using the calculated values, and the measured nutrient values from the system and ocean (mmol.m^{-3}), the budget of non-conservative materials can be constructed. To complete this, individual fluxes are needed, which follow the equations (in mmol.d^{-1}),

$$Q_Q{}^{DIX} = DIX_Q \,.\, V_Q \quad (7)$$

$$Q_G{}^{DIX} = DIX_G \,.\, V_G \quad (8)$$

$$Q_O{}^{DIX} = DIX_O \,.\, V_O \quad (9)$$

$$Q_R{}^{DIX} = [(DIX_{OCEAN} + DIX_{SYS}) / 2] \,.\, V_R \quad (10)$$

$$Q_X{}^{DIX} = (DIX_{OCEAN} - DIX_{SYS}) \,.\, V_X \quad (11)$$

where *DIX* stands for either dissolved inorganic nitrogen or dissolved inorganic phosphorus, depending on which budget is being calculated. The net flux out of the system as a whole follows equation (12), where *DIX* represents either dissolved inorganic nitrogen or phosphorus (in mmol.d^{-1}),

$$\Delta DIX_{SYS} = -(Q_X{}^{DIX} + Q_R{}^{DIX} + Q_O{}^{DIX} + Q_G{}^{DIX} + Q_Q{}^{DIX}) \quad (12)$$

The biological cycles of carbon, nitrogen and phosphorus are intimately linked, but while both carbon and nitrogen have a gaseous phase, phosphorus does not. It is therefore assumed that the internal flux of phosphorus is proportional to the production and

consumption of particulate material (generally dominated by organic matter) (Gordon *et al.*, 1996). The net biological metabolism (production minus respiration) can be calculated as (in mmol.C.d^{-1}),

$$(p - r) = -\Delta DIP \,.\, r_{C/P} \qquad (13)$$

where $-\Delta DIP$ equals the observed consumption of phosphate and $r_{C/P}$ is the ratio of carbon to phosphorus in organic matter. This value can be divided by the area of the system of interest (mmol.C.m^{-2}.d^{-1}) and compared to other systems. The change in DIN can be represented by the difference in observed DIN consumption and the expected consumption of DIN, computed from the observed phosphate consumption multiplied by the N:P ratio in organic matter. Hence the loss of DIN by denitrification or gain of DIN by nitrogen fixation, is expressed as (in mmol.N.d^{-1}),

$$(nfix - denit) = \Delta DIN - \Delta DIP.\, r_{N/P} \qquad (14)$$

This value can again be divided by the area of the system (mmol.N.m^{-2}.d^{-1}) to allow for comparison. The stoichiometric ratios of C:P and N:P used are those typically found in organic matter, 106:1 and 16:1, respectively, according to the Redfield ratio.

2.4.2 Two-layer model

This model is more complex than the one box model due to a vertical stratification in salinity, creating surface and bottom layers. The model is based on a number of assumptions: (1) fresh water inflow (equaling $V_Q + V_O + V_G + V_P - V_E$) is added to the surface layer; (2) a net inflow of sea water (V_D) enters the bottom layer across the open boundary from the outside ocean; (3) there is a corresponding flow ($V_{D'}$) into the surface layer from the bottom layer; and (4) there is a flow across the open boundary to the outside ocean from the surface layer (V_S) that equals the inflows ($V_R - V_{D'}$) to this layer. Finally, the salt budget of the two layers is balanced by a vertical mixing flux (V_Z) between the surface and bottom layers. The boundary between the two layers is chosen according to hydrological conditions with the thickness of the surface layer extending from the surface

down to the pycnocline and the bottom layer from the pycnocline to the bottom (Nitishinsky *et al.*, 2005).

Using these parameters, the following equations are resolved. The water budget for the surface layer (values in m^3d^{-1}) equals,

$$V_Q + V_O + V_G + V_P - |V_E| + V_{D'} + V_S = 0 \quad (15)$$

where V_E and V_S are negative. The water budget of the deep layer equals,

$$V_D - V_{D'} = 0 \quad (16)$$

The vertical mixing term (V_Z) is not included in the water budget as it has the same flux in as out for both layers. Assuming the same terms to have a salinity of zero as in the one box model, the salt budget for the surface layer is (in m^3.psu.d^{-1}),

$$V_S.S_{SYS-S} + V_D.S_{SYS-D} + V_Z.(S_{SYS-D} - S_{SYS-S}) = 0 \quad (17)$$

where S_{SYS-S} equals average salinity of surface layer in the system, and S_{SYS-D} equals average salinity of the bottom layer of the system. The salt flowing into the ocean is balanced by the vertical advection flux and exchange flow. The salt budget of the bottom layer equals (in m^3.psu.d^{-1}),

$$V_D.S_{OCEAN} - V_{D'}.S_{SYS-D} - V_Z.(S_{SYS-D} - S_{SYS-S}) = 0 \quad (18)$$

Combining (15) with the residual flow volume equation (19) (in $m^3.d^{-1}$)

$$V_R = -(V_Q + V_O + V_G + V_P + |V_E|) \quad (19)$$

gives (20) (in m^3d^{-1}),

$$V_S = V_R - V_{D'} \quad (20)$$

In the above equations there are two unknowns, $V_{D'}$ and V_Z, which can be expressed in known parameters according to (21) and (22) (in $m^3.d^{-1}$),

$$V_{D'} = V_R \,.\, S_{SYS-S} / (S_{SYS-S} - S_{OCEAN}) \quad (21)$$

and

$$V_Z = V_D \,.\, (S_{OCEAN} - S_{SYS-D}) / (S_{SYS-D} - S_{SYS-S}) \quad (22)$$

Using these calculated values, and the measured nutrient values from the system and ocean ($mmol.m^{-3}$), as in the one-box model, the budget of non-conservative materials can be constructed. Although some of the individual fluxes are the same as in the one-box model, additional terms are also included (in $mmol.d^{-1}$),

$$Q_Q{}^{DIX} = DIX_Q \,.\, V_Q \quad (23)$$

$$Q_G{}^{DIX} = DIX_G \,.\, V_G \quad (24)$$

$$Q_O{}^{DIX} = DIX_O \,.\, V_O \quad (25)$$

$$Q_D{}^{DIX} = DIX_{OCEAN} \,.\, V_D \quad (26)$$

$$Q_S{}^{DIX} = DIX_{SYS\text{-}S} \,.\, V_{SURF} \quad (27)$$

$$Q_{D'}{}^{DIX} = DIX_{SYS\text{-}D} \,.\, V_{D'} \quad (28)$$

$$Q_{Z-SYS\text{-}S}{}^{DIX} = (DIX_{SYS\text{-}D} - DIX_{SYS\text{-}S}) \,.\, V_Z \quad (29)$$

$$Q_{Z-SYS\text{-}D}{}^{DIX} = (DIX_{SYS\text{-}S} - DIX_{SYS\text{-}D}) \,.\, V_Z \quad (30)$$

where *DIX* stands for either dissolved inorganic nitrogen or dissolved inorganic phosphorus, depending on which budget is being calculated. The net flux out of the surface layer, and the deep layer, and the system as a whole follow equations (31 – 33) respectively, where *DIX* represents either dissolved inorganic nitrogen or phosphorus (in mmol.d^{-1}),

$$\Delta DIX_{SYS-S} = -(Q_S{}^{DIX} + Q_Q{}^{DIX} + Q_O{}^{DIX} + Q_{D'}{}^{DIX} + Q_{Z-SYS-S}{}^{DIX}) \quad (31)$$

$$\Delta DIX_{SYS-D} = -[Q_D{}^{DIX} + Q_G{}^{DIX} + Q_{Z-SYS-D}{}^{DIX} + (-Q_D{}^{DIX})] \quad (32)$$

$$\Delta DIX_{SYS} = \Delta DIX_{SYS-S} + \Delta DIX_{SYS-D} \quad (33)$$

The stoichiometric calculations follow the same principle as in the one-box model, except ($p - r$) (34 – 36, in mmol.C.d^{-1}) and (*nfix – denit*) (37 – 39, in mmol.N.d^{-1}) are calculated for the surface and bottom layers and the system as a whole,

$$(p-r)_{SYS\text{-}S} = -\Delta DIP_{SYS-S} \,.\, r_{C/P} \quad (34)$$

$$(p-r)_{SYS\text{-}D} = -\Delta DIP_{SYS-D} \,.\, r_{C/P} \quad (35)$$

$$(p-r)_{SYS} = (p-r)_{SYS-S} + (p-r)_{SYS-D} \quad (36)$$

$$(nfix-denit)_{SYS\text{-}S} = \Delta DIN_{SYS-S} - \Delta DIP_{SYS-S}.\, r_{N/P} \quad (37)$$

$$(nfix-denit)_{SYS\text{-}D} = \Delta DIN_{SYS-D} - \Delta DIP_{SYS-D}.\, r_{N/P} \quad (38)$$

$$(nfix-denit)_{SYS} = (nfix-denit)_{SYS-S} + (nfix-denit)_{SYS\text{-}D} \quad (39)$$

These values can again be divided by the area of the system to allow for comparison.

2.5 STATISTICAL ANALYSIS

To asses if there were any significant differences in salinity and temperature values and nutrient concentrations in and between the Kariega and Great Fish estuaries and the marine nearshore environment adjacent to the estuaries, analysis of variance tests were employed using the computer package Statistica (ver. 7). As the distribution of the results was non-normal, as most water quality tends to be (Sanders *et al.*, 1987, as cited in Grange and Allanson, 1995), non-parametric tests were used based on the median values. When two factors were being compared, the Mann-Whitney U test was used (significant results represented by $p<0.05$), while the Kruskal-Wallis test was used when comparing more than two factors (significant results represented by $p<0.05$). When using subsequent Mann-Whitney U tests to further test relationships deemed to be significantly different by the Kruskal-Wallis test, 90% confidence level (0.1) was divided by the number of initial comparisons in order to obtain a p-value below which differences were regarded as significant, according to the Bonferroni adjustment (Quinn and Keough, 2002).

Mixing plots of nutrient concentrations and salinity values for the estuarine and marine environments were created using the Statistica computer package. Visual representation of the data was achieved through the use of the computer profiling program SigmaPlot.

CHAPTER 3 - RESULTS

Due to the non-normal distribution of the data sets and resultant use of non-parametric statistical analyses, median values are reported here. Mean values, together with the median and inter-quartile range values, are presented in Tables 3.1 to 3.4. For each survey, a full table of results can be found in Appendix I (Tables A1.1.1 to A1.4.4). Appendix II contains the results of the statistical analyses (Tables A2.1.1 to A2.1.7). In the figures of the two estuaries in this chapter, station 10 and 8 are shown as being 1000 m from the mouth in the Kariega and Great Fish estuaries, respectively, with stations occurring at 1000 m intervals upstream in each estuary.

3.1 JUNE SURVEY

3.1.1 Introduction

The winter month of June is historically a dry time of year in the Eastern Cape region, with peaks in rainfall occurring, on average, in the autumn and spring months. During the three days of sampling no rain fell at Port Alfred, with only 2 mm falling in the thirty days preceding the sampling trip, and 6.8 mm in the month of June. The mean monthly rainfall at Port Alfred is 49.95 $mm.month^{-1}$. The flow rate in the Great Fish River on the day of sampling the estuary was 8.48 $m^3.s^{-1}$. The mean flow rate for the thirty days preceding sampling was 7.86 $m^3.s^{-1}$. These were both lower than the mean monthly flow rate of the year-long study period of 13.12 $m^3.s^{-1}$. The flow rate in the Kariega River was 0.003 $m^3.s^{-1}$ on the day of sampling the Kariega estuary, as well as every day for the thirty days prior to sampling. The mean monthly flow rate over the course of the sampling period in the Kariega River was 0.006 $m^3.s^{-1}$.

Rough sea conditions during the Great Fish marine environment sampling trip resulted in only stations in transects 1, 2 and 3 being occupied. In addition, no Marine Control station was occupied.

Table 3.1 Mean (Mn), median (Mdn) and inter-quartile range (IQR) values of salinities (psu), temperatures (^{o}C) and nutrient concentrations (mmol.m^{-3}) for June. KE = Kariega estuary, GFE = Great Fish estuary, KM = Kariega marine environment, GFM = Great Fish marine environment.

	Depth (m)	Salinity			Temperature			DIN			Nitrate		
		Mn	Mdn	IQR	Mn	Mdn	IQR	Mn	Mdn	IQR	Mn	Mdn	IQR
KE	**0**	36.68	36.67	1.91	16.41	16.25	0.54	14.20	5.71	24.21	10.88	3.65	19.73
	1.5	36.73	36.73	1.59	16.12	15.96	0.73	28.01	29.81	32.16	24.04	23.8	26.60
	System	36.70	36.73	1.73	16.26	16.19	0.67	21.11	15.37	29.51	17.46	11.43	24.52
GFE	**0**	7.56	8.06	9.78	14.09	14.12	0.75	112.08	108.57	34.64	107.15	103.16	35.10
	1.5	21.93	23.57	19.89	15.10	15.13	0.38	67.89	51.35	61.27	63.36	46.28	57.15
	System	14.75	12.51	18.65	14.60	14.57	1.01	89.99	95.09	64.85	85.25	88.76	64.87
KM	**0**	35.33	35.34	0.02	16.34	16.38	0.35	22.94	22.22	23.56	17.49	15.12	18.88
	5	35.34	35.34	0.01	16.26	16.29	0.25	23.25	29.98	25.25	17.59	21.20	21.61
	10	35.29	35.35	0.12	16.25	16.25	0.19	20.68	12.62	28.07	15.92	8.98	24.01
	System	35.33	35.34	0.02	16.29	16.30	0.27	22.61	22.22	25.58	17.22	15.12	21.46
GFM	**0**	32.58	33.92	1.27	15.86	15.83	0.37	22.29	16.02	26.97	19.25	13.44	27.05
	5	35.27	35.28	0.05	15.90	15.90	0.04	11.24	10.45	4.29	8.73	7.96	4.94
	10	35.32	35.32	0.10	15.67	15.70	0.11	9.82	10.41	4.53	7.88	7.10	5.20
	System	34.29	35.23	1.17	15.83	15.83	0.20	14.93	11.38	6.51	12.38	9.11	5.98

	Depth (m)	Nitrite			Ammonium			Phosphate			Silicate		
		Mn	Mdn	IQR	Mn	Mdn	IQR	Mn	Mdn	IQR	Mn	Mdn	IQR
KE	**0**	2.49	1.13	4.70	0.83	0.74	0.61	1.45	1.45	0.86	64.08	50.31	78.37
	1.5	3.39	5.29	5.21	0.58	0.55	0.56	1.57	1.71	1.31	64.18	52.37	56.21
	System	2.94	2.97	4.93	0.71	0.72	0.58	1.51	1.49	1.07	64.13	52.09	69.16
GFE	**0**	1.43	1.14	0.94	3.50	3.69	1.13	3.58	3.61	1.73	141.07	147.99	18.70
	1.5	1.48	1.21	0.77	3.05	2.70	2.39	2.26	1.98	1.14	141.88	144.33	12.91
	System	1.46	1.18	0.79	3.27	3.31	1.41	2.92	2.79	1.77	141.48	145.93	16.97
KM	**0**	3.87	4.15	4.23	1.58	1.59	0.49	0.95	0.92	0.32	10.67	10.83	2.30
	5	3.88	5.00	4.38	1.77	1.69	0.36	0.95	0.96	0.23	9.81	9.79	2.84
	10	3.10	1.81	4.28	1.66	1.73	0.45	0.79	0.79	0.08	10.90	10.69	1.51
	System	3.72	4.57	4.40	1.67	1.67	0.37	0.92	0.87	0.27	10.37	10.26	1.99
GFM	**0**	1.67	1.55	2.12	1.37	1.45	0.71	1.12	0.98	0.55	65.25	39.80	88.70
	5	1.43	1.56	1.21	1.08	1.10	0.52	1.07	0.86	0.57	25.27	20.13	11.40
	10	0.89	0.75	1.26	1.05	0.89	0.16	0.90	0.93	0.46	16.27	14.81	6.68
	System	1.37	1.36	1.41	1.18	1.03	0.64	1.05	0.90	0.53	37.63	24.12	25.70

June mean, median and inter-quartile range physico-chemical and nutrient concentration values are presented in Table 3.1. Full tables of results for the June survey can be found in Appendix 1 (Tables A1.1.1 to A1.1.4). The results of the statistical analyses for the Kariega and Great Fish estuaries and marine environments are shown in Appendix 2 (Tables A2.1.1 to A2.1.4).

3.1.2 Physico-Chemical Factors

3.1.2.1 Kariega estuary

The Kariega estuary during the June survey was well mixed with no salt-wedge or vertical stratification evident (Figure 3.1). A very small horizontal gradient in salinity and temperature was evident, with the highest salinity and lowest temperature values recorded in the upper reaches (37.5psu and 16.26^{o}C at station 2B) and lowest salinities and warmest temperatures near the mouth (35.34psu and 16.75^{o}C at station 10A). The median salinity value was 36.73psu with no significant difference between the surface and bottom median layer concentrations ($p>0.05$). The median surface temperature (16.25^{o}C) was significantly higher ($U = 24.00$; $p = 0.049$) than the median bottom temperature (15.96^{o}C).

3.1.2.2 Great Fish Estuary

The salinity profile of the Great Fish estuary during the June survey was that of a typical salt-wedge type estuary, with less dense fresher river water found on the surface and bottom in the upper reaches (0.76psu and 1.30psu at stations 1A and 1B, respectively), overlying saline water intruding through the mouth in the lower reaches at the bottom (34.58psu at station 8B) (Figure 3.2). Entrainment of the salty water caused mixing in the middle reaches of the estuary. Cooler river water (13.57^{o}C at station 1A) was found on top of the warmer marine water (15.44^{o}C at station 7B), trapped underneath the fast flowing surface layer. The median surface salinity and temperature values (8.06psu and 14.12^{o}C, respectively) were significantly higher than the median bottom salinity and temperature

values (23.57psu and 15.13^{o}C, respectively) (U = 11.00; p < 0.027 and U = 3.00; p = 0.0023, respectively).

3.1.2.3 Kariega Marine Environment

Salinity offshore of the Kariega estuary during the June survey showed little variation with no significant difference between median surface, 5 m and 10 m values (p>0.05). Bodies of slightly less saline water were present at stations 1A and 1B (35.28psu and 35.32psu, respectively) adjacent to the mouth. This was, however, only 0.04psu lower than the surrounding surface water and only 0.02psu less than the ambient water at 5 m (both with a median value of 35.34psu). The lowest salinity was found at station 12C (35.15psu) at a depth of 10 m, where the median salinity value was 35.35psu. A temperature gradient was recorded at the surface as well as at 5 and 10 m from east (16.10^{o}C, 16.07^{o}C and 16.06^{o}C at stations 8A, B and C, respectively) to west (16.68^{o}C, 16.39^{o}C and 16.34^{o}C at stations 23A, B and C, respectively) of the mouth, however, the variation was less than 0.6^{o}C and more than likely attributed to the time of day the samples were taken and warming due to the sun (transects east of the mouth were completed in the early morning, and those west in the afternoon). The median temperature values showed a slight and expected decrease with depth from the surface layer (16.38^{o}C), to the 5 m layer (16.29^{o}C) to the median 10 m temperature (16.25^{o}C). Differences between the three depths were, however, not significant (p>0.05).

3.1.2.4 Great Fish Marine Environment

Offshore of the Great Fish estuary a body of fresher water (25.95psu at station 11A) was found leaving the inshore area as a plume 500 m west of the mouth on the surface during the June survey. The plume flowed out into the surrounding marine water (34.98psu at station 9A and 33.60psu at station 18A, either side of the plume of fresher water) and eventually dissipated due to mixing (Figure 3.3). The fresher water was, however, confined to the surface layer, the lowest salinities at 5 and 10 m being 35.13psu at station 5B and 35.15psu at station 18C. There was a significant decrease in median salinity values from

the surface (33.92psu) to 5 m (35.28psu) ($U < 0.001$; $p < 0.001$), as well as to 10 m (35.32psu) ($U < 0.001$; $p < 0.001$), with no significant difference between 5 and 10 m median salinity values ($p>0.05$). Cooler water was found coinciding with the fresher water at station 11A (15.70^{o}C), but the lowest temperature on the surface was found at station 3A (15.54^{o}C), again likely due to the transect opposite the mouth being undertaken in the early morning. There was a significant difference between the three depth layers, the median 10 m temperature (15.70^{o}C) being significantly lower than the median surface (15.86^{o}C) ($U = 34.50$; $p = 0.0017$) and 5 m (15.90^{o}C) ($U = 45.50$; $p = 0.0072$) temperatures. There was no significant difference in temperature between the surface and 5 m layers ($p>0.05$).

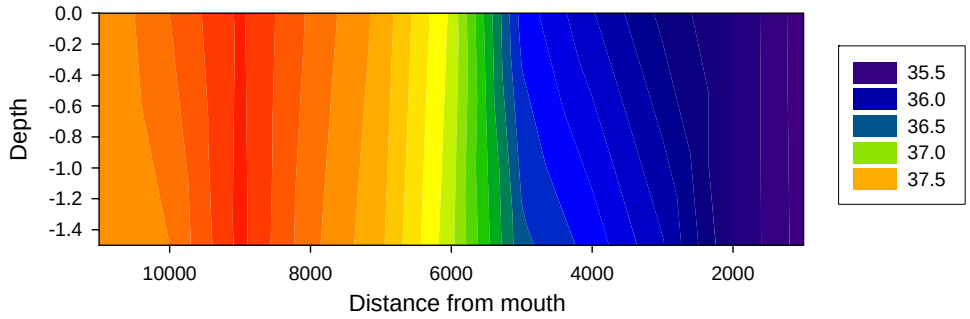


Figure 3.1 Salinity profile (psu) of the Kariega estuary in June. Distance from mouth and depth in m.

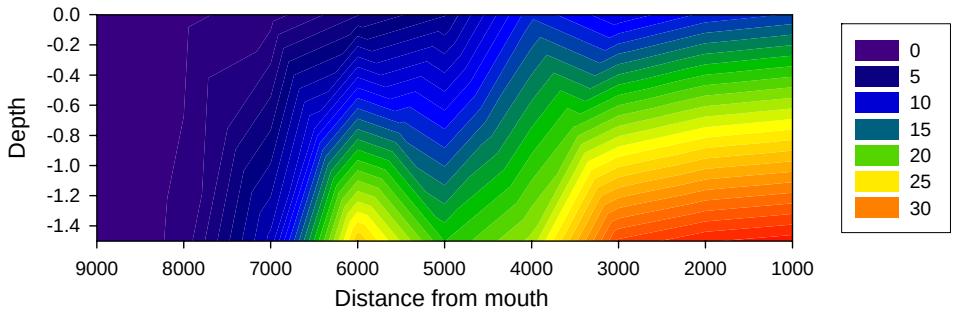


Figure 3.2 Salinity profile (psu) of the Great Fish estuary in June. Distance from mouth and depth in m.

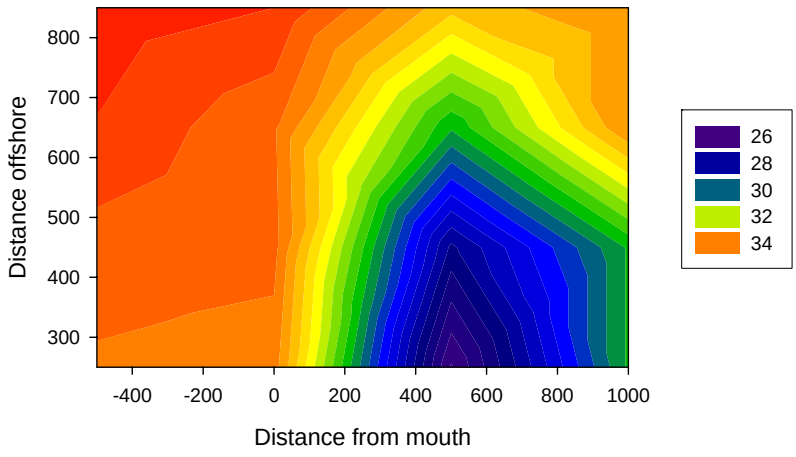


Figure 3.3 Surface salinity plot (psu) of the Great Fish marine environment in June. Distances in m. Positive and negative distances from the mouth represent west and east, respectively.

3.1.3 Nutrient Concentrations

3.1.3.1 Kariega Estuary

There were no clear trends in dissolved inorganic nitrogen (DIN) in the Kariega estuary during the June survey. The water generally showed little horizontal stratification in DIN concentration, with no significant difference between top and bottom median concentrations ($p>0.05$). The highest concentration was found in the lower reaches where the bottom water had higher concentrations (113.05 mmol.m^{-3} at station 10B) than the surface water. Further peaks were found at station 5 (43.61 mmol.m^{-3} on the surface and 29.75 mmol.m^{-3} on the bottom), station 1 (25.87 mmol.m^{-3} at the surface and 39.04 mmol.m^{-3} at the bottom) and station 3A (30.37 mmol.m^{-3}). These peaks were due to peaks in nitrate concentrations (with a median value of 11.43 mmol.m^{-3} for the system) which were higher than nitrite and ammonium concentrations (median values of 2.97 mmol.m^{-3} and 0.72 mmol.m^{-3}, respectively). The nitrite did, however, mirror nitrate in terms of peaks in concentration. Phosphate concentration showed little vertical stratification (no significant difference between surface (1.45 mmol.m^{-3}) and bottom (1.71 mmol.m^{-3}) median concentrations, $p>0.05$) with highest concentrations recorded in the middle reaches (2.53 mmol.m^{-3} at station 4B), while values in the upper and lower reaches were lower (1.52 mmol.m^{-3} at station 1A and 0.57 mmol.m^{-3} at station 10B). Silicate displayed horizontal stratification from the headwaters (152.77 mmol.m^{-3} at station 2B) to the mouth (9.56 mmol.m^{-3} at station 10A), with a median concentration of 52.09 mmol.m^{-3} (Figure 3.4).

3.1.3.2 Great Fish Estuary

In the Great Fish estuary during the June survey, DIN-rich river water was found flowing out above the relatively DIN-poor marine water intruding through the mouth (Figure 3.5). Higher DIN concentrations were recorded at the surface at all stations, except station 2, where the highest concentration was recorded at the bottom (165.65 mmol.m^{-3} at station 2B). Nitrate contributed the most to DIN concentrations, with a median concentration of

103.16 mmol.m^{-3} in the surface layer, significantly higher (U = 12.00; p = 0.036) than the median concentration of 46.28 mmol.m^{-3} for the bottom layer. The DIN median concentration of the surface (108.57 mmol.m^{-3}) was significantly higher (U = 12.00; p = 0.036) than the median DIN concentration for the bottom layer (51.35 mmol.m^{-3}). Nitrite and ammonium showed no clear trends or significant difference between median surface and bottom concentrations (p>0.05). Minor peaks in nitrite were found at station 1B (3.57 mmol.m^{-3}, with a median concentration of 1.18 mmol.m^{-3} for the system) and in ammonium at station 3B (6.67 mmol.m^{-3}, with a median concentration of 3.31 mmol.m^{-3} for the system). Phosphate concentrations showed a similar yet less pronounced pattern to that of DIN. The surface median concentration (3.61 mmol.m^{-3}) was significantly higher (U = 10.00; p = 0.021) than the bottom median concentrations (1.98 mmol.m^{-3}). The highest phosphate concentration was recorded at station 2A (5.22 mmol.m^{-3}). A general decrease in phosphate concentrations from the head to the mouth was evident, except for stations 6A and 7A (3.67 mmol.m^{-3} and 3.54 mmol.m^{-3}, respectively) where higher concentrations were found than at station 5A (2.19 mmol.m^{-3}). Silicate concentrations showed no clear trends and little vertical or horizontal stratification. The median surface concentration was 147.99 mmol.m^{-3}, which was not significantly different to the median bottom concentration of 144.33 mmol.m^{-3} (p>0.05).

3.1.3.3 Kariega Marine Environment

DIN concentrations at the surface in the Kariega marine environment during the June survey were patchy, with a median value of 22.22 mmol.m^{-3} and three areas of higher concentrations, at stations 8A (47.28 mmol.m^{-3}), 11A (45.91 mmol.m^{-3}) and 22A (47.89 mmol.m^{-3}). Next to station 22A, however, at 23A, the lowest surface DIN concentration was found (6.33 mmol.m^{-3}). At 5 m, the stations with the highest concentrations did not correspond with those above in the surface layer and showed a gradient increasing from east of the mouth (9.1 mmol.m^{-3} at station 3B) to west (reaching 39.59 mmol.m^{-3} at station 12B). The overall median concentration at 5 m (29.98 mmol.m^{-3}) was higher but not significantly different from the surface layer value (p>0.05). The 10 m layer bore little resemblance to the layers above in terms of peaks in concentration, and a lower median

concentration of 12.62 mmol.m^{-3}, yet not significantly different to the layers above ($p>0.05$). As in the Kariega estuary, the DIN was comprised predominantly of nitrate, with minor contributions of ammonium and nitrite, the latter showing a similar trend to nitrate, but with lower concentrations. The ammonium surface, 5 m and 10 m concentrations bore little resemblance to each other and showed no distinct patterns with no significant differences between the median layer concentrations ($p>0.05$). Phosphate concentrations showed little variation in and between the surface and 5 m layers, with median concentrations of 0.92 mmol.m^{-3} and 0.96 mmol.m^{-3}, respectively. Both were, however, significantly higher than the median 10 m concentration of 0.79 mmol.m^{-3} ($U = 50.00$; $p = 0.027$ and $U = 31.00$; $p = 0.002$, respectively). Silicate concentrations showed no distinct trends, except for the highest concentrations occurring at the same stations at 5 m and 10 m, 14.36 mmol.m^{-3} and 13.26 mmol.m^{-3} at stations 9B and 9C, respectively. The median surface, 5 m and 10 m concentrations were 10.83 mmol.m^{-3}, 9.79 mmol.m^{-3} and 10.69 mmol.m^{-3}, respectively, with no significant differences between the three layers ($p>0.05$).

3.1.3.4 Great Fish Marine Environment

In the Great Fish marine environment during the June survey, DIN-rich water was found leaving the estuary 500 m west of the mouth as a plume, coinciding with the fresher water in the region. Highest concentrations were recorded at stations 11A and 14A (47.60 mmol.m^{-3} and 49.98 mmol.m^{-3}, respectively), with a median surface concentration of 16.02 mmol.m^{-3} (Figure 3.6). At 5 m, the water with the highest concentration was below the position of the plume, reaching 26.78 mmol.m^{-3} but dissipating closer inshore than the surface water to give a median 5 m concentration of 10.45 mmol.m^{-3}, significantly lower than the median surface concentration ($U = 46.00$; $p = 0.017$). The 10 m layer had a lower median concentration (10.41 mmol.m^{-3}), again significantly different to the surface layer ($U = 28.00$; $p = 0.014$). Nitrate, as in the Great Fish estuary, contributed the most to total DIN. Nitrite concentrations showed a slight yet not significant decrease with depth ($p>0.05$), with median values of 1.55 mmol.m^{-3}, 1.56 mmol.m^{-3} and 0.75 mmol.m^{-3} for the surface, the 5 and 10 m layers, respectively. Ammonium median layer concentrations were 1.45 mmol.m^{-3}, 1.10 mmol.m^{-3} and 0.89 mmol.m^{-3} for the surface, the 5 and the 10 m layers,

respectively, with no significant differences between the layers ($p>0.05$). Phosphate concentrations did not show the expected increase in concentration in the fresher water leaving the estuary. There were no significant differences between surface (0.98 mmol.m^{-3}), 5 (0.86 mmol.m^{-3}) and 10 m (0.93 mmol.m^{-3}) median concentrations ($p>0.05$). Highest concentrations were recorded at stations 10A and 1B (both 2.59 mmol.m^{-3}). Highest silicate concentrations were found within the plume of DIN-rich fresher water, reaching 161.61 mmol.m^{-3} at station 12A. The median surface concentration was 39.80 mmol.m^{-3}, which was significantly higher than the median 5 m concentration of 20.13 mmol.m^{-3} ($U = 23.00$; $p < 0.001$) as well as the median 10 m concentration of 14.81 mmol.m^{-3} ($U = 5.00$; $p < 0.001$). There were no significant differences in median silicate concentration between the deeper layers ($p>0.05$). At 5 m the highest concentrations were found close inshore below the plume (94.50 mmol.m^{-3} at station 11B), with lower concentrations found at 10 m in the same region (29.86 mmol.m^{-3} at station 12C).

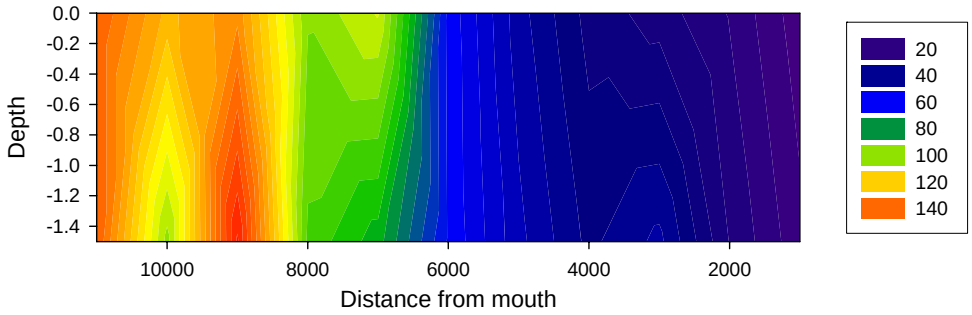


Figure 3.4 Silicate profile (mmol.m^{-3}) of the Kariega estuary in June. Distance from mouth and depth in m.

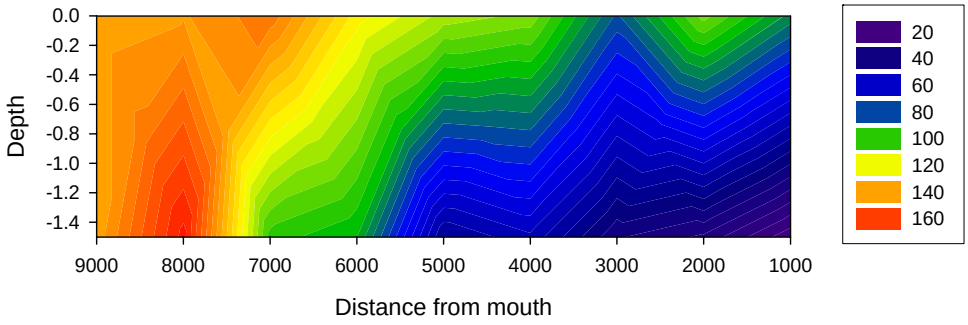


Figure 3.5 DIN (mmol.m^{-3}) profile of the Great Fish estuary in June. Distance from mouth and depth in m.

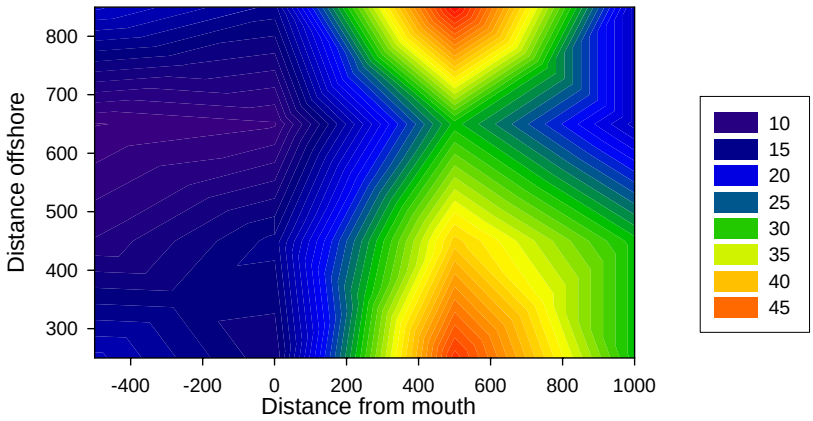


Figure 3.6 Surface DIN plot (mmol.m^{-3}) of the Great Fish marine environment in June. Distances in m. Positive and negative distances from the mouth represent west and east, respectively.

3.2 SEPTEMBER SURVEY

3.2.1 Introduction

Spring is historically one of the bimodal peaks in rainfall in the Eastern Cape region, and this proved to be true as 161.5 mm of rain fell in the month of September at Port Alfred. Of this total, however, 87 mm fell on the day after samples were taken, with 23 mm falling on the day when sampling the in Kariega marine environment took place. At Port Alfred, 41.4 mm of rain fell in the thirty days leading up to the sampling period. The flow rate in the Kariega River, however, did not change from the drier winter months, remaining at 0.003 m^3s^{-1} on the day the estuary was sampled, as well as for the thirty days prior to sampling. This was, as in June, lower than the mean monthly flow rate for the study period of 0.006 m^3s^{-1} in the Kariega River. In the Great Fish River, the flow rate on the day of sampling was 3.46 m^3s^{-1}, with a mean flow rate of 5.51 m^3s^{-1} for the thirty days preceding sampling. These were lower than the winter June flow rates (and hence the mean monthly flow rate).

At sea, calmer conditions allowed more transects to be occupied in the Great Fish marine environment. Unfortunately, due to a faulty sampling bottle, only two samples were collected at 10 m in the Great Fish marine grid. A Marine Control site was occupied between the two estuaries.

September mean, median and inter-quartile range physico-chemical and nutrient concentration values are presented in Table 3.2. Full tables of results for the September survey can be found in Appendix 1 (Tables A1.2.1 to A1.2.4). The results of the statistical analyses for the Kariega and Great Fish estuaries and marine environments are shown in Appendix 2 (Tables A2.1.1 to A2.1.4).

Table 3.2 Mean (Mn), median (Mdn) and inter-quartile range (IQR) values of salinities (psu), temperatures (^{o}C) and nutrient concentrations (mmol.m^{-3}) for September. KE = Kariega estuary, GFE = Great Fish estuary, KM = Kariega marine environment, GFM = Great Fish marine environment.

	Depth	Salinity			Temperature			DIN			Nitrate		
	(m)	Mn	Mdn	IQR	Mn	Mdn	IQR	Mn	Mdn	IQR	Mn	Mdn	IQR
KE	**0**	36.79	37.16	1.72	21.86	21.98	0.86	1.53	1.52	0.91	0.57	0.41	0.50
	1.5	35.74	35.70	2.35	20.29	20.32	0.39	1.27	1.11	0.30	0.36	0.22	0.27
	System	36.27	36.67	1.77	21.07	20.59	1.70	1.40	1.14	0.81	0.47	0.32	0.55
GFE	**0**	15.50	9.46	25.50	18.65	18.49	0.84	10.39	11.40	7.12	3.48	3.67	1.18
	1.5	24.52	25.95	10.84	17.99	17.96	0.84	10.28	8.62	7.51	3.31	3.27	0.60
	System	20.01	24.05	25.79	18.32	18.33	0.73	10.33	9.78	7.50	3.39	3.44	0.77
KM	**0**	35.29	35.30	0.01	18.02	18.03	0.05	3.14	2.98	0.42	2.44	2.31	0.44
	5	35.29	35.31	0.00	18.01	18.02	0.06	3.06	2.89	0.28	2.42	2.29	0.37
	10	35.31	35.31	0.00	18.02	18.02	0.06	2.89	2.65	0.49	2.25	2.05	0.41
	System	35.29	35.31	0.02	18.02	18.03	0.06	3.06	2.90	0.40	2.40	2.27	0.41
GFM	**0**	35.14	35.19	0.10	17.25	17.21	0.17	5.82	5.44	1.71	3.02	2.97	1.22
	5	35.20	35.23	0.09	17.21	17.17	0.19	5.57	5.15	0.99	3.06	2.74	0.58
	10	35.19	35.19	0.01	16.99	16.99	0.06	5.14	5.14	0.01	2.92	2.92	0.26
	System	35.17	35.20	0.08	17.21	17.18	0.18	5.66	5.20	1.26	3.03	2.84	0.70

	Depth	Nitrite			Ammonium			Phosphate			Silicate		
	(m)	Mn	Mdn	IQR	Mn	Mdn	IQR	Mn	Mdn	IQR	Mn	Mdn	IQR
KE	0	0.01	0.00	0.03	0.94	0.94	0.50	1.33	1.35	1.28	94.41	83.71	77.74
	1.5	0.04	0.01	0.05	0.87	0.84	0.13	1.33	1.41	1.19	101.08	92.97	76.31
	System	0.03	0.00	0.03	0.91	0.84	0.36	1.33	1.41	1.24	97.74	92.17	77.95
GFE	0	0.65	0.68	0.22	6.27	7.37	5.64	1.28	1.30	0.56	44.78	46.56	36.74
	1.5	0.65	0.57	0.40	6.32	5.04	6.87	1.30	1.33	1.02	59.16	33.16	60.20
	System	0.65	0.64	0.33	6.29	6.45	6.07	1.29	1.30	0.96	51.97	39.11	43.91
KM	0	0.10	0.10	0.03	0.61	0.60	0.21	0.37	0.36	0.13	4.59	4.17	1.62
	5	0.10	0.11	0.03	0.54	0.55	0.25	0.36	0.34	0.11	4.24	3.96	1.73
	10	0.10	0.09	0.04	0.54	0.54	0.10	0.38	0.36	0.18	2.85	2.92	0.62
	System	0.10	0.10	0.03	0.57	0.58	0.23	0.37	0.36	0.13	4.13	3.74	2.02
GFM	0	0.47	0.44	0.15	2.33	2.12	0.66	0.31	0.27	0.15	6.62	6.48	1.64
	5	0.44	0.40	0.13	2.07	1.86	0.35	0.23	0.22	0.06	6.75	6.54	1.34
	10	0.63	0.63	0.03	1.59	1.59	0.28	0.31	0.31	0.05	5.65	5.65	0.30
	System	0.47	0.42	0.14	2.16	1.99	0.49	0.27	0.23	0.08	6.62	6.49	1.45

3.2.2 Physico-Chemical Factors

3.2.2.1 Kariega Estuary

In September during the Kariega estuary survey, hypersaline conditions were recorded in the upper reaches, except at three stations where relatively fresher water (below standard sea water salinity) was found on the bottom at stations 1B, 2B and 4B (33.48psu, 34.21psu and 34.53psu, respectively) (Figure 3.7). This caused the median bottom layer salinity value (35.70psu) to be significantly lower ($U = 24$; $p = 0.049$) than the median surface salinity value (37.16psu). The middle to lower reaches showed no vertical stratification, and salinities decreased to the mouth where values closer to that of marine water were measured (35.58psu at station 10A and B). Warmer temperatures were recorded at the surface in the middle and upper reaches. The median surface temperature (21.98^{o}C) was significantly higher ($U = 10.00$; $p = 0.002$) than the median of on bottom temperature (20.32^{o}C).

3.2.2.2 Great Fish Estuary

Salinity in the Great Fish estuary during the September survey displayed a classic salt-wedge, with fresher river water lying above the denser marine water between stations 2 and 5 (Figure 3.8). Upstream of this region fresh water was found at the surface and bottom (3.33psu at station 1B). Towards the mouth, the vertical stratification broke down due to the pushing of the tide (34.93psu at stations 8A and 8B). The surface layer of the estuary had a median salinity value (9.46psu) less than that of the bottom layer (25.95psu), but without a significant difference ($p>0.05$). Cooler, denser marine water was found pushing in through the mouth at the bottom of the estuary (17.88^{o}C at station 8B). The river water (18.20^{o}C) was warmer than the marine water, while the warmest water was found in the middle reaches at the surface (19.61^{o}C at station 4A), giving the surface layer a median temperature value (18.49^{o}C) significantly higher ($U = 12.50$; $p = 0.04$) than that of the bottom layer (17.96^{o}C).

3.2.2.3 Kariega Marine Environment

There were no significant spatial or vertical differences in salinity or temperature values in the marine environment opposite the Kariega estuary during the September survey ($p>0.05$). The lowest salinity recorded was 35.00psu at station 1B. The surface had a median salinity of 35.30psu, similar to the 5 and 10 m layers (35.31psu), all close to the Marine Control salinities of 35.20psu, 35.34psu and 35.34psu for the surface, 5 and 10 m, respectively. Similar to salinity, temperature showed very little variation between or within the layers. The surface layer had a median temperature value of 18.03°C, the same as the Marine Control surface temperature, while the 5 and 10 m median temperatures (both 18.02°C) were less than the corresponding Marine Control temperatures of 18.18°C and 18.17°C, respectively. The lowest temperature recorded in the grid was at station 1B (17.83°C).

3.2.2.4 Great Fish Marine Environment

Offshore of the Great Fish estuary during the September survey, no evidence of fresher water was recorded leaving the mouth, although median salinities were less than the salinities at the September Marine Control site (see above). The median surface salinity was 35.19psu, the same as the 10 m layer and slightly less than the 5 m median salinity (35.23psu), with no significant differences between the three layers ($p>0.05$). The lowest salinity was recorded at station 24A at the most south-western corner of the grid (34.73psu). Cooler water was found east of the mouth at the surface as well as at 5 and 10 m, with a 0.5°C difference between the warmest (17.62°C at station 24A) and coolest stations (17.12°C at station 5A) at the surface. The surface water over the grid (17.21°C) was slightly warmer than the 5 m and 10 m layers (17.17°C and 16.99°C, respectively), with a significant difference between the surface and 5 m median temperatures ($U < 0.001$; $p = 0.024$). Median temperatures offshore of the Great Fish estuary were cooler than at the September Marine Control site temperatures (see above).

3.2.3 Nutrient Concentrations

3.2.3.1 Kariega Estuary

There was no significant difference between median surface and bottom concentrations in any of the nutrients measured in the Kariega estuary during the September survey ($p>0.05$). The estuary was characterized by oligotrophic conditions, with a DIN median concentration of 1.14 mmol.m^{-3}. The highest concentration was found in the mouth region, 2.91 mmol.m^{-3} at station 10B, consisting primarily of the nitrate. For the rest of the estuary, however, ammonium contributed most to the DIN, with a median concentration of 0.84 mmol.m^{-3} for the system, while the nitrate value was less (0.32 mmol.m^{-3}) and nitrite lower still (a median concentration of less than 0.01 mmol.m^{-3}). Phosphate concentrations were highest in the upper reaches of the estuary (2.51 mmol.m^{-3} at station 2A) and decreased along the length of the estuary to 0.33 mmol.m^{-3} at station 10B at the mouth, with a median concentration of 1.41 mmol.m^{-3} (Figure 3.9). Silicate showed no vertical stratification, although a strong horizontal gradient was evident, decreasing from 225.86 mmol.m^{-3} at station 1A in the upper reaches, to 10.39 mmol.m^{-3} at station 10A at the mouth (Figure 3.10). The median silicate concentration in the estuary was 92.17 mmol.m^{-3}.

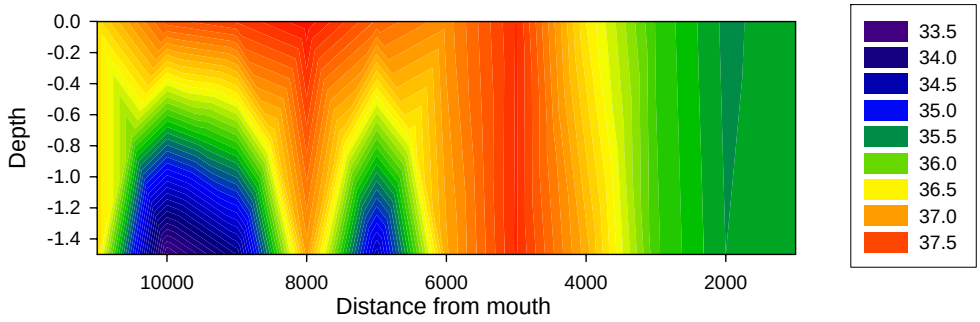


Figure 3.7 Salinity profile (psu) of the Kariega estuary in September. Distance from mouth and depth in m.

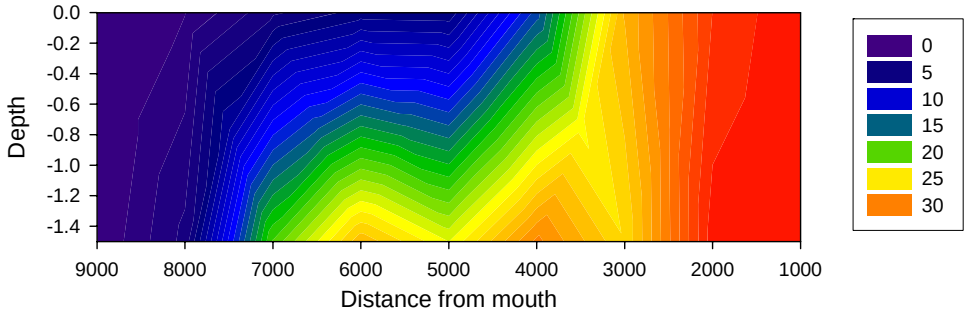


Figure 3.8 Salinity profile (psu) of the Great Fish Kariega estuary in September. Distance from mouth and depth in m.

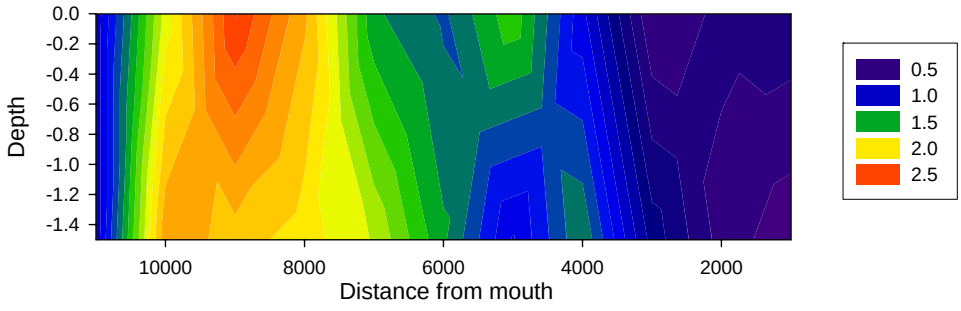


Figure 3.9 Phosphate profile (mmol.m^{-3}) of the Kariega estuary in September. Distance from mouth and depth in m.

3.2.3.2 Great Fish Estuary

As in the Kariega estuary, there were no significant differences between median surface and bottom concentrations in any of the nutrients measured in the Great Fish estuary during the September survey ($p>0.05$). Nitrate showed little vertical stratification, with the lowest concentration recorded in the waters at the head of the estuary at both the surface (1.97 $mmol.m^{-3}$) and bottom (2.00 $mmol.m^{-3}$). The fresh river water registered a nitrate concentration of 0.69 $mmol.m^{-3}$. Concentrations increased downstream to a peak at the surface at station 5A (4.46 $mmol.m^{-3}$), and then decreased towards the mouth (3.11 $mmol.m^{-3}$ at station 8A). Median surface nitrate and nitrite concentrations (3.67 $mmol.m^{-3}$ and 0.68 $mmol.m^{-3}$, respectively) were similar to median bottom concentrations (3.27 $mmol.m^{-3}$ and 0.57 $mmol.m^{-3}$, respectively). Ammonium, however, contributed the most to total DIN, with a median concentration of 7.37 $mmol.m^{-3}$ on the surface and 5.04 $mmol.m^{-3}$ on the bottom, with a peak on the bottom at station 2B (15.81 $mmol.m^{-3}$) (Figure 3.11). The median DIN concentration was 9.78 $mmol.m^{-3}$. A low phosphate content was found in the fresh river water (0.73 $mmol.m^{-3}$), with concentrations peaking a in the upper reaches downstream at station 2 (2.28 $mmol.m^{-3}$ on the surface and 2.05 $mmol.m^{-3}$ on the bottom) and then decreasing towards the mouth (0.60 $mmol.m^{-3}$ at station 8B). The median surface and bottom phosphate concentrations were similar (1.30 $mmol.m^{-3}$ and 1.33 $mmol.m^{-3}$, respectively). Silicate showed a similar pattern to the ammonium (and hence DIN), with a peak at station 2B (157.84 $mmol.m^{-3}$). The median silicate concentration was 46.56 $mmol.m^{-3}$ on the surface, and lower on the bottom, 33.16 $mmol.m^{-3}$.

3.2.3.3 Kariega Marine Environment

In the Kariega marine environment during the September survey, nitrate contributed the most to total DIN, with a peak in concentrations east of mouth at the surface and at 5 m at stations 8A and 8B (4.02 $mmol.m^{-3}$ and 4.52 $mmol.m^{-3}$, respectively). The remainder of the stations at the three depths showed little variation, with a median nitrate concentration of 2.31 $mmol.m^{-3}$ for the surface, 2.29 $mmol.m^{-3}$ for 5 m and 2.05 $mmol.m^{-3}$ for 10 m. There were no significant differences in median layer concentrations in any of the forms of

nitrogen measured ($p>0.05$). All median concentrations were similar to corresponding values at the Marine Control site. Nitrite concentrations were low at all three depths, reaching a maximum of 0.14 mmol.m^{-3} at station 5A, while ammonium showed a similar pattern to nitrate, peaking east of the mouth at stations 8A and 8B (1.02 mmol.m^{-3} and 0.94 mmol.m^{-3}, respectively). Phosphate concentrations were low, peaking at the surface, at 5 and 10 m in the vicinity of station 19, reaching a maximum concentration of 0.59 mmol.m^{-3} at station 19A, with no significant difference between the three layers ($p>0.05$). Phosphate concentrations of the Marine Control site were higher than the median concentrations found in the Kariega marine grid. Surface, 5 and 10 m silicate concentrations showed little in common, with peaks on the surface at station 23A on the western side of the grid (9.36 mmol.m^{-3}) and at 5 m at station 11B (8.06 mmol.m^{-3}), inshore and 500 m west of the mouth. The median surface, 5 and 10 m concentrations were 4.17 mmol.m^{-3}, 3.96 mmol.m^{-3} and 2.92 mmol.m^{-3}, respectively, with the 10 m median concentration significantly less than the surface ($U = 9.00$; $p < 0.001$) and 5 m median values ($U = 14.00$; $p = 0.001$). Median silicate concentrations were lower than the 7.87 mmol.m^{-3}, 6.70 mmol.m^{-3} and 4.76 mmol.m^{-3} measured at the surface, at 5 and at 10 m at the Marine Control site.

3.2.3.4 Great Fish Marine Environment

There were no significant differences between the median surface and 5 m concentrations of any of the nutrients measured in the Great Fish estuary during the September survey ($p>0.05$). Surface nitrate concentrations were highest in a plume of relatively nitrate-rich water leaving the mouth, reaching maximum concentrations at stations 2A (4.10 mmol.m^{-3}) and 4A (4.61 mmol.m^{-3}) opposite the mouth (Figure 3.12). At 5 m the highest concentration of nitrate was again found opposite the mouth, but confined to station 1B (6.01 mmol.m^{-3}), 250 m offshore and opposite the mouth. Median surface and 5 m nitrate concentrations were 2.97 mmol.m^{-3} and 2.74 mmol.m^{-3}, respectively, and contributed the most to total DIN in both layers. DIN median concentrations were 5.44 mmol.m^{-3} at the surface and 5.15 mmol.m^{-3} at 5 m, higher than the surface and 5 m concentrations of the Marine Control site (3.06 mmol.m^{-3} and 3.00 mmol.m^{-3}, respectively). Nitrite concentrations were lower than nitrate values, but above Marine Control surface and 5 m

concentrations (0.03 mmol.m^{-3} and 0.12 mmol.m^{-3}, respectively). Peaks in nitrate at the surface and at 5 m (median values of 0.44 mmol.m^{-3} and 0.40 mmol.m^{-3}, respectively) were found away form the plume of nitrate-rich water, reaching 0.72 mmol.m^{-3} at station 12A. Highest ammonium concentrations were recorded in association with the higher nitrate concentrations, reaching 3.95 mmol.m^{-3} and 4.92 mmol.m^{-3} opposite the mouth at stations 1A and 1B, respectively. Ammonium had a median value of 2.12 mmol.m^{-3} on the surface and 1.86 mmol.m^{-3} at 5 m, above those measured at the Marine Control site at the surface and 5 m (0.56 mmol.m^{-3} and 0.50 mmol.m^{-3}, respectively). Phosphate concentrations were generally low, with no evidence of phosphate-rich water leaving the estuary. The surface layer had a median value of 0.27 mmol.m^{-3} and the 5 m layer 0.22 mmol.m^{-3}, with phosphate reaching a maximum concentration of 0.44 mmol.m^{-3} at stations 12A and 1B. These were, however, below Marine Control concentrations. Low silicate concentrations were found opposite the mouth on the surface and at 5 m, while the highest concentration (10.81 mmol.m^{-3}) was recorded 850 m offshore and east of the mouth at station 9A on the surface. Surface and 5 m median concentrations (6.48 mmol.m^{-3} and 6.54 mmol.m^{-3}, respectively) were similar to those measured at the Marine Control site.

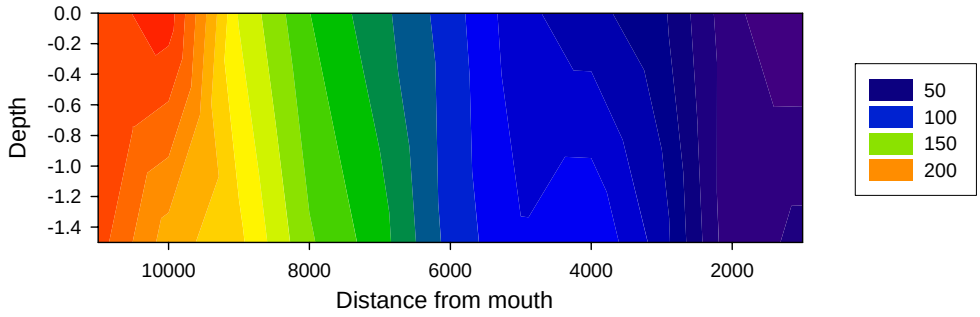


Figure 3.10 Silicate profile (mmol.m^{-3}) of the Kariega estuary in September. Distance from mouth and depth in m.

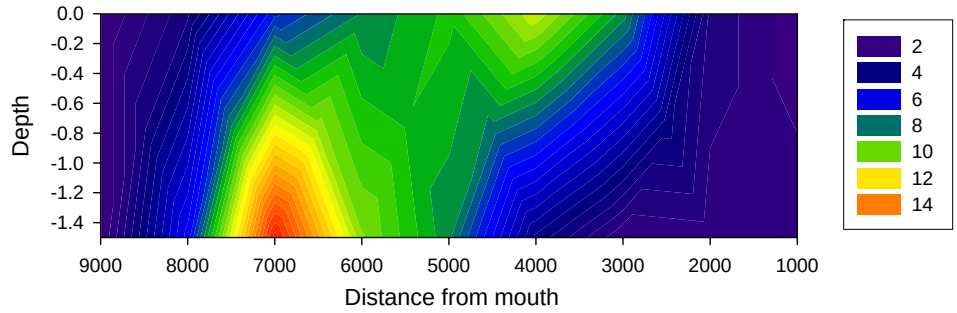


Figure 3.11 Phosphate profile (mmol.m^{-3}) of the Great Fish estuary in September. Distance from mouth and depth in m.

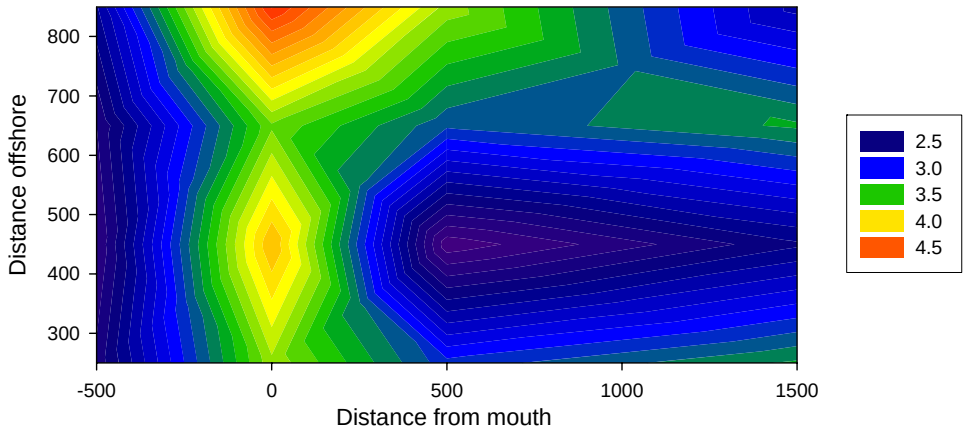


Figure 3.12 Surface nitrate plot (mmol.m^{-3}) of the Great Fish marine environment in September. Distances in m. Positive and negative distances from the mouth represent west and east, respectively.

3.3 DECEMBER SURVEY

3.3.1 Introduction

The summer samples were taken in early December, historically a dry period of the year in the Eastern Cape region. Towards the end of the month, however, heavy rain fell in Port Alfred, causing the monthly total to rise to 51.0 mm. During the thirty days prior to sampling, 41.2 mm of rain fell in Port Alfred. The flow rate in the Kariega River was 0.003 $m^3.s^{-1}$ on the day of sampling. The mean flow rate for the thirty days prior to sampling, however, was 0.004 $m^3.s^{-1}$ due to a slight increase in flow rates at the beginning of November in response to local rainfall. This was, however, still less than the mean monthly flow rate in the Kariega River for the study period. In the Great Fish River, the flow rate was 4.98 $m^3.s^{-1}$ on the day of sampling, with a similar mean flow rate of 4.30 $m^3.s^{-1}$ for the thirty days preceding sampling. These were higher than September flow rates, but lower than the June and mean monthly flow rates for the study period in the Great Fish River.

Due to technical problems with the probe, a hand-held refractometer was used to determine the salinity in both the estuarine and marine environments. A Marine Control station was occupied between the two estuaries.

December mean, median and inter-quartile range physico-chemical and nutrient concentration values are presented in Table 3.3. Full tables of results for the December survey can be found in Appendix 1 (Tables A1.3.1 to A1.3.4). The results of the statistical analyses for the Kariega and Great Fish estuaries and marine environments are shown in Appendix 2 (Tables A2.1.1 to A2.1.4).

Table 3.3 Mean (Mn), median (Mdn) and inter-quartile range (IQR) values of salinities (psu), temperatures (^{o}C) and nutrient concentrations (mmol.m^{-3}) for December. KE = Kariega estuary, GFE = Great Fish estuary, KM = Kariega marine environment, GFM = Great Fish marine environment.

	Depth	Salinity			Temperature			DIN			Nitrate		
	(m)	Mn	Mdn	IQR	Mn	Mdn	IQR	Mn	Mdn	IQR	Mn	Mdn	IQR
KE	**0**	34.10	34.00	1.00	26.81	27.40	2.00	4.47	2.97	3.76	1.78	1.05	2.44
	1.5	34.30	34.50	1.00	26.50	26.95	1.50	3.86	3.25	3.12	1.86	1.31	2.70
	System	34.20	34.00	1.00	26.66	27.20	1.85	4.16	2.97	3.24	1.82	1.05	2.57
GFE	**0**	9.38	9.50	13.50	25.58	25.70	0.60	3.41	3.39	2.36	1.01	0.58	1.60
	1.5	19.50	23.00	21.00	23.91	23.60	1.40	6.64	6.54	1.58	2.02	2.04	0.79
	System	14.44	13.00	18.00	24.74	25.05	2.10	5.02	5.38	3.15	1.51	1.83	1.62
KM	**0**	35.00	35.00	0.00	22.07	22.10	0.40	3.51	3.40	0.99	1.54	1.46	0.66
	5	35.00	35.00	0.00	22.03	22.05	0.40	3.45	3.41	0.79	1.55	1.39	0.71
	10	35.00	35.00	0.00	21.75	21.80	0.30	3.92	3.81	1.09	1.81	1.66	0.49
	System	35.00	35.00	0.00	21.98	22.00	0.40	3.57	3.52	1.03	1.60	1.53	0.69
GFM	**0**	31.47	32.00	3.00	21.48	21.50	0.10	1.45	1.44	0.53	0.49	0.52	0.17
	5	32.00	33.00	2.50	21.30	21.30	0.10	1.26	1.29	0.58	0.53	0.51	0.23
	10	33.08	33.50	3.00	21.04	21.15	0.40	1.40	1.16	1.18	0.64	0.58	0.52
	System	32.06	33.00	3.00	21.31	21.40	0.30	1.37	1.30	0.62	0.54	0.53	0.22

	Depth	Nitrite			Ammonium			Phosphate			Silicate		
	(m)	Mn	Mdn	IQR	Mn	Mdn	IQR	Mn	Mdn	IQR	Mn	Mdn	IQR
KE	**0**	0.25	0.24	0.07	2.43	1.80	0.89	0.90	0.91	0.75	86.20	83.28	74.19
	1.5	0.25	0.24	0.08	1.76	1.72	0.57	0.88	0.93	0.63	88.86	87.89	74.49
	System	0.25	0.24	0.08	2.09	1.77	0.58	0.89	0.93	0.67	87.53	87.12	74.34
GFE	**0**	0.57	0.67	0.83	1.84	1.76	0.34	2.30	2.32	0.57	185.09	182.55	12.30
	1.5	0.84	0.89	0.31	3.77	3.77	2.03	2.55	1.60	3.12	139.05	129.94	114.65
	System	0.71	0.77	0.49	2.80	2.38	2.02	2.42	2.20	1.46	162.07	180.99	68.54
KM	**0**	0.61	0.61	0.11	1.36	1.31	0.37	0.30	0.26	0.13	4.99	4.85	0.86
	5	0.62	0.64	0.12	1.27	1.29	0.42	0.31	0.28	0.16	4.97	4.87	1.04
	10	0.61	0.66	0.18	1.49	1.51	0.91	0.33	0.27	0.18	5.47	5.64	0.73
	System	0.62	0.62	0.12	1.35	1.33	0.47	0.31	0.27	0.14	5.08	4.95	1.04
GFM	**0**	0.20	0.20	0.12	0.77	0.79	0.40	0.13	0.08	0.15	4.21	4.30	0.84
	5	0.20	0.21	0.11	0.54	0.55	0.23	0.09	0.05	0.10	3.75	3.81	0.74
	10	0.18	0.17	0.17	0.59	0.46	0.35	0.13	0.12	0.10	4.53	4.35	2.26
	System	0.19	0.20	0.12	0.64	0.57	0.37	0.11	0.08	0.11	4.11	3.95	1.19

3.3.2 Physico-Chemical Factors

3.3.2.1 Kariega Estuary

Relatively fresher water was found above the causeway (31.00psu), feeding the Kariega estuary during the December survey. This resulted is lower salinities at stations 1A and B (both 32.00psu). By station 2, however, the salinity was 34.00psu on the surface and bottom, and other than at station 8A (33.00psu), the salinity remained either 34.00psu or 35.00psu, lacking vertical stratification (Figure 3.13). No hypersaline stations were recorded, resulting in a median salinity value of 34.00psu without any significant difference between surface and bottom median salinity values ($p>0.05$). The system was horizontally stratified with respect to temperature (no significant difference between median surface (27.40^{o}C) and bottom (26.95^{o}C) temperatures, $p>0.05$), decreasing from the upper stations (28.00^{o}C at station 1A) to the mouth (23.50^{o}C at station 10A) (Figure 3.14).

3.3.2.2 Great Fish Estuary

In Great Fish estuary, a well-defined salt-wedge was observed during the December survey, with fresh or very low salinity water dominating the upper reaches on both the surface and bottom (1.00psu at station 2A and 5.00psu at station 2B) (Figure 3.15). In the middle reaches, vertical stratification was evident, the greatest salinity difference at a station being 16.00psu between station 6A (15.00psu) and 6B (31.00psu). More saline marine water in the mouth (29.00psu at station 8B) was recorded undercutting the less dense, fresher water above. The median salinity value was 9.50psu for the surface and 23.00psu for the bottom layer, with no significant difference between the two ($p>0.05$). Cooler, denser marine water was found on the bottom in the lower reaches of the estuary (22.60^{o}C at station 6B), spreading out as a layer beneath the significantly warmer ($U = 2.00$; $p = 0.002$) river water above (26.20^{o}C at station 2A) (Figure 3.16). The median temperature was 25.70^{o}C for the surface layer, and 23.60^{o}C for the bottom layer.

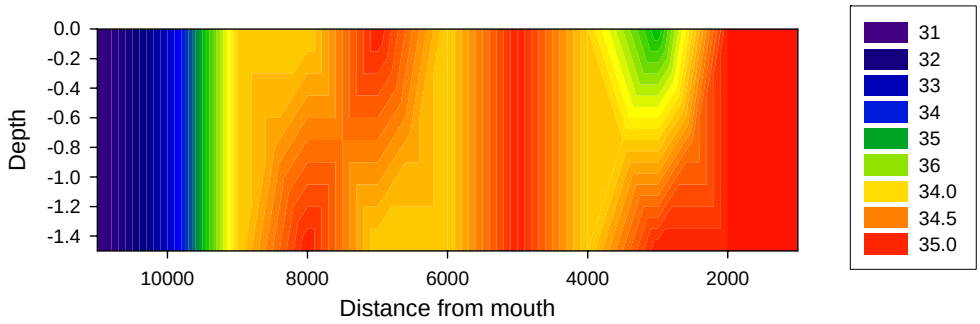


Figure 3.13 Salinity profile (psu) of the Kariega estuary in December. Distance from mouth and depth in m.

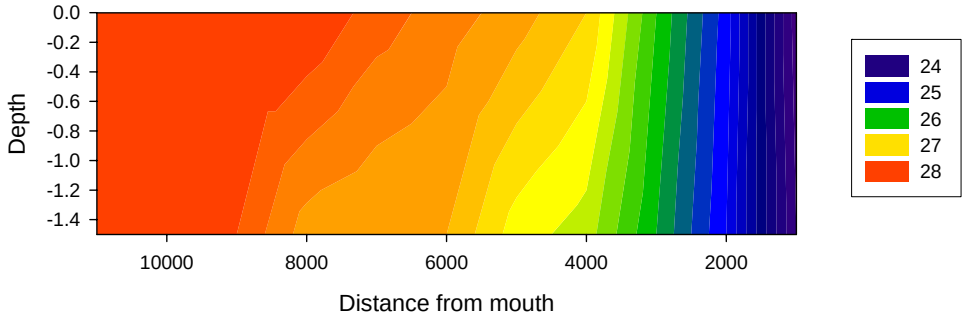


Figure 3.14 Temperature (^{o}C) profile of the Kariega estuary in December. Distance from mouth and depth in m.

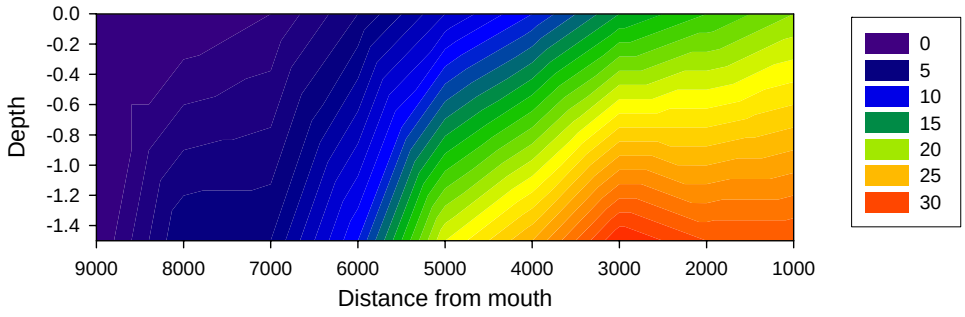


Figure 3.15 Salinity profile (psu) of the Great Fish estuary in December. Distance from mouth and depth in m.

3.3.2.3 Kariega Marine Environment

Due to technical problems with both the probe and refractometer in the Kariega marine environment during the December survey, salinity throughout the grid as well as at the Marine Control station, was assumed to be 35.00psu. The water west of the mouth was cooler at the surface as well as at 5 and 10 m (21.70^{o}C, 21.60^{o}C and 21.40^{o}C at stations 22A, 18B and 24C, respectively), with warmer water recorded east of the mouth, reaching 22.50^{o}C at stations 7A and 2B. The median 10 m temperature value (21.80^{o}C) was significantly cooler (U = 34.50; p = 0.002) than both and surface (22.10^{o}C) and 5 m (22.05^{o}C) median salinity values (U = 45.50; p = 0.007). Median temperatures were warmer than the Marine Control site temperatures of 21.80^{o}C for the surface and 5 m and 21.40^{o}C at 10 m.

3.3.2.4 Great Fish Marine Environment

During the December survey, an area of less saline water was found leaving the inshore region of the Great Fish marine environment 500 m west of the mouth and spreading offshore (26.00psu at station 12A and 27.00 at station 18A) (Figure 3.17). The fresher water was also traced at 5 m, but only dropped to a salinity of 28.00psu, again at stations 12B and 18B. At 10 m, the lowest salinity recorded was 30.00psu at station 12C. The median salinities at the surface, 5 and 10 m were 32.00psu, 33.00psu and 33.50psu, respectively, which were not significantly different from one another (p>0.05). In the vicinity of the less saline water, cooler water was found, dropping to 21.40^{o}C at station 12A, although there was little variation between this and the warmest station on the surface, 21.70^{o}C at station 22A. The surface layer had a median temperature of 21.50^{o}C, significantly warmer than both the 5 m, 21.30^{o}C (U = 76.5; p = 0.002), and the 10 m layers, 21.15^{o}C (U = 5.50; p < 0.001). Median temperatures were lower than at the Marine Control site temperatures of 21.8^{o}C at the surface and 5 m, and 21.4^{o}C at 10 m.

3.3.3 Nutrient Concentrations

3.3.3.1 Kariega Estuary

No significant differences were found between median surface and bottom concentrations in any of the nutrients measured in the Kariega estuary during the December survey ($p>0.05$). DIN concentrations were highest in the middle reaches of the estuary, where nitrate was recorded in higher concentration (3.8 $mmol.m^{-3}$ between stations 6 and 8) than ammonium (2.35 $mmol.m^{-3}$ in the same region). In the upper reaches, as well as at stations occupied in the vicinity of the mouth, ammonium concentrations were greater than nitrate values. For the estuary as a whole, DIN, nitrate and ammonium median concentrations were 2.97 $mmol.m^{-3}$, 1.05 $mmol.m^{-3}$ and 1.77 $mmol.m^{-3}$, respectively. Phosphate concentrations increased from 0.82 $mmol.m^{-3}$ in the upper reaches (at station 1A) to a maximum of 1.67 $mmol.m^{-3}$ in the middle reaches (at station 3A), then decreased towards the mouth with a total depletion at stations 10A and 10B (less than 0.01 $mmol.m^{-3}$). The median phosphate concentration was 0.93 $mmol.m^{-3}$. Silicate concentrations, as in previous surveys, showed no vertical stratification but a strong horizontal gradient, decreasing from a maximum concentration of 190.82 $mmol.m^{-3}$ above the causeway to 5.81 $mmol.m^{-3}$ at station 10A, located at the mouth of the estuary.

3.3.3.2 Great Fish Estuary

In the Great Fish estuary during the summer December survey, the DIN median concentration in the bottom layer (6.54 $mmol.m^{-3}$) was significantly higher than the median DIN concentration in the surface layer (3.39 $mmol.m^{-3}$) ($U = 0.00$; $p < 0.001$). Ammonium contributed more than nitrate to total DIN, particularly at the bottom in the upper reaches, reaching a maximum concentration of 5.22 $mmol.m^{-3}$ at station 2B. The surface waters were significantly lower in median ammonium concentration (1.76 $mmol.m^{-3}$) ($U = 1.00$; $p = 0.001$) than the bottom waters (3.77 $mmol.m^{-3}$). Nitrate concentrations were higher in the more saline waters intruding through the mouth than in the fresher river water entering at the head of the estuary (Figure 3.18), where concentrations were totally depleted (less than

0.01 mmol.m^{-3}). Highest concentrations were recorded in the middle reaches (3.84 mmol.m^{-3} at station 4B). The median concentration of the surface layer (0.58 mmol.m^{-3}) was significantly lower (U = 12.0; p = 0.036) than that of the bottom layer (2.04 mmol.m^{-3}). Phosphate concentrations in the upper reaches were higher in the bottom layer than the surface layer, reaching a maximum of 5.60 mmol.m^{-3} at station 1B. In the lower reaches, however, this trend was reversed, resulting in no significant difference between median surface (2.32 mmol.m^{-3}) and bottom concentrations (1.60 mmol.m^{-3}) ($p>0.05$). Silicate concentrations decreased from the upper reaches, where concentrations were high in the fresher river water (210.29 mmol.m^{-3} at station 3B), to the lower reaches, where the water column was vertically stratified with respect to silicate, (166.35 mmol.m^{-3} at the surface at station 8A and 87.25 mmol.m^{-3} at the bottom at station 8B in the more saline water). The median surface (182.55 mmol.m^{-3}) and bottom (129.94 mmol.m^{-3}) concentrations were not significantly different ($p>0.05$).

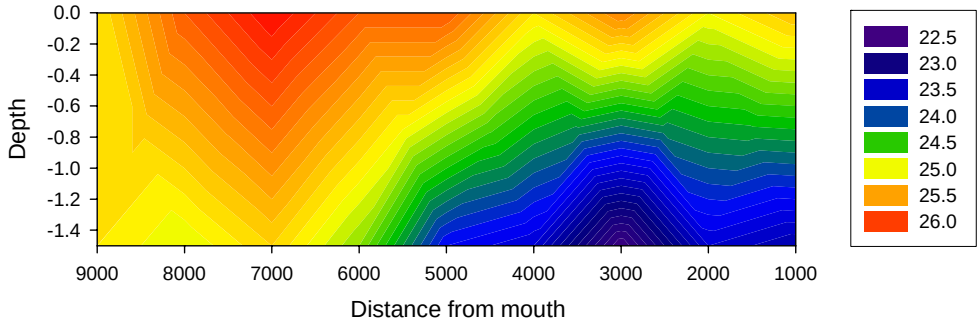


Figure 3.16 Temperature profile (^{o}C) of the Great Fish estuary in December. Distance from mouth and depth in m.

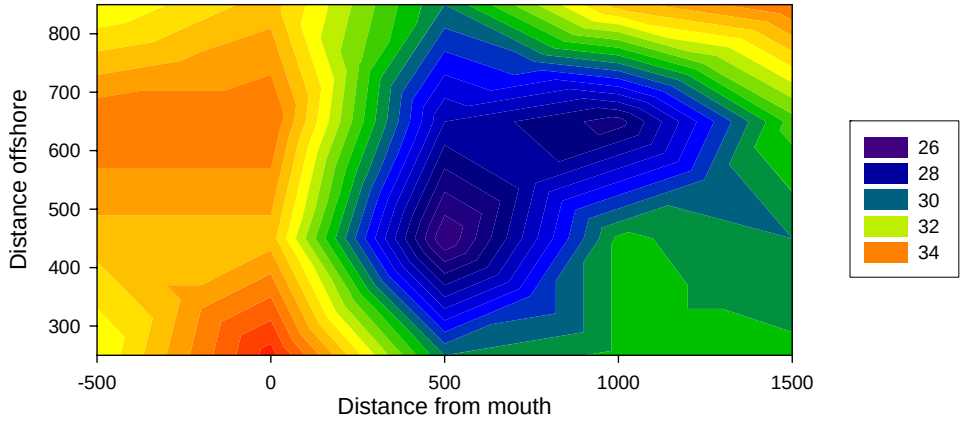


Figure 3.17 Surface salinity plot (psu) of the Great Fish marine environment in December. Distances in m. Positive and negative distances from the mouth represent west and east, respectively.

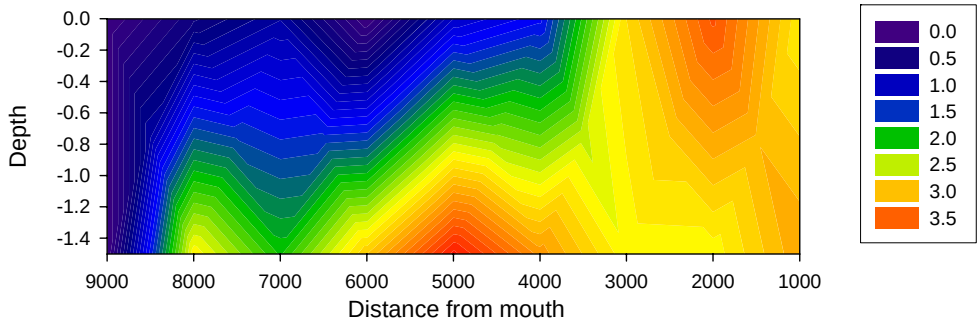


Figure 3.18 Nitrate profile (mmol.m^{-3}) of the Great Fish estuary in December. Distance from mouth and depth in m.

3.3.3.3 Kariega Marine Environment

Highest surface DIN concentrations in the Kariega marine environment during the December were found the inshore opposite the mouth (station 1A) and in the cooler waters west of the mouth (station 18A). The inshore peak was due to elevated ammonium concentrations (1.97 mmol.m^{-3} at station 1A and 2.40 mmol.m^{-3} at station 10A). Median nitrate concentrations between the three depths were not significantly different ($p>0.05$) and were 1.46 mmol.m^{-3} for the surface, 1.39 mmol.m^{-3} for the 5 m layer, and 1.66 mmol.m^{-3} for the 10 m layer. These were similar to the Marine Control nitrate concentrations. Ammonium had median concentrations of 1.31 mmol.m^{-3} at the surface, 1.29 mmol.m^{-3} for the 5 m and 1.51 mmol.m^{-3} for the 10 m layers. There were no significant differences in median concentrations between the three depths ($p>0.05$), which were similar to Marine Control ammonium concentrations. Nitrite, reaching a maximum of 0.74 mmol.m^{-3} on the far south-west corner of the grid at station 24A, maintained a median concentration in the region of 0.63 mmol.m^{-3} for the three layers, similar to concentrations recorded at the Marine Control site. Phosphate showed no definite trends in concentration with no significant differences ($p>0.05$) between the median concentrations at the three layers (0.26 mmol.m^{-3}, 0.28 mmol.m^{-3} and 0.27 mmol.m^{-3} for the surface, 5 m and 10 m layers, respectively), which were all above the Marine Control concentrations. Highest silicate concentrations were found west of the mouth (7.51 mmol.m^{-3} at station 18A). The 10 m layer median silicate concentration (5.64 mmol.m^{-3}) was significantly higher than the surface (4.85 mmol.m^{-3}) ($U = 49.00$; $p = 0.012$) but not the 5 m layer median silicate concentration (4.87 mmol.m^{-3}) ($p>0.05$). Median concentrations of all three layers were lower than the Marine Control site concentrations.

3.3.3.4 Great Fish Marine Environment

Nitrate, nitrite and ammonium concentrations were low offshore of the Great Fish estuary in December, and showed no increase in the fresher water leaving the estuary, with no significant difference in the three layers in nitrate, nitrite or total DIN ($p>0.05$). The median concentrations of nitrate, nitrite and ammonium in the surface layer were 0.52

mmol.m^{-3}, 0.2 mmol.m^{-3} and 0.79 mmol.m^{-3}, respectively. These values were all below Marine Control concentrations. The median nitrate concentration increased slightly with depth (0.58 mmol.m^{-3} at 10 m), while nitrite values remained constant. Ammonium values decreased to a significantly lower concentration at 5 m, 0.55 mmol.m^{-3} ($U = 83.50$; $p = 0.005$) as well as at 10 m, 0.46 mmol.m^{-3} ($U = 58.50$; $p = 0.024$). These values were all below Marine Control concentrations. The maximum total DIN concentrations were recorded in the north-eastern most corner of the grid (at station 9A and 9C), where the surface water had a concentration of 2.13 mmol.m^{-3} and the 10 m water a concentration of 2.36 mmol.m^{-3}. Phosphate concentrations were low, with median values of 0.08 mmol.m^{-3}, 0.05 mmol.m^{-3} and 0.12 mmol.m^{-3} for the surface, 5 m and 10 m, respectively, all below Marine Control concentrations with no significant differences between the layers ($p>0.05$). Median silicate concentrations were below Marine Control values. The surface layer (4.30 mmol.m^{-3}), however, was significantly higher in median concentration than the 5 m layer (3.81 mmol.m^{-3}) ($U = 105.5$; $p = 0.003$), and less but not significantly different from the median 10 m concentration (4.35 mmol.m^{-3}) ($p>0.05$).

3.4 MARCH SURVEY

3.4.1 Introduction

Heavy rainfall (37.4 mm on the 7th of March) before the autumn sampling trip, undertaken in March, resulted in increased flow rates in the Great Fish River. Whilst only 64.8 mm of rain fell in Port Alfred in March, 125.4 mm fell in the thirty days before sampling the estuaries and marine environments. The flow rate in the Great Fish River was 32.92 $m^3.s^{-1}$ on the day the estuary was sampled, with a lower mean flow rate for the thirty days preceding sampling of 20.87 $m^3.s^{-1}$. These were higher than the mean monthly flow rate in Great Fish River for the study period. The increased rainfall resulted in a mean flow rate of 0.005 $m^3.s^{-1}$ in the Kariega River for the thirty days prior to sampling, as well as on the day the estuary was sampled. This was the highest flow rate of any of the four sampling trips, but still, however, below the mean monthly flow rate in the Kariega River for the study period.

Conditions at sea were calm, allowing all transects and most stations to be occupied in both the Great Fish and Kariega marine environments. A Marine Control station was occupied between the two estuaries.

March mean, median and inter-quartile range physico-chemical and nutrient concentration values are presented in Table 3.4. Full tables of results for the March survey can be found in Appendix 1 (Tables A1.4.1 to A1.4.4). The results of the statistical analyses for the Kariega and Great Fish estuaries and marine environments are shown in Appendix 2 (Tables A2.1.1 to A2.1.4).

Table 3.4 Mean (Mn), median (Mdn) and inter-quartile range (IQR) values of salinities (psu), temperatures (^{o}C) and nutrient concentrations (mmol.m^{-3}) for March. KE = Kariega estuary, GFE = Great Fish estuary, KM = Kariega marine environment, GFM = Great Fish marine environment.

	Depth (m)	Salinity			Temperature			DIN			Nitrate		
		Mn	Mdn	IQR	Mn	Mdn	IQR	Mn	Mdn	IQR	Mn	Mdn	IQR
KE	**0**	35.68	35.26	1.61	23.29	24.19	2.58	3.24	2.74	2.65	2.00	1.78	2.00
	1.5	34.58	35.00	1.84	23.35	24.25	2.83	3.83	3.22	4.53	2.52	2.39	3.10
	System	35.13	35.05	1.67	23.32	24.20	2.70	3.54	3.10	3.53	2.26	1.98	2.28
GFE	**0**	0.68	0.56	0.41	24.04	24.13	0.27	88.43	88.46	3.80	77.77	79.15	6.12
	1.5	8.79	8.40	9.84	23.70	23.78	0.85	90.14	91.64	5.88	76.67	79.23	12.73
	System	4.73	1.09	7.91	23.87	24.04	0.51	89.29	89.34	5.97	77.22	79.15	9.83
KM	**0**	34.57	34.87	0.87	20.19	20.16	0.28	1.41	1.39	0.54	0.32	0.27	0.20
	5	34.61	34.92	0.91	20.10	20.13	0.12	0.95	0.92	0.50	0.34	0.28	0.22
	10	34.71	34.89	0.55	20.12	20.14	0.08	0.96	0.86	0.42	0.33	0.30	0.11
	System	34.61	34.89	0.89	20.14	20.14	0.11	1.14	1.09	0.57	0.33	0.28	0.19
GFM	**0**	33.18	34.07	1.84	18.77	18.72	0.31	19.25	19.49	16.36	12.23	11.96	10.77
	5	34.86	34.90	0.09	18.52	18.60	0.06	10.02	9.67	4.13	3.47	2.59	2.82
	10	34.91	34.94	0.05	18.60	18.60	0.11	7.81	8.50	3.57	2.80	2.68	1.04
	System	34.24	34.81	0.52	18.63	18.60	0.19	12.93	10.01	6.53	6.59	3.38	5.42

	Depth (m)	Nitrite			Ammonium			Phosphate			Silicate		
		Mn	Mdn	IQR	Mn	Mdn	IQR	Mn	Mdn	IQR	Mn	Mdn	IQR
KE	**0**	0.22	0.22	0.06	1.02	0.93	0.57	3.24	3.04	1.29	137.05	122.74	142.88
	1.5	0.27	0.24	0.15	1.04	0.79	1.08	3.54	3.71	0.73	129.22	115.97	126.44
	System	0.24	0.22	0.05	1.03	0.86	0.97	3.39	3.49	1.07	133.13	121.47	134.66
GFE	**0**	1.78	1.29	1.71	8.88	7.76	7.19	18.60	17.94	15.47	690.77	641.05	244.51
	1.5	2.78	2.23	2.85	10.69	9.70	10.02	20.99	22.44	19.35	671.99	640.63	104.27
	System	2.28	1.48	2.02	9.79	8.73	7.83	19.80	19.69	18.23	681.38	641.05	207.69
KM	**0**	0.32	0.18	0.38	0.76	0.83	0.51	1.04	0.68	1.17	19.43	18.37	4.18
	5	0.30	0.19	0.35	0.31	0.32	0.32	1.25	0.87	1.50	17.34	15.26	5.15
	10	0.27	0.16	0.34	0.36	0.32	0.47	1.41	1.42	1.15	17.10	15.16	6.61
	System	0.30	0.18	0.36	0.50	0.39	0.63	1.20	1.01	1.20	18.13	17.98	5.44
GFM	**0**	0.23	0.22	0.09	6.79	7.85	4.40	1.57	1.45	0.99	59.38	48.47	79.22
	5	0.22	0.21	0.08	6.33	6.17	2.87	0.84	0.81	0.58	17.47	13.59	4.29
	10	0.20	0.19	0.03	4.82	5.41	3.64	0.94	0.99	0.70	13.38	11.49	2.33
	System	0.22	0.20	0.07	6.12	6.36	3.78	1.14	1.07	0.75	32.16	14.77	17.46

3.4.2 Physico-Chemical Factors

3.4.2.1 Kariega Estuary

Hypersaline conditions were recorded in the surface and bottom waters in the upper reaches of the Kariega estuary during the March sampling trip (37.05psu at station 3A and 36.79psu at station 3B). Less saline water was recorded above the causeway (33.03psu) and at the bottom in the middle reaches (30.00psu at station 5B and 30.72psu at station 6B) (Figure 3.19). In the lower reaches of the estuary the salinity was closer to that of sea water, giving the estuary a median salinity of 35.05psu, with no significant difference between the top and bottom median salinity layers ($p>0.05$). Top and bottom median temperatures showed no significant difference ($p>0.05$) but a gradient from the upper (25.20^{o}C at station 1B) to lower reaches (19.72^{o}C at station 10B) was evident. The median temperature of the estuary was 24.20^{o}C.

3.4.2.2 Great Fish Estuary

Fresh water was recorded on the surface and bottom in the upper reaches of the Great Fish estuary, and all the way to the mouth at the surface (1.28psu at station 8A) during the March survey (Figure 3.20). In the middle reaches, the salinity rose to 7.30psu at station 3B, while the more saline water was confined to the mouth region (21.43psu at station 8B). The median salinity of the surface layer (0.56psu) was significantly lower ($U = 8.00$; $p = 0.012$) than the median salinity of the bottom layer (8.40psu). Warm river water was found in the upper reaches (24.14^{o}C at station 1A) overlying the cooler marine water in the middle and lower reaches (24.00^{o}C at station 6A and 22.70^{o}C at station 6B). The median surface temperature (24.13^{o}C) was not significantly different to the median bottom temperature (23.78^{o}C) ($p>0.05$).

3.4.2.3 Kariega Marine Environment

Offshore of the Kariega estuary during the March survey, less saline water was found east of the mouth compared to west, but the difference between the lowest surface salinities (34.00psu at stations 2A, 3A, 7A and 8A) and the highest (34.95psu at stations 19A and 23A), was marginal (less than 1psu). At 5 m, the east-west gradient was still present, but even weaker. There were no significant differences in median salinity values between the three depths ($p>0.05$). The median salinities were 34.87psu at the surface, 34.92psu at 5 m and 34.899psu at 10 m. These values were higher than the Marine Control salinities, which were 34.05psu for the surface and 34.00psu for 5 and 10 m. A temperature gradient was evident between east and west, with 0.5°C separating station 1A (19.93°C) and 24A (20.43°C). Although the gradient was also evident at 5 m, the difference was minimal (less than 0.2°C). Median temperatures showed no significant differences from one another ($p>0.05$), and were 20.16°C on the surface, 20.13°C at 5 m, and 20.14°C at 10 m. These were generally cooler than the Marine Control temperatures (20.45°C, 20.26°C and 20.12°C for the surface, 5 and 10 m, respectively).

3.4.2.4 Great Fish Marine Environment

In the Great Fish marine environment during the March survey, a body of fresher water was present at the surface opposite the mouth, where salinities at stations 2A and 3A were 24.45psu and 28.50psu, respectively (Figure 3.21). Relatively fresher water was also found at stations 10A, 11A and 12A, all inshore and close to the mouth. The surface median salinity was 34.07psu, which was similar to the Marine Control surface salinity (34.05psu). Significantly higher median salinities were recorded at 5 (34.90psu) ($U = 7.00$; $p < 0.001$) and 10 m (34.94psu) ($U = 0.00$; $p < 0.001$). The 5 m layer median salinity was significantly lower ($U = 49.50$; $p = 0.011$) than that of the 10 m layer, but both were above Marine Control 5 and 10 m salinities (both 34.00psu). Warmer water was recorded on the surface where the less saline water was positioned (19.78°C at station 2A), while the rest of the surface temperatures varied little. The median surface temperature was 18.72°C,

significantly warmer than the median 5 (U = 81.00; p 0.010) and 10 m temperatures (U = 49.5; p = 0.011), both 18.60^{o}C. Temperatures were cooler than at the Marine Control site.

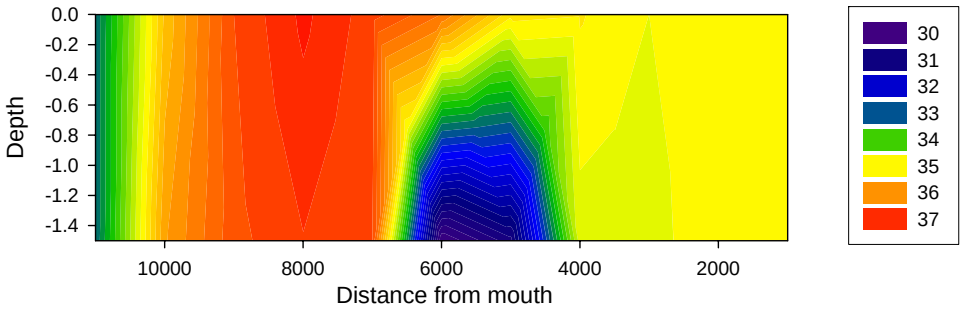


Figure 3.19 Salinity profile (psu) of the Kariega estuary in March. Distance from mouth and depth in m.

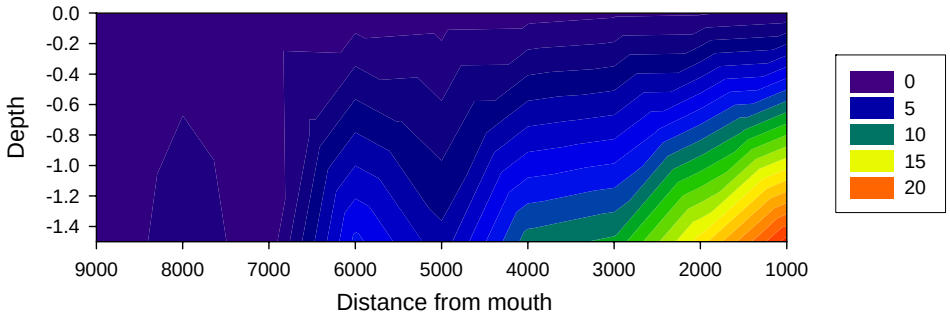


Figure 3.20 Salinity profile (psu) of the Great Fish estuary in March. Distance from mouth and depth in m.

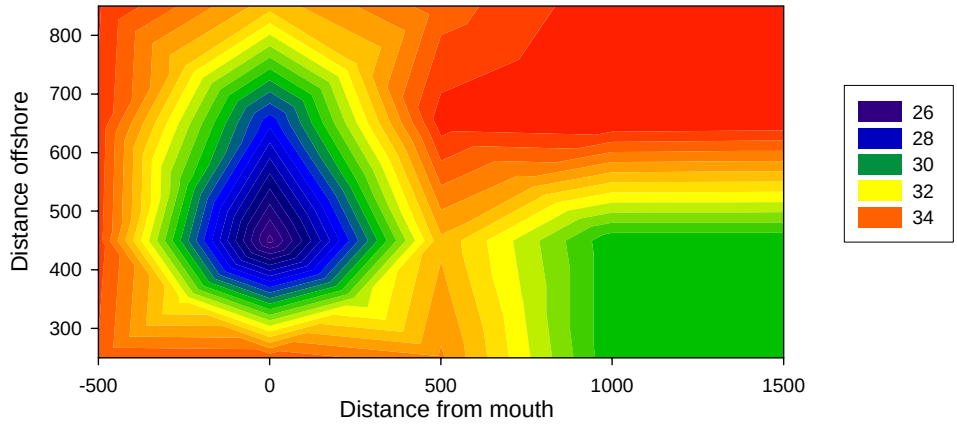


Figure 3.21 Surface salinity plot (psu) of the Great Fish marine environment in March. Distances in m. Positive and negative distances from the mouth represent west and east, respectively.

3.4.3 Nutrient Concentrations

3.4.3.1 Kariega Estuary

There were no significant differences between median surface and bottom concentrations of any of the nutrients measured in the Kariega estuary during the March survey ($p>0.05$). The middle reaches, where salinity values were lowest, were characterised by the highest DIN concentrations (7.02 mmol.m^{-3} at station 7B) (Figure 3.22). Lower concentrations were recorded in the upper (0.93 mmol.m^{-3} at station 1A) and lower reaches (2.21 mmol.m^{-3} at station 10A) of the estuary. The maximum nitrate concentration was recorded at station 6B (4.54 mmol.m^{-3}), while ammonium concentration was at its highest one station further downstream, at 7B (2.51 mmol.m^{-3}). Nitrite concentrations remained fairly constant throughout the estuary, giving a median value of 0.22 mmol.m^{-3}. The median DIN concentration was 3.10 mmol.m^{-3}. Phosphate concentrations were highest in the middle reaches in the vicinity of the less saline water, reaching a concentration of 6.02 mmol.m^{-3} at stations 4B and 5A, with median concentration of 3.49 mmol.m^{-3} for the estuary. Silicate showed a horizontal gradient from a maximum of 302.85 mmol.m^{-3} at station 1A to a minimum of 24.82 mmol.m^{-3} at station 9B, near the mouth of the estuary. The median silicate concentration was 121.47 mmol.m^{-3}.

3.4.3.2 Great Fish Estuary

There were no significant differences between median surface and bottom concentrations of any of the nutrients measured in the Great Fish estuary during the March survey. Nitrate concentrations decreased from the upper (81.58 mmol.m^{-3} and 84.71 mmol.m^{-3} at stations 1A and 1B, respectively) to the lower reaches (66.86 mmol.m^{-3} and 64.13 mmol.m^{-3} at stations 8A and 8B, respectively), with a median value of 79.15 mmol.m^{-3} in the surface waters and 79.23 mmol.m^{-3} in the bottom layer (Figure 3.23). Both ammonium and nitrite increased in concentration in the lower reaches in the presence of the cooler more saline water. Ammonium reached a maximum concentration of 18.32 mmol.m^{-3} at station 6B, with a median concentration of 7.76 mmol.m^{-3} on the surface and 9.70 mmol.m^{-3} on the

bottom, while nitrite reached a maximum concentration of 5.40 mmol.m^{-3} at station 5B, with a median concentration of 1.29 mmol.m^{-3} on the surface and 2.23 mmol.m^{-3} on the bottom. The median DIN concentration was 89.34 mmol.m^{-3}. Phosphate concentrations showed little vertical stratification and were highest in the middle to lower reaches, reaching 32.51 mmol.m^{-3} at station 7B. The median concentration for the estuary was 19.69 mmol.m^{-3}. Silicate concentrations were high throughout the estuary, peaking in the middle reaches (835.73 mmol.m^{-3} at stations 5A, 5B and 6A) with a median value of 641.05 mmol.m^{-3}.

3.4.3.3 Kariega Marine Environment

The median DIN surface concentration (1.39 mmol.m^{-3}) offshore of the Kariega estuary during the March survey was significantly higher ($U = 74.00$; $p < 0.001$) than both the 5 m (0.92 mmol.m^{-3}), and 10 m median concentrations (0.86 mmol.m^{-3}) ($U = 36.00$; $p = 0.005$). The median DIN surface concentration was higher than the corresponding Marine Control value (0.88 mmol.m^{-3}), but the lower layers were below the values recorded at the Marine Control site at 5 and 10 m (1.40 mmol.m^{-3} and 1.33 mmol.m^{-3}, respectively). The highest DIN concentration (2.12 mmol.m^{-3}) was recorded at the surface at the furthest offshore eastern-most station, station 9A. Ammonium contributed more than nitrate to total DIN, with the median concentration at the surface layer (0.83 mmol.m^{-3}) being significantly higher ($U = 57.50$; $p < 0.001$) than the median values at 5 (0.32 mmol.m^{-3}) and 10 m (0.32 mmol.m^{-3}) ($U = 33.00$; $p = 0.003$). Nitrate maintained a median concentration of between 0.16 mmol.m^{-3} and 0.19 mmol.m^{-3} over the three layers, which were higher than the corresponding Marine Control values. Nitrite concentrations showed an east (0.64 mmol.m^{-3} at station 3A) to west (0.14 mmol.m^{-3} at station 18A) gradient at the surface and at 5 m. Median concentrations were 0.27 mmol.m^{-3}, 0.28 mmol.m^{-3} and 0.30 mmol.m^{-3} for the surface, 5 and 10 m, respectively. There were no significant differences in nitrate and nitrite median concentration values between the three depths ($p>0.05$). Highest phosphate concentrations were found on the western side of the grid, reaching 3.05 mmol.m^{-3} at station 14B and 20B at 5 m, and 2.67 mmol.m^{-3} at station 22A on the surface. Median phosphate concentrations increased with depth, but without a significant difference, from

0.68 mmol.m^{-3} at the surface to 0.87 mmol.m^{-3} at 5 m and 1.42 mmol.m^{-3} for the 10 m layer. All three median layer concentrations were below the Marine Control values. Silicate showed no distinct patterns, except for highest concentrations on the surface and at 5 m being opposite the mouth (23.52 mmol.m^{-3} and 31.49 mmol.m^{-3} at stations 1A and 1B, respectively). Median concentrations decreased significantly from the surface (18.37 mmol.m^{-3}), to 5 m (15.26 mmol.m^{-3}) ($U = 113.00$; $p = 0.019$) and from the surface to 10 m (15.16 mmol.m^{-3}) ($U = 50.50$; $p = 0.029$). All three median layer concentrations were below the Marine Control values.

3.4.3.4 Great Fish Marine Environment

A distinct plume of DIN-rich water was found leaving the Great Fish estuary in March and entering the nearshore area 500 m west of the mouth (Figure 3.24). Station 10A had the highest DIN concentration (40.79 mmol.m^{-3}), while concentrations east of the mouth, in the more saline water, were lower. The median surface DIN concentration (19.49 mmol.m^{-3}) was significantly higher than the median 5 (9.67 mmol.m^{-3}) ($U = 79.00$; $p = 0.008$) and 10 m concentrations (8.50 mmol.m^{-3}) ($U = 35.00$; $p = 0.002$). All three median values were well above Marine Control DIN concentrations. Nitrate was the most abundant form of nitrogen, with a median concentration of 11.96 mmol.m^{-3} for the surface layer and a maximum concentration of 28.70 mmol.m^{-3} at station 10A, in the plume. The nitrate-rich water was confined to the surface layer, with significantly lower median 5 (2.59 mmol.m^{-3}) and 10 m (2.68 mmol.m^{-3}) concentrations ($U = 49.00$; $p < 0.001$ and $U = 27.00$; $p < 0.001$, respectively). The median values of all three depths were above Marine Control nitrate concentrations. Ammonium levels were elevated within in the plume. The highest surface concentrations were found at stations 10A (11.87 mmol.m^{-3}) and 13A (10.62 mmol.m^{-3}) 500 m west of the mouth. The maximum concentration of ammonium within the grid, however, was recorded in the 5 m layer (15.02 mmol.m^{-3} at station 10B). There were no significant differences in the median values of the surface (7.85 mmol.m^{-3}), 5 (6.17 mmol.m^{-3}) and 10 m layers (5.41 mmol.m^{-3}) ($p>0.05$). All were, however, higher than Marine Control values. The median nitrite concentrations were 0.22 mmol.m^{-3}, 0.21 mmol.m^{-3} and 0.19 mmol.m^{-3} for the surface, 5 and 10 m layers, respectively. These values

were all above Marine Control levels, with no significant differences between the three layers ($p>0.05$). The waters east of the mouth were depleted of phosphate, with higher concentrations opposite the mouth and higher still at 500 m west of the mouth. The highest concentration were recorded at station 10A (3.19 $mmol.m^{-3}$), 250 m west of the mouth at the furthest inshore station of the grid. The surface layer had a median concentration of 1.45 $mmol.m^{-3}$, lower than the Marine Control site but significantly higher than the median 5 (0.81 $mmol.m^{-3}$) and 10 m (0.99 $mmol.m^{-3}$) concentrations ($U = 62.00$; $p = 0.002$ and $U = 51.00$; $p = 0.016$, respectively). Higher silicate concentrations were recorded in the plume, with maximum concentrations at station 10A (170.54 $mmol.m^{-3}$), 12A (114.99 $mmol.m^{-3}$) and 4A (118.34 $mmol.m^{-3}$), all in the surface layer. The surface silicate median concentration of 48.47 $mmol.m^{-3}$ was significantly higher than the median 5 (13.59 $mmol.m^{-3}$) and 10 m (11.49 $mmol.m^{-3}$) concentrations ($U = 39.50$; $p < 0.001$ and $U = 15.00$; $p < 0.001$, respectively). Marine Control concentrations were lower at the surface (25.07 $mmol.m^{-3}$) than the median value for the grid offshore of the Great Fish estuary, but higher at 5 and 10 m (20.08 and 15.74, respectively).

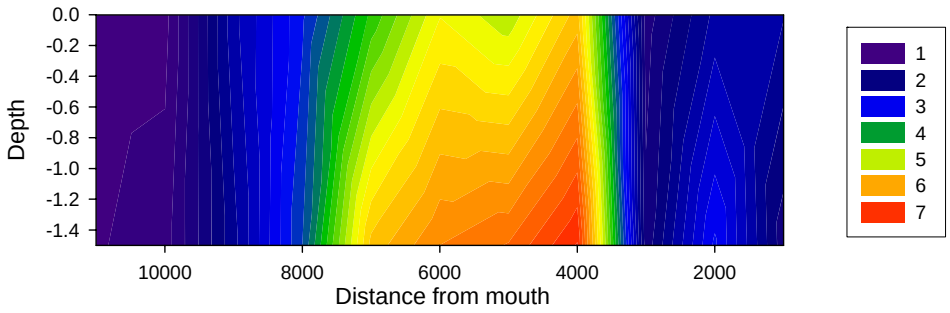


Figure 3.22 DIN profile (mmol.m^{-3}) of the Kariega estuary in March. Distance from mouth and depth in m.

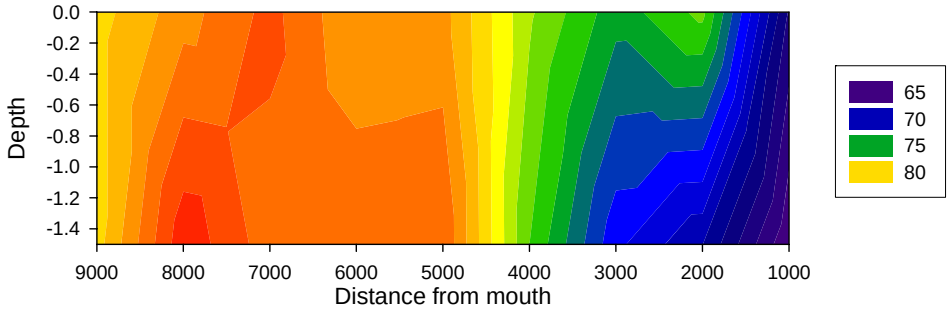


Figure 3.23 Nitrate profile (mmol.m $^{-3}$) of the Great Fish estuary in March. Distance from mouth and depth in m.

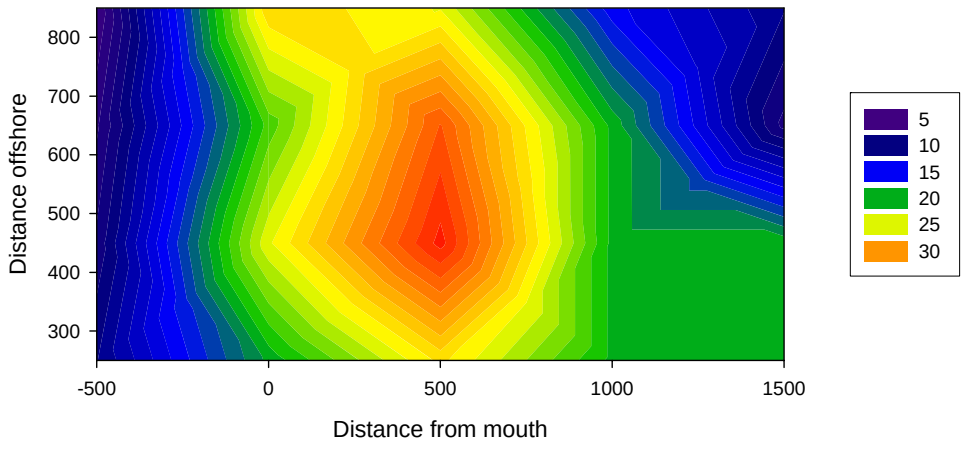


Figure 3.24 Surface DIN plot (mmol.m^{-3}) of the Great Fish marine environment in March. Distances in m. Positive and negative distances from the mouth represent west and east, respectively.

3.5 SEASONAL TRENDS

Median values of the four systems were each compared over the four surveys to test for significant differences in salinity, temperature and the concentrations of the nutrients measured. Median values used were for the system, combining all depth layers. Appendix 2 (Tables A2.1.5 and A2.1.6) contains the results of the analyses of the two estuaries and two marine environments.

3.5.1 Kariega Estuary

There were no distinct trends in the Kariega estuary, with no surveys being consistently significantly higher in median nutrient concentrations and salinity values than the remaining surveys. There was, however, a significant difference in median salinity between all surveys, except June and September, when median salinities were hypersaline. The median DIN concentration in September was significantly lower than the remaining surveys. In terms of nitrate median concentrations, June proved to be significantly higher than the remaining surveys, while March and December were significantly higher than September. December was significantly higher than all other surveys in terms of ammonium. In terms of median phosphate concentration, March was significantly higher than the remaining surveys, while June which was significantly higher than December. No significant difference was found in median silicate concentrations over the four surveys, the exception being March and June, when March was significantly higher. Median temperature, as expected, was significantly different in all surveys.

3.5.2 Great Fish Estuary

Median nutrient concentrations and salinity values in the Great Fish estuary were largely determined by flow rate. Increased flow rates in March and June were associated with reduced salinity values and increased levels of nutrients in the estuary. The highest median concentrations were in March, which was significantly lower in median salinity value than the remaining surveys. March was significantly higher in median concentration of all

nutrients than either September or December, an exception being ammonium in September. March was significantly higher in median ammonium, phosphate and silicate concentrations than June. June was significantly higher in the majority of median nutrient concentrations than in September and December, when lower concentrations were recorded. December was, however, significantly higher than September in median phosphate and silicate concentrations, but significantly lower in DIN, nitrate and nitrite median concentrations. In response to the changing seasons, all surveys were significantly different in terms of median temperature, except December and March, where warmer than expected temperatures were recorded on March

3.5.3 Kariega Marine Environment

All salinity, temperature and nutrient median concentrations were significantly different between all surveys in the Kariega marine environment, except June and March in terms median phosphate concentration. As in the estuary, high DIN concentrations were recorded in June and high silicate concentrations measured in March in the marine environment. Generally speaking, June and March had significantly higher median nutrient concentrations than December (an exception being DIN in March, which had the lowest median concentration of the surveys), which was in turn significantly higher in median concentrations then September (an exception being for phosphate, which was significantly lower in median concentration in December).

3.5.4 Great Fish Marine Environment

As in the Kariega marine environment, June and March in the Great Fish marine environment contained the highest median nutrient concentrations (no significant differences in terms of DIN, phosphate and silicate median concentrations), significantly higher than September which was in turn significantly higher than December in all median nutrient concentrations. December, however, had the lowest median salinity value, significantly lower than March, which was significantly lower than September and June (which were not significantly different from one another). There was also no significant

difference between September and March in terms of median nitrate concentration, and between December and March in terms of median nitrite concentration. All median temperature vales were significantly different from one another.

3.6 INTERSYSTEM RELATIONS

The median values of the two estuaries and two marine environments, as well as the corresponding estuaries and marine environments were compared over the four surveys to test for significant differences in median salinity, temperature and the nutrient concentrations. Median values used were once again for the system, combining all depth layers. Appendix 2 (Table A2.1.7) contains the results of the analysis.

3.6.1 Kariega Estuary vs. Great Fish Estuary

The median salinity and temperature values in the Kariega estuary were significantly higher than in the Great Fish estuary in all surveys. An exception was recorded in March, when there was no significant difference in median temperature values between the two systems. The concentrations of nutrients in the Great Fish estuary were significantly higher than the Kariega estuary during all four surveys. Exceptions, when there was no significant difference between the two systems, were recorded in December in terms of median DIN and nitrate concentrations, in June in terms of median nitrite concentration and in September in median phosphate concentration. During the September survey, silicate was significantly higher in median concentration in the Kariega estuary.

3.6.2 Kariega Marine Environment vs. Great Fish Marine Environment

The Kariega marine environment was significantly higher in median salinity and temperature values than the Great Fish marine environment in all four surveys, with an exception in March, when there was no significant difference in median salinity value. In terms of median nutrient concentrations, the Kariega marine environment was significantly higher in all nutrients measured in September and in DIN, nitrate and ammonium in June.

There were no significant differences in median concentration of nitrate and phosphate in June between the two marine environments. The Great Fish marine environment, however, was significantly higher in all median nutrient concentrations in March (exceptions being median nitrite, phosphate and silicate concentrations which were not significantly different from the Kariega marine environment), September (exceptions being median phosphate concentration, which was significantly higher in the Kariega marine environment), and June (an exception being median phosphate concentration, which was not significantly different to that of the Kariega marine environment).

3.6.3 Kariega Estuary vs. Kariega Marine Environment

The Kariega estuary was significantly higher in median salinity than the Kariega marine environment in all surveys except December, in which the median salinity value of the estuary was significantly lower. In terms of median temperature, the estuary was significantly warmer in all surveys except June, when there was no significant difference with the marine environment. The marine environment was significantly higher in DIN, nitrate and nitrite median concentrations in September, as well as in median nitrite concentration in June and December and in median ammonium concentration in June. There was no significant difference between the estuary and marine environment in median DIN and nitrate concentrations in June and December and in nitrite in March. The estuary was significantly higher than the marine environment in all surveys in terms of phosphate and silicate median concentrations, as well as median ammonium concentration, except in June, as already stated. The estuary was also significantly higher in DIN and nitrate median concentrations in March.

3.6.4 Great Fish Estuary vs. Great Fish Marine Environment

The Great Fish marine environment was consistently significantly higher in all surveys in median salinity than the Great Fish estuary, and lower in median temperature in all surveys except June, when the estuary was significantly cooler. In terms of median nutrient concentrations, the estuary was significantly higher in median concentration of all nutrients

measured in all surveys, except for one occasion in June, when there was no significant difference between the estuary and marine environment in median nitrite concentration.

CHAPTER 4 – LOICZ BUDGETS

4.1 KARIEGA ESTUARY

4.1.1 Water and Salt balance

For the Kariega estuary, a simple one-box one-layer model was used for all surveys due to the lack of horizontal or vertical stratification in salinity within the system. The absence of any gradients was due to the low flow rate (V_Q), exceeded by both precipitation (V_P) and evaporation (V_E) in all surveys except June, the driest month (Table 4.1). Salinity in the system (S_{SYS}) exceeded the salinity of the sea (S_{OCN}) in all surveys except December. The residual salinity (S_R) is included in order to highlight the high salinities exchanged across the estuarine-ocean boundary. The residual flow (V_R) was positive in all surveys, i.e. movement of water from the sea into the estuary. In December, however, the system was deemed to be in an 'unsteady state' as the relevant ocean and estuary salinities were such that a negative V_R term was required in order to balance the lower salinity in the estuary. This resulted in a negative mixing flux (V_X) and water residence time (τ) in December, and unreliable nutrient flux and system metabolism rates. The water residence time ranged from approximately two and a half months in June, to almost eight months in March. Figure 4.1 illustrates the water and salt budgets for the estuary.

Table 4.1 Water flux, salinity and water exchange time for the Kariega estuary.

	Water Flux ($10^3.m^3.day^{-1}$)					**Salinity** (psu)			**τ** (days)
	V_Q	V_P	V_E	V_R	V_X	S_{OCN}	S_{SYS}	S_R	$_{SYS}$
June	0.26	0.11	2.11	1.7	51.4	35.32	36.70	36.01	72
Sep	0.26	2.20	2.93	0.5	26.3	35.19	36.23	35.71	143
Dec	0.35	2.20	5.81	3.3	-125.1	35.20	34.20	34.70	-32
March	0.43	3.34	3.90	0.1	16.4	34.05	35.13	34.59	233

4.1.2 Budgets of nonconservative materials

The nonconservative dissolved inorganic phosphorus (DIP) flux (ΔDIP) of the system was positive for June, September and March, implying the estuary was a weak source of DIP in all surveys except December, when the estuary acted as a sink for phosphate (Table 4.2). In December, however, flux rates were unreliable due to the system being in an 'unsteady' state. ΔDIP remained constant in June and September (+0.017 $mmolm^{-2}day^{-1}$ and +0.016 $mmolm^{-2}day^{-1}$, respectively) and was higher in September (+0.024 $mmolm^{-2}day^{-1}$). ΔDIP was dominated by the mixing flux ($V_X DIP_X$, where $DIP_X = DIP_{OCN} - DIP_{SYS}$) in all surveys due to a relatively small residual flux ($V_R DIP_R$) because of the similarity of the ocean and system salinities, as well as a small flow flux ($V_Q DIP_Q$) because of the low flow rates (Figure 4.2). The nonconservative dissolve inorganic nitrogen (DIN) flux (ΔDIN) of the system was negative in June, September and December (although December is not taken into consideration) behaving as a net sink for DIN. The flux decreased from -48 $mmolm^{-2}day^{-1}$ in September to -139 $mmolm^{-2}day^{-1}$ in June. For March, the system flux was positive +35 $mmolm^{-2}day^{-1}$, implying a source of DIN (Table 4.2). As with phosphate, ΔDIN was determined principally by the mixing flux (Figure 4.3), which in March was negative i.e. out of the system due to higher DIN concentrations in the system than the adjacent ocean, while in June and September (and December), the mixing flux was positive.

Table 4.2 Nonconservative fluxes of DIP (ΔDIP) and DIN (ΔDIN) for the Kariega estuary.

	ΔDIP		**ΔDIN**	
	($mol.day^{-1}$)	($mmol.m^{-2}.day^{-1}$)	($mol.day^{-1}$)	($mmol.m^{-2}.day^{-1}$)
June	+27	+0.017	-139	-0.09
September	+25	+0.016	-48	-0.03
December	-76	-0.048	-95	-0.06
March	+38	+0.024	+35	+0.02

4.1.3 Stoichiometric calculations of aspects of net system metabolism

In June, September and March respiration in the estuary exceeded primary production, rendering the system net heterotrophic. In December, the opposite trend was observed, with autotrophic processes dominating (Table 4.3). The December results however, were discounted due the unsteady nature of the system. Apparent system net nitrogen metabolism indicates that in June, September and March the estuary exhibited primarily denitrification, with the expected DIN flux (ΔDIN_{EXP}) greater than the observed DIN flux (ΔDIN_{OBS}). In December, nitrogen fixation dominated over denitrification (Table 4.3). The December results are again, however, unreliable.

Table 4.3 Apparent net ecosystem metabolism for the Kariega estuary.

	(*p* – *r*) (mmol.C.m^{-2}.day^{-1})	**(*nfix* – *denit*)** (mmol.N.m^{-2}.day^{-1})
June	-1.8	-0.36
September	-1.7	-0.29
December	+5.1	+0.71
March	-2.5	-0.36

4.1.4 Kariega Estuary 'box diagrams'

Figure 4.1 Water and salt budgets for the Kariega estuary in (a) June, (b) September, (c) December and (d) March. Water flux in 10^3 ^{m3}.day^{-1} and salt flux in 10^3psu-m^3.day^{-1}.

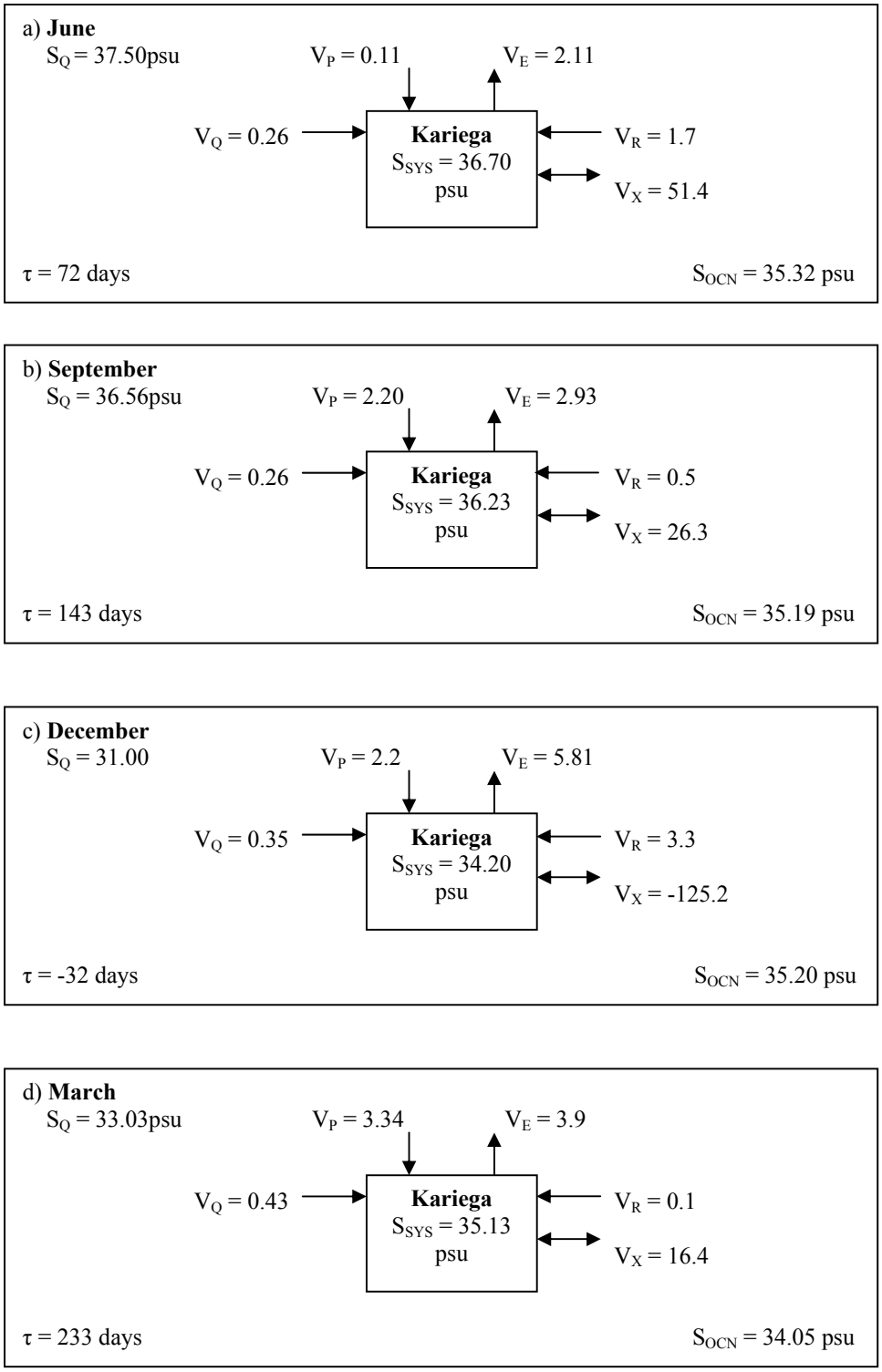


Figure 4.2 DIP budget for the Kariega estuary in (a) June, (b) September, (c) December and (d) March. Flux in mol.day^{-1}.

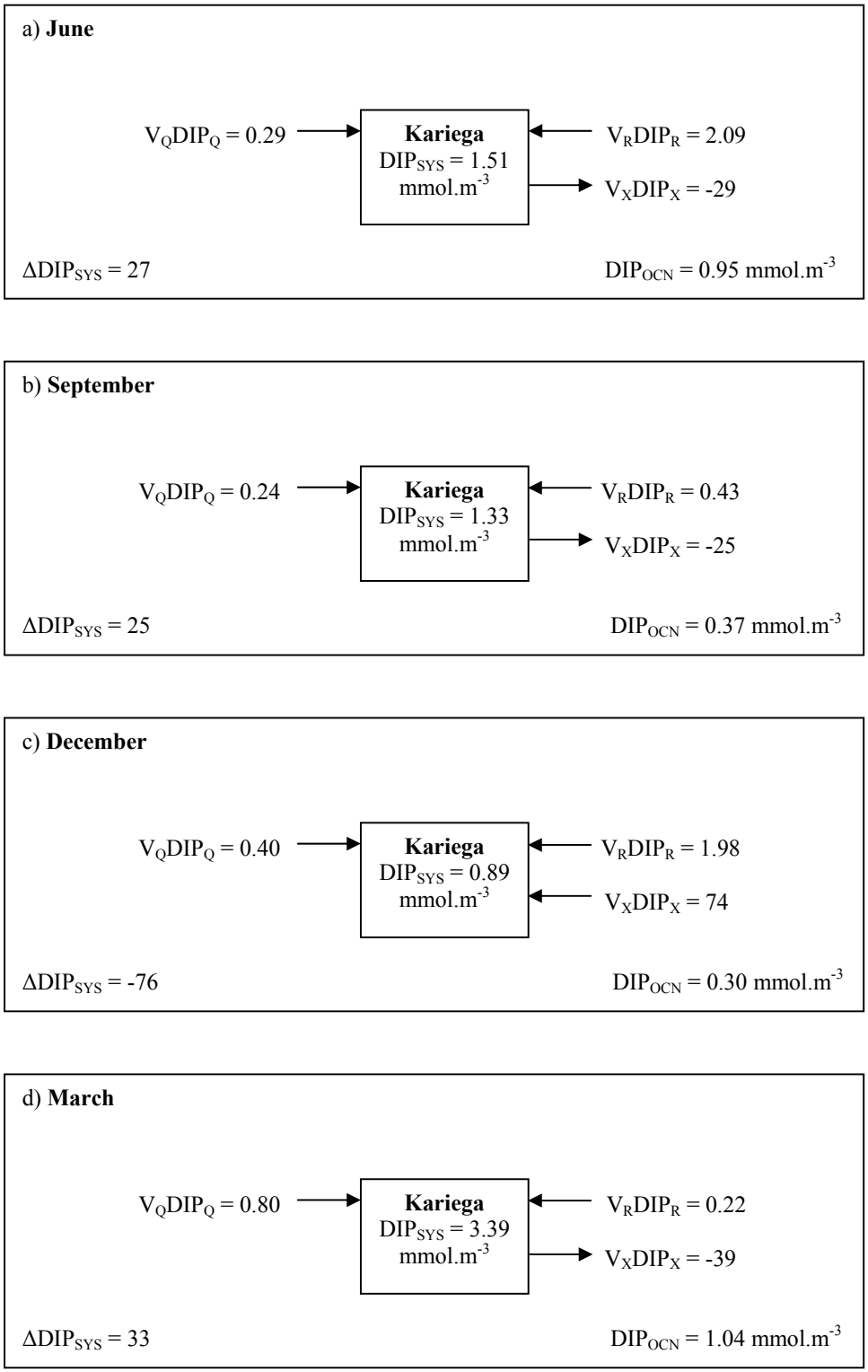
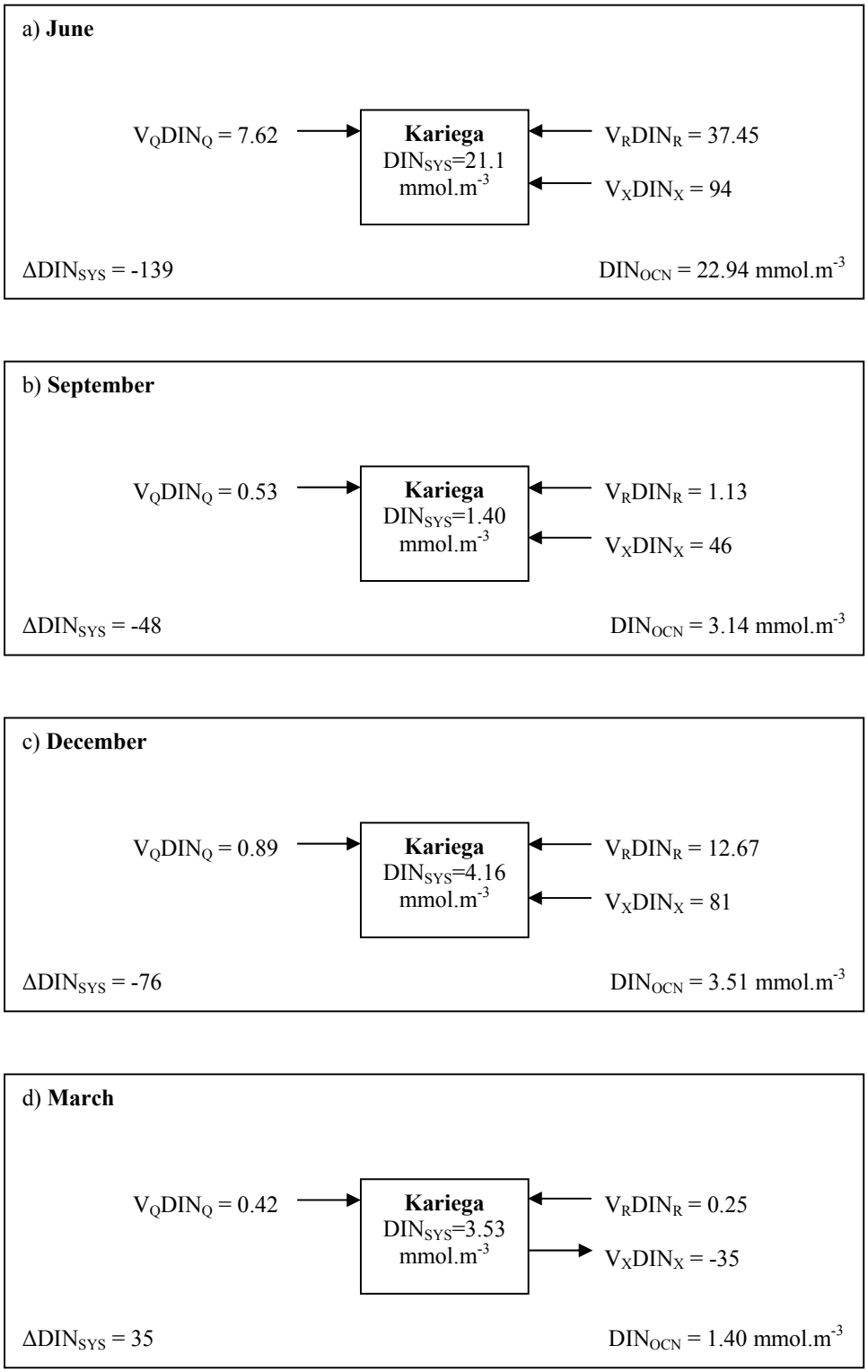


Figure 4.3 DIN budget for the Kariega estuary in (a) June, (b) September, (c) December and (d) March. Flux in mol.day^{-1}.



4.2 GREAT FISH ESTUARY

4.2.1 Water and Salt balance

For the Great Fish estuary, a one-box two-layer model was used to accommodate the persistent vertical salinity gradient found within the system due to the inter-basin transfer of fresh water to the Great Fish River. The results of the water and salt budgets are illustrated in Figure 4.4. Evaporation (V_E) exceeded precipitation (V_P) in all surveys, but the contribution of both was insignificant when compared to the high river discharge (V_Q), resulting in a highly negative residual flow (V_R) value in all surveys (Table 4.4). Water exchange time for the whole system was always less than three days (one day in March).

Table 4.4 Water flux, salinity and water exchange time for the Great Fish estuary.

	Water Flux (10^3.m^3.day^{-1})							**Salinity** (psu)		**τ**	
	V_Q	V_P	V_E	V_R	V_{SRF}	V_Z	V_D	S_{OCN}	S_{SYS}	days	
June	679.0	0.06	1.32	-667.7	-872.9	163.5	195.2	33.94	7.59	1	srf
									21.93	3	bot
									14.76	2	sys
Sep	476.0	1.38	1.83	-475.6	-850.9	441.9	375.3	35.14	15.50	1	srf
									24.52	1	bot
									20.01	2	sys
Dec	371.5	1.37	3.63	-369.2	-526.0	189.6	156.8	31.47	9.38	1	srf
									19.38	3	bot
									14.38	3	sys
Mar	1803	2.09	2.44	-1803	-1840	156.1	36.9	33.90	0.68	1	srf
									7.03	5	bot
									3.85	1	sys

4.2.2 Budgets of nonconservative materials

The nonconservative DIP flux (Δ*DIP*) of the system was positive (source of DIP) in all surveys in both the surface and bottom layers and therefore the system as a whole (Table 4.5; Figure 4.5). The flux increased from +0.027 mmol.m^{-2}.day^{-1} in June to +13.26 mmol.m^{-2}.day^{-1} in March, corresponding with the increase in flow rate. The nonconservative DIN flux (Δ*DIN*) in the system and bottom layer was positive (source of DIN) in all surveys as well as in the surface layer in September and March, and negative in the surface layer in June and December (a sink for DIN). The flux in the system was lowest in June (+0.15 mmol.m^{-2}.day^{-1}) and highest in March (+6.37 mmol.m^{-2}.day^{-1}) (Table 4.5;Figure 4.6).

Table 4.5 Nonconservative fluxes of DIP and DIN for the Great Fish estuary.

	Δ*DIP*		**Δ*DIN***	
	(mol.day^{-1})	(mmol.m^{-2}.day^{-1})	(mol.day^{-1})	(mmol.m^{-2}.day^{-1})
June				
surface	+21	+0.021	-1521	-1.52
bottom	+6	+0.006	+1676	+1.68
system	+27	+0.027	+155	+0.15
September				
surface	+245	+0.25	+3561	+3.56
bottom	+381	+0.38	+1625	+1.63
system	+626	+0.63	+5186	+5.19
December				
surface	+180	+0.18	-944	-0.94
bottom	+427	+0.43	+1426	+1.43
system	+607	+0.61	+482	+0.48
March				
surface	+12172	+12.17	+3484	+3.48
bottom	+1090	+1.09	+2883	+2.88
system	+13262	+13.26	+6367	+6.37

4.2.3 Stoichiometric calculations of aspects of net system metabolism:

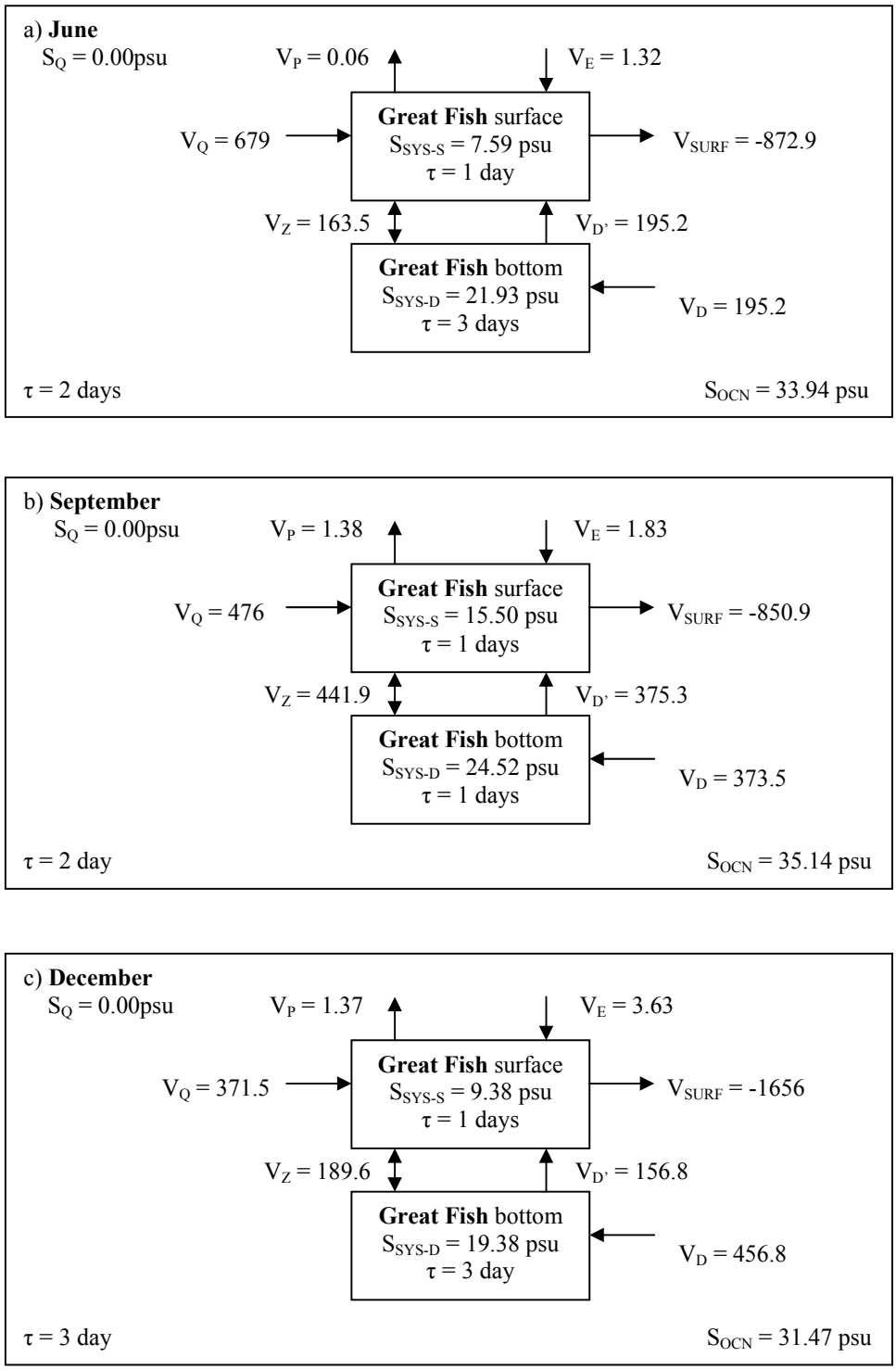
In all surveys, in both the surface and bottom layers and therefore the system as a whole, respiration in the estuary exceeded primary production, rendering the system heterotrophic at all times (Table 4.6). Values of (*p-r*) decreased in proportion to the Δ*DIP* increase, from -2.8 mmol.C.m^{-2}.day^{-1} in June to -1405.7 mmol.C.m^{-2}.day^{-1} in March. The system acted as a net denitrifyer in all surveys in the surface and bottom layers and the system overall, except in the bottom layer in June (+1.6 mmol.N.m^{-2}.day^{-1}), when nitrogen fixing processes dominated (Table 4.6).

Table 4.6 Apparent net ecosystem metabolism for the Great Fish estuary.

	(*p – r*) (mmol.C.m^{-2}.day^{-1})	**(*nfix – denit*)** (mmol.N.m^{-2}.day^{-1})
June		
Surface	-2.2	-1.9
Bottom	-0.6	+1.6
System	-2.8	-0.3
September		
Surface	-26.0	-0.4
Bottom	-40.4	-4.5
System	-66.4	-4.8
December		
Surface	-19.1	-3.8
Bottom	-45.3	-5.4
System	-64.4	-9.2
March		
Surface	-1290.2	-191.3
Bottom	-115.5	-14.6
System	-1405.7	-205.8

4.2.4 Great Fish Estuary 'box diagrams'

Figure 4.4 Water and salt budgets for the Great Fish estuary in (a) June, (b) September, (c) December and (d) March. Water flux in 10^{3} m^3.day^{-1} and salt flux in 10^{3}psu-m^3.day^{-1}.



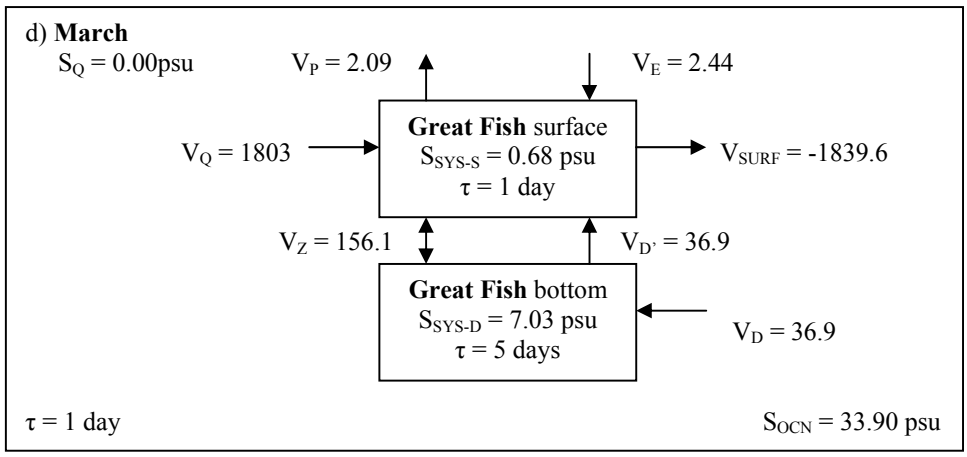
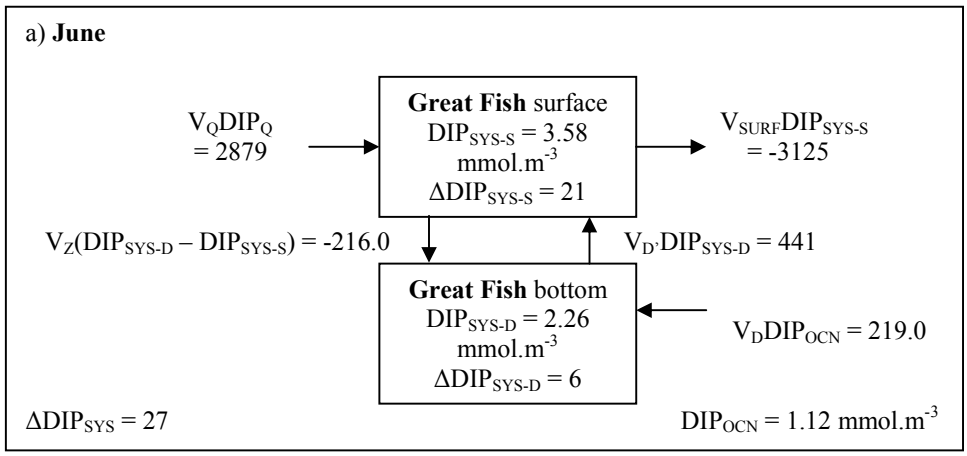
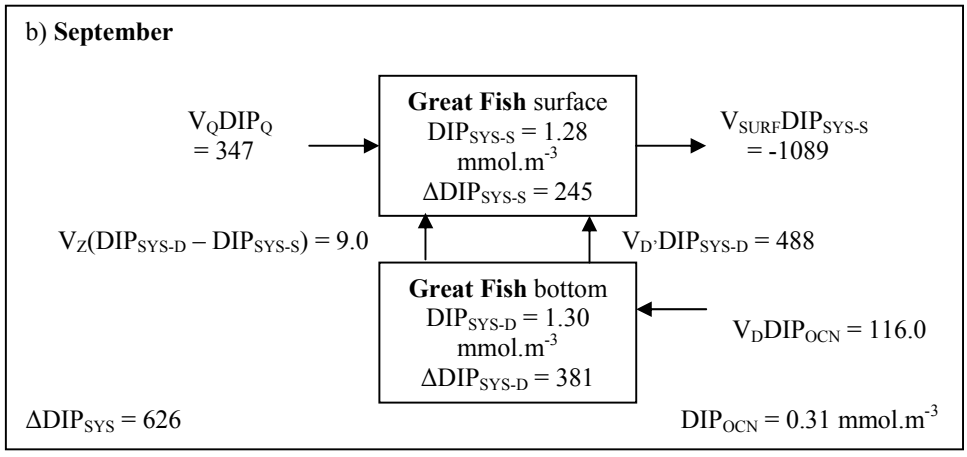
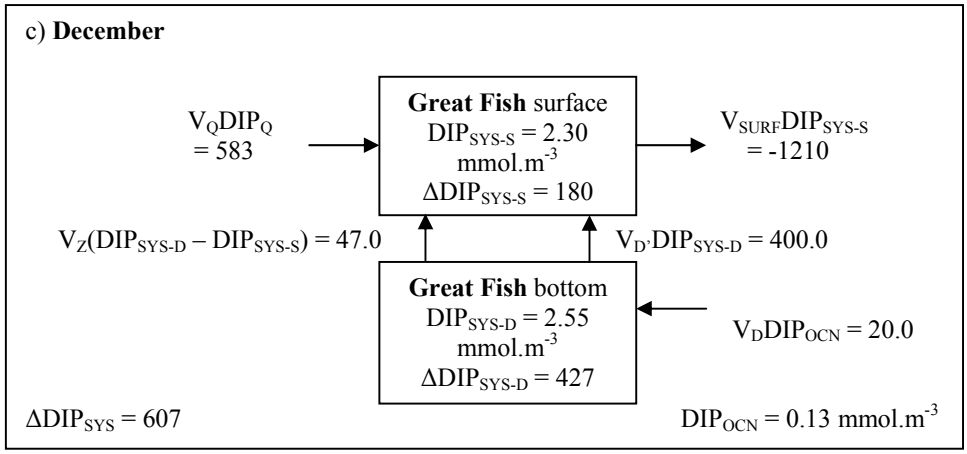


Figure 4.5 DIP budget for the Great Fish estuary in (a) June, (b) September, (c) December and (d) March. Flux in mol.day^{-1}.







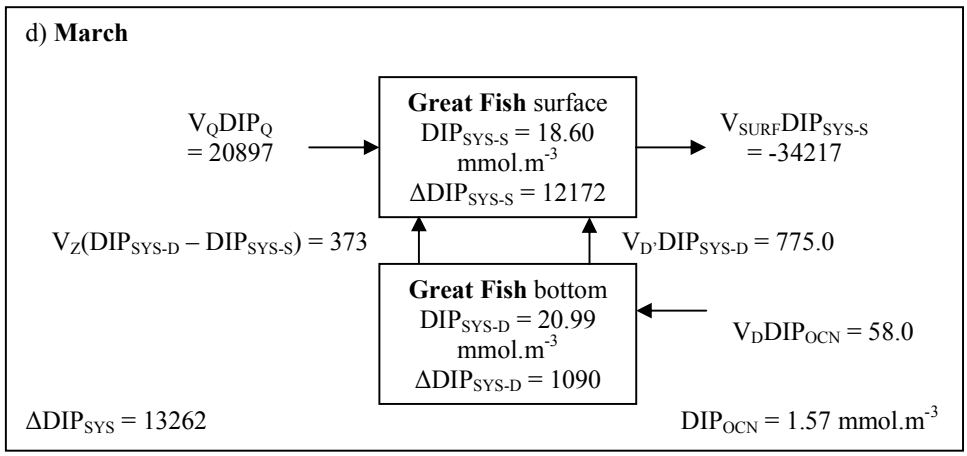
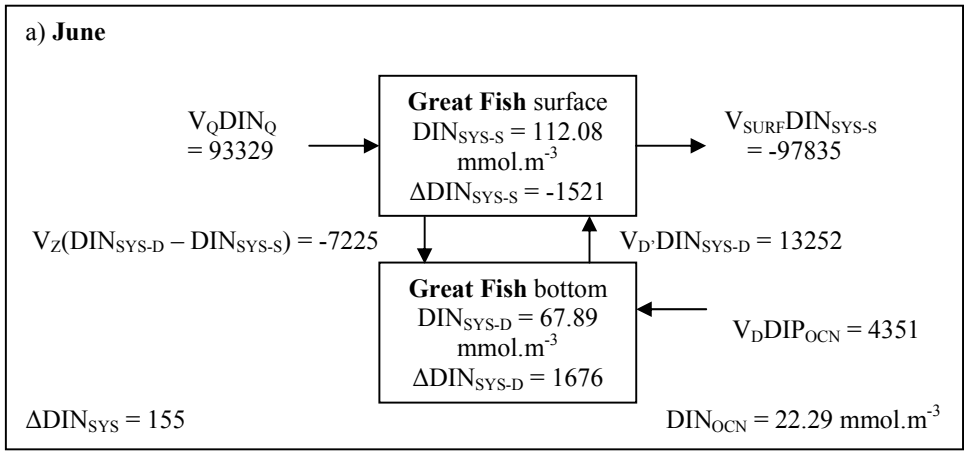
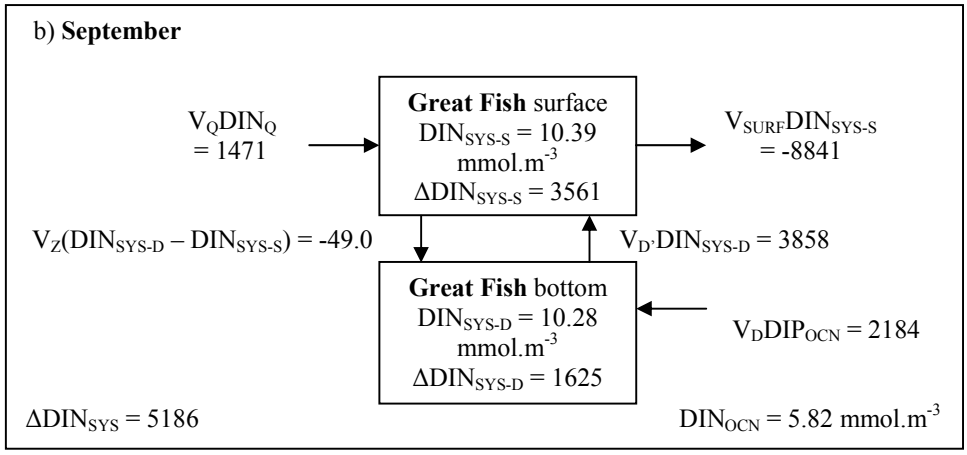
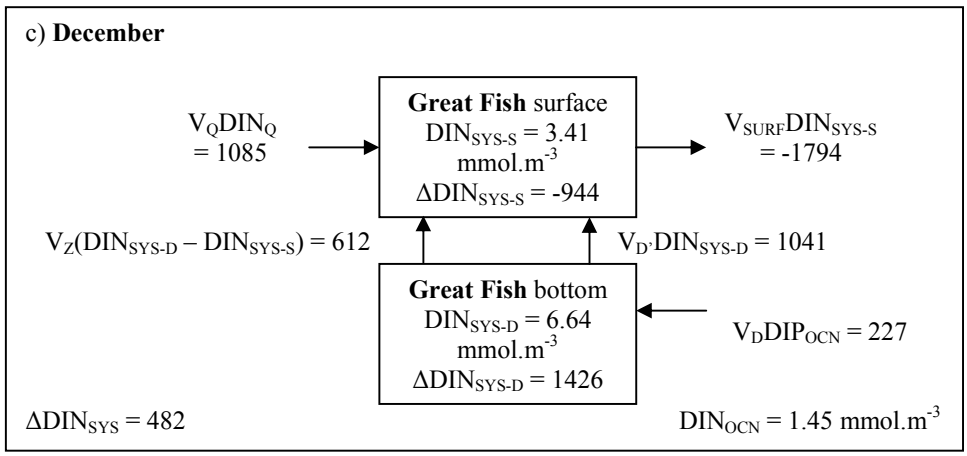
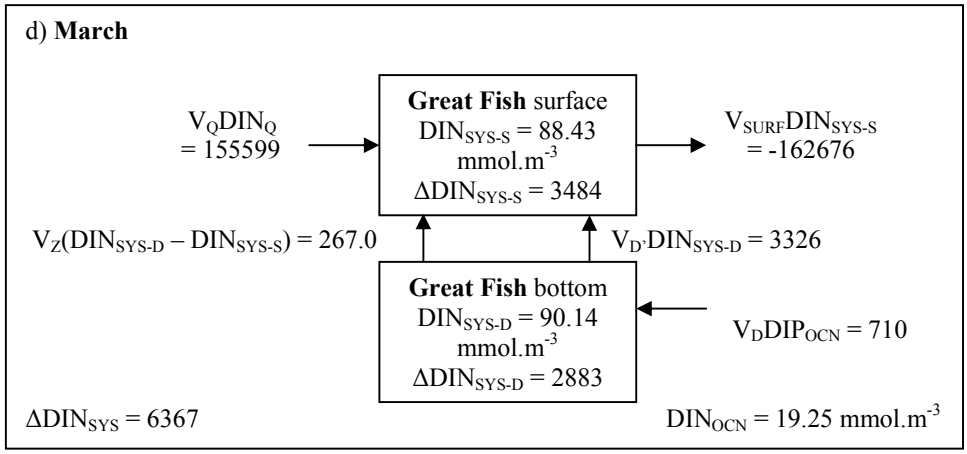


Figure 4.6 DIN budget for the Great Fish estuary in (a) June, (b) September, (c) December and (d) March. Flux in mol.day^{-1}.




b) **September**
$V_Q DIN_Q$ = 1471
Great Fish surface
DIN_{SYS-S} = 10.39 mmol.m^{-3}
ΔDIN_{SYS-S} = 3561
$V_{SURF} DIN_{SYS-S}$ = -8841
$V_Z(DIN_{SYS-D} - DIN_{SYS-S})$ = -49.0
$V_D \cdot DIN_{SYS-D}$ = 3858
Great Fish bottom
DIN_{SYS-D} = 10.28 mmol.m^{-3}
ΔDIN_{SYS-D} = 1625
$V_D DIP_{OCN}$ = 2184
ΔDIN_{SYS} = 5186
DIN_{OCN} = 5.82 mmol.m^{-3}


c) **December**
$V_Q DIN_Q$ = 1085
Great Fish surface
DIN_{SYS-S} = 3.41 mmol.m^{-3}
ΔDIN_{SYS-S} = -944
$V_{SURF} DIN_{SYS-S}$ = -1794
$V_Z(DIN_{SYS-D} - DIN_{SYS-S})$ = 612
$V_D \cdot DIN_{SYS-D}$ = 1041
Great Fish bottom
DIN_{SYS-D} = 6.64 mmol.m^{-3}
ΔDIN_{SYS-D} = 1426
$V_D DIP_{OCN}$ = 227
ΔDIN_{SYS} = 482
DIN_{OCN} = 1.45 mmol.m^{-3}


d) **March**
$V_Q DIN_Q$ = 155599
Great Fish surface
DIN_{SYS-S} = 88.43 mmol.m^{-3}
ΔDIN_{SYS-S} = 3484
$V_{SURF} DIN_{SYS-S}$ = -162676
$V_Z(DIN_{SYS-D} - DIN_{SYS-S})$ = 267.0
$V_D \cdot DIN_{SYS-D}$ = 3326
Great Fish bottom
DIN_{SYS-D} = 90.14 mmol.m^{-3}
ΔDIN_{SYS-D} = 2883
$V_D DIP_{OCN}$ = 710
ΔDIN_{SYS} = 6367
DIN_{OCN} = 19.25 mmol.m^{-3}

CHAPTER 5 – DISCUSSION

Estuaries are dynamic systems, constantly changing in response to changes in river flow and the regular pulsing of the tide, which affect a range of factors from hydrodynamic to autochthonous biological processes occurring within them (Allanson and Winter, 1999). Although the inherent variability in both the Kariega and Great Fish estuaries has largely been reduced due to anthropogenic activities (Whitfield and Bruton, 1989; O'Keefe and de Moor, 1988), the aforementioned factors are still responsible for determining the chemistry of the water column. For example, in the Kariega estuary, cold, marine, nutrient-rich water has been reported after an upwelling event (Taylor, 1992), and flooding has been reported to elevate nutrient concentrations in the estuary to levels similar to that of the permanently open Swartkops estuary, affected by discharge from sewage works (Allanson and Read, 1995). Similarly, in the Great Fish estuary, estuarine phytoplankton have been shown to increase in abundance due to elevated nutrient levels following peaks in flow rate (Grange and Allanson, 1995), while on the other hand, a dependence upon tidal input of nutrients has been noted under low flow conditions (Allanson and Read, 1995). Thus, while the results of the four surveys over the course of the year-long study period are likely to give a good indication of mean conditions within the two estuaries given the reduction in variability of the flow rates, they must still be interpreted with caution.

5.1 THE ESTUARIES

For the purposes of comparison with previous studies, the mean concentration and standard deviations of nitrate, phosphate and silicate were calculated for June and March, representing 'wet' periods when flow rates were higher (in the Great Fish River), and September and December, representing 'dry' periods with associated lower flow rates (Table 5.1).

Table 5.1 Mean concentration and standard deviation (mmol.m^{-3}) for 'dry' (September and December) and 'wet' periods (June and March).

	nitrate	**phosphate**	**Silicate**
Kariega estuary			
Sep + Dec	1.14 +/- 1.18	1.11 +/- 0.64	92.63 +/- 55.02
June + March	9.86 +/- 18.93	2.44 +/- 1.30	98.63 +/- 76.04
Great Fish estuary			
Sep + Dec	2.45 +/- 1.25	1.86 +/- 1.51	107.02 +/- 70.00
June + March	81.24 +/- 30.12	11.36 +/- 10.59	411.43 +/- 285.74

The mean nitrate concentrations in Kariega estuary during the present study during both the wet and dry periods were below those reported by Allanson and Read (1995) in a 1985 study in wet and dry periods. Mean phosphate and silicate concentrations in the dry period of the present study were similar to values reported by Allanson and Read (1995) during the dry period, but did not reach the levels of the 1985 study in the corresponding wet period. The higher concentrations recorded in the 1985 survey were due to elevated flow rates in both the dry (and particularly) the wet periods. On the other hand, the mean nitrate and phosphate concentrations in the Great Fish estuary during the present study were below those reported by Allanson and Read (1995) in the dry period, and above those reported for the wet period. In the present study dry period, the mean silicate concentration fell within the range reported from the 1985 survey of the Great Fish estuary, while the mean concentration from the wet period was above the same range. In the 1985 study, nitrate and phosphate concentrations decreased with the onset of flooding, while in the present study, levels were elevated during periods of high flow.

The concentrations of the selected nutrients in the Kariega estuary recorded during the present study were broadly in the same range as those reported by Froneman (2000) for a 1999 survey of the Kariega estuary. In the Great Fish estuary, the mean nitrate concentration during the dry period of the present study was below the range of nitrate concentrations reported by Froneman (2000), while the mean nitrate concentration in the wet period was above the same range. The mean phosphate concentration from the dry

period of the present study fell within the range of phosphate concentrations reported for the 1999 study of the Great Fish estuary, while the mean concentration in the wet period was above the same range. The flow rate was not reported for the 1999 study, but is presumed, according to the results, to be between the flow rates of the wet and dry periods in the present study of the Great Fish estuary.

In common with these previous studies, nutrient concentrations were consistently higher in the present study in the Great Fish estuary than in the Kariega estuary, particularly in the wetter periods, when flow rates in the Great Fish River rose while the flow rate of the Kariega River remained similar to those of the drier periods. This, as has previously been shown, is due to different sets of processes regulating the two rivers, namely damming and water abstraction from the Kariega River, and augmented flow through an inter-basin transfer scheme in the Great Fish River.

5.1.1 The Kariega Estuary

With the exception of the June survey, nutrient concentrations in the Kariega estuary were reflective of an oligotrophic system. Nutrient concentrations were generally below the levels stated in the SAWQG as the maximum concentrations for a healthy aquatic ecosystem. In June, however, in the absence of increased flow rates, relatively high dissolved inorganic nitrogen (DIN) concentrations were found in the lower reaches at the bottom of the estuary, suggesting the presence of upwelled water intruding through the mouth. While this has been previously reported (Taylor, 1992), the reduced water temperatures characteristic of upwelling events were not recorded, suggesting some other allochthonous source. As similar DIN concentrations were found in the upper reaches, it is tempting to suggest that the elevated nutrient levels could possibly be in response to run-off of nitrates found in fertilizers used by farmers in the intensively cultivated catchment of the Kariega estuary (Allanson and Read, 1995). Even with the long residence time of the water, inverse density driven circulation would move the hyper-saline water and associated nutrients seawards along the bottom of the estuary (Schumann *et al.*., 1999), explaining the higher DIN concentrations in the lower reaches.

However, rainfall in June was low (only 2 mm in the 30 days prior to sampling) and chicory, the dominant crop in the catchment, is a dry crop (i.e. is not irrigated) meaning nutrients from fertilizers would require a mechanism of transport into the estuary, which was lacking. In addition, phosphate concentrations in the estuary were generally low. It appears, therefore, that the most probable source of DIN in the estuary was the adjacent sea (due to low river inflow) and tidal intrusion up the estuary. The dominance of the sea in terms of DIN input is reflected in the best-fit line through the mixing plot for DIN in June, shown in Figure 5.1 (Note: salinity of 35.20psu represent the sea, increasing to 38.00psu at the head of the estuary). Whilst nitrate and nitrite were at their highest levels of the four surveys due to the allochthonous import, ammonium was at its lowest mean concentration in June. In September and December however, when inflow into the estuary remained minimal, ammonium had a higher mean concentration then nitrate (or nitrite). This is attributed to the reductive process of nitrate ammonification, where nitrate is converted to into ammonium by heterotrophic bacteria. Under low nitrate conditions, nitrate ammonifying bacteria have been shown to out compete denitrifying bacteria (Herbert, 1999), accounting for the (relatively) higher ammonium concentrations. Although more rain fell in September than in December, heavy rain in late September and early October would have had the effect of flushing any available nutrients in the catchment of the estuary into the system (run-off form the catchment of the Kariega River would make its way into one of the dams above the estuary, effectively locking away potential nutrient supplies until sufficient rain falls in order to breach the dam wall). This, in combination with the long residence time of the water in fresh water deprived estuaries (approximately three months according to the September Land-Ocean Interactions in the Coastal Zone (LOICZ) results), would explain the marginally higher DIN concentrations and lower salinities in December, when compared to September. Grange and Allanson (1995) reported a minor pulse of fresh water to have the effect of reducing salinities in the upper reaches of the Kariega estuary for a period of five months. Such a pulse occurred during the present study on the 10th of October when the flow rate rose from the standard 0.003 $m^3.s^{-1}$ to 0.041 $m^3.s^{-1}$ in the space of a day, and declined steadily to a flow rate of 0.004 $m^3.s^{-1}$ reached a month later, and was again 0.003 $m^3.s^{-1}$ during the December survey. A second, stronger pulse in flow rate occurred (reaching

0.063 $m^3.s^{-1}$) on the 26th December, except that on this occasion the flow rate remained elevated for longer and was 0.005 $m^3.s^{-1}$ at the time of sampling in March. This had the effect of elevating DIN in March in the Kariega estuary to concentrations above those of September or December, but still below the peaks reached in June. This again suggests an allochthonous, high concentration source of DIN in June. In March, the middle reaches of the estuary had the highest nitrate and ammonium concentrations and represented a source of DIN. This attributed to the relatively higher flow rates and associated elevated nutrient concentrations combined with the long residence time of the water within the estuary.

Phosphate, on the other hand, did not show a corresponding influx of phosphate-rich water from the sea in June as was the case with DIN, and was reliant on river flow and internal recycling as a source phosphate, resulting in low concentrations. Figure 5.2 shows the phosphate mixing plot for the Kariega estuary in June, with higher salinities and phosphate concentrations representing the estuary, decreasing to a salinity of 35.20psu at the mouth. Mixing plots for the remaining surveys are more difficult to interpret, as salinities did not increase or decrease linearly along the length of the estuary, but showed low concentrations throughout the system in response to the low flow. This again highlights the importance of fresh water inflow, widely considered to be the dominant source of phosphate to estuaries (DWAF, 1996). The highest concentrations were, as expected, recorded in March when the highest flow rate during the four surveys was recorded.

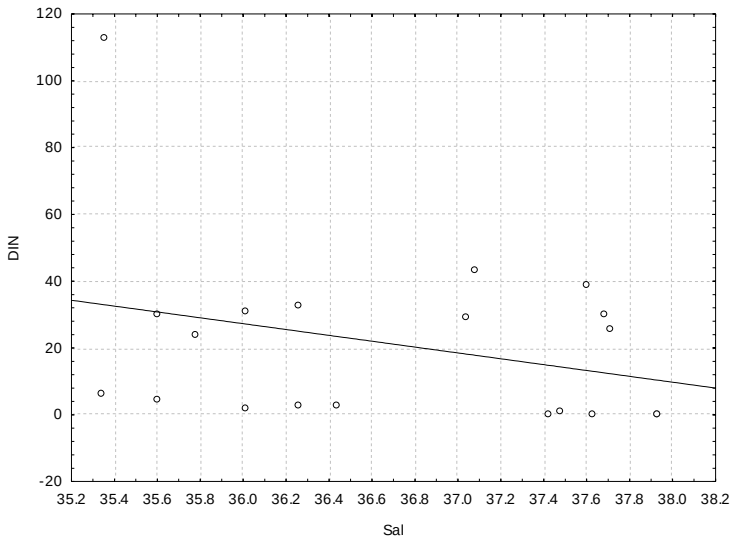


Figure 5.1 Mixing plot of DIN (mmol.m^{-3}) and salinity (psu) in the Kariega estuary in June.

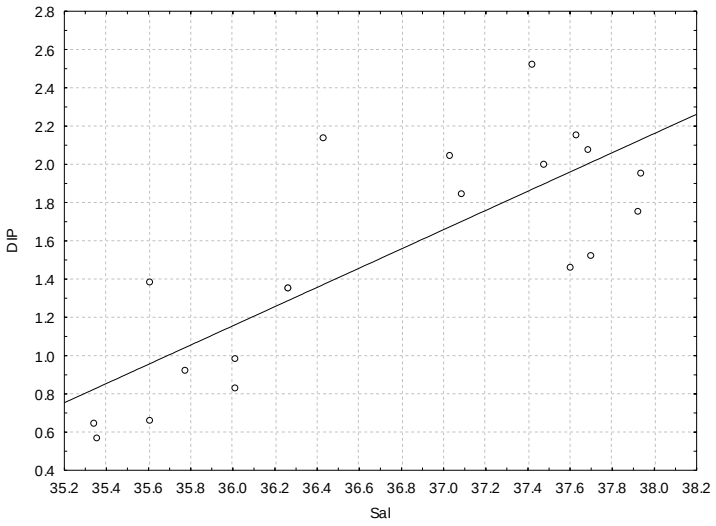


Figure 5.2 Mixing plot of phosphate (mmol.m^{-3}) and salinity (psu) in the Kariega estuary in June.

Silicate displayed a consistent horizontal gradient in concentration from the headwaters to the mouth, where the silicate-rich estuarine water was diluted by the inflow of sea water due to the action of the tides (indicated by the mixing plot for June, Figure 5.3). The upper reaches contained the highest concentrations due to a gradual build-up of silicate-rich clays washed into the estuary through ground water discharge and weathering of the catchment (DWAF, 1996), combined with the long residence time of the water. It follows then, that the highest silicate concentrations were found in March, following the heavy rain in December and March. Generally speaking, silicate was less depleted than DIN or phosphate within the estuary due to the lack of large phytoplankton cells in the water column, which require silicate for growth (Froneman, 2000).

The high DIN concentrations in the Kariega estuary in June resulted in a N:P ratio of 14:1, approximating the Redfield ratio of 16:1, the atomic ratio of cellular N:P in phytoplankton (Valiela, 1980). In June, therefore, sustained algal growth would be expected. During the remaining surveys, however, phytoplankton growth would have been nutrient limited as is evident from an N:P ratio of 5:1 for December and 1:1 for September and March. Historically, nitrogen limits phytoplankton growth in coastal waters, while phosphate is the limiting nutrient in rivers (Tett *et al.*, 2003). With a reduction in fresh water discharge, one would thus expect a shift from phosphate to nitrogen limitation, which, with the exception of June, is the case in the Kariega estuary. This is in agreement with the studies conducted by Allanson and Read (1995) (for the majority of the study period) and Froneman (2000). In response to the nutrient limitation due to reduced fresh water inflow, decreasing turbidity and current velocities are accompanied by a shift from pelagic phytoplankton production dominated systems to one where submerged macrophytes are the dominant producers in the more stable sediment and salinity environments (Adams *et al.*., 1999). Froneman (2000) showed that phytoplankton standing stocks, represented by chlorophyll-a, were an order of magnitude lower in the Kariega estuary than in the fresh water dominated Great Fish estuary. Rather than being consumed directly, as in the case of the phytoplankton, the majority of the macrophyte production enters the food chain as detritus (Mann, 1988), where it is initially manipulated by the microbial community (Baird, 1999). Grange and Allanson

(1995) reported that in the Kariega estuary, the organic fraction of seston was dominated by material detrital in origin. Submerged macrophytes, primarily the eelgrass *Zostra capensis*, are found extensively along the middle and upper reaches of the Kariega estuary (Cowley and Danial, 2001). The presence of the eelgrass allows for an anchoring of sediment and a dampening of wave action, leading to improved water clarity. This allows for the growth of microphytobenthic algae on the sediment surface, which has the effect of taking up nutrients released from the sediment, further reducing the nutrient concentrations within the water column (Adams *et al.*., 1999). In fact, in systems characterized by low fresh water inflow and associated oligotrophic conditions, microphytobenthic biomass of chlorophyll-a can be up to three orders of magnitude greater than pelagic phytoplankton biomass (Adams *et al.*., 1999). The reduced concentrations of nutrients in the water column promote the growth of small phytoplankton cells (<2μm) which are more efficient at taking up nutrients in low concentration than larger cells due to their favourable surface area to volume ratio (Froneman, 2000). The small cells are in turn consumed by micro-heterotrophs (<200μm). This version of the food web is known as the microbial loop (Froneman and McQuaid, 1997), in which all steps are mediated by heterotrophic bacteria. Energy transfer between trophic levels is based on the flow of detrital particles of inferior quality (Grange and Allanson, 1995) and is characteristically inefficient (Froneman, 2000), relying on recycled carbon rather than an allochthonous source.

A study in the Kromme estuary, also on the south-east coast of South Africa and not unlike the Kariega estuary in that the flow regime has been altered due to the construction of a dam in the catchment, revealed several changes from 1984, pre-construction, to 1992, subsequent to the building of the dam. While the rate of primary production was reported to have increased, phytoplankton biomass decreased and was replaced by increased submerged macrophyte presence. It was suggested that the Kromme estuary had become more dependant on recycled material and a detrital food web, with declined levels of system maturity and oganisation in the absence of fresh water inflow (Baird, 1999). A similar situation would be expected in the Kariega estuary.

5.1.2 The Great Fish Estuary

The Great Fish estuary is generally considered to contain high levels of nutrients due to the sustained fresh water inflow resulting from an inter-basin transfer of water from the Gariep Dam to the Great Fish River (Grange *et al.*., 2000). In addition, livestock farming is widely practiced in the catchment, while some of the low-lying floodplain areas have been cleared of natural vegetation and cultivated with maize and pineapple plantations, due to the availability of fresh water from the inter-basin transfer scheme (Cowley and Danial, 2001). The land-use patterns in close proximity to the river could therefore further contribute to elevated nutrient concentrations in the estuary. The water quality is, however, described as generally being good (Cowley and Danial, 2001), largely due to the rapid flushing time which prevents the build up of pollutants in the system (less than three days during all surveys in the present study). Nutrient levels within the estuary were regularly indicative of a eutrophic system, particularly in the higher flow rate months of June and March. DIN and phosphate in these months were well above the levels recommended in the SAWQG for a healthy aquatic ecosystem. In the lower flow months of September and December, DIN concentrations dropped to acceptable levels, while phosphate concentrations were generally of a meso-eutrophic level (DWAF, 1996).

In June, DIN was comprised predominantly of nitrate, with highest concentrations found at the surface in the fresher water washed down from the river. The mixing plot of DIN (Figure 5.4) shows no marked deviation from the theoretical dilution line. Of interest was a peak in ammonium at the bottom in the lower reaches. This was again apparent in September and December, suggesting a source of ammonium in this region. In both September and December, ammonium proved to be the dominant form of nitrogen in the water column. This was due to lower flow rates and associated lower nitrate concentrations, under which conditions nitrate ammonifying bacteria convert nitrate to ammonium, as opposed to high nitrate concentrations when nitrate is converted to nitrous oxide (N_2O) or dinitrogen (N_2) during denitrification (Herbert, 1999). During nitrate ammonification, nitrate is not lost from the system, but rather converted into another form of nitrogen, thereby conserving DIN within the system. Nitrate concentrations in

both September and December were highest in association with a salinity front, represented by a horizontal halocline in the vicinity of station 5 on the surface in September, and on the bottom in December. These areas have been documented as being of importance in mixing processes and transport of suspended sediment (Schumann *et al.*, 1999). In September, the intrusion of the tidal waters was evident with saline water on the surface and bottom in the middle reaches of the estuary. The marine water was low in ammonium concentration, as was the fresh river water entering at the head, resulting in the highest DIN (as ammonium was the principal from of nitrogen) occurring in the middle reaches in the zone of maximum mixing. This is reflected in the DIN mixing plot for September (Figure 5.5), showing elevated concentrations in the middle reaches, above the theoretical dilution line from the head of the estuary to the mouth, therefore representing a source of DIN (Allanson, 2001). In December, nitrate concentrations showed a reversed trend, with lower concentrations occurring at the surface in the fresher water than at depth in association with the saline water intruding through the mouth (Figure 5.6). This is in agreement with Allanson and Read (1995), who noted the dependence of the Great Fish estuary on marine-derived nutrients during times of low flow. In December, which had the lowest flow rate averaged over the thirty days prior to sampling, the river water was depleted of nitrate (less than 0.01 $mmol.m^{-3}$). In March, high runoff from the catchment due to heavy rainfall coupled with high flow rates resulted in the estuary being more typical of a river mouth (Whitfield, 1992). Nitrate was again, as with the higher flow rates of June, the dominant form of nitrogen in the fresher water. High nitrate concentrations reflective of eutrophic levels were recorded throughout the estuary, with a slight decrease in concentration at the mouth due to dilution. Ammonium concentrations were highest in the mouth region, where the only salt marsh is located along the Great Fish estuary. Ammonification is an important process in vegetated areas (Herbert, 1999), and the elevated flow rates would have had the effect of flushing out the salt marsh and associated ammonium, released from decomposing nitrogenous matter during ammonification, explaining the higher concentrations in this region.

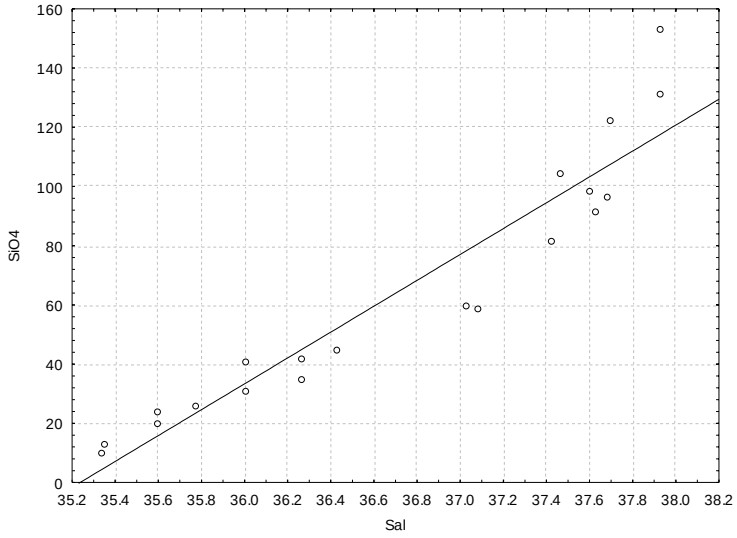


Figure 5.3 Mixing plot of silicate (mmol.m^{-3}) and salinity (psu) in the Kariega estuary in June.

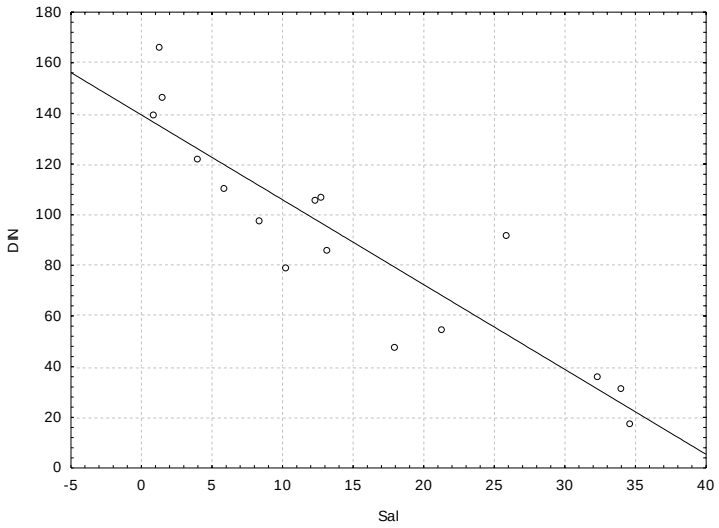


Figure 5.4 Mixing plot of DIN (mmol.m^{-3}) and salinity (psu) in the Great Fish estuary in June.

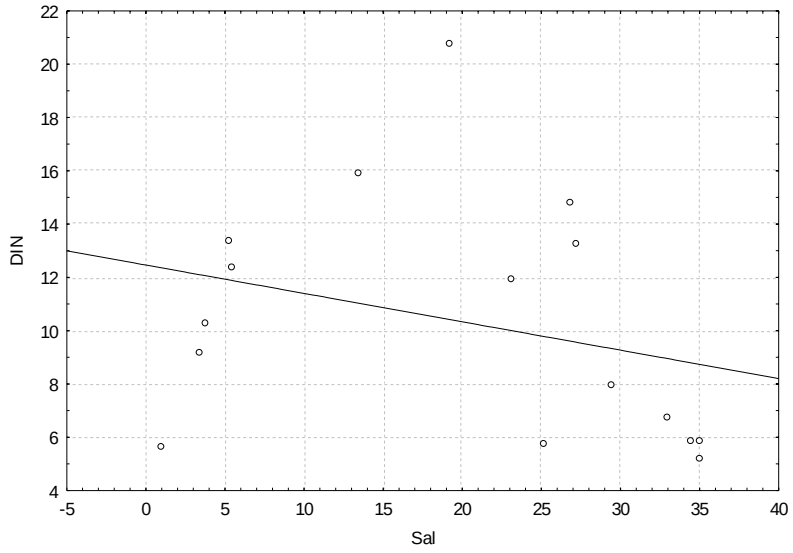


Figure 5.5 Mixing plot of DIN (mmol.m^{-3}) and salinity (psu) in the Great Fish estuary in September.

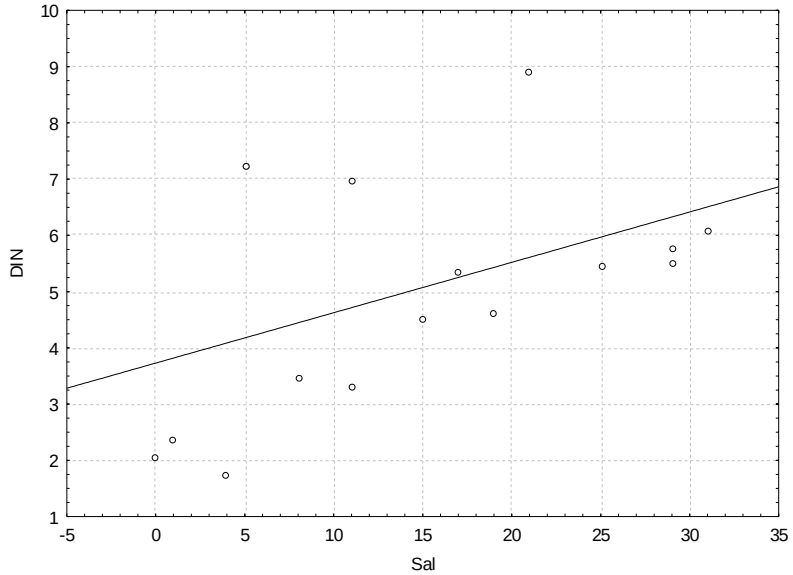


Figure 5.6 Mixing plot of DIN (mmol.m^{-3}) and salinity (psu) in the Great Fish estuary in December.

Phosphate concentrations generally showed a correlation with salinity, decreasing in concentration as salinity increased towards the mouth of the estuary. The phosphate mixing plot for June is shown in Figure 5.7. Allanson and Read (1995) commented on the lack of relation between phosphate concentrations and salinity, with decreased concentrations with the onset of flooding. This was not true for the present study, as the highest phosphate levels were recorded in association with the elevated flow rates of March when high concentrations were recorded throughout the estuary. During the remaining surveys, concentrations decreased linearly with salinity, with DIN, highest concentrations were found in the upper to middle reaches and lower concentrations at the mouth. In December, there was no evidence of phosphate-rich saline water in the lower reaches, as was the case with DIN, the highest phosphate concentrations occurring in the upper reaches in association with the fresher water extending to the bottom. This resulted in a best-fit line approximating the theoretical dilution line through the mixing plot (similar to Figure 5.7).

Silicate is thought to act conservatively, i.e. decrease linearly with decreasing salinity (Allanson and Winter, 1999). This was partially observed in the Great Fish estuary, although a patchy distribution resulted in a sporadic mixing plot in June. In September, during the lowest flow rates, silicate occurred in its lowest concentration in the estuary, which is to be expected. Strong peaks in concentration in September and December were found in the lower reaches on the bottom, where highest ammonium concentrations were measured, again suggest a source region. In December, concentrations decreased from head to mouth waters with increasing salinity, resulting in a relatively linear mixing plot, Figure 5.8. In March, silicate concentrations were abnormally high throughout the estuary in response to the influx of Orange River water, highlighting the fact that this originates from a different catchment to the Great Fish River water (O'Keefe and de Moor, 1988).

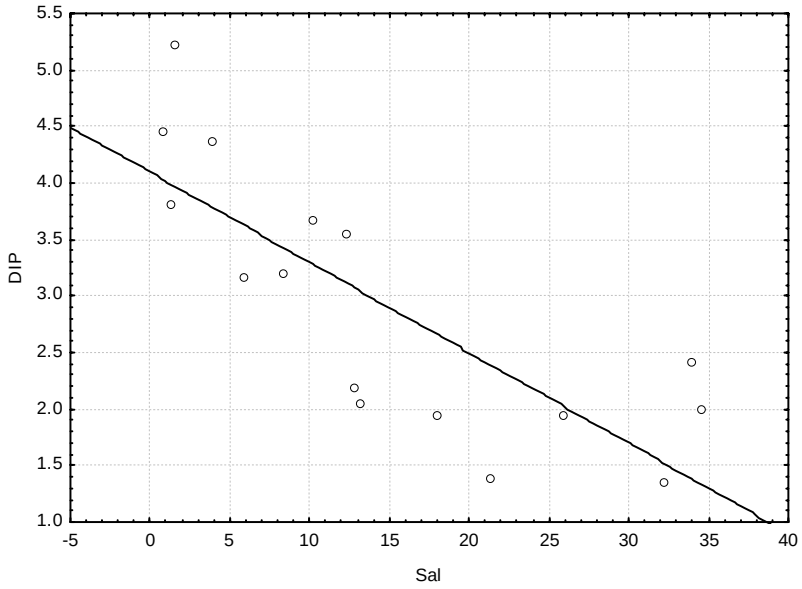


Figure 5.7 Mixing plot of phosphate (mmol.m^{-3}) and salinity (psu) in the Great Fish estuary in June.

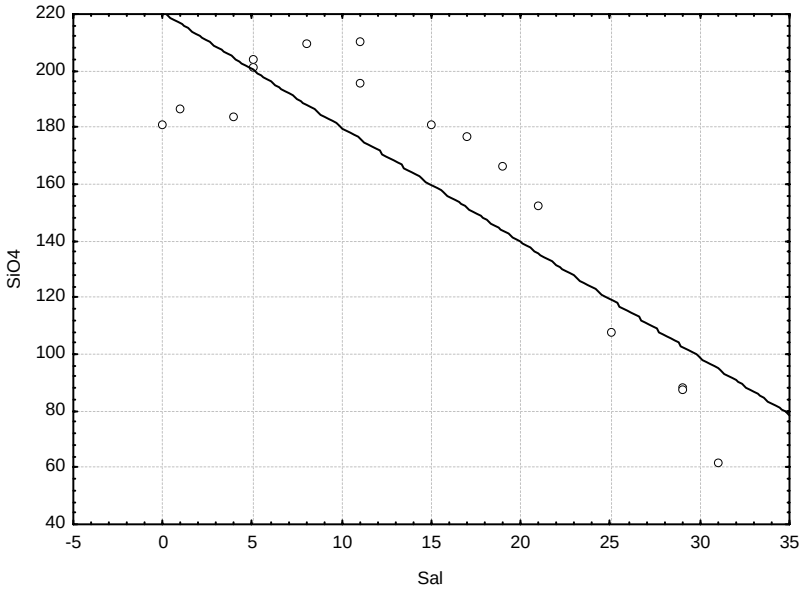


Figure 5.8 Mixing plot of silicate (mmol.m^{-3}) and salinity (psu) in the Great Fish estuary in December.

The N:P ratio in the Great Fish estuary has previously been reported as favourable for algal growth (20:1 as found by both Allanson and Read (1995) and Froneman (2000)). In this study, the ratio deviated from the ideal 16:1 (according to the Redfield ratio), with phosphate limiting growth in June and the opposite occurring in the remaining surveys. In June, an N:P ratio of 30:1 was found in response to the high flow rate and associated dominance of fresh water in the estuary. In September a low flow rate resulted in a ratio of 8:1, while in December, when the dominant source of nitrate was the ocean, a ratio of 2:1 indicates severe nitrogen limitation. In March under the flooding conditions, a ratio of 5:1 was due to higher phosphate concentrations (the highest values over the four surveys) rather than lower DIN values. Therefore, growth by assimilation would occur before 'stoichiometric limitation' occurred, as relatively higher DIN and phosphate concentrations meant a lower 'probable limitation' (Justic *et al.*, 1995).

Seasonal changes in fresh water flow in unaltered catchments cause substantial changes in circulation and stratification stability in estuaries with important consequences for nutrient dynamics and primary production (Schumann *et al.*, 1999). While the low flow conditions which would have persisted through the drier months (eventually causing closure through marine sediment deposition in the mouth) in the Great Fish estuary no longer occur, episodic high discharge rates associated with high rainfall coupled with the release of water from the inter-basin transfer perform the function of floods. Flood-tide deltas are scoured out reducing the depth of the sill and any resident marine water is flushed out to sea. Under large scale flooding, stratification can occur seawards (Schumann *et al.*, 1999). Under these conditions, however, flushing time is minimal (0.8 days, as reported by Grange *et al.* (2000), similar to the flushing rate of one day calculated for the present survey) meaning rates of physical removal of phytoplankton and nutrients are greater than rates of *in-situ* production (Adams *et al.*, 1999). Associated with high flow rates and increased freshwater content is an increase in turbidity. Turbidity reduces the depth of the euphotic zone, meaning algal cells are exposed to a favourable light environment for shorter periods of time. This is due to the allochthonous import of suspended particulates in association with the lower salinity water, or due to turbulence causing benthic particles to be lifted off the bottom and held in suspension,

increasing light attenuation (Adams *et al.*, 1999). In Great Fish estuary, however, turbidity has been shown not to limit phytoplankton growth due to the shallow nature of the estuary in combination with the regular tidal intrusions creating sufficient flux to lift algal cells off the bottom and in to the euphotic zone allowing for autochthonous production (Allanson and Winter, 1999). Grange and Allanson (1995) showed that high phytoplankton standing stocks generally develop following high freshwater inflow. The observed pattern was, however, due more likely to an accumulation of phytoplankton of riverine origin by hydrodynamic trapping rather than due to an increase in available nutrients (as was the case following high March flow rates in the present study). This highlights the importance of allochthonous production in the estuary. Even in the absence of high flow, phytoplankton biomass, represented by chlorophyll-a, has been shown to be an order of magnitude higher in the Great Fish estuary than in the Kariega estuary (Froneman, 2000). Blooms have been shown to be dominated by diatoms (Allanson and Read, 1995), making use of the readily available silicate in the water. These larger phytoplankton cells are then consumed directly by copepods and mysids in a classic food web characterized by high trophic efficiency and greater secondary and tertiary production (Froneman, 2000).

5.2 LOICZ BUDGETS

Results of the LOICZ budgets for the Kariega estuary were similar to the findings of Allanson and Smith in a 1984 study (Dupra *et al.*, 2002), in that the estuary behaved as a net source of phosphate and a net sink for DIN, and was net heterotrophic with denitrification processes dominating in both wet and dry seasons of the previous survey, as well as for the majority of surveys in the present study. The major differences occurred in the flow rate and residence time. In the wet season (November to December), Allanson and Smith reported a flow rate of 250 x 10^3 $m^3.day^{-1}$ in the Kariega River with salinities in the upper estuary dropping to 4.5psu and an exchange time (flushing rate) of one day. This flow rate was three orders of magnitude higher than the flow rate recorded at the same time of year in the present study. While it is appreciated that rainfall and flooding occur episodically at unpredictable times of year, it is quite

clear that the flow rates recorded during previous years are unlikely to be recorded in the Kariega River in the near future owing to the state of alteration in the catchment. In the dry season, when the flow rate was reported as zero, flushing time for the system was calculated to be 10 days, less than any of the reliable estimates from this study.

Budgets of the Great Fish estuary were less similar to previous studies. When compared to the budget calculated by Smith and Allanson (Dupra *et al.*, 2002), several differences were apparent. In the present study the estuary proved to be a source of phosphate and DIN, net heterotrophic and a denitrifyer in all surveys. In contrast, during the Smith and Allanson survey, the estuary acted as a net sink for phosphate in the dry season, as well as for DIN in both the wet and dry seasons, while net system metabolism indicated the estuary to be primarily autotrophic and a nitrogen fixer. This was attributed mainly to high phytoplankton activity in the estuary. Results of the present study were more consistent with results obtained for budgets constructed for the Mhlatize and Thukela estuaries of Kwa-Zulu Natal (Dupra *et al.*, 2001). Both estuaries are highly altered and dominated by fresh water, the former discharging into Richards Bay via the harbour, and the latter supplying water to the Vaal River through an inter-basin transfer of water, but still considered a river mouth due to the large volume of freshwater discharging into the sea. Both estuaries proved to be sources of nutrients, heterotrophic and chiefly denitrifying.

5.2.1 The Kariega Estuary

The Kariega budgets show little variation over the four surveys, the exception being December. In the remaining surveys, salinity in the system was higher than the salinity of the adjacent ocean. Residual flow (V_R) was positive i.e. a flow into the estuary from the sea to compensate for water lost via evaporation (V_E), which was greater than the combined contributions of rainfall (V_P) and river flow (V_Q). In December, however, salinity in the system was lower than in the ocean, which would require V_R to be negative i.e. from the estuary into the ocean. This was, however, not the case as V_E was again greater than the sum of inflows (V_P and V_Q were both low), meaning the system was not

in a 'steady state' at the time of sampling, resulting in a negative exchange time unreliable flux values. This raises the question: what was responsible for the lowered salinities in the upper reaches in December? It is unlikely that the flow rate was responsible, as higher V_Q and V_P rates were measured in March, when salinities were higher than in December. Unfortunately, the most likely answer is therefore a combination of human-induced error and faulty measuring equipment. In December, a hand-held refractometer was used to measure salinity in the estuary, while all salinities offshore of the Kariega estuary, including the Marine Control salinity, were taken to be 35.00psu, the standard salinity of sea water (DWAF, 1995). In order for V_R to be positive, the salinity of the ocean would have had to be lower than the mean salinity of 34.20psu calculated for the estuary, and while this is unlikely in the absence of fresh water outflow, it is interesting to note that all surface and 5 m stations (with the exception of station 1A) in the Great Fish marine grid, even those east of and not directly by the fresh water discharge, were below 35.00psu (although, again, these were measured with the hand-held refractometer).

During the remainder of the survey, the estuary acted as a source for phosphate. This is thought to be related to the low production in the estuary, with no sink in terms of phytoplankton assimilation, but rather a slow release from the numerous salt marshes along the banks (Taylor, 1992). *ΔDIN* in the estuary switched from a weak sink in the first three surveys (even in June when high concentrations were measured in the estuary, as higher concentrations were measured in the sea), to a weak source in March in the relatively higher flow rates (but with lowest river DIN recorded) remobilizing DIN in the estuary. The negative (*p*-*r*) values, derived from the negative of the *ΔDIP* flux multiplied by the atomic ratio of C:P (106:1), implies a dominance heterotrophic organisms, known to be involved in all stages of the microbial loop. Production was low, as stated previously, due to low nutrient availability, with organic matter entering the system as detritus. If *ΔDIP* values are a measure of the net production or consumption of organic matter in the system, as per Gordon *et al.* (1996), then the expected *ΔDIN* would be the *ΔDIN* for the system multiplied by the N:P ration of reacting organic matter (assumed to be 16:1). Differences between the expected *ΔDIN* and the *ΔDIN* calculated through the

equations provided by the LOICZ budgeting procedures are deemed to be due to nitrogen fixation or denitrification, the two principal processes governing the state of nitrogen in the coastal environment (Herbert, 1999). The *ΔDIN* derived from the system was less than the expected *ΔDIN* due to the low N:P ratios, resulting in the system acting as a net denitrifyer. Whilst nitrogen fixation may be expected to be the dominant process in the low DIN conditions, this is limited by the availability of organic carbon in oligotrophic systems, as low C:N ratios promote denitrification (Herbert, 1999).

5.2.2 The Great Fish Estuary

The *ΔDIP* fluxes of the Great Fish estuary indicate that the estuary behaved as a net source of phosphate in all surveys. The amount of phosphate released into the ocean form the surface layer of the estuary was more than the sum of the fluxes from the river and from circulation from the ocean. This was largely due to low phosphate concentrations recorded in the fresh river water, and the rapid flushing time, preventing a build-up of phosphate within the estuary. In March, high flow rates would have had the effect of remobilizing phosphate by resuspension and flushing from the estuary floor (DWAF, 1996), resulting in the estuary in March representing the greatest source of phosphate. The estuary was also a source of DIN during all surveys, largely in response to lower than expected DIN levels measured in the fresh river water i.e. in December the nitrate content of the river water was less than 0.01 $mmol.m^{-3}$. June and December were weaker sources of DIN than September and March. In June and December the surface layers represented sinks – in June due to the high DIN load in the river water, and in December due to the inverse trends in concentration in the water column, with surface DIN concentrations less then bottom concentrations. As in the Kariega, and as indicated by the (*p-r*) results, there was little production in the water column (the estuary was net heterotrophic). The high chlorophyll-a traditionally associated with the fresh water of the Great Fish estuary would have been washed down from the river, acting as an allochthonous source of phytoplankton. The short residence time of the water (less than three days in all surveys), prevented phytoplankton growth within the estuary. Generally low N:P ratios resulted in lower than expected *ΔDIN* fluxes derived from the *ΔDIP* flux,

resulting in the estuary acting as a net denitrifyer, with nitrate converted by denitrifying bacteria into nitrous oxide (N_2O) and dinitrogen (N_2) which are lost from the system. Denitrification rates were highest in March due to highest nitrate concentrations in the estuary.

5.3 THE MARINE ENVIRONMENTS

Reference values for coastal nutrient concentrations were less available in the literature than comparative estuarine values. The absence of this data is largely due to the difficult working environment due to high wave activity and often swirling currents creating an unstable and ever changing environment, making measurement taking and sample collecting difficult. While the exchange between the estuarine and nearshore environment has come under scrutiny in the past (e.g. Winter and Baird, 1991; numerous LOICZ studies), thorough studies undertaken in the nearshore wave zone have been lacking. Although nearshore concentrations are variable, mesoscale processes such as persistent upwelling or riverine outflow can elevate nutrient concentrations in particular regions. Such is the case with the Great Fish marine nearshore environment, dominated by relatively fresh water outflow, while in the Kariega marine nearshore environment, marine water extends into the estuary to be governed by the processes therein. Due to the lack of data in the literature, the nearshore concentrations from the two sites were compared to average south coast values stated in the SAWQG for marine coastal areas, to concentrations from the Marine Control site without any estuarine influence, as well as, of course, to each other.

5.3.1 The Kariega Marine Nearshore Environment

The results of the Kariega estuary LOICZ budgets suggest that in terms of DIN, the marine environment has a greater influence on the estuary than vice versa. A positive V_R term and a calculated net sink for DIN in June and September, combined with the low river flow and nutrient concentrations point to the sea as the dominant source of DIN within the estuary. This is in agreement with the long held view that the Kariega estuary

is in fact an extension of the sea or a marine embayment. De Villiers (1990) commented that the Kariega estuary, due to the low fresh water inflow, acted as a detrital trap and did not readily export accumulated detritus to the marine environment.

In June high DIN concentrations, above standard south coast values (DWAF, 1995) at all depths, suggests upwelled water. The characteristic cooler water temperatures were, however, absent. The nutrient-rich water could not have been derived from the estuary due to the positive V_R term and low flow rates. Furthermore, the fact that the mean concentration of DIN in the marine environment was higher than that of the estuary, indicates that the marine environment was the more likely source of DIN. The high DIN concentrations offshore of the Kariega estuary could be accounted for by discharge from the Great Fish estuary, some 50 km away. Strong outflow in June could have resulted in water of Great Fish estuarine origin washing down the coast following the dominant south westward flowing inshore currents eventually delivering nutrient-rich water to the Kariega nearshore environment. According to those who frequent the nearshore area between the two estuaries, this is a regular occurrence, but not consistent due to the variable nature of the inshore currents, with a counter-current at times dominating (Van der Walt[1], pers. comm.) Figure 5.9, a satellite photo of surface chlorophyll-a concentration of a section of the Eastern Cape coastline, shows the effect the high volume of fresh water discharging from the Great Fish River through the estuary has on the nearshore environment south-west of the estuary, reaching as far as the Kariega estuary. The light blue zones indicate regions of higher chlorophyll-a concentration, eminating from the Great Fish estuary. Unfortunately, due to adverse weather conditions, no Marine Control station, which was in later surveys positioned between the two estuaries, was occupied in June. This would have provided further evidence to support this theory, as the nutrient concentrations of an area between the two nearshore zones would have been known. Lower DIN concentrations, below south coast standards (DWAF, 1995), characterised the remaining three surveys, with March the lowest, accounting for the estuary being a source of DIN as described in the LOICZ budget for March. September and December in the Great Fish River were characterised by low flow rates, while in

[1] Keryn Van der Walt, Station Commander, National Sea Rescue Institute (NSRI), Port Alfred.

March, high discharge into the estuary resulted in river mouth conditions (in the sense of Whitfield, 1992) and would have resulted in freshwater pushing out further from the immediate coastal and off into deeper water. DIN concentrations in the water offshore of the Kariega estuary were therefore similar to the naturally occurring concentrations of the Marine Control site.

In the absence of nutrient delivery via fresh water from the Kariega estuary (resulting in sporadic mixing plots in the marine grid with a small range of salinities and nutrient concentrations), phosphate concentrations were due to decomposition and excretion of organisms in the nearshore environment (Valiela, 1980). This is verified by mean concentrations in the grid being similar or less than concentrations from the Marine Control site in the corresponding surveys, which were generally less than south coast standard phosphate concentrations (DWAF, 1995). An N:P ratio of 25:1 in the Kariega marine nearshore environment in June indicates phosphate limitation, accounting for the low phosphate concentrations recorded due to the assimilation by phytoplankton present in the grid. The remaining surveys were characterised by low N:P ratios, 8:1, 12:1 and 1:1 for September, December and March, respectively, indicative of nitrate limitation common in coastal waters.

Silicate concentrations in the Kariega marine nearshore environment were above average south coast levels (DWAF, 1995) in June and March. In March, this was due to high silicate concentrations in the estuary in response to local rainfall, and tidal exchange with the nearshore water. In June, however, the estuary was generally low in silicate concentration (the lowest of the four surveys), again suggesting the allochthonous delivery of nutrient-rich water from the Great Fish estuary. In September and December, concentrations were equal to or less than standard south coast silicate concentrations (DWAF, 1995). Silicate concentrations in the Kariega marine grid were less than concentrations at the Marine Control site in all surveys (that the Marine Control site was occupied). The atomic ratio of silicate:DIN:phosphate in the marine environment is 16:16:1 (Justic *et al.*, 1995). Where anthropogenic loading in river catchments is severe, a decrease in silicate availability in the coastal zone can arise from high nutrient

stimulated fresh water diatom production (Turner and Rabalais, 1991). This can result in silicate limitation in the coastal zone, with coastal eutrophication implications due to non-siliceous phytoplankton production (Justic *et al.*, 1995). According to the criteria in Justic *et al.* (1995), however, the Kariega marine grid was always nutrient limited in terms of DIN (Si:N>1), except in June when DIN concentrations were high due to the effects of the Great Fish estuary outflow, while in terms of phosphate, the Redfield ratio was approximated (10<Si:P>22).

5.3.2 The Great Fish Marine Nearshore Environment

Nutrient concentrations in the Great Fish marine environment, represented by a median value from the grid as a whole, were often significantly less or showed no significant difference from those in the Kariega marine grid. This was due to the higher concentrations expected in response to the outflow of nutrient-rich water being confined to a plume leaving the estuary. Indeed, with the exception of December, the highest individual station concentrations were always in the Great Fish marine grid, associated with the plume. Grange *et al.* (2000) commented that during ebb tides, large quantities of terrestrially-driven material and nutrients are washed out into the sea from the Great fish estuary to be utilized in the coastal zone. This can be seen in Figure 5.10, a section through the water column 250 m offshore in March, showing DIN-rich in the top layer, flowing out as defined plume into the Great Fish marine nearshore environment.

Figure 5.9 Satellite photograph showing chlorophyll-a concentration of nearshore surface waters between the Great Fish and Kariega estuaries.

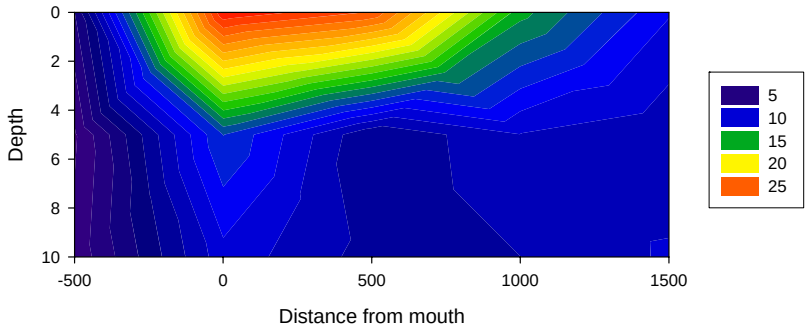


Figure 5.10 Section through water column showing DIN concentration (mmol.m^{-3}) 250 m offshore of the Great Fish estuary in March. Distance and depth in m. Positive and negative distances from the mouth represent west and east, respectively.

DIN concentrations in June and March were above standard south coast concentrations (DWAF, 1995), as well as the Marine Control station in March. This was due to delivery from the estuary under high flow and lower salinity conditions, as is visible on the DIN mixing plot of June (Figure 5.11). In September and December, associated with lower flow, DIN concentrations were below those stated as standard for the south coasts in the SAQWG for coastal marine environments, and generally equal to concentrations recorded at the Marine Control site. This highlights the importance of the high flow through the Great Fish estuary as a source of DIN for the adjacent marine nearshore environment. DIN concentrations in the nearshore were generally higher in the surface layer than at depth due to the buoyancy of the fresher river water, as can be seen in Figure 5.10.

Phosphate generally did not show as much of an increase in the fresher water discharging from the estuary, with concentrations in June equal to or less than those stated as average for the south coast (DWAF, 1995). This also was true for September and December, in which phosphate concentrations adjacent to the estuary were less than at the Marine Control site. In March, however, due to higher phosphate concentrations in the estuary, concentrations in the nearshore grid were higher than south coast averages, as well as those of the Marine Control station (in the surface layer). The N:P ratios of the surface layers were generally higher than those of the three combined depths. Ratios of 14:1 in June (20:1 at the surface), 20:1 in September (and at the surface), 12:1 in December (18:1 at the surface) and 11:1 in March (12:1 at the surface) were calculated, meaning however, with the exception of March, sustained algal growth would be expected in the surface layer (Allanson and Read, 1995). In March, the ratio was due to higher phosphate concentrations (the highest values over the four surveys) rather than lower DIN values. Therefore, as in Great Fish estuary in March, growth by assimilation would occur before 'stoichiometric limitation' occurred, as relatively higher DIN and phosphate concentrations meant a lower 'probable limitation' (Justic *et al.*, 1995).

Silicate values were generally high due to the outflow of silicate-rich estuarine water (Figure 5.12). Concentrations in the grid were above south coast standards (DWAF,

1995) in all surveys except December, when lowest flow conditions were recorded in the Great Fish River. Concentrations in the nearshore were similar to Marine Control concentrations in September and December, and, as with DIN and phosphate, higher in March. As with the Kariega marine nearshore environment, diatom production was nutrient limited in terms of DIN as well as phosphate (Si:P ratio of 37:1 in December). This suggests there is no severe loading of DIN and phosphate from agricultural activity in the upper catchment of the Great Fish River.

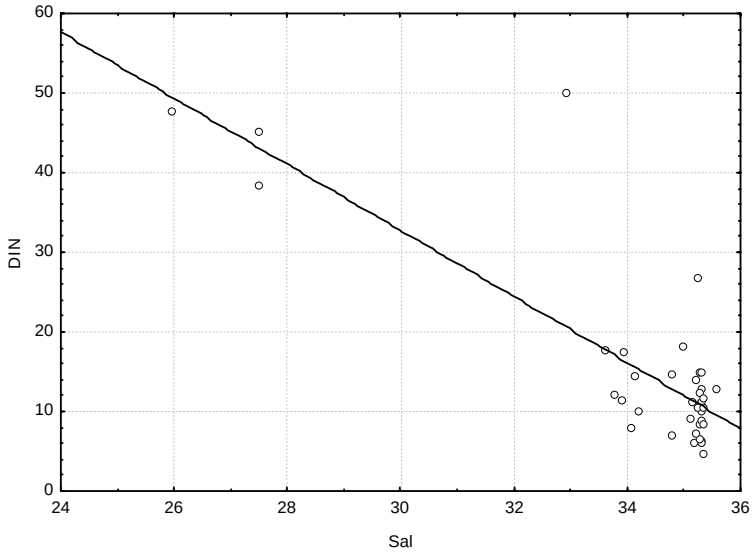


Figure 5.11 Mixing plot of DIN (mmol.m^{-3}) and salinity (psu) in the Great Fish marine environment in June.

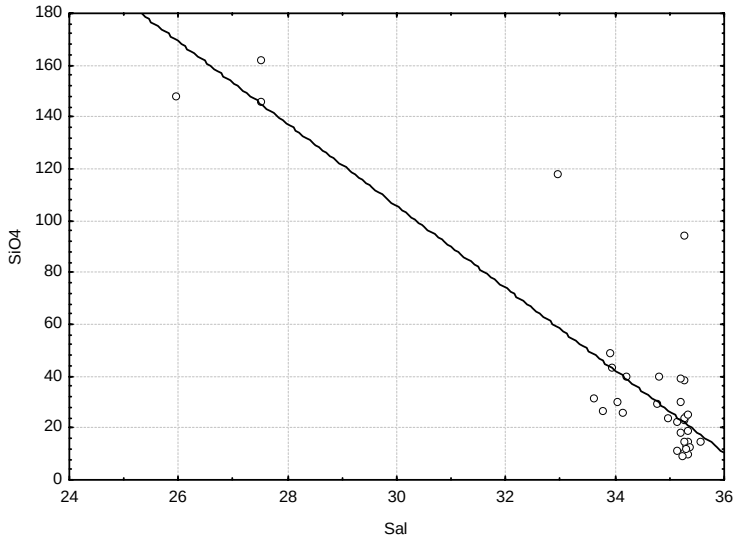


Figure 5.12 Mixing plot of Silicate (mmol.m^{-3}) and salinity (psu) in the Great Fish marine environment in June.

CHAPTER 6 – SUMMARY

The results of the estuarine survey are consistent with previous studies in that the nutrient concentrations in the Great Fish estuary were consistently higher than those recorded in the Kariega estuary, particularly during periods of elevated flow. Periods of lower flow rates in the Great fish River, which were two orders of magnitude greater than the highest flow rates recorded in the Kariega River, resulted in lowered nutrient concentrations in the Great Fish estuary, where the sea became the most important source of dissolved inorganic nitrogen (DIN). These were due to decreased release of water form the inter-basin transfer, rather than seasonal changes in rainfall within the catchment. Due to the lack of variation in riverine inflow into the estuary, seasonal variation in physico-chemical properties and nutrient concentrations in the Kariega estuary was minimal. Exception were recorded in March, when a marginal increase in flow resulted in reduced salinities (in the context of the Kariega estuary) and higher nutrient concentrations within the estuary, and in June, when DIN concentrations were elevated due to allochthonous import from the adjacent ocean. Results of the Land-Ocean Interactions in the Coastal Zone (LOICZ) budgets reveal that, despite the hydrodynamic differences in the two estuaries, they behave in largely the same manner, in that both systems were sources of nutrients with heterotrophic process dominating over autotrophic actions and both were net denitrifyers for the majority of the sampling trips (discounting December in the Kariega estuary). The Great Fish estuary was, however, a greater source of dissolved inorganic phosphorus (DIP) per unit area in all surveys, up to two orders of magnitude higher than the Kariega estuary. In terms of DIN, in March, when both the estuaries were a source of DIN, the Great Fish estuary was a greater source per unit area. In June and September, the Kariega estuary was a sink for DIN. When compared to the larger systems of Europe and the Americas, however, the DIN flux results in the Kariega estuary were neutral. For Italian systems, a ΔDIN of +/- 0.5 $mmol.m^{-2}.day^{-1}$ and a ΔDIP of +/- 0.01 $mmol.m^{-2}.day^{-1}$ is considered to represent neither a sink nor a source of DIN or DIP, respectively (Giordani, 2005). This highlights the lack of fresh water flow into the Kariega estuary. In both estuaries respiration exceeded primary production. In the Kariega estuary, this was due to low productivity resulting from the low nutrient

concentrations. In the Great Fish estuary, the rapid flushing time (less than three days in all surveys) prevented build-up of biomass within the system. Both systems were net denitrifyers, again, however, for different reasons. In the Kariega estuary, this was a consequence of low nitrogen concentrations and an unfavourable C:N ratio (common to oligotrophic systems) preventing nitrogen fixation. The higher nitrate concentrations in the Great fish estuary allowed bacteria to utilize nitrate as a terminal electron acceptor in respiration and reduce it during denitrification.

Anthropogenic activities have been shown to adversely affect the water quality of estuaries. While there is no doubt that the Kariega and Great Fish estuaries have been anthropogenically altered, have they been degraded? The greatest threats to the estuaries of Kwa-Zulu Natal have been reported to be agrochemical leaching from farmlands, fecal contamination from unserviced informal settlements and effluents from industries (Morant and Quinn, 1999). The two estuaries in question have none of these problems, although the changes in flow have lead to other consequences. The Kariega estuary has been shown to be low in productivity while in the Great Fish estuary the variability and diversity associated with natural periods of high and low flow has been lost. These are due to anthropogenic induced changes in flow, which translate into the different physico-chemical properties and nutrient concentrations found in the nearshore environments adjacent to the two estuaries.

The nearshore environment adjacent to the Great Fish estuary was generally characterised by the presence of a surface plume of decreased salinity and increased nutrient concentrations flowing out of the estuary, with an exception recorded during December. During the December survey, no evidence nutrient-rich estuarine outflow was recorded. This corresponds to the period lowest flow in the Great Fish River. Concentrations within the plume leaving the Great Fish estuary for the remainder of the surveys were generally higher than those in the Kariega marine nearshore environment, as well as at the Marine Control station, not directly under the influence of estuarine outflow. Concentrations in the Kariega marine grid were generally similar to Marine Control concentrations. The absence of elevated nutrient concentrations delivered by the Kariega

estuary highlights the lack of outflow due to regular impoundments along the Kariega River. On the basis of these findings, the validity of the 'outwelling hypothesis' in the Kariega estuary has to be questioned. This is in agreement with Taylor and Allanson (1995), who suggested that micro-tidal estuaries with low discharges may in fact be 'inwellers' of dissolved nutrients and particulate material. The fact that the Kariega estuary was a weak sink for DIN in June and September, with similar nutrient concentrations to the adjacent nearshore, stands in agreement with this theory. The Great Fish estuary, on the other hand, was a source of DIN and DIP during all surveys and exhibited a consistent strong outflow into the nearshore environment as indicated by the high residual flux (V_R) value described in the LOICZ budgets. The outflow of nutrient-rich waters was evident the nearshore zone adjacent to the Great Fish estuary. The observed pattern was due to the inter-basin transfer of water from the Orange River system to the Great Fish River. Partial evidence was recorded to suggest that the outflow of riverine water from the Great Fish estuary may be evident in the marine environment adjacent to the Kariega estuary.

As further development in the Eastern Cape coastal belt, and indeed in South Africa, is inevitable, so river catchments will be further altered in order to supply adequate fresh water needed to sustain development. These alterations are historically made without concern for the potentially adverse effects felt downstream in estuaries, and ultimately in the adjacent nearshore environment. Future studies should therefore concentrate on providing those in the position to make decisions regarding catchment management with as much information as possible about estuarine and nearshore nutrient dynamics and how to minimize the potential threats of eutrophication and mouth closure. This is best achieved by long-term monitoring at short enough intervals in order to properly asses both short-term fluctuations as well as long-term variability. Whether this information is considered, and what the consequences of a failure to consider the fragile nature of the estuarine environment will be, remains to be seen.

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APPENDIX 1

Table A1.1.1 June survey salinity (psu), temperature (^{o}C) and nutrient concentration (mmol.m^{-3}) results in the Kariega estuary. Srf = surface layer; bot = bottom layer, R = river.

Station	Salinity		Temperature		DIN		Nitrate		Nitrite		Ammonium		Phosphate		Silicate	
	srf	bot	srf	bot	srf	bot	Srf	bot	srf	bot	srf	bot	srf	bot	srf	bot
R	37.50		16.20		29.44		22.85		5.93		0.66		1.10		140.08	
1	37.70	37.60	16.26	16.04	25.87	39.04	20.07	32.99	5.48	5.93	0.32	0.12	1.52	1.47	122.73	98.37
2	37.92	37.93	16.03	15.88	0.62	0.37	0.12	0.11	0.00	0.00	0.50	0.26	1.75	1.95	130.73	152.77
3	37.68	37.63	16.21	16.25	30.37	0.32	24.42	0.00	5.67	0.00	0.28	0.32	2.07	2.16	96.51	91.09
4	37.47	37.42	16.17	16.00	1.21	0.64	0.04	0.00	0.41	0.26	0.76	0.38	2.00	2.53	104.43	81.77
5	37.08	37.03	16.15	15.88	43.61	29.75	37.87	24.11	5.24	5.28	0.50	0.36	1.84	2.05	58.91	59.47
6	36.26	36.43	16.23	15.87	3.18	2.77	0.43	1.31	0.54	0.58	2.21	0.88	1.36	2.14	41.70	45.26
7	36.01	36.26	17.00	15.84	1.66	32.80	0.34	26.71	0.60	5.31	0.72	0.78	0.98	1.36	30.50	34.88
8	35.77	36.01	16.55	15.92	24.07	31.51	18.24	25.08	4.68	5.47	1.15	0.96	0.92	0.83	26.06	41.13
9	35.60	35.60	16.71	16.77	4.77	29.87	2.66	23.49	1.00	5.33	1.11	1.05	1.39	0.67	19.66	23.87
10	35.34	35.35	16.75	16.76	6.66	113.05	4.63	106.63	1.27	5.70	0.76	0.72	0.64	0.57	9.56	13.19

Table A1.1.2 June survey salinity (psu), temperature (^{o}C) and nutrient concentration (mmol.m^{-3}) results in the Great Fish estuary. Srf = surface layer; bot = bottom layer, R = river.

Station	Salinity		Temperature		DIN		Nitrate		Nitrite		Ammonium		Phosphate		Silicate	
	srf	bot	srf	bot	srf	bot	Srf	bot	srf	bot	srf	bot	srf	bot	srf	bot
R	0.00		13.50		137.45		133.34		0.78		3.33		4.48		150.41	
1	0.76	1.30	13.57	14.37	139.53	165.65	135.66	159.10	1.14	3.57	2.73	2.98	4.45	3.81	152.87	152.81
2	1.53	8.33	13.61	15.07	146.71	98.05	139.94	93.15	2.65	1.21	4.12	3.69	5.22	3.19	149.15	144.55
3	3.95	25.85	13.78	15.35	121.95	92.13	117.91	84.37	1.13	1.09	2.91	6.67	4.36	1.95	148.68	153.36
4	5.91	17.98	13.89	15.41	110.43	47.71	104.37	41.37	2.43	2.12	3.63	4.22	3.17	1.95	129.41	136.52
5	12.75	21.30	14.38	15.18	106.71	54.98	101.95	51.18	0.98	1.38	3.78	2.42	2.19	1.38	131.66	143.84
6	10.20	32.20	14.34	15.06	79.09	36.52	73.97	33.88	1.37	0.87	3.75	1.77	3.67	1.35	149.31	164.92
7	12.28	33.88	14.50	15.44	105.70	31.12	100.49	29.34	0.81	0.42	4.40	1.36	3.54	2.41	120.20	94.95
8	13.13	34.58	14.63	14.95	86.50	16.99	82.89	14.50	0.94	1.21	2.67	1.28	2.04	2.00	147.30	144.10

Table A1.1.3 June survey salinity (psu), temperature (^{o}C) and nutrient concentration (mmol.m^{-3}) results in the Kariega marine environment. MC = Marine Control.

Station	Salinity			Temperature			DIN			Nitrate		
	0m	5m	10m	0m	5m	10m	0m	5m	10m	0m	5m	10m
1	35.28	35.32		16.09	16.13		9.99	10.56		6.64	5.59	
2	35.32	35.34	35.34	16.09	16.07	16.08	8.44	8.22		4.47	6.07	
3	35.32	35.33	35.04	16.13	16.13	16.14	8.79	9.1	8.51	6.22	6.16	5.18
4	35.32	35.34	35.35	16.22	16.16	16.13	11.48	11.28	15.47	7.40	7.85	11.77
5	35.33	35.34	35.33	16.09	16.08	16.07	19.68	9.44		14.12	6.25	
7	35.32	35.34		16.12	16.06		15.52	16.59		10.09	10.68	
8	35.33	35.34	35.33	16.10	16.07	16.06	47.28	30.95		39.31	23.58	
9	35.34	35.36	35.36	16.26	16.25	16.24	24.76	7.58	7.64	16.12	4.54	5.22
10	35.34	35.32	35.23	16.40	16.31	16.18	33.27	35.54	36.35	25.68	27.53	29.36
11	35.34	35.35		16.30	16.30		45.91	30.11		38.63	19.74	
12	35.34	35.35	35.15	16.40	16.31	16.26	9.25	39.59	8.28	5.49	32.52	5.35
13	35.33	35.35		16.35	16.28		8.55	36.29		6.10	29.35	
14	35.34	35.36	35.35	16.50	16.19	16.15	29.16	34.32	9.76	22.26	27.11	6.19
17	35.35	35.35	35.30	16.42	16.34	16.31	7.97	32.34		5.43	25.19	
18	35.35	35.34	35.35	16.58	16.37	16.34	31.88	37.75	41.42	24.40	30.47	33.99
19	35.33	35.34	35.35	16.55	16.41	16.37	29.65	29.84	34.3	22.61	22.66	26.78
20	35.34	35.35		16.45	16.40		36.84	8.04		29.06	4.86	
22	35.34	35.35	35.30	16.44	16.48	16.45	47.89	34.37		43.04	27.91	
23	35.34	35.34	35.33	16.68	16.39	16.34	6.33	34.66	7.75	3.74	28.35	5.59
24	35.33	35.34	35.35	16.60	16.40	16.37	26.24	8.35	37.3	19.03	5.39	29.76

Station	Nitrite			Ammonium			Phosphate			Silicate		
	0m	5m	10m	0m	5m	10m	0m	5m	10m	0m	5m	10m
1	1.31	3.30		2.04	1.67		0.87	0.80		9.49	7.70	
2	2.75	1.22		1.22	0.93		1.08	1.13		8.84	9.77	
3	1.61	1.27	1.40	0.96	1.67	1.93	1.01	1.23	0.69	12.44	9.10	10.63
4	2.49	1.65	2.22	1.59	1.78	1.48	0.96	0.99	0.92	9.10	7.36	10.31
5	4.45	1.26		1.11	1.93		0.87	1.19		8.39	9.71	
7	3.84	4.76		1.59	1.15		0.76	0.85		9.85	10.86	
8	6.27	5.67		1.70	1.70		0.66	0.80		12.87	11.98	
9	7.75	1.26	1.31	0.89	1.78	1.11	1.06	1.05	0.79	11.27	14.36	13.26
10	5.59	5.79	5.51	2.00	2.22	1.48	1.13	0.83	0.78	10.81	10.20	11.68
11	5.80	5.52		1.48	4.85		0.78	0.74		12.14	11.63	
12	1.20	5.29	1.12	2.56	1.78	1.81	1.01	0.83	0.73	11.48	10.74	12.55
13	1.12	5.61		1.33	1.33		1.46	1.10		9.49	7.18	
14	5.42	5.80	1.24	1.48	1.41	2.33	1.10	1.06	0.87	10.84	11.09	10.74
17	1.10	5.71		1.44	1.44		1.29	0.73		12.69	8.57	
18	5.70	5.72	5.76	1.78	1.56	1.67	1.10	0.87	0.81	10.88	9.10	11.28
19	5.93	5.48	5.52	1.11	1.70	2.00	0.85	0.93	0.73	9.67	7.22	8.43
20	5.67	1.22		2.11	1.96		0.69	1.01		11.28	7.22	
22	3.11	5.24		1.74	1.22		0.75	0.99		9.53	9.81	
23	0.89	4.68	1.12	1.70	1.63	1.04	0.74	0.83	0.81	12.47	12.62	10.17
24	5.47	1.18	5.76	1.74	1.78	1.78	0.83	0.99	0.73	9.81	9.95	9.99

Table A1.1.4 June survey salinity (psu), temperature (^{o}C) and nutrient concentration (mmol.m^{-3}) results in the Great Fish marine environment. MC = Marine Control.

Station	Salinity			Temperature			DIN			Nitrate		
	0m	5m	10m	0m	5m	10m	0m	5m	10m	0m	5m	10m
1	33.79	35.19	35.28	15.76	15.86	15.77	12.15	5.96	6.63	8.45	4.12	5.44
2	34.14	35.31	35.35	15.62	15.88	15.57	14.37	8.82	10.36	10.35	4.89	7.97
3	34.06	35.31	35.36	15.54	16.06	15.72	7.86	6.25	8.35	6.09	4.57	5.11
4	34.80	35.31	35.35	15.96	15.93	15.77	14.68	6.04	4.73	12.05	5.05	3.60
5	33.90	35.13	35.19	15.80	15.90	15.90	9.46	5.80		9.46	5.80	
6	33.94	35.27	35.29	15.83	15.92	15.99	17.36	10.85		14.82	8.28	
7	34.21	35.32	35.25	15.92	15.90	15.66	10.09	12.7	10.46	7.30	8.99	6.07
8	34.78	35.28	35.34	16.07	15.97	15.80	6.93	8.41	11.68	4.92	6.27	10.64
9	34.98	35.33	35.57	16.11	15.89	15.37	18.26	10.05	12.77	15.06	7.64	11.76
10	27.50	35.28	35.29	15.68	15.88	15.66	40.30	11.94		40.30	11.94	
11	25.95	35.26	35.20	15.70	15.80	15.70	47.6	26.78		43.13	23.56	
12	27.50	35.20	35.20	15.82	15.92	15.66	38.45	13.89	7.15	35.50	11.35	6.23
14	32.94	35.33	35.30	16.09	15.92	15.67	49.98	11.28	14.92	46.84	9.78	12.72
18	33.60	35.27	35.15	16.11	15.79	15.73	17.59	12.32	11.1	15.26	9.99	9.23

Station	Nitrite			Ammonium			Phosphate			Silicate		
	0m	5m	10m	0m	5m	10m	0m	5m	10m	0m	5m	10m
1	2.99	0.68	0.29	0.71	1.16	0.90	1.29	2.59	1.10	26.82	17.85	14.75
2	2.76	2.48	1.65	1.26	1.45	0.74	1.31	1.35	1.04	25.74	13.37	24.85
3	0.51	0.39	2.21	1.26	1.29	1.03	0.87	0.83	0.69	30.01	13.13	12.59
4	1.92	0.54	0.26	0.71	0.45	0.87	0.93	0.84	1.33	39.64	24.53	18.65
5	0.49	1.78		1.53	1.45		1.03	1.23		48.85	22.40	
6	0.64	1.38		1.90	1.19		1.74	0.73		43.53	23.18	
7	1.34	1.84	1.52	1.45	1.87	2.87	0.76	0.62	0.60	39.96	10.67	9.03
8	0.36	1.20	0.14	1.65	0.94	0.90	0.86	0.60	1.19	29.58	10.17	14.86
9	2.49	1.89	0.30	0.71	0.52	0.71	0.67	0.76	0.99	23.71	9.92	15.00
10	2.81	2.32		2.13	0.68		2.59	1.33		146.19	38.22	
11	2.86	2.28		1.61	0.94		1.08	1.42		148.14	94.50	
12	1.05	1.73	0.05	1.90	0.81	0.87	1.33	0.98	0.64	161.61	39.07	29.86
14	1.70	0.17	1.30	1.44	1.33	0.90	0.51	0.85	0.60	118.28	13.26	11.97
18	1.39	1.30	1.20	0.94	1.03	0.67	0.76	0.86	0.86	31.37	23.49	11.16

Table A1.2.1 September survey salinity (psu), temperature (^{o}C) and nutrient concentration (mmol.m^{-3}) results in the Kariega estuary. Srf = surface layer; bot = bottom layer, R = river.

Station	Salinity		Temperature		DIN		Nitrate		Nitrite		Ammonium		Phosphate		Silicate	
	srf	bot	srf	bot	srf	bot	srf	bot	srf	bot	srf	bot	srf	bot	srf	bot
R	36.56		20.89		2.03		0.62		0.00		1.41		0.93		214.64	
1	37.35	33.48	21.96	20.42	0.73	1.11	0.01	0.32	0.00	0.00	0.72	0.79	1.85	2.18	225.86	184.65
2	37.51	34.21	21.92	20.12	1.08	0.82	0.38	0.05	0.00	0.00	0.70	0.77	2.51	2.05	159.10	172.51
3	37.77	36.94	23.04	21.06	1.69	1.10	0.44	0.02	0.03	0.17	1.22	0.91	2.12	1.95	130.15	141.45
4	37.28	34.53	22.00	20.66	1.54	1.79	0.76	0.65	0.04	0.03	0.74	1.11	1.42	1.79	113.11	124.52
5	37.04	36.88	22.52	20.51	0.93	0.68	0.34	0.04	0.00	0.00	0.59	0.64	1.28	1.42	94.62	96.21
6	37.61	37.62	22.73	20.34	1.49	1.17	0.26	0.31	0.00	0.00	1.23	0.86	1.57	0.99	72.79	80.93
7	36.50	36.85	22.38	20.26	1.84	1.23	0.58	0.31	0.00	0.14	1.26	0.78	1.03	1.39	63.30	89.72
8	35.79	35.82	21.66	19.35	0.83	0.93	0.05	0.09	0.00	0.00	0.78	0.84	0.40	0.76	52.41	65.14
9	35.47	35.50	20.52	20.30	2.28	0.97	1.16	0.12	0.03	0.01	1.09	0.84	0.53	0.46	22.10	21.95
10	35.58	35.58	19.85	19.84	2.84	2.91	1.73	1.71	0.00	0.05	1.11	1.15	0.57	0.33	10.66	33.69

Table A1.2.2 September survey salinity (psu), temperature (^{o}C) and nutrient concentration (mmol.m^{-3}) results in the Great Fish estuary. Srf = surface layer; bot = bottom layer, R = river.

Station	Salinity		Temperature		DIN		Nitrate		Nitrite		Ammonium		Phosphate		Silicate	
	srf	bot	srf	bot	srf	bot	srf	bot	Srf	bot	srf	bot	srf	bot	srf	bot
R	0.00		18.20		3.09		0.69		0.84		1.56		0.73		20.79	
1	0.97	3.33	18.33	18.49	5.69	9.21	1.97	2.00	0.61	1.02	3.11	6.19	1.36	1.69	25.79	31.50
2	3.80	19.15	18.60	18.62	10.34	20.75	2.75	4.04	0.89	0.90	6.70	15.81	2.28	2.05	43.39	157.84
3	5.45	26.80	19.25	18.32	12.45	14.83	3.72	3.96	0.69	0.82	8.04	10.05	1.57	1.79	49.73	92.06
4	5.30	23.00	19.61	18.03	13.44	11.91	3.81	3.22	0.72	0.58	8.91	8.11	1.19	1.79	55.96	81.82
5	13.46	29.32	18.95	17.59	15.92	8.03	4.46	3.59	0.76	0.55	10.70	3.89	1.24	0.97	70.31	34.82
6	27.09	25.10	18.20	17.42	13.28	5.77	4.40	3.26	0.66	0.47	8.22	2.04	1.37	0.93	68.34	24.18
7	33.01	34.50	18.38	17.54	6.79	5.90	3.61	3.28	0.44	0.45	2.74	2.17	0.64	0.56	25.04	29.30
8	34.93	34.93	17.88	17.88	5.21	5.83	3.11	3.13	0.40	0.44	1.70	2.26	0.60	0.62	19.65	21.72

Table A1.2.3 September survey salinity (psu), temperature (^{o}C) and nutrient concentration (mmol.m^{-3}) results in the Kariega marine environment. MC = Marine Control.

Station	Salinity			Temperature			DIN			Nitrate		
	0m	5m	10m	0m	5m	10m	0m	5m	10m	0m	5m	10m
1	35.32	35.00		17.88	17.83		2.88	3.73		2.17	3.11	
2	35.23	35.31		17.99	17.97		3.05	2.84		2.45	2.28	
3	35.29	35.31		18.03	18.03		3.13	2.88		2.54	2.49	
4	35.30	35.31	35.31	18.04	18.05	18.03	3.06	2.58	4.11	2.26	2.12	3.46
5	35.29	35.29		18.05	18.00		2.72	2.79		2.36	2.49	
7	35.29	35.31	35.31	18.03	18.03	18.02	4.39	3.44		3.82	2.53	
8	35.30	35.30	35.05	18.00	18.01	17.99	5.15	5.57		4.02	4.52	
9	35.29	35.31		17.97	17.97		3.23	3.07		2.39	2.30	
10	35.25	35.31	35.22	18.00	17.99	17.95	3.04	3.07		2.41	2.37	
11	35.30	35.31		18.10	18.10		2.65	3.23		2.13	2.49	
12	35.29	35.32	35.31	18.06	18.06	18.06	3.26	2.90	3.09	2.69	2.34	2.43
13	35.30	35.32	35.31	18.06	18.06	18.05	2.85	2.83	2.56	2.10	2.04	1.99
14	35.25	35.31	35.31	17.99	17.99	17.98	2.92	2.39	2.69	2.17	2.02	2.08
17	35.31	35.31		18.10	18.10		2.89	2.96		2.23	2.36	
18	35.31	35.31	35.31	18.01	18.00	18.00	2.30	2.80	2.54	1.80	2.24	2.02
19	35.31	35.31	35.31	18.00	18.01	17.99	3.73	2.67	2.53	2.75	1.98	1.89
22	35.30	35.31	35.31	18.05	18.04	18.04	2.56	3.06		1.74	2.27	
23	35.30	35.33	35.31	18.08	18.06	18.05	2.52	2.52	2.61	1.84	1.91	1.89
24	35.28	35.31	35.30	18.05	18.05	18.01	2.81	3.04	2.98	2.09	2.22	2.27
MC	35.32	35.34	35.34	18.02	18.18	18.17	3.06	3.00	3.13	2.47	2.38	2.46

Station	Nitrite			Ammonium			Phosphate			Silicate		
	0m	5m	10m	0m	5m	10m	0m	5m	10m	0m	5m	10m
1	0.09	0.11		0.62	0.51		0.39	0.35		2.98	2.76	
2	0.10	0.12		0.50	0.44		0.28	0.31		3.68	2.76	
3	0.11	0.15		0.48	0.24		0.22	0.24		3.65	5.18	
4	0.11	0.13	0.13	0.69	0.33	0.52	0.27	0.18	0.25	4.13	5.36	3.30
5	0.14	0.10		0.22	0.20		0.42	0.42		4.17	3.96	
7	0.00	0.11		0.57	0.80		0.15	0.42		5.24	5.36	
8	0.11	0.11		1.02	0.94		0.36	0.33		3.65	6.26	
9	0.12	0.07		0.72	0.70		0.45	0.33		3.59	4.57	
10	0.17	0.12		0.46	0.58		0.42	0.42		4.17	3.96	
11	0.08	0.11		0.44	0.63		0.40	0.27		4.48	8.06	
12	0.11	0.12	0.12	0.46	0.44	0.54	0.32	0.33	0.36	3.09	3.79	2.67
13	0.09	0.10	0.11	0.66	0.69	0.46	0.39	0.28	0.29	5.27	3.45	3.11
14	0.06	0.07	0.07	0.69	0.30	0.54	0.29	0.32	0.28	5.27	2.98	2.73
17	0.08	0.00		0.58	0.60		0.36	0.30		5.84	3.17	
18	0.06	0.08	0.08	0.44	0.48	0.44	0.52	0.53	0.59	5.97	4.16	3.24
19	0.08	0.09	0.08	0.90	0.60	0.56	0.59	0.54	0.57	3.28	3.51	2.44
22	0.10	0.11		0.72	0.68		0.50	0.40		4.22	4.85	
23	0.1	0.11	0.1	0.58	0.5	0.62	0.35	0.4	0.35	9.36	3.52	2.16
24	0.08	0.1	0.07	0.64	0.72	0.64	0.36	0.43	0.36	5.14	6.67	3.11
MC	0.03	0.12	0.07	0.56	0.5	0.6	0.87	0.6	2.33	7.87	6.7	4.76

Table A1.2.4 September survey salinity (psu), temperature (^{o}C) and nutrient concentration (mmol.m^{-3}) results in the Great Fish marine environment. MC = Marine Control.

Station	Salinity			Temperature			DIN			Nitrate		
	0m	5m	10m	0m	5m	10m	0m	5m	10m	0m	5m	10m
1	35.21	35.21	35.21	17.21	17.22	17.17	8.03	11.35		3.67	6.01	
2	35.19	35.24	35.25	17.21	17.15	17.00	6.69	6.10		4.10	3.45	
3	35.21	35.25	35.26	17.20	17.18	17.12	6.04	5.15		3.58	2.99	
4	35.22	35.26	35.26	17.14	17.12	17.07	7.81	5.75		4.61	3.27	
5	34.98	35.06	35.10	17.12	17.16	17.17	5.52	4.84		2.89	2.71	
6	35.09	35.14	35.12	17.23	17.08	17.07	4.45	5.28		2.33	2.71	
7	35.13	35.16	35.18	17.18	17.07	17.02	4.23	4.90	5.13	2.20	2.64	2.79
8	35.17	35.19	35.19	17.13	17.11	16.96	4.82	4.62	5.14	2.30	2.61	3.05
9	35.16	35.22	35.22	17.09	17.00	16.97	5.11	4.66		2.59	2.50	
10	35.19	35.24	35.25	17.32	17.32	17.25	7.18	5.73		3.06	3.07	
11	35.22	35.26	35.25	17.32	17.30	17.29	6.13	5.37		3.04	2.52	
12	35.22	35.26	35.27	17.31	17.30	17.14	4.68	4.67		2.03	2.57	
13	35.20	35.27	35.26	17.21	17.18	17.30	5.36	5.15		3.12	2.96	
14	35.24	35.27	35.27	17.16	17.16	17.16	6.65	6.12		3.66	3.76	
22	35.10	35.19	35.27	17.53	17.45	17.22	5.25	4.35		2.48	2.36	
24	34.73	34.99	35.27	17.62	17.50	17.23	5.11	5.04		2.66	2.76	
MC	35.32	35.34	35.34	18.02	18.18	18.17	3.06	3.00	3.13	2.47	2.38	2.46

Station	Nitrite			Ammonium			Phosphate			Silicate		
	0m	5m	10m	0m	5m	10m	0m	5m	10m	0m	5m	10m
1	0.41	0.42		3.95	4.92		0.26	0.44		5.77	6.56	
2	0.42	0.38		2.17	2.27		0.11	0.22		5.53	5.63	
3	0.39	0.38		2.07	1.78		0.18	0.00		5.98	6.03	
4	0.40	0.39		2.80	2.09		0.22	0.24		6.51	7.71	
5	0.41	0.40		2.22	1.73		0.28	0.26		6.58	7.08	
6	0.45	0.51		1.67	2.06		0.28	0.22		8.66	6.82	
7	0.55	0.46	0.61	1.48	1.80	1.73	0.46	0.20	0.28	5.35	8.24	5.80
8	0.56	0.50	0.64	1.96	1.51	1.45	0.48	0.28	0.33	5.28	5.72	5.50
9	0.53	0.52		1.99	1.64		0.22	0.30		10.81	6.66	
10	0.59	0.60		3.53	2.06		0.22	0.17		5.25	6.09	
11	0.49	0.63		2.60	2.22		0.06	0.28		6.51	6.40	
12	0.72	0.37		1.93	1.73		0.44	0.22		5.56	5.19	
13	0.47	0.36		1.77	1.83		0.22	0.22		6.45	7.87	
14	0.39	0.37		2.60	1.99		0.86	0.22		7.20	6.51	
22	0.36	0.38		2.41	1.61		0.30	0.17		7.17	6.47	
24	0.38	0.40		2.07	1.88		0.30	0.22		7.29	8.97	
MC	0.03	0.12	0.07	0.56	0.50	0.60	0.87	0.60	2.33	7.87	6.70	4.76

Table A1.3.1 December survey salinity (psu), temperature (^{o}C) and nutrient concentration (mmol.m^{-3}) results in the Kariega estuary. Srf = surface layer; bot = bottom layer, R = river.

Station	Salinity		Temperature		DIN		Nitrate		Nitrite		Ammonium		Phosphate		Silicate	
	srf	bot	srf	bot	srf	bot	srf	bot	srf	bot	srf	bot	srf	bot	srf	bot
R	31.00		28.00		2.53		1.00		0.20		1.33		1.15		190.82	
1	32.00	32.00	28.00	27.90	2.93	2.20	1.01	0.75	0.26	0.21	1.66	1.24	0.82	0.84	165.69	170.73
2	34.00	34.00	28.00	27.80	2.40	2.13	0.81	0.57	0.26	0.17	1.33	1.39	1.40	1.47	147.97	151.83
3	34.00	35.00	28.00	27.30	2.78	2.36	0.66	0.70	0.22	0.20	1.90	1.46	1.67	1.29	129.25	128.22
4	35.00	34.00	27.70	27.20	2.16	2.76	0.57	0.90	0.18	0.25	1.41	1.61	1.33	1.31	108.28	110.32
5	34.00	34.00	27.50	27.20	11.00	5.36	3.54	3.40	0.23	0.37	7.23	1.59	1.41	1.34	93.79	95.33
6	35.00	35.00	27.30	26.70	6.17	6.02	3.47	3.68	0.29	0.24	2.41	2.10	0.99	0.99	72.76	80.44
7	34.00	34.00	27.00	26.50	5.30	5.76	2.99	3.45	0.30	0.28	2.01	2.03	0.73	0.87	64.81	74.08
8	33.00	35.00	26.00	25.80	6.58	5.49	3.10	2.80	0.32	0.30	3.16	2.39	0.65	0.68	55.06	53.73
9	35.00	35.00	25.10	25.00	2.34	2.74	0.61	0.58	0.21	0.24	1.52	1.92	0.02	0.00	18.53	17.62
10	35.00	35.00	23.50	23.60	3.01	3.73	1.09	1.72	0.22	0.18	1.70	1.83	0.00	0.00	5.81	6.27

Table A1.3.2 December survey salinity (psu), temperature (^{o}C) and nutrient concentration (mmol.m^{-3}) results in the Great Fish estuary. Srf = surface layer; bot = bottom layer, R = river.

Station	Salinity		Temperature		DIN		Nitrate		Nitrite		Ammonium		Phosphate		Silicate	
	srf	bot	srf	bot	srf	bot	srf	bot	Srf	bot	srf	bot	srf	bot	srf	bot
R	0.00		25.10		2.92		0.00		0.00		2.92		1.57		186.14	
1	0.00	5.00	25.80	24.90	2.05	8.55	0.48	2.68	0.02	1.32	1.55	4.55	2.44	5.60	181.16	201.22
2	1.00	5.00	26.20	25.20	2.51	8.06	0.79	1.98	0.17	0.86	1.55	5.22	1.31	4.41	186.37	203.68
3	4.00	11.00	25.80	24.70	1.72	7.93	0.00	2.90	0.00	0.96	1.72	4.07	2.20	4.08	183.94	210.29
4	8.00	21.00	25.80	23.70	4.29	9.86	1.00	3.84	0.81	0.98	2.48	5.04	3.14	1.41	209.64	152.26
5	11.00	25.00	25.10	23.50	4.00	6.03	1.26	3.16	0.71	0.59	2.03	2.28	2.70	0.84	195.73	107.62
6	15.00	31.00	25.60	22.50	5.52	6.83	2.80	2.63	1.04	0.73	1.68	3.47	2.51	1.67	180.81	61.68
7	17.00	29.00	25.00	23.50	6.48	5.89	3.53	2.64	1.16	0.38	1.79	2.87	2.20	1.52	176.69	88.36
8	19.00	29.00	25.30	23.30	5.24	6.68	2.72	3.08	0.64	0.93	1.88	2.67	1.88	0.85	166.35	87.25

Table A1.3.3 December survey salinity (psu), temperature (^{o}C) and nutrient concentration (mmol.m^{-3}) results in the Kariega marine environment. MC = Marine Control.

Station	Salinity			Temperature			DIN			Nitrate		
	0m	5m	10m	0m	5m	10m	0m	5m	10m	0m	5m	10m
1	35.00	35.00		21.90	22.00		4.39	3.35		1.78	1.38	
2	35.00	35.00		22.00	22.50		3.39	3.13		1.40	1.21	
3	35.00	35.00	35.00	22.30	22.20	21.90	2.78	2.73	3.76	0.91	1.06	1.58
4	35.00	35.00	35.00	22.30	22.30	21.70	3.87	2.99	4.24	1.68	1.31	2.07
5	35.00	35.00		22.40	22.40		3.29	3.19		1.43	1.28	
7	35.00	35.00		22.50	22.40		3.01	3.58		1.27	1.18	
8	35.00	35.00	35.00	22.30	22.20		3.52	3.60		1.03	1.25	
9	35.00	35.00	35.00	22.10	22.10	22.10	2.54	4.35	4.55	0.93	1.37	1.53
10	35.00	35.00	35.00	22.10	22.10	22.00	4.11	2.72		1.16	1.17	1.25
11	35.00	35.00		22.10	22.10		3.37	3.70		1.45	1.54	
12	35.00	35.00	35.00	22.10	22.00	21.80	3.33	2.78	2.83	1.49	1.47	1.66
13	35.00	35.00	35.00	22.20	21.80	21.80	2.48	3.53	4.15	1.28	1.97	2.59
14	35.00	35.00	35.00	22.20	22.10	21.80	2.84	2.84	3.68	1.47	1.39	1.93
17	35.00	35.00		21.80	21.70		3.40	3.47		2.02	2.14	
18	35.00	35.00	35.00	21.80	21.60	21.60	4.45	3.20	3.81	2.00	1.56	1.58
19	35.00	35.00	35.00	22.00	22.00	21.60	3.12	3.06	3.43	1.35	1.17	1.61
20	35.00	35.00		21.80	21.70		4.18	4.29		2.17	2.32	
22	35.00	35.00		21.70	21.80		4.25	4.17		2.20	2.21	
23	35.00	35.00	35.00	21.80	21.80	21.50	3.92	4.34	4.52	1.88	2.12	1.91
24	35.00	35.00	35.00	21.90	21.80	21.40	3.99	3.92	4.88	1.98	1.91	2.23
MC	35.00	35.00	35.00	21.80	21.80	21.40	2.69	3.41	4.43	0.92	1.38	2.60

Station	Nitrite			Ammonium			Phosphate			Silicate		
	0m	5m	10m	0m	5m	10m	0m	5m	10m	0m	5m	10m
1	0.64	0.59		1.97	1.38		0.24	0.13		4.37	4.68	
2	0.57	0.52		1.42	1.40		0.24	0.21		4.14	2.53	
3	0.45	0.59	0.60	1.42	1.08	1.58	0.27	0.26	0.40	4.60	4.83	5.67
4	0.59	0.46	0.66	1.60	1.22	1.51	0.49	0.57	0.65	4.45	4.29	4.98
5	0.57	0.58		1.29	1.33		0.46	0.48		4.29	4.41	
7	0.63	0.57		1.11	1.83		0.26	0.40		4.91	5.25	
8	0.59	0.66		1.90	1.69		0.29	0.34		4.87	4.60	
9	0.46	0.67	0.69	1.15	2.31	2.33	0.10	0.10	0.06	4.49	4.72	4.37
10	0.55	0.58	0.53	2.40	0.97	1.49	0.35	0.56	0.67	4.79	4.49	5.06
11	0.68	0.67		1.24	1.49		0.24	0.38		4.45	4.26	
12	0.71	0.70	0.72	1.13	0.61	0.45	0.38	0.29	0.26	4.72	4.83	5.14
13	0.70	0.72	0.72	0.50	0.84	0.84	0.24	0.27	0.32	4.83	5.52	5.64
14	0.56	0.66	0.69	0.81	0.79	1.06	0.18	0.10	0.26	5.37	4.91	5.48
17	0.57	0.61		0.81	0.72		0.26	0.24		5.52	5.90	
18	0.60	0.49	0.47	1.85	1.15	1.76	0.54	0.34	0.22	7.51	6.02	6.21
19	0.62	0.53	0.49	1.15	1.36	1.33	0.26	0.27	0.27	4.87	4.95	6.10
20	0.63	0.68		1.38	1.29		0.34	0.24		5.41	6.21	
22	0.67	0.74		1.38	1.22		0.19	0.29		5.71	6.1	
23	0.71	0.73	0.51	1.33	1.49	2.1	0.24	0.22	0.19	5.14	5.64	5.75
24	0.74	0.72	0.68	1.27	1.29	1.97	0.48	0.41	0.38	5.29	5.25	5.79
MC	0.44	0.65	0.77	1.33	1.38	1.06	0.22	0.24	0.24	5.83	6.02	7.51

Table A1.3.4 December survey salinity (psu), temperature (^{o}C) and nutrient concentration (mmol.m^{-3}) results in the Great Fish marine environment. MC = Marine Control.

Station	Salinity			Temperature			DIN			Nitrate		
	0m	5m	10m	0m	5m	10m	0m	5m	10m	0m	5m	10m
1	35.00	33.00		21.50	21.40		1.43	0.78		0.55	0.30	
2	33.00	33.50	34.00	21.50	21.40	21.10	1.18	0.94	1.24	0.42	0.51	0.58
3	34.00	34.00	34.00	21.50	21.50	21.20	1.44	1.19	1.18	0.53	0.44	0.50
4	33.00	34.00	35.00	21.60	21.40	21.20	1.71	1.29	0.99	0.61	0.50	0.38
5	33.00	31.00		21.40	21.30		2.04	1.56	0.00	0.68	0.73	
6	32.00	32.00		21.50	21.30		1.91	1.88		0.69	0.73	
7	33.00	32.00	31.00	21.50	21.30	20.80	1.53	1.49	2.34	0.48	0.66	1.25
8	34.00	34.00	34.00	21.50	21.20	20.90	1.39	0.98	2.10	0.52	0.43	1.02
9	32.00	33.00	35.00	21.40	21.20	20.60	2.13	1.60	2.36	0.71	0.54	0.74
10	30.00	33.00		21.40	21.30		1.57	1.37	0.00	0.41	0.55	
11	30.00	33.00		21.40	21.30		1.63	1.00		0.44	0.41	
12	26.00	28.00	30.00	21.40	21.40	21.00	1.81	1.30	0.93	0.57	0.48	0.33
13	28.00	29.50	31.00	21.40	21.40	21.30	1.23	1.49	1.14	0.54	0.65	0.61
14	30.00	31.00	32.00	21.40	21.30	21.20	0.85	1.01	0.54	0.03	0.38	0.26
18	27.00	28.00		21.30	20.70		0.85	1.72		0.38	0.63	
19	33.00	33.00	33.00	21.50	20.70	20.50	1.02	1.92	2.18	0.32	0.92	1.13
22	30.00	30.00		21.70	21.60		1.06	0.44		0.40	0.27	
23	31.00	32.00	33.00	21.60	21.50	21.30	1.27	1.15	0.83	0.37	0.56	0.34
24	34.00	34.00	35.00	21.60	21.50	21.40	1.50	0.92	1.02	0.57	0.42	0.57
MC	35.00	35.00	35.00	21.80	21.80	21.40	2.69	3.41	4.43	0.92	1.38	2.60

Station	Nitrite			Ammonium			Phosphate			Silicate		
	0m	5m	10m	0m	5m	10m	0m	5m	10m	0m	5m	10m
1	0.23	0.14		0.65	0.34		0.20	0.13		4.30	3.90	
2	0.19	0.21	0.24	0.57	0.22	0.42	0.07	0.08	0.16	3.99	3.37	4.56
3	0.24	0.20	0.26	0.67	0.55	0.42	0.36	0.33	0.39	5.15	3.54	3.04
4	0.29	0.24	0.17	0.81	0.55	0.44	0.02	0.02	0.16	5.59	2.91	2.91
5	0.19	0.24		1.17	0.59		0.07	0.10		2.62	2.46	
6	0.27	0.24		0.95	0.91		0.07	0.08		3.73	2.79	
7	0.20	0.26	0.30	0.85	0.57	0.79	0.03	0.05	0.07	3.19	3.24	5.94
8	0.26	0.19	0.33	0.61	0.36	0.75	0.29	0.00	0.07	4.56	3.89	5.55
9	0.25	0.25	0.21	1.17	0.81	1.41	0.02	0.02	0.08	4.04	3.81	6.76
10	0.19	0.27		0.97	0.55		0.05	0.05		3.87	3.95	
11	0.22	0.23		0.97	0.36		0.08	0.08		2.95	3.11	
12	0.27	0.25	0.07	0.97	0.57	0.53	0.15	0.02	0.07	4.15	3.84	4.75
13	0.21	0.29	0.05	0.48	0.55	0.48	0.05	0.05	0.18	3.62	4.26	4.13
14	0.13	0.15	0.10	0.69	0.48	0.18	0.13	0.03	0.03	4.40	3.21	2.93
18	0.12	0.08		0.35	1.01		0.10	0.03		4.49	5.88	
19	0.13	0.13	0.16	0.57	0.87	0.89	0.05	0.20	0.15	4.52	5.59	5.94
22	0.11	0.11		0.55	0.06		0.2	0.15		4.57	3.61	
23	0.11	0.11	0.07	0.79	0.48	0.42	0.2	0.03	0.02	5.23	3.95	3.95
24	0.14	0.14	0.15	0.79	0.36	0.3	0.29	0.23	0.2	5.01	3.94	3.94
MC	0.44	0.65	0.77	1.33	1.38	1.06	0.22	0.24	0.24	5.83	6.02	7.51

Table A1.4.1 March survey salinity (psu), temperature (^{o}C) and nutrient concentration (mmol.m^{-3}) results in the Kariega estuary. Srf = surface layer; bot = bottom layer, R = river.

Station	Salinity		Temperature		DIN		Nitrate		Nitrite		Ammonium		Phosphate		Silicate	
	srf	bot	srf	bot	srf	bot	srf	bot	srf	bot	srf	bot	srf	bot	srf	bot
R	33.03		24.36		0.98		0.55		0.14		0.29		1.86		374.17	
1	35.45	35.77	24.70	25.20	0.93	1.10	0.69	0.34	0.17	0.47	0.07	0.29	1.69	1.97	302.85	296.08
2	36.60	36.53	24.54	24.65	2.33	2.13	1.32	1.17	0.22	0.24	0.79	0.72	1.74	2.03	239.99	228.39
3	37.05	36.79	24.94	24.95	3.16	3.41	1.94	2.77	0.21	0.21	1.01	0.43	3.38	3.71	203.24	181.97
4	36.69	36.60	24.89	24.90	4.25	5.67	2.80	3.60	0.23	0.35	1.22	1.72	2.59	6.02	156.83	150.06
5	36.19	30.00	24.69	24.69	5.19	6.20	3.12	4.44	0.34	0.26	1.72	1.51	6.02	3.94	131.92	129.39
6	35.07	30.72	23.83	23.85	4.86	6.42	3.40	4.54	0.17	0.37	1.29	1.51	2.98	3.71	113.55	102.55
7	35.02	34.70	23.57	23.56	5.69	7.02	3.46	4.27	0.22	0.24	2.01	2.51	3.09	3.60	102.19	95.66
8	34.80	34.69	22.12	22.07	1.50	1.67	0.55	1.19	0.23	0.19	0.72	0.29	3.88	3.71	60.36	55.53
9	34.99	35.00	19.84	19.86	2.25	3.04	1.62	2.02	0.13	0.16	0.50	0.86	4.16	2.98	30.14	24.82
10	34.98	35.00	19.74	19.72	2.21	1.67	1.12	0.90	0.23	0.20	0.86	0.57	2.87	3.71	29.41	27.72

Table A1.4.2 March survey salinity (psu), temperature (^{o}C) and nutrient concentration (mmol.m^{-3}) results in the Great Fish estuary. Srf = surface layer; bot = bottom layer, R = river.

Station	Salinity		Temperature		DIN		Nitrate		Nitrite		Ammonium		Phosphate		Silicate	
	srf	bot	srf	bot	srf	bot	srf	bot	srf	bot	srf	bot	srf	bot	srf	bot
R	0.00		24.16		86.30		79.56		1.29		5.46		11.59		640.21	
1	0.45	1.68	24.14	24.46	87.29	19.72	81.58	84.71	0.68	1.25	5.03	6.54	14.01	17.49	554.41	513.92
2	0.45	0.34	24.20	24.22	89.32	16.74	83.33	82.45	0.97	1.42	5.03	4.81	10.74	10.18	554.41	835.73
3	0.40	7.30	24.21	23.71	87.59	16.87	81.12	82.87	1.37	1.54	5.10	4.53	10.41	10.24	628.04	641.05
4	0.54	4.35	24.18	24.07	86.66	15.69	81.38	82.90	0.76	1.30	4.53	12.36	10.41	30.99	641.05	628.04
5	0.58	9.50	24.12	23.84	89.35	34.05	77.18	76.00	1.75	5.40	10.42	13.08	21.88	28.52	835.73	835.73
6	0.82	10.22	24.00	22.70	94.32	49.23	74.40	71.28	3.39	5.31	16.53	18.32	29.31	27.39	835.73	640.21
7	0.90	15.49	23.85	23.00	92.21	39.06	76.32	69.04	4.10	2.92	11.78	18.83	23.18	32.51	641.05	641.05
8	1.28	21.43	23.65	23.60	80.72	42.77	66.86	64.13	1.21	3.10	12.65	7.04	28.91	10.58	835.73	640.21

Table A1.4.3 March survey salinity (psu), temperature (^{o}C) and nutrient concentration (mmol.m^{-3}) results in the Kariega marine environment. MC = Marine Control.

Station	Salinity			Temperature			DIN			Nitrate		
	0m	5m	10m	0m	5m	10m	0m	5m	10m	0m	5m	10m
1	34.05	34.07		19.93	19.96		1.77	1.06		0.24	0.18	
2	34.00	34.00		20.03	20.02		1.30	1.33		0.33	0.30	
3	34.07	34.00	34.30	20.08	20.05	20.05	1.93	0.74	0.93	0.42	0.22	0.27
4	34.03	34.89	34.75	20.10	20.04	20.03	1.39	0.82	0.66	0.13	0.18	0.17
5	34.00	34.03		20.00	19.98		1.88	1.20		0.22	0.23	
7	34.40	34.00		19.96	19.99		0.82	1.15		0.26	0.34	
8	34.05	34.00		20.05	20.07		2.03	0.91		0.41	0.37	
9	34.00	34.03	34.04	20.13	20.13	20.13	2.12	1.33	1.87	0.54	0.45	0.57
10	34.89	34.91		20.15	20.10		1.53	0.63		0.35	0.44	
11	34.88	34.90		20.14	20.13		1.56	0.94		0.59	0.67	
12	34.86	34.92	34.41	20.16	20.15	20.15	1.04	1.39	0.62	0.44	0.56	0.45
13	34.87	34.93	34.95	20.23	20.16	20.16	1.35	1.01	0.84	0.38	0.40	0.38
14	34.80	34.94	34.96	20.22	20.17	20.14	1.24	0.39	0.79	0.21	0.23	0.32
17	34.93	34.94	34.94	20.31	20.16	20.16	1.08	0.83		0.28	0.50	
18	34.91	34.93	34.95	20.38	20.16	20.15	1.09	0.70	1.29	0.16	0.27	0.26
19	34.94	34.95	34.96	20.40	20.15	20.13	0.61	0.54	1.07	0.22	0.24	0.28
20	34.91	34.94		20.38	20.19		1.40	0.62		0.21	0.23	
22	34.92	34.93	34.93	20.24	20.22	20.21	1.16	1.45		0.58	0.65	
23	34.92	34.95	34.82	20.40	20.14	20.14	1.43	0.81	0.65	0.23	0.26	0.33
24	34.95	34.94	34.96	20.43	20.08	20.07	1.44	1.25	0.88	0.25	0.16	0.26
MC	34.05	34.00	34.00	20.45	20.26	20.12	0.89	1.40	1.33	0.38	0.42	0.49

Station	Nitrite			Ammonium			Phosphate			Silicate		
	0m	5m	10m	0m	5m	10m	0m	5m	10m	0m	5m	10m
1	0.58	0.56		0.95	0.32		0.00	0.60		23.52	31.49	
2	0.57	0.55		0.39	0.47		0.38	0.05		22.16	14.19	
3	0.64	0.43	0.50	0.87	0.08	0.16	0.00	0.60	0.71	18.08	21.38	24.10
4	0.54	0.48	0.49	0.71	0.16	0.00	0.49	0.71	0.22	19.44	15.55	14.19
5	0.55	0.57		1.11	0.40		0.60	0.22		20.21	14.38	
7	0.49	0.42		0.08	0.39		0.44	0.16		18.27	18.46	
8	0.51	0.54		1.11	0.00		0.60	0.33		18.85	16.52	
9	0.55	0.56	0.67	1.03	0.32	0.63	1.09	0.33	0.76	18.46	19.63	15.55
10	0.15	0.19		1.03	0.00		0.27	1.04		18.27	18.46	
11	0.18	0.19		0.79	0.08		0.60	0.71		22.35	13.99	
12	0.20	0.20	0.16	0.39	0.63	0.00	1.36	1.36	1.25	18.08	13.61	22.35
13	0.18	0.15	0.14	0.79	0.47	0.32	0.71	0.71	2.24	17.88	14.58	14.19
14	0.16	0.16	0.15	0.87	0.00	0.32	0.65	3.05	0.98	22.74	13.61	16.33
17	0.17	0.17		0.63	0.16		1.64	1.85		23.52	19.83	
18	0.14	0.12	0.16	0.79	0.32	0.87	1.58	2.78	1.58	17.30	14.97	13.99
19	0.16	0.15	0.16	0.24	0.16	0.63	1.64	1.42	1.64	21.57	13.99	14.77
20	0.16	0.15		1.03	0.24		1.8	3.05		16.91	19.24	
22	0.18	0.17		0.39	0.63		2.67	1.75		16.91	14.38	
23	0.17	0.158	0.163	1.03	0.39	0.16	2.02	2.18	1.91	16.52	23.91	14.77
24	0.16	0.14	0.145	1.03	0.95	0.47	2.29	2.07	2.84	17.49	14.58	20.80
MC	0.11	0.11	0.13	0.40	0.87	0.71	2.24	1.91	2.51	25.07	20.08	15.74

Table A1.4.4 March survey salinity (psu), temperature (^{o}C) and nutrient concentration (mmol.m^{-3}) results in the Great Fish marine environment. MC = Marine Control.

Station	Salinity			Temperature			DIN			Nitrate		
	0m	5m	10m	0m	5m	10m	0m	5m	10m	0m	5m	10m
1	33.90	34.69		18.70	18.27		19.30	11.65		11.18	5.65	
2	25.45	34.67	34.90	19.78	18.61	18.60	24.83	13.66	7.42	16.26	2.21	2.44
3	28.50	34.91	34.90	19.39	18.79	18.60	21.43	13.59	9.07	12.73	2.04	1.91
4	32.59	34.90	34.95	18.87	18.60	18.56	26.90	12.03	9.62	18.34	2.52	3.47
5	34.32	34.81		18.35	18.24		13.70	11.89		6.33	5.01	
6	33.96	34.70		18.24	18.27		9.93	7.90		8.09	6.97	
7	34.18	34.90	34.80	18.25	18.60	18.49	8.25	6.05	4.21	6.23	3.60	2.84
8	34.32	34.90	34.93	18.39	18.60	18.63	6.82	3.07	4.04	4.65	1.57	2.15
9	34.46	34.94	34.95	18.60	18.79	18.81	5.00	2.87	3.26	2.89	1.98	1.87
10	32.52	34.93		18.92	18.54		40.79	5.40		28.70	5.40	
11	33.26	34.71		18.77	17.83		26.30	14.24		17.00	7.84	
12	32.70	34.90	34.94	18.85	18.60	18.54	34.41	8.16	11.47	24.59	2.22	4.71
13	34.61	34.90	34.94	18.71	18.60	18.54	32.09	9.09	9.00	21.21	2.67	2.32
14	33.80	34.90	34.96	18.69	18.60	18.64	24.89	7.03	7.58	15.80	1.80	3.25
18	34.73	34.94		18.73	18.68		19.68	10.97		14.90	2.85	
19	34.70	34.90	34.96	18.70	18.60	18.66	14.39	8.96	7.99	7.49	2.27	2.83
23	34.67	34.90	34.79	18.91	18.60	18.38	7.67	10.25	10.95	1.55	3.68	3.29
24	34.54	34.90	34.95	18.94	18.60	18.73	10.09	8.24	9.14	2.11	2.19	2.53
MC	34.05	34.00	34.00	20.45	20.26	20.12	0.89	1.40	1.33	0.38	0.42	0.49

Station	Nitrite			Ammonium			Phosphate			Silicate		
	0m	5m	10m	0m	5m	10m	0m	5m	10m	0m	5m	10m
1	0.17	0.26		7.94	5.74		1.10	0.35		62.47	71.84	
2	0.24	0.16	0.19	8.33	11.29	4.78	1.28	0.52	0.29	70.33	13.86	10.85
3	0.18	0.16	0.18	8.52	11.39	6.99	1.28	0.23	0.70	78.43	12.59	11.03
4	0.32	0.23	0.31	8.23	9.28	5.84	2.15	0.58	0.35	118.34	16.87	12.31
5	0.29	0.28		7.08	6.60		0.35	0.64		19.97	13.04	
6	0.31	0.35		1.53	0.57		0.99	0.87		20.70	23.81	
7	0.30	0.25	0.22	1.72	2.20	1.15	0.46	0.35	1.10	18.06	11.86	12.77
8	0.15	0.16	0.18	2.01	1.34	1.72	1.39	0.75	0.41	18.06	10.58	10.40
9	0.19	0.22	0.15	1.91	0.67	1.24	0.70	0.87	1.05	14.77	10.76	10.85
10	0.22	0.30		11.87	15.02		3.19	0.81		170.54	18.88	
11	0.21	0.27		9.09	6.12		1.45	1.16		73.14	16.23	
12	0.25	0.20	0.16	9.57	5.74	6.60	2.55	0.81	1.22	114.99	14.77	31.46
13	0.26	0.20	0.18	10.62	6.22	6.51	2.09	1.28	1.28	101.50	15.87	13.31
14	0.19	0.16	0.21	8.90	5.07	4.11	2.21	0.75	0.81	97.28	12.49	11.95
18	0.29	0.18		4.50	7.94		2.03	1.16		27.36	14.32	
19	0.20	0.18	0.19	6.70	6.51	4.98	2.09	0.99	0.93	34.47	11.95	10.58
23	0.18	0.25	0.197	5.93	6.32	7.46	1.45	1.57	1.57	10.85	13.31	14.77
24	0.22	0.21	0.20	7.75	5.84	6.41	1.51	1.39	1.63	17.51	11.40	10.21
MC	0.11	0.11	0.13	0.40	0.87	0.71	2.24	1.91	2.51	25.07	20.08	15.74

APPENDIX 2

Table A2.1.1 Mann-Whitney U Test results of surface vs. bottom salinity, temperature and nutrient concentration median values of the Kariega (KE) and Great Fish (GFE) estuaries. Significant results ($p < 0.05$) are denoted with an 'S'.

	Season	Salinity	Temperature	DIN	Nitrate	Nitrite	Ammonium	Phosphate	Silicate
KE	June	U = 49.5 p = 0.97	U = 24.0 S P = 0.049	U = 43.0 p = 0.60	U = 42.0 p = 0.55	U = 43.0 p = 0.60	U = 38.0 p = 0.36	U = 42.5 p = 0.57	U = 49.0 p = 0.94
	Sep	U = 26.5 p = 0.076	U = 10.0 S p = 0.002	U = 39.5 p = 0.43	U = 32.5 p = 0.19	U = 37.5 p = 0.29	U = 48.0 p = 0.88	U = 49.5 p = 0.97	U = 44.0 p = 0.65
	Dec	U = 43.5 p = 0.59	U = 36.5 p = 0.31	U = 43.0 p = 0.60	U = 50.0 p = 1.0	U = 43.0 p = 0.60	U = 41.0 p = 0.50	U = 47.5 p = 0.85	U = 47.0 p = 0.82
	March	U = 35.5 p = 0.27	U = 46.5 p = 0.79	U = 43.0 p = 0.60	U = 40.0 p = 0.45	U = 33.0 p = 0.20	U = 46.5 p = 0.79	U = 39.0 p = 0.40	U = 44.0 p = 0.65
GFE	June	U = 11.0 S p = 0.027	U = 3.0 S p = 0.002	U = 12.0 S p = 0.036	U = 12.0 S p = 0.036	U = 30.0 p = 0.83	U = 22.0 p = 0.29	U = 10.0 S p = 0.021	U = 29.0 p = 0.75
	Sep	U = 22.5 p = 0.32	U = 12.5 S p = 0.040	U = 31.0 p = 0.92	U = 28.0 p = 0.67	U = 31.5 p = 0.96	U = 29.0 p = 0.75	U = 31.0 p = 0.92	U = 29.0 p = 0.75
	Dec	U = 13.5 p = 0.052	U = 2.0 S p = 0.002	U = 0.0 S p < 0.001	U = 12.0 S p = 0.036	U = 21.0 p = 0.25	U = 1.0 S p = 0.001	U = 27.0 p = 0.60	U = 22.0 p = 0.29
	March	U = 8.0 S p = 0.012	U = 21.0 p = 0.25	U = 19.0 p = 0.17	U = 31.0 p = 0.92	U = 18.0 p = 0.14	U = 25.5 p = 0.49	U = 30.0 p = 0.83	U = 29.5 p = 0.79

Table A2.1.2 Kruskal-Wallis ANOVA Test results of surface vs. 5 m vs. 10 m salinity, temperature and nutrient concentration median values of the Kariega (KM) and Great Fish marine (GFM) environments. Significant results ($p < 0.05$) are denoted with an 'S'.

	Season	Salinity	Temperature	DIN	NO_3	NO_2	NH_4	PO_4	SiO_4
KM	June	H = 5.9 p = 0.052	H = 2.6 p = 0.27	H = 0.30 p = 0.86	H = 0.20 p = 0.91	H = 0.64 p = 0.73	H = 0.72 p = 0.70	H = 8.4 S p = 0.015	H = 3.7 p = 0.16
	Sep	H = 13.4 S p = 0.001	H = 0.15 p = 0.93	H = 1.7 p = 0.43	H = 2.0 p = 0.38	H = 1.0 p = 0.60	H = 1.5 p = 0.46	H = 0.04 p = 0.98	H = 14.0 S p < 0.001
	Dec	H = 0.00 p = 1.0	H = 10.7 S p = 0.005	H = 4.2 p = 0.12	H = 4.3 p = 0.12	H = 0.26 p = 0.88	H = 2.2 p = 0.32	H = 0.17 p = 0.92	H = 6.1 S p = 0.047
	March	H = 3.5 p = 0.17	H = 2.78 p = 0.25	H = 14.2 S p < 0.001	H = 0.37 p = 0.83	H = 2.4 p = 0.31	H = 17.4 S p < 0.001	H = 1.8 p = 0.41	H = 7.3 S p = 0.03
GFM	June	H = 26.5 S p = 0.00	H = 13.9 S p = 0.001	H = 8.2 S p = 0.016	H = 7.6 S p = 0.023	H = 5.6 p = 0.061	H = 5.4 p = 0.067	H = 0.97 p = 0.62	H = 18.5 S p < 0.001
	Sep	H = 4.5 p = 0.11	H = 6.2 S p = 0.045	H = 1.3 p = 0.53	H = 0.086 p = 0.96	H = 5.7 p = 0.059	H = 6.7 S p = 0.036	H = 3.5 p = 0.17	H = 2.6 p = 0.28
	Dec	H = 3.9 p = 0.14	H = 24.8 S p < 0.001	H = 1.8 p = 0.41	H = 1.1 p = 0.58	H = 0.62 p = 0.73	H = 9.3 S p = 0.009	H = 2.6 p = 0.27	H = 6.1 S p = 0.048
	March	H = 34.5 S p < 0.001	H = 7.5 S p = 0.023	H = 12.4 S p = 0.002	H = 17.1 S p < 0.001	H = 4.1 p = 0.13	H = 4.5 p = 0.11	H = 11.6 S p = 0.003	H = 23.2 S p < 0.001

Table A2.1.3 Mann-Whitney U Test results of surface vs. 5 m, surface vs. 10 m and 5 m vs. 10 m salinity, temperature and nutrient concentration median values of the Kariega marine environment. Significant results ($p < 0.033$) are denoted with an 'S'.

	Depth (m)	Salinity	Temperature	DIN	Nitrate	Nitrite	Ammonium	Phosphate	Silicate
June	**0 vs. 5**							U = 196.5 p = 0.92	
	0 vs. 10							U = 50.0 S p = 0.028	
	5 vs. 10							U = 31.0 S p = 0.002	
September	**0 vs. 5**	U = 67.0 S p = 0.003							U = 138.5 p = 0.46
	0 vs. 10	U = 24.0 S p = 0.008							U = 9.0 S p < 0.001
	5 vs. 10	U = 65.5 p = 0.72							U = 14.0 S p = 0.001
December	**0 vs. 5**		U = 182.0 p = 0.63						U = 184.0 p = 0.66
	0 vs. 10		U = 34.5 S p = 0.002						U = 49.0 p = 0.012
	5 vs. 10		U = 45.5 S p = 0.008						U = 65.5 S p = 0.066
March	**0 vs. 5**			U = 74.0 S p < 0.001			U = 57.5 S p < 0.001		U = 113.0 S p = 0.019
	0 vs. 10			U = 36.0 S p = 0.005			U = 33.0 S p = 0.003		U = 50.5 S p = 0.029
	5 vs. 10			U = 93.0 p = 0.76			U = 92.0 p = 0.72		U = 94.5 p = 0.81

Table A2.1.4 Mann-Whitney U Test results of surface vs. 5 m, surface vs. 10 m and 5 m vs. 10 m salinity, temperature and nutrient concentration median values of the Great Fish marine environment. Significant results ($p < 0.033$) are denoted with an 'S'

	Depth (m)	Salinity	Temperature	DIN	Nitrate	Nitrite	Ammonium	Phosphate	Silicate
June	**0 vs. 5**	U = 0.00 S p < 0.001	U = 83.0 p = 0.49	U = 46.0 S p = 0.017	U = 46.0 S p = 0.017				U = 23.0 S p < 0.001
	0 vs. 10	U = 0.00 S p < 0.001	U = 30.5 S p = 0.021	U = 28.0 S p = 0.014	U = 31.0 S p = 0.022				U = 5.0 S p < 0.001
	5 vs. 10	U = 48.5 p = 0.21	U = 1.5 S p < 0.001	U = 63.0 p = 0.68	U = 70.0 p = 1.0				U = 56.0 p = 0.41
September	**0 vs. 5**		U = 99.5 S p = 0.28				U = 80.0 p = 0.07		
	0 vs. 10		U = 0.0 p = 0.024				U = 2.00 p = 0.049		
	5 vs. 10		U = 1.0 p = 0.035				U = 4.0 p = 0.090		
December	**0 vs. 5**		U = 76.5 S p = 0.002				U = 83.5 S p = 0.005		U = 105.5 S p = 0.029
	0 vs. 10		U = 5.5 S p < 0.001				U = 58.5 S p = 0.024		U = 100.5 p = 0.58
	5 vs. 10		U = 43.5 S p = 0.004				U = 108.0 p = 0.81		U = 67.0 p = 0.056
March	**0 vs. 5**	U = 7.0 S p < 0.001	U = 81.0 S p = 0.010	U = 79.0 S p = 0.009	U = 49.0 S p < 0.001			U = 62.0 p = 0.002	U = 39.5 S p < 0.001
	0 vs. 10	U = 0.0 S p < 0.001	U = 63.5 p = 0.059	U = 35.0 S p = 0.002	U = 27.0 S p < 0.001			U = 51.0 p = 0.016	U = 15.0 S p < 0.001
	5 vs. 10	U = 49.5 S p = 0.011	U = 96.0 p = 0.60	U = 74.0 p = 0.15	U = 99.0 p = 0.70			U = 90.5 p = 0.46	U = 60.0 p = 0.042

Table A2.1.5 Mann-Whitney U Test results of June (J) vs. September (s), June vs. December (D), June vs. March (M), September vs. December, September vs. March and December vs. March salinity, temperature and nutrient concentration median values for the Kariega (KE) and Great Fish (GFE) estuaries. All test were significant ($p < 0.016$), except those denoted with an 'NS', Not Significant.

	Season	Salinity	Temperature	DIN	Nitrate	Nitrite	Ammonium	Phosphate	Silicate
KE	**J vs. S**	U = 155.0 NS p = 0.22	U = 0.0 p < 0.001	U = 97.0 p = 0.005	U = 102.5 p = 0.008	U = 42.0 p < 0.001	U = 113.5 NS p = 0.019	U = 168.0 NS p = 0.39	U = 136.0 NS p = 0.083
	J vs. D	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 150.0 NS p = 0.18	U = 157.0 NS p = 0.24	U = 67.0 p < 0.001	U = 16.0 p < 0.001	U = 93.5 p = 0.004	U = 152.0 NS p = 0.19
	J vs. M	U = 74.5 p < 0.001	U = 0.0 p < 0.001	U = 143.0 NS p = 0.12	U = 160.0 NS p = 0.28	U = 65.0 p < 0.001	U = 140.0 NS p = 0.10	U = 29.0 p < 0.001	U = 100.0 p = 0.007
	S vs. D	U = 35.0 p < 0.001	U = 0.0 p < 0.001	U = 21.0 p < 0.001	U = 47.0 p < 0.001	U = 0.0 p < 0.001	U = 1.0 p < 0.001	U = 127.0 NS p = 0.05	U = 180.0 NS p = 0.59
	S vs. M	U = 111.0 p = 0.015	U = 81.5 p = 0.001	U = 56.0 p < 0.001	U = 33.0 p < 0.001	U = 4.0 p < 0.001	U = 190.0 NS p = 0.79	U = 22.0 p < 0.001	U = 152.0 NS p = 0.19
	D vs. M	U = 94.0 p = 0.004	U = 28.0 p < 0.001	U = 163.0 NS p = 0.32	U = 157.0 NS p = 0.24	U = 161.0 NS p = 0.29	U = 63.0 p < 0.001	U = 0.0 p < 0.001	U = 135.0 NS p = 0.079
GFE	**J vs. S**	U = 96.0 NS p = 0.23	U = 0.0 p < 0.001	U = 1.0 p < 0.001	U = 0.0 p < 0.001	U = 24.0 p < 0.001	U = 76.0 NS p = 0.05	U = 23.0 p < 0.001	U = 15.0 p < 0.001
	J vs. D	U = 125.0 NS p = 0.91	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 42.0 p = 0.001	U = 99.5 NS p = 0.28	U = 97.0 NS p = 0.24	U = 67.0 NS p = 0.02
	J vs. M	U = 50.0 p = 0.003	U = 0.0 p < 0.001	U = 115.0 NS p = 0.62	U = 96.0 NS p = 0.23	U = 81.0 NS p = 0.076	U = 7.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001
	S vs. D	U = 92.0 NS p = 0.17	U = 0.0 p < 0.001	U = 35.0 p < 0.001	U = 13.0 p < 0.001	U = 102.0 NS p = 0.33	U = 55.0 p = 0.006	U = 53.0 p = 0.005	U = 11.0 p < 0.001
	S vs. M	U = 33.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 13.0 p < 0.001	U = 75.0 NS p = 0.046	U = 0.0 p < 0.001	U = 0.0 p < 0.001
	D vs. M	U = 53.0 p = 0.005	U = 70.0 NS p = 0.029	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 25.0 p < 0.001	U = 13.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001

Table A2.1.6 Mann-Whitney U Test results of June (J) vs. September (s), June vs. December (D), June vs. March (M), September vs. December, September vs. March and December vs. March salinity, temperature and nutrient concentration median values for the Kariega (KM) and Great Fish marine (GFM) environments. All test were significant ($p < 0.016$), except those denoted with an 'NS', Not Significant.

	Season	Salinity	Temperature	DIN	Nitrate	Nitrite	Ammonium	Phosphate	Silicate
KM	**J vs. S**	U = 186.5 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 4.0 p < 0.001	U = 0.0 p < 0.001	U = 6.0 p < 0.001	U = 0.0 p < 0.001	U = 12.0 p < 0.001
	J vs. D	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 797.5 p = 0.001	U = 1.0 p < 0.001	U = 4.0 p < 0.001
	J vs. M	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 27.0 p < 0.001	U = 1220.0 NS p = 0.84	U = 8.0 p < 0.001
	S vs. D	U = 25.5 p < 0.001	U = 0.0 p < 0.001	U = 532.5 p < 0.001	U = 221.5 p < 0.001	U = 0.0 p < 0.001	U = 103.5 p < 0.001	U = 731.5 p = 0.004	U = 524.0 p < 0.001
	S vs. M	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 39.0 p < 0.001	U = 909.0 p = 0.15	U = 388.0 p < 0.001	U = 0.0 p < 0.001
	D vs. M	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 211.5 p < 0.001	U = 152.0 p < 0.001	U = 382.0 p < 0.001	U = 0.0 p < 0.001
GFM	**J vs. S**	U = 589.5 NS p = 0.52	U = 0.0 p < 0.001	U = 79.5 p < 0.001	U = 16.0 p < 0.001	U = 295.0 p < 0.001	U = 108.0 p < 0.001	U = 16.5 p < 0.001	U = 4.0 p < 0.001
	J vs. D	U = 253.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 128.5 p < 0.001	U = 297.5 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001
	J vs. M	U = 515.0 p < 0.001	U = 0.0 p < 0.001	U = 796.0 NS p = 0.31	U = 428.0 p < 0.001	U = 159.0 p < 0.001	U = 140.0 p < 0.001	U = 848.5 NS p = 0.58	U = 716.0 NS p = 0.088
	S vs. D	U = 12.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 256.0 p < 0.001	U = 77.0 p < 0.001
	S vs. M	U = 26.5 p < 0.001	U = 0.0 p < 0.001	U = 238.0 p < 0.001	U = 672.0 NS p = 0.18	U = 0.0 p < 0.001	U = 306.0 p < 0.001	U = 63.0 p < 0.001	U = 5.0 p < 0.001
	D vs. M	U = 389.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 968.0 NS p = 0.099	U = 48.0 p < 0.001	U = 16.0 p < 0.001	U = 0.0 p < 0.001

Table A2.1.7 Mann-Whitney U Test results of Kariega estuary (KE) vs. Great Fish estuary (GFE), Kariega marine environment (KM) vs. Great Fish marine environment (GFM), Kariega estuary vs. Kariega marine environment and Great Fish estuary vs. Great Fish marine environment salinity, temperature and nutrient concentration median values for the in June, September, December and March. All test were significant ($p < 0.05$), except those denoted with an 'NS', Not Significant.

	Season	Salinity	Temperature	DIN	Nitrate	Nitrite	Ammonium	Phosphate	Silicate
KE vs GFE	**June**	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 27.0 p < 0.001	U = 24.0 p < 0.001	U = 142.0 NS p = 0.57	U = 3.0 p < 0.001	U = 51.5 p < 0.001	U = 20.0 p < 0.001
	Sep	U = 8.0 p < 0.001	U = 1.0 p < 0.001	U = 0.0 p < 0.001	U = 0.00 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 153.0 NS p = 0.82	U = 83.0 p = 0.014
	Dec	U = 0.0 p < 0.001	U = 44.5 p < 0.001	U = 120.0 NS p = 0.20	U = 135.0 NS p = 0.43	U = 60.0 p = 0.001	U = 88.5 p = 0.022	U = 33.0 p < 0.001	U = 45.0 p < 0.001
	March	U = 0.0 p < 0.001	U = 144.5 NS p = 0.62	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 P < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001
KM vs GFM	**June**	U = 286.0 p < 0.001	U = 24.0 p < 0.001	U = 700.5 p = 0.036	U = 772.5 NS p = 0.13	U = 405.0 p < 0.001	U = 407.0 p < 0.001	U = 861.0 NS p = 0.45	U = 155.0 p < 0.001
	Sep	U = 85.0 p < 0.001	U = 0.0 p < 0.001	U = 40.0 p < 0.001	U = 262.5 p < 0.001	U = 34.0 p < 0.001	U = 3.0 p < 0.001	U = 323.5 p < 0.001	U = 139.0 p < 0.001
	Dec	U = 102.0 p < 0.001	U = 42.5 p < 0.001	U = 0.0 p < 0.001	U = 17.0 p < 0.001	U = 0.0 p < 0.001	U = 216.5 p < 0.001	U = 272.5 p < 0.001	U = 506.5 p < 0.001
	March	U = 1064.0 NS p = 0.33	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 1106.0 NS p = 0.50	U = 37.0 p < 0.001	U = 1187.0 NS p = 0.92	U = 983.0 NS P = 0.12
KE vs KM	**June**	U = 34.0 p < 0.001	U = 406.5 NS p = 0.22	U = 350.0 NS p = 0.051	U = 364.0 NS p = 0.077	U = 339.5 p = 0.037	U = 65.5 p < 0.001	U = 222.5 p < 0.001	U = 37.0 P < 0.001
	Sep	U = 132.0 p < 0.001	U = 0.0 p < 0.001	U = 40.5 p < 0.001	U = 0.0 p < 0.001	U = 109.0 p < 0.001	U = 77.0 p < 0.001	U = 56.5 p < 0.001	U = 0.0 p < 0.001
	Dec	U = 229.5 p < 0.001	U = 0.0 p < 0.001	U = 471.0 NS p = 0.62	U = 447.0 NS p = 0.42	U = 0.0 p < 0.001	U = 203.5 p < 0.001	U = 205.5 p < 0.001	U = 8.0 p < 0.001
	March	U = 194.5 p < 0.001	U = 200.0 p < 0.001	U = 76.0 p < 0.001	U = 25.0 p < 0.001	U = 443.0 NS p = 0.46	U = 254.0 p = 0.001	U = 58.0 p < 0.001	U = 4.0 p < 0.001
GFE vs GFM	**June**	U = 20.0 p < 0.001	U = 2.0 p < 0.001	U = 17.0 p < 0.001	U = 18.0 p < 0.001	U = 302.5 NS p = 0.98	U = 34.0 p < 0.001	U = 20.5 p < 0.001	U = 33.0 p < 0.001
	Sep	U = 2.0 p < 0.001	U = 6.0 p < 0.001	U = 67.0 p < 0.001	U = 161.0 p = 0.021	U = 102.0 p < 0.001	U = 71.5 p < 0.001	U = 4.0 p < 0.001	U = 0.0 p < 0.001
	Dec	U = 24.5 p < 0.001	U = 0.0 p < 0.001	U = 18.0 p < 0.001	U = 167.0 p < 0.001	U = 130.5 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001
	March	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 0.0 p < 0.001	U = 250.0 p = 0.038	U = 0.0 p < 0.001	U = 0.0 p < 0.001