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Regional Coastal Ecosystem Assessment for Development

Nutrient Cycling and Transformation in Coastal Ecosystems, Focussing on Estuaries and the Influence of Catchment Fluxes

A South African Perspective

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INTRODUCTION

South Africa's coastline is characterised by a significant number of small, estuarine systems that link (terrestrial) catchments to the sea. According to Whitfield (1992), there are about 250 functional estuaries and of these more than 75% are temporarily open/closed systems, i.e. systems that are occasionally cut off from the sea, particularly during the dry season.

This study aims to provide preliminary conceptual models of nutrient cycling and transformation within South African estuarine systems, focussing on the role of catchment fluxes, amongst other factors. Estuaries form part of the coastal ecosystem. The coastal ecosystem, as investigated here, comprises estuarine, nearshore and coastal shelf systems, recognizing the functional links with adjacent catchments (terrestrial) and offshore (oceanic) environments (Figure A.1). This zone has also been referred to as the *land-sea margin* (Nixon *et al*., 1996).

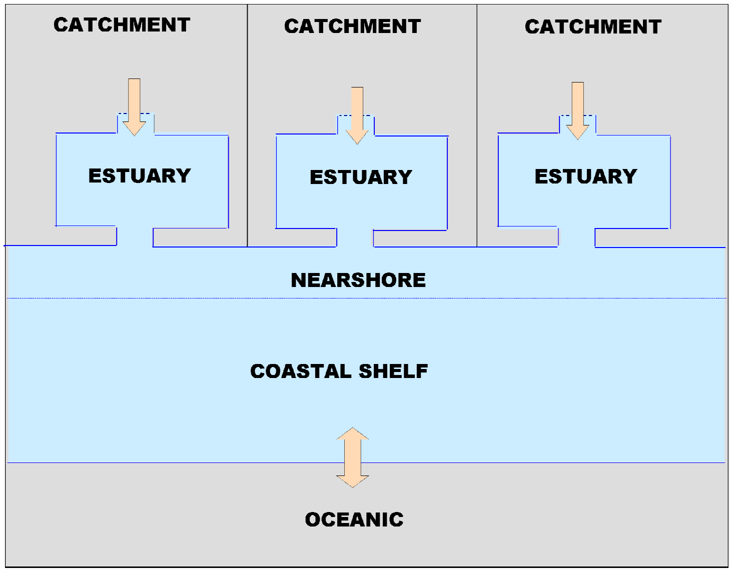


Figure A.1: Schematic illustration of the coastal ecosystem

Nutrient cycling and transformation are some of the key components that drive biological production in coastal ecosystems. However, the complex nature of nutrient cycling and transformation in these ecosystems is easily perturbed by external (anthropogenic) forces that may lead to changes in the trophic status, ultimately impacting on the ability of the system to support higher trophic orders (Ferguson *et al*., 2004). Therefore, human activities that change the processes influencing nutrient cycling and transformation in coastal ecosystems (e.g. waste loading and alteration in transport and dispersion mechanisms) can potentially impact on the ecological services provided by these ecosystems, not only locally but also on larger (regional) scales.

External sources of nutrients to coastal ecosystems are mainly derived from catchments (i.e. river and groundwater inflow), upwelling (external input via the oceanic boundary) and atmospheric inputs (Nixon *et al*., 1996; US-EPA, 2004). Nutrient cycling and transformation can also be influenced by *in situ* chemical, biochemical and biological processes occurring within coastal ecosystems. These often involve complex inter-relationships between water column (pelagic) and bottom sediment (benthic) components – referred to as pelagic-benthic coupling (Eyre, 1994; Eyre and Balls, 1999; Roy *et al*., 2001; Dagg *et al*., 2004; McKee *et al*., 2004).

Estuaries, in particular, are highly dynamic transition zones between river catchments and the coastal ecosystem. Because estuaries can act as a filter, or transformer, of nutrients, the (nutrient) chemistry of river water may be extensively modified as it passes from the catchment to the nearshore (Eyre, 1994; Mortimer *et al*., 1998; Ferguson *et al.*, 2004). The unique hydrodynamic and chemical regime created within estuaries plays a key role in the extent to which nutrients are cycled and transformed within these systems. There are also instances, e.g. during flood events or high flow periods, in which estuaries merely act as conduits for catchment flows to the nearshore and coastal shelf environments, in which case the cycling and transformation of catchment-derived nutrients largely occur at sea.

The objective here is to provide a review of existing information on nutrient cycling and transformation processes in estuaries, particularly focussing on the influence of catchment fluxes. The direct influence of catchment fluxes (river plumes) on nutrient cycling and transformation in nearshore and coastal shelf environments is also briefly reviewed (Section A).

Key factors influencing nutrient cycling and transformation in estuaries are then assessed within the South African context (Section B). Based on this information, preliminary conceptual models for nutrient cycling and transformation, of particular relevance to South African estuaries, are proposed and tested using selected case studies (Section B). Preliminary conceptual models of the water quality characteristics (including inorganic nutrients) of temporarily open/closed estuaries in South Africa have been proposed by Snow & Taljaard (2006). The aim of this study is to further refine those conceptual models in terms of nutrient cycling and transformation processes, as well as to extend those models to other types of estuarine systems. The direct influence of catchment fluxes (river plumes) on nutrient cycling and productivity in the nearshore and coastal shelf environment is not well documented and is therefore not dealt with here in further detail, other than to identify future research opportunities (Section C).

This project will facilitate the development of expertise and capabilities within the CSIR (and southern Africa) that will enable better quantification and prediction of:

- The temporal and spatial scales of nutrient fluxes and transformation from catchments, through estuaries, into nearshore and coastal shelf waters, which constitute important input data to regional biological predictive models (coastal scales)
- Cause-effect relationships between catchment practices (e.g. waste loading and freshwater abstraction) and modification of coastal ecosystems through changes in nutrient fluxes, cycling and transformation processes.

SECTION A

OVERVIEW

A.1 LIMITING NUTRIENTS IN COASTAL ECOSYSTEMS

Nitrogen (N), phosphorous (P) and silicon (Si) are considered to be the primary limiting macro-nutrients for production in coastal ecosystems. Although iron (Fe) has been implicated as a limiting nutrient is some systems, it is usually not limited in river-dominated coastal shelf ecosystems (Dagg *et al.,* 2004). Therefore, taking the above into account, this report focuses on the cycling and transformation of N, P and Si, and their role in (primary) production of coastal ecosystems, particularly those influenced by fluxes from catchments (river run-off).

The major forms of nitrogen in aquatic ecosystems include (NSW Department of Natural Resources, 2005):

- Dissolved nitrogen (N_2) and nitrous oxide (N_2O) gases
- Dissolved inorganic nitrogen (DIN), i.e. ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-)
- Dissolved organic nitrogen (DON), e.g. urea and uric acid
- Particulate organic nitrogen (PON), e.g. as in detritus.

The nitrogen cycle within coastal ecosystems is complex, but the most common pathways are illustrated in Figure A.2.

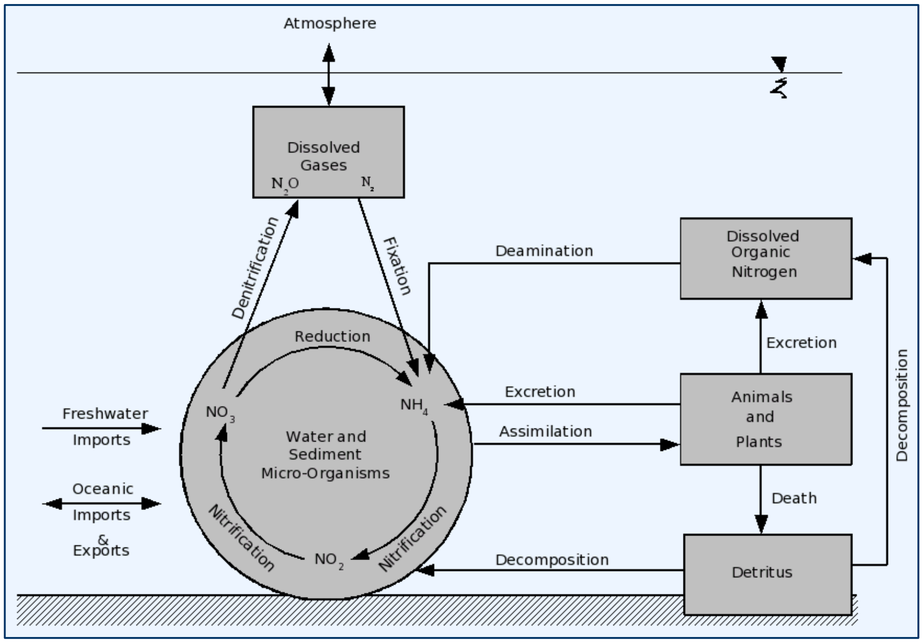


Figure A.2: Nitrogen cycling (Source: NSW Department of Natural Resources, 2005)

The main forms of phosphorous (P) in aquatic ecosystems are (Roy *et al.*, 2001; NSW Department of Natural resources, 2005):

- Dissolved inorganic phosphate (DIP), i.e. PO_4^{3-}
- Dissolved organic phosphorous (DOP)
- Particulate (insoluble) inorganic phosphate (PIP), adsorbed onto cohesive sediment or organic particles
- Particulate organic phosphorous (POP), e.g. as in detritus.

Figure A.3 provides a schematic summary of the major components affecting phosphorus cycling in coastal ecosystems (NSW Department of Natural Resources, 2005).

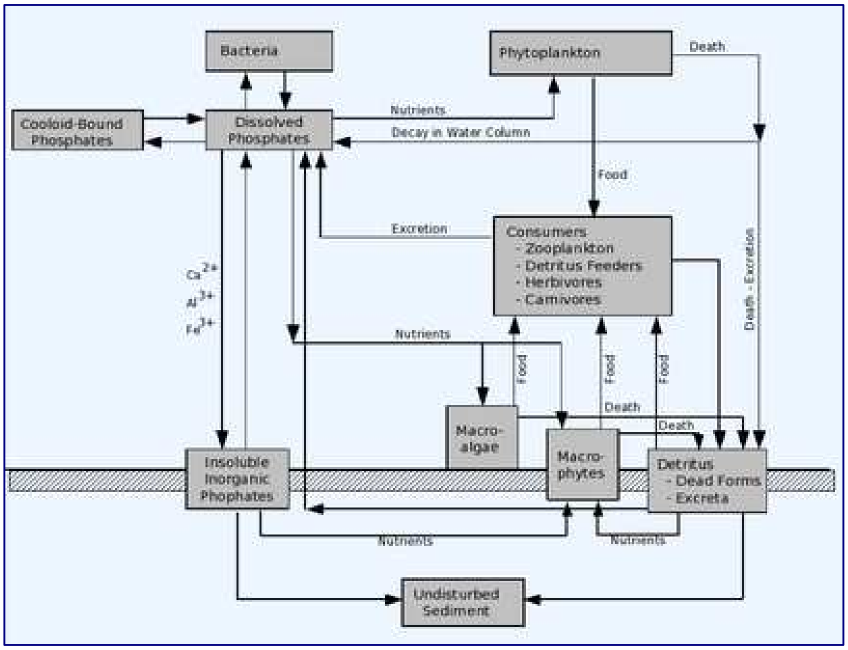


Figure A.3: Phosphorus cycle (Source: NSW Department of Natural Resources, 2005)

Silica (Si) in coastal ecosystems is mainly present as:

- Inorganic silicate (dissolved reactive silicate – DRS)
- Particulate biogenic silica (Conley, 1997; Kemmerer, 2004) - Biogenic silica in coastal ecosystems is usually associated with phytoplankton (diatom) and radiolaria (animals) growth.

A.2 KEY PROCESSES AFFECTING NUTRIENT CYCLING AND TRANSFORMATION

External sources of nutrients to coastal ecosystems are mainly derived from catchments (i.e. river and groundwater inflow), upwelling (via the oceanic boundary) and atmospheric sources (Nixon *et al*, 1996). However, in addition to external sources, there are a number of *in situ* physical, chemical, biochemical and biological processes within coastal ecosystems that also influence nutrient cycling and transformation (Eyre, 1994; Eyre and Balls, 1999; Roy *et al*., 2001). A brief overview of some of the important processes is provided below.

A.2.1 Physical Processes

Key physical processes influencing nutrient dynamics in coastal systems, such as estuaries, include *mixing, flushing and sedimentation/re-suspension* (Eyre and Balls, 1999),

Mixing refers to the extent which river water entering from the catchment mixes with seawater entering as a result of tidal exchange through the mouth. Mixing is largely influenced by factors such as volume of river inflow, the size and shape of an estuary, state of the mouth, tidal exchange, wind and stratification.

Flushing refers to the time that it takes to replace water within a particular area. For estuaries, this is mainly dependent on the volume of river inflow and the size and shape of the estuary. Tidal exchange and the state of the mouth (e.g. restricted, unrestricted or closed) can also significantly influence flushing in an estuary, especially the lower reaches. Flushing time is one of the dominant factors that control the degree to which nutrients passing from the catchment to the sea are modified within an estuary. The extent to which biochemical and biological processes influence nutrient cycling in estuaries is especially controlled by flushing times (Eyre and Balls, 1999).

Sedimentation/re-suspension processes primarily influence nutrient dynamics in terms of nutrients being associated with suspended particles, e.g. through adsorption or flocculation (see below). The settling characteristics of the suspended particles depend on the specific gravity, size and shape of the particles as well as the specific gravity and viscosity of the receiving water. The physical fate of suspended material, with regards to possible re-suspension after deposition, is primarily related to current and wave dynamics.

A.2.2 Geochemical Processes

Key geochemical processes that influence nutrient dynamics in coastal ecosystems include *adorption/desorption, flocculation and dissolution*.

i. Adsorption-desorption

Adsorption-desorption processes have been linked mainly to phosphorous (P) chemistry. Adsorption of P occurs onto particulate phases (suspended or bottom sediments), which can be either cohesive (non-biological) particles (e.g. silt and clay, < 50 µm fraction, on which adsorption phases such as aluminium hydroxides, manganese hydroxides and iron hydroxides are common) or organic particles (e.g. phytoplankton and debris). These particulate phases have their origin either within coastal ecosystems (e.g. estuarine sediments or phytoplankton blooms), from the catchment through river inflow (suspended sediment loads and debris) or from mixing processes between fresh and saline water.

Literature studies suggest that, in the water column, partially reversible adsorption onto suspended particulate phases regulates the dissolved phosphate-P (DIP) concentrations within the range 20 µg/ℓ – 43 µg/ℓ (0.6 – 1.4 µmol/ℓ). This mechanism predicts that, when DIP concentrations are low (below 20 ug/ℓ), inorganic phosphate will desorb from particulate phases into the dissolved pool. This partially reversible adsorption is dominantly controlled by pH (and DIP levels), but other parameters such as ionic strength, temperature, amount of suspended material and its composition, Eh (redox potential - an indicator of oxygen levels), time and biological activity can also be important (based on a literature review conducted by Eyre, 1994; Kemmerer, 2004). In the Moresby Estuary (Australia) it was suggested that low DIP concentrations in the water column were probably being maintained by low pH values (below 7.8) that favoured adsorption (Eyre, 1994). In another study on the Richmond Estuary (Australia), DIP concentrations in the water column showed a large departure from conservative mixing. This was attributed to adsorption onto suspended sediments at low salinities (and lower pH) and desorption from suspended sediments at higher salinities (rising pH levels). However, this only occurred during periods when flushing times of the estuary were very long (~ 200 days) (Eyre and Twigg, 1997).

At the sediment-water interface, studies showed that adsorption-desorption of P is also controlled by the supply of oxygen, where oxygenated conditions generally favour adsorption and reduced (or anoxic) conditions favour desorption or mobilization of P (Biggs and Cronin, 1981; Roy *et al.,* 2001, Compton *et al*., 2000; Nielsen *et al*., 2001).

ii. Flocculation

In terms of nutrients, it is mainly the dynamics of P that are affected by these processes, either through flocculation of the organic phases (DOP and POP) or through adsorption onto cohesive particles (PIP) (Compton *et al*, 2000; Nielsen *et al*, 2001). Particulate organic nitrogen (PON) associated with organic particles that flocculate will obviously also be affected by this process.

Flocculation is known to occur at the river-estuary interface where it is usually triggered by the marked difference in salinity between the two water types. This process typically affects organic matter and cohesive sediments (e.g. sediments with a high clay content) entering from catchments. Research conducted by Jiang *et al.* (2004) highlighted the following factors as being of importance in the flocculation and deposition of mud particles at these interfaces:

- Flow velocities greater than 80 cm/s markedly reduce flocculation of mud particles (Ruan, 1991)
- Salinities between 2 and 7 ppt are optimal for mud flocculation (Ruan, 1991), while Jiang *et al.* (2004) found a marked increase in flocculation at 10 ppt
- Flocculation of mud particles greater than 32 µm was not found to occur (Zhang, 1992)
- Organic aggregates and bio-flocculation can play an important role in mud flocculation (Van Leussen, 1988)
- Water temperature lower than 25^{o}C were found to markedly inhibit flocculation and deposition of mud particles (Jiang *et al*., 2004).

iii. Dissolution

Once marine organisms such as diatoms die their siliceous remains settle to the bottom and undergo dissolution (Kamatani *et al.*, 1980; Berner, 1980). Dissolution of biogenic silica is presented by the equation (Kamatani *et al.*, 1980):

$$SiO_2 \text{ (solid)} + 2H_2O \rightarrow H_4SiO_4$$

This process is controlled by the diffusion of dissolved silica at the surface of the solid (e.g. diatom skeleton). The rate of dissolution is controlled by factors such as surface area of solid biogenic silica, temperature and diatom species (Kamatani *et al*., 1980) and saturation state of water at sediment-water interface with respect to silica.

A.2.3 Biochemical (Bacterial) Processes

Biochemical processes are usually most intense in muddy sediments where organic matter and bacterial densities are typically high. In contrast to muddy areas, sandy sediments typically have low organic loads and bacterial densities (possibly an order of magnitude lower compared with muds), resulting in smaller stores of nutrients available for biochemical processing. Important biochemical (bacterial) processes that influence nutrient dynamics in coastal ecosystems include:

i. Remineralisation

- Remineralisation refers to the process whereby nutrients (ammonium-N and DIP) are released from ‘labile’ organic matter through heterotrophic bacterial decomposition. This bacterial decomposition can occur under both aerobic and anaerobic conditions.

'Labile' is the term used to describe organic matter with low TOC:TN ratios (e.g. phytoplankton) that breaks down easily, whereas 'refractory' organic compounds (woody debris made of lignin and cellulose) have very high TOC:TN ratios and are highly resistant to degradation (Enriquez et al., 1993).

Under aerobic conditions, organic matter is oxidised by aerobic bacteria that utilize dissolved oxygen very efficiently, with the products (or metabolites) of the reaction being carbon dioxide and the recycled nutrients (the reaction is the reverse of photosynthesis) (www.ozestuaries.org/oracle/ozestuaries/indicators/In_Nutrients_f.html):

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 106O_2 \rightarrow 106\ CO_2 + 16\ NH_3 + PO_4^{3-} + 3H^+ + 106H_2O$$

As oxygen becomes depleted, the decomposition (or oxidation of organic matter) can proceed in a series of reactions which represent successively lower redox states as illustrated in Figure A.4.

Remineralisation/ammonification has also been described as a two-way process with remineralisation being the conversion of organic materials from the particulate to the dissolved state (e.g. PON → DON) and ammonification the conversion of DON to ammonium (DON → NH_4^+). These two processes occur through the decay of plants and animals mediated by heterotrophic bacteria, or through excretion from animals. They occur both in sediments and in the water column, although in shallow coastal environments, a larger proportion of the remineralisation takes place in sediments as particles tend to settle more rapidly (Libes, 1992).

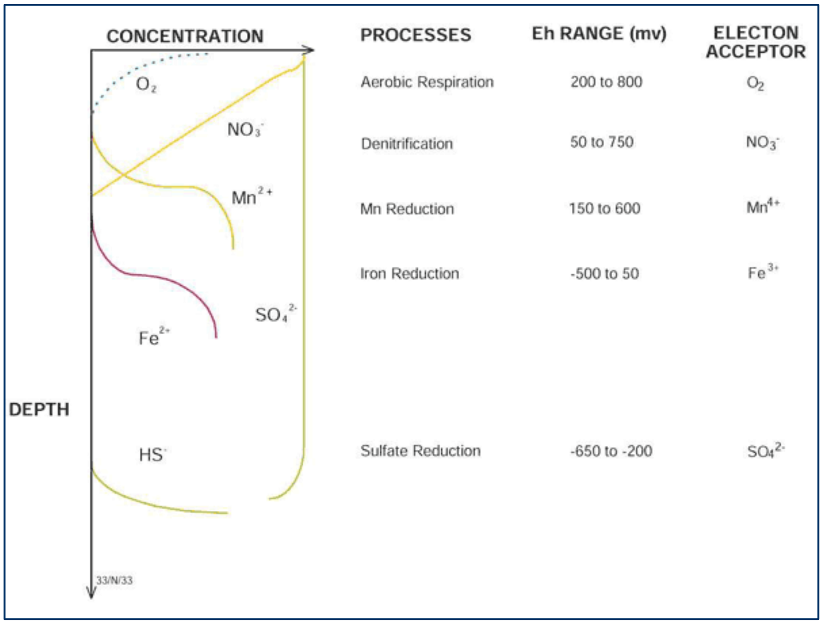


***Figure A.4:** Schematic illustration of processes governing mineralization of organic matter in sediments with changing depth and redox potential (Eh) (Source: www.ozestuaries.org/oracle/ozestuaries/indicators/)*

Benthic remineralisation of organic (or detrital) matter is often an important source of nutrients in coastal ecosystems. However, an important point that is often overlooked is that in many instances the organic matter in sediments came originally from the catchment and is therefore an external source. Thus, It is important not only to quantify inorganic nutrient fluxes from catchments but also organic nutrient fluxes, as the latter can become a major source of inorganic nutrients to coastal ecosystems through recycling (or remineralisation).

ii. *Nitrification*

Nitrification or 'ammonium oxidation' is a two-step respiratory process occurring in sediment (benthic nitrification) or the water column (pelagic nitrification) in which bacteria oxidise ammonium (NH_4^+) first to nitrite (NO_2^-) and then to nitrate (NO_3^-).

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+ \quad (1)$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \quad (2)$$

Nirtosomonas spp. and *Nitrobacter* spp. (both bacterial chemoautotrophs) are the main organisms responsible for steps (1) and (2) respectively.

Nitrifiers rely on oxygen and NH_4^+/NH_3 diffusing from the sediments or from decomposing suspended organic matter. Nitrification is therefore often concentrated at the oxic-anoxic interfaces of pycnoclines, sediments, biofilms, mats, and detrital particles. Nitrification may, however, also occur in fully oxygenated environments as long as NH_4^+/NH_3 are readily available (Paerl & Pinckney, 1996).

Water temperature was found to be an important factor influencing benthic (and probably also pelagic) nitrification, with rates increasing with increase in temperature (Berounsky and Nixon, 1990).

Nitrification in coastal ecosystems is important to consider as it (Henriksen & Kemp, 1988):

- modifies the form of DIN released during the decomposition of organic matter (or remineralisation)
- produces nitrate (NO_3^-) that can feed into denitrification pathways
- competes with heterotrophic bacteria for dissolved oxygen supplies.

iii. *Denitrification*

Denitrification is the microbial reduction of nitrate to dinitrogen gas (N_2), carbon dioxide and DIP using organic matter as an electron acceptor (heterotrophic process). The denitrification reaction of organic matter with Redfield molar proportions is as follows (Froelich *et al*., 1979):

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 94HNO_3 \rightarrow 106CO_2 + H_3PO_4 + 177H_2O + 55.2N_2$$

Because NO_3^- is reduced but not incorporated into microbial tissue, the reaction is also called dissimilatory nitrate reduction.

Although denitrifying bacteria are anaerobic they require an oxidised form of N for the respiratory process, in this case nitrate (NO_3^-), which can be derived from the water column (e.g. introduced through river inflow) or from nitrification. In the absence of external NO_3^- sources, denitrification is controlled mainly by nitrification. The denitrification supported by external sources of NO_3^- is referred to as direct denitrification, whereas denitrification using NO_3^- from nitrification is referred to as coupled nitrification-denitrification (Jenkins & Kemp, 1984; Paerl & Pinckney, 1996).

Denitrification efficiency referrs to the percentage DIN released as N_2 during organic matter decomposition. Studies showed that the rate of carbon decomposition (a proxy for organic loading) appears to play an important role in denitrification efficiency (Eyre & Ferguson, 2002). For example, at higher decomposition rates (or high organic loading), the efficiency decreased with most of the recycled DIN returning to the water column as ammonium. This was mainly attributed to inhibition of the nitrification process (that supplies NO_3^- for the reaction), either through a lack of available oxygen or by exposure of sulphides, which are the product of nitrification.

The presence of seagrass and other benthic plants and algae may enhance coupled nitrification-denitrification because they oxygenate the upper sediment layers, oxygen being required for nitrification. However, saturating the upper sediment layers with oxygen can have the reverse effect in that it inhibits denitrification rates that require sub-oxic conditions (<10 µM O_2) (Paerl & Pinckney, 1996). If water column DIN concentrations are really low, benthic microalgae may also inhibit coupled nitrification-denitrification, by competing for NO_3^- produced during nitrification (Risgaard-Petersen & Jensen, 1997; Krause-Jensen *et al*., 1999).

Denitrification can also be enhanced by the presence of benthic infauna by increasing sediment surface area (producing burrows) and re-oxygenating surface sediments. Benthic invertebrates also cause localised increases in organic matter concentrations and solutes (*i.e.* ammonium) and ultimately enhance microbial activity through their burrow linings, excreta and organic particles (Harris, 1999).

Denitrifying activity was found to be highest in warmer water temperatures (summer), while it varied inversely, with ionic strength being highest at salinities <10 ppt. High concentrations of the heavy metals cadmium, copper and zinc in sediment were also found to inhibit denitrification (Rysgaard *et al*., 1999; Sakadevan *et al*., 1999).

iv. Nitrogen fixation

Nitrogen fixation is the reduction of dinitrogen gas (N_2) to ammonia (NH_3). The reaction can be represented as:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

The process is catalysed by the enzyme nitrogenase and is conducted by a large range of nitrogen-fixing bacteria referred to as diazotrophs. These include (Postgate 1998):

- *Free-living diazotrophs*, such as *Azotobacter* spp. - an aerobe that requires oxygen to grow, but have the ability to protect their nitrogenase from oxygen damage. This group also includes photosynthetic bacteria (cyanobacteria) with specialised heterocysts (i.e. cells that lack the oxygen generating steps of photosynthesis). There are also other cyanobacteria that lack heterocysts, but that can still fix nitrogen under low light and low oxygen levels.
- *Symbiotic diazotrophs*, such as *Rhizobia,* which are associated with legumes and plant roots. In their case, oxygen bound to the root nodules (that house the bacterial symbionts) is only supplied at rates that will not harm the nitrogenase. There are also symbiotic cyanobacteria, for example those associated with the water fern *Azolla*.

The enzymatic nitrogenase reaction is energetically costly. Amongst photosynthetic bacteria, energy demands are met by photosynthesis, while for heterotrophic and chemolithotrophic bacteria these are met by the oxidation of organic matter or redox reactions, respectively.

To fix nitrogen, diazotrophs therefore generally require access to light (photosynthetic bacteria), labile organic matter (heterotrophs), electron donors (chemolithotrophic bacteria) and anoxic conditions (Paerl & Pinckney, 1996).

Nitrogen fixation by bacteria in estuarine and coastal sediments is considered to be generally low, with deficiencies in organic matter considered one of the main reasons for this (Paerl et al, 1987). It is suggested that the fact that many estuaries and other coastal ecosystems are nitrogen limited is in part due to these generally low rates of nitrogen fixation (Howarth *et al.*, 1988).

v. Anaerobic Ammonium Oxidation

Recently, studies in the Black Sea have revealed another process whereby inorganic nitrogen can be converted to N_2 (Kuypers *et al*., 2003). The reaction occurs in anoxic basins characterised by high ammonium concentrations. Here bacteria referred to as 'anammox' bacteria can oxidise ammonium to N_2 using nitrite as the electron acceptor:

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$$

A.2.4 Photochemical processes

In coastal ecosystems, where refractory matter is sufficiently exposed to solar radiation, photochemical processes have been known to regenerate ammonium and phosphate, referred to as photodegradation or photo-oxidation (Dagg *et al*., 2004). The susceptibility of organic matter to photo-oxidation is largely dependent on its chemical composition, with aromatic compounds being particularly photo-reactive. Aromatic structures are characteristic components of refractory terrestrial-derived organic matter (e.g. tannins and lignins).

A.2.5 Biological Processing (Production)

Biological uptake of nutrients can be through autotrophic (or primary) or heterotrophic production:

- *Autotrophic production* occurs where organisms utilize inorganic carbon (CO_2) as the main source of carbon and obtain energy for life processes from the oxidation of inorganic elements (chemotrophic) or from radiant energy (phototrophic). Green plants, algae, and certain bacteria are autotrophs. Autotrophic production can be restricted by low light energy levels and a shortage of nutrient salts.
- *Heterotrophic production* occurs where organisms derive energy for life processes from the decomposition of organic matter and are incapable of using inorganic compounds as sole sources of energy or for organic synthesis. Energy is released from these compounds through respiration. All animals and certain bacteria are classified as heterotrophs (or consumers).

Heterotrophic bacterial processes that are important in terms of nutrient cycling in coastal ecosystems include remineralisation, denitrification and nitrogen fixation that were discussed earlier.

Autotrophic production (uptake of inorganic nutrients) in coastal ecosystems varies greatly. For example, all plants require nitrogen and phosphorus, whereas the uptake of silica is restricted to a few taxonomic groups, mainly diatoms (low silicon concentrations can therefore limit diatom production even when other nutrients are plentiful) (Kemmerer, 2004). The rate of nutrient assimilation by primary producers also depends on many factors (including uptake capabilities, interaction with grazers, water temperature, amount of turbulence and turbidity [light availability]) and does not necessarily correlate with the rate of nutrient supply (Anderson *et al.*, 2002).

Within estuaries, primary producers constitute an array of different floral types which are typically sub-divided into:

- Microalgae (phytoplankton, benthic microalgae or microphytobenthos & epiphytes)

- Submerged Macrophytes (including seagrasses)
- Macroalgae
- Reeds and sedges
- Saltmarsh
- Mangroves.

In nearshore and coastal shelf systems, phytoplankton is usually the dominant primary producer (limited light availability usually inhibits benthic primary production). However, macroalgae and other marine plants (e.g. kelp) can become important, for example, along rocky coastlines. For the purposes of this review, the focus will, however, be on phytoplankton and the primary producers characteristic of estuaries.

Different estuarine floral types can result in significantly different nutrient cycling and transformation processes as is highlighted below.

i. Microalgae (phytoplankton and benthic microalgae)

Uptake of nutrients by primary producers can usually be described by Michaelis-Menton kinetics where growth rates increase with an increase in concentration, but levels off at higher concentrations (Figure A.5).

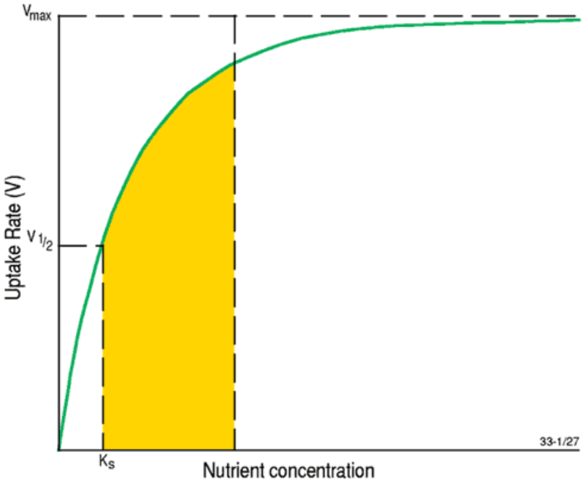


Figure A.5: Relationship between plant uptake rate and nutrient concentrations in water

Phytoplankton typically takes up inorganic nutrients from the water column (although nutrients could have originated from sediments e.g. remineralisation), while benthic microalgae can assimilate nutrients from both the water column and pore water (sediment), although the sediment nutrients are probably more common (Eyre & Ferguson, 2002). Epiphyte microalgae are small primary producers that grow on other estuarine plants. These organisms are not parasitic but use the host plant for support only. Epiphytes are fast growing and obtain all their nutrients from the water column. These organisms are not competitive when nutrient concentrations are relatively low, but when nutrient levels increase in the water column, they become more competitive by capturing and using light more efficiently (www.nrm.gov.au/monitoring/indicators/estuarine/biomass-of-epiphytes.html). In estuaries, epiphyte growth is often associated with plants such as seagrasses (e.g. *Zostera marina*), reeds, saltmarsh vegetation (e.g. *Spartina*) and mangroves (Wright *et al*., 1995; Riber *et al*., 1984; Zoraida & Fleeger, 2005). Growth is usually enhanced in nutrient enriched systems and epiphytic growth on

Zostera leaves have inhibited growth of these plants by intercepting light before it reaches the leaves (Wright *et al*., 1995).

A simple first order approach to assess potential nutrient limitation for microalgae is to examine periods when nutrient concentrations are below the theoretical half-saturation constant (K_s) for uptake and to compare the stoichiometry of key elements (C:N:P) to expected optimal growth ratios. Although crude, this is a robust approach to determine which nutrient is most limiting. K_s values reported for marine phytoplankton are:

- 2 µM (28µg N/ℓ) for DIN
- 0.2 µM (6.2 µg P/ℓ) for DIP
- 2 µM (56µg Si/ℓ) for DRS

The optimal growth ratio for marine phytoplankton for C:N:P is 106:16:1, based on molar concentrations (known as the Redfield ratio). Optimal growth ratios for diatoms for Si:N and Si:P are 1:1 and 16:1 respectively (based on molar concentrations), indicating that for diatoms the abundance of Si relative to N and P affects growth (Fisher *et al*., 1992; Ærtebjerg *et al*., 2003). Optimal growth ratios (C:N:P) for benthic microalgae have been reported as 119:17:1, slightly higher than the Redfield ratio (106:6:1) describing optimal growth for phytoplankton (Hillebrand & Sommer, 1999).

Certain forms of cyanobacteria (e.g. hetercystic cyanobacteria) are also able to fix nitrogen, but high rates of fixation are usually only recorded in systems where cyanobacteria make up a significant proportion of the phytoplankton. However, in most estuaries, species of nitrogen-fixing cyanobacteria are absent or make up only a small portion of the phytoplankton biomass (Howarth *et al.*, 1988).

ii. Submerged Macrophytes and Macroalgae

Submerged macrophytes (plants that are rooted both in soft subtidal and low intertidal substrata and whose leaves and stems are submersed for most states of the tide – Adams *et al*., 1999) derive N and P from sediment pore water and the water column. For example, *Zostera* (eelgrass) beds generally exhibit high annual primary production rates, requiring significant amounts of nitrogen to support this growth, of which a large fraction (~80%) is taken up from the sediment and water column of estuaries (Risgaard-Petersen *et al.*, 1998).

Submerged macrophytes (such as sea grasses) appear to have significantly different optimal growth ratios (C:N:P) compared with microalgae with median ratios reported as 550:30:1 (Atkinson ratio) (Baird & Middleton, 2004). These plants may be N-limited in nutrient-poor waters with sandy or (less so) organic sediments, and P-limited in carbonate sediments. While some species of submerged macrophytes follow classic Michaelis-Menten kinetics for N uptake (Figure A.5), others have exhibited sustained linear uptake with limited or negligible product feedback inhibition, perhaps in adaptation to oligotrophic environments. *Zostera marina*, for example, is able to maintain nitrate reductase activity during dark periods if adequate carbohydrate reserves and substrate are available. Thus, this species can respond to inorganic N pulses throughout a diel cycle, rather than being limited, as most plants, to N-uptake during the light period. However, excessive DIN loading to the water column can inhibit submerged macrophyte growth (e.g. eelgrass) and survival, not only as an indirect effect by stimulating algal (e.g. epiphytes, phytoplankton, macroalgae) overgrowth and associated light reduction, but for some species, as a direct physiological effect (Touchette & Burkholder, 2000).

The importance of leaves versus roots in nutrient acquisition in macrophytes depends, in part, on the concentrations in the water column and sediment. For example, a shift from reliance on sediment pore water to increased reliance on the overlying water for N and P supplies has been observed under progressive water column nutrient enrichment (Touchette & Burkholder, 2000). In one example, ammonium uptake by *Zostera marina* roots met 100% of the N demand although leaf N uptake represented a periodically significant source, e.g. when tidal exchange introduced nutrients to the beds. Ammonium was the preferred DIN source, as demonstrated by its rapid uptake in both leaves and roots (Short and McRoy, 1984).

Relative surface areas and biomass of leaves and roots were also reported as possible factors influencing N uptake. For example, studies on *Potamogeton perfoliatus* showed that with similar DIN concentrations in the water column and pore water, higher leaf biomass and surface area (compared with roots) were the main reason for higher DIN uptake by leaves. Studies on *Potamogeton pectinatus* showed that, although both roots and leaves absorbed P, the microscopic periphyton, which develops on the leaves at an early stage in growth, may account for a significant fraction of 'leaf' absorption (Howard-Williams and Allanson, 1981).

Submerged macrophytes (e.g. *Potamogeton* and *Zostera*) also have a mechanism (referred to as nutrient translocation) whereby nutrients can be transferred from the site of uptake (e.g. roots) to growing tissues (e.g. leaves) (Caffrey and Kemp, 1992).

In estuaries, submerged macrophytes generally act as sinks of inorganic N, where assimilated N is retained within the tissue. These plants decompose relatively slowly and, as a result, N is temporarily immobilized and made unavailable for other autotrophs (e.g. phytoplankton and macroalgae). Submerged macrophyte beds can also be efficient sinks for particulate nitrogen, where decreased current velocity in the macrophyte canopy favours sedimentation and accumulation of suspended matter. This mechanism also supplements sediment pools of nitrogen available for plant uptake (Risgaard-Petersen *et al.*, 1998).

Nitrogen fixation in seagrass beds may also be an important supplementary N source for their growth, particularly in N limiting ecosystems. For example, it has been shown in seagrass beds up to 50% of the N requirements for plant growth was supported by bacterial nitrogen fixation (O'Donohgue *et al.*, 1991). However, other studies showed the contrary where for examples N fixation rates in *Zostera* beds in North Carolina and Alaska were found to be negligible (McRoy *et al.*, 1973).

Interestingly, the aquatic fern *Azolla* (floating macrophyte), an exotic species also found in South African estuaries, fixes nitrogen by virtue of a symbiotic association with a cyanobacterium (*Anabaena azollae*) (http://academic.reed.edu/biology/Nitrogen/Nfix1.html).

Rooted macrophytes may also promote loss of nitrogen through enhancing coupled nitrification-denitrification. The plants transport oxygen from leaves to roots via an air-lacuna system, from where it diffuses into the sediments. Here it can be used for nitrification ($N0_3^-$ production) from where the $N0_3^-$ can undergo denitrification in the sub-oxic sediment surrounding the roots (Risgaard-Petersen *et al.*, 1998).

Foliar release of soluble P by macrophytes (e.g. *Zostera and Potamogeton*) is also a well documented component of P cycling in estuaries (McRoy *et al.*, 1972; Adams *et al.*. 1999). Through this mechanism, P taken up by the roots (interstitial water) is translocated to the leaves and released into the water column as DIP. McRoy *et al.* (1972) in their studies on *Zostera* beds in a lagoon found that a significant portion of DIP released in this manner was exported to the adjacent coastal waters. However, in a study by Howard-Williams and Allanson (1981) on Swartvlei (South Africa), exchange of DIP from *Potamogeton beds* located in the littoral zone of the lake to open waters was low. This was attributed to effective cycling of this nutrient within the beds (by components such as periphyton, *Chladophora*, filter-feeders and sediment). Slow exchange between the littoral zone and the open water was considered an important physical factor contributing to this ‘closed’ cycling of P in the *Potamogeton* beds.

Macrophytes are considered to be important sources of particulate organic nutrients - particularly N (e.g. via loss of leaves). Their production often forms the basis of detrital food chains and other secondary production in estuaries, where these vascular plants also provide habitat and nursery areas for many aquatic organisms (Short, 1987; Risgaard-Petersen *et al.*, 1998).

iii. Macroalgae

Macroalgae (which may be attached to hard or soft substrates or floating) usually take up nutrients from the water column. Significantly different optimal growth ratios (C:N:P) have been reported for benthic macroalgae compared with those for microalgae, with estimated median values similar to those of seagrasses (550:30:1 - Atkinson ratio) (Baird and Middleton, 2004). The limiting nutrient for macroalgal growth and production depends on the time of year, nature of the sedimentary substrate and taxonomic composition of the bed. The limiting nutrient may also depend on the macroalgal taxon. For example, in the Peel-Harvey Estuary (Australia), *Ulva* was found to be N limiting, while *Cladophora* was P limited. Too little is known about the reasons for such differences to generalize freely on limiting nutrients for macroalgae (Valiela *et al*., 1997).

Excessive nutrient loading, favours macroalgae (and phytoplankton) production over benthic primary production (e.g. seagrasses and benthic microalgae), which has a ripple effect on other nutrient cycling and transformation processes. Rooted plants (e.g. seagrasses) and benthic microalgae usually oxygenate the upper sediment layer, enhancing coupled nitrification-denitrification (removing excessive N through N_2). With faster-growing plants (such as macroalgae and phytoplankton), decomposition (remineralisation) is quicker due to their higher nutrient and low fibre content. Oxygen can therefore be rapidly depleted, inhibiting coupled nitrification-denitrification (Eyre and Ferguson, 2002).

Macroalgal blooms also tend to decouple biogeochemical cycles between sediments and the water columns. Under higher rates of nutrient loading, macroalgae (taking up nutrients for the water column) replace plants that extract nutrients from sediments using roots (e.g. seagrasses). Macroalgal canopies over the sediment-water interface also tend to intercept recycled nutrients from sediments (that would have entered the water column (Valiela *et al.*, 1997)).

iv. Reeds and Sedges

Reeds and sedges are plants rooted in soft intertidal or shallow subtidal substrata with photosynthetic aerial portions which are partially or occasionally submersed (Adams *et al*., 1999). These plant communities also play a significant role in the cycling and transformation of nutrients in estuarine systems, often acting as nutrient sinks. For this same reason, reeds are widely used in the construction of artificial wetlands to remove excess nutrients from waste streams. For example, the reed, *Phragmites*, is known to sequestrate inorganic nutrients (in particular N) quite effectively. Detritus (organic matter) generated from *Phragmites* contains large refractory fractions that inhibit rapid decomposition (although the leaves tend to decompose fairly rapidly). This rapid uptake and transformation into refractory organic matter provides an effective mechanism whereby inorganic nutrients (e.g. N) are made inaccessible to other primary producers or for export to adjacent coastal ecosystems (Meyerton *et al*., 2000).

Comparative studies conducted on the common reed, *Phragmites australis*, and short saltmarsh grass (e.g. *Spartina patens*) showed distinctly different nutrient (N) dynamics, in that (Windham and Ehrenfeld, 2003):

- Remineralisation (production of NH_3 from organic matter) rates in sediment covered by *Phragmites* were much higher (~300%) than in *Spartina* beds, but then the uptake rates of inorganic N (mainly NH_3 from sediments) by *Phragmites* were markedly higher (~60%) than by *Spartina*
- Nitrification ($NH_3 \rightarrow NO_3$) and denitrification (organic matter + $NO_3 \rightarrow N_2$) were much higher in sediment underlying *Phragmites* beds than *Spartina* beds
- Rates of litter N-immobilization (see text box) were about 500% higher on *Phragmites* litter (detritus) than on *Spartina,* measured over a year.

Immobilization is the microbial conversion of inorganic N (ammonium and nitrate) into organic forms. This reaction is carried out by heterotrophic microorganisms that obtain energy from the aerobic decomposition of organic matter containing a high C/N ratio that requires additional uptake of N by microorganisms (Lindau et al., 1994).

Numerous studies have shown that nitrogen enrichment of plant litter (e.g. reeds, saltmarsh vegetation and mangroves) increases its nutritional value – often referred to as nitrogen immobilization (N is removed from the environment and incorporated into the microbial biomass on the litter, making it unavailable for other primary producers) (Windham & Ehrenfeld, 2003; Woitchik et al., 1997). In their studies, White & Howes (1994) estimated that microbial biomass can contribute 20 to 25% of the leaf litter N of **Spartina.**

Most of the differences between *P. australis* and *S. patens* may be attributable to morphologic and physiological differences. For example, *P. australis* has large below and above ground rhizomes, which generate stout (up to 2 cm diameter), erect (up to 4 m), hollow culms at densities up to 100 culms m^{-2} with relatively large leaves up to 40 cm long and 5 cm wide. Roots originate from widely and deeply dispersed rhizomes (up to 1.5 m) below ground and the high rates of transpiration and Venturi-enhanced convective ventilation promote a more oxidized rhizosphere than *S. patens* (i.e. providing conditions conducive to remineralisation, denitrification and coupled nitrification-denitrification). In contrast, *S. patens* forms tussocks of shorter, thin tillers up to 1 m tall and 2-3 mm in diameter; with stem densities between 1200-2000 stems m^{-2}. Its roots are clustered under tussocks and penetrate to 40 cm depth, at most. The higher N-immobilization rate on *Phragmites* litter was attributed to higher fractions of refractory (recalcitrant) matter that have slower decomposition rates and therefore the ability to retain exogenous N over more than a year (Windham & Ehrenfeld, 2003).

N-fixation is also known to occur in reed beds. For example, significant N-fixation associated with the roots and rhizomes of the reed *Typha latifolia* have been observed in Minnesota (USA), although sediments associated with these plants did not show large N-fixation activity (Bieboer, 1984).

Although nutrient cycling and transformation in reed beds are complex, these plants primarily act as sinks of inorganic nutrients (particularly N), taking into account: a) the high rates of inorganic N uptake, b) relatively high denitrification rates (losing N to atmosphere), c) the production of large amounts of refractory detritus (trapping N in particulate fractions that do not decompose easily) and d) the ability of reed litter to effectively immobilize N.

Reed litter (detritus) can be a significant source of organic nutrients (C, N & P) to heterotrophs in coastal ecosystems, although the relative importance of this source compared to other sources of organic nutrients (e.g. algal detritus) differs from system to system (Kang *et al*., 2003). Here some studies suggest that even though algae and marsh vascular plant production are of similar magnitude and equally available, algae will contribute more dominantly to the production of higher trophic levels because of the higher digestibility of most algae compared to vascular plants (Deegan & Garritt, 1997). *Phragmites* also appeared to have made little contribution to the diets of consumers in Korean coastal bay systems (Kang *et al*., 2003). In contrast, studies in North America found that reeds (*Phragmites*) make an important contribution (though less nutritious) to aquatic food webs in reed-grass-dominated systems (Wainright *et al*. 2000). Factors that were attributed to such differences included: a) lower digestibility to some consumers, b) disconnection between intertidal marsh areas and aquatic food webs (e.g. small tidal ranges usually result in less effective inundation of intertidal areas) (Kang *et al*., 2003), and probably also c) the extent of microbial N-enrichment of detritus (it is assumed that retention time plays an important role in the extent to which N-enrichment [through nitrogen immobilization] increases nutritional value). In the Mhlanga Estuary (South Africa), litter (detritus) from both *P. australis* and *Scoenoplectus triqueter* beds was found to be the most important food source to about 90% of the fish community in the estuary, particularly during die-back in late summer (Whitfield, 1980).

v. Saltmarsh

Saltmarshes can be described as areas of alluvial deposits colonised by herbaceous and small shrubby terrestrial vascular plants, almost permanently wet and frequently inundated with saline water (Long and Mason, 1983). Intertidal saltmarshes are typically sub-divided into different zones, from 'low marsh' areas (usually inundated on every high tide), colonised by plants such as *Spartina*, through to 'high marsh' areas (usually only inundated during spring high tides), colonised by plants such as *Sarcocornia.*

Nitrogen (N) limitation of primary production is common in temperate saltmarshes (Valiela *et al*., 1978; Tyler *et al*., 2003). In addition to receiving nutrients from the river, through tidal exchange and *in situ* microbial processes, marsh areas can also receive nutrients from groundwater flow and local precipitation. Nutrient cycling in these marshes involves a large number of individual biochemical processes, affecting both fluxes within the system and interchanges with the surrounding environment.

Nutrient cycling (in particular remineralisation, nitrification-denitirification and N immobilization) in lower saltmarsh vegetation (e.g. *Spartina)*, compared with that in reed-beds (e.g. *P. australis*), was discussed earlier (see *Reeds and Sedges*). Nitrogen fixation, by both free-living bacteria in sediments and bacteria associated with the rhizosphere of marsh plants, is considered to be a significant new source of inorganic nitrogen to saltmarsh habitats, although it might not always be sufficient to support the entire N budget (Teal *et al.*, 1979; Tyler *et al.*, 2003; Tibbles *et al*., 1994). With increasing marsh age, there are changes in the magnitude of a number of factors that may limit N fixers, for example, sediment organic matter, ammonium and sulphide concentrations in the pore water. High ammonium concentrations in pore water (>100-200 µM) were found to inhibit N-fixation (Carpenter *et al*., 1978). Benthic microalgae are often associated with intertidal marsh areas, in which case light limitation may result in lower microalgal productivity beneath aging dense stands of marsh vegetation (e.g. *Spartina* beds) (Tyler *et al*., 2003).

Significant changes can take place in the nutrient exchange across the open water-saltmarsh boundary, where marshes sometimes act as nutrient sinks, but at times saltmarshes are known to be significant sources of nutrients to aquatic coastal systems. For example, Valiela *et al.* (1978) found that, during the growing season, saltmarsh *Spartina alterniflora* imported large quantities of DIN (both nitrate and ammonia), but when the growing season ceased and senescence began, the marsh exported large quantities of DIN. Plants are most subject to leaching at maturity and senescence, so that the large export could be due to leaching as well as reduced uptake rates (Valiela *et al*., 1978). However, despite the large variability in exchange, several studies found saltmarshes to be overall net exporters of inorganic and organic nutrients (e.g. litter) to aquatic coastal ecosystems. The extent of such exchange is obviously also influenced by physical factors such as tidal range (determining the extent of tidal flushing of intertidal marsh areas). The energy of tidal flows and other factors, such as the bathymetry of estuaries, also determine the extent to which nutrients are exported into the sea (i.e. nearshore and coastal shelf systems) (Valiela *et al*., 1978).

vi. Mangroves

Mangroves comprise several species of trees and shrubs that grow along sheltered intertidal shores, mainly in tropical and subtropical coastal areas. Mangrove forests are characterised by distinctive tree-height gradients that reflect complex spatial, within-stand differences in environmental factors, including nutrient dynamics, salinity, and tidal inundation, across narrow gradients (Feller *et al*., 2003).

Most research indicates that mangroves are limited by a single nutrient, usually nitrogen (N). However, recent work in mangrove forests has shown that there may be more than one limiting nutrient (e.g. N and P) and that not all processes in mangrove wetlands are limited by the same nutrient. It has also been shown that nutrient availability varies within mangrove forests and can switch from N limitation (e.g. older fringing trees) to P limitation (e.g. dwarf trees further inland) across narrow environmental gradients (Feller *et al*., 2003).

Nitrogen enters mangrove areas in organic and inorganic forms from different sources, including river run-off, tidal exchange and N-fixation. N-fixation is known to occur in mangrove forests, usually associated with roots (Lee and Joye, 2006). These plants stimulate nitrogen fixation by providing the rhizosphere habitat (Hicks and Silvester, 1985).

In these habitats, inorganic N is removed by four major processes: a) uptake by plants, b) immobilization by microorganisms into microbial cells during decomposition of plant material low in N, c) sorption of ammonium onto the organic matter and the clay cation exchange complex and, d) most importantly, mineralization-nitrification-denitrification reactions. Sequential mineralization-nitrification-denitrification reactions occur through interaction between aerobic-anaerobic soil layers. Mineralization takes place where there is organic matter, resulting in a release of ammonium. Nitrification creates a concentration gradient causing ammonium to diffuse from the anaerobic layer into the aerobic layer. Nitrate does not build up in the aerobic zone because nitrate diffusion and denitrification are faster than the nitrification reactions. Nitrate can diffuse both up into the water column and down into the anaerobic soil layer. Net nitrate diffusion is downward where denitrification occurs in the sediments. Inorganic N concentrations (sediment plus water column), a liable organic carbon source and temperature govern denitrification rates (Lindau *et al*., 1994).

Mangrove leaf litter has been identified as an organic nutrient source to heterotrophs (e.g. bacteria and detritus feeders) in coastal ecosystems, including southern African systems such as Gazi Bay, Kenya (Woitchik *et al*., 1997), St Lucia (Steinke and Ward, 1987) and Mngazana (Emmerson and McGwynne, 1992). However, senescent leaves (older leaves just fallen from trees) have fairly low nutritional value (e.g. high tannin content and C:N ratios >>17 - maximum ratio for sustainable animal nutrition) and it is not always clear why these are consumed in significant amounts. Some studies have found that consumers tend to feed on aged leaves that have lower tannin content and reduced C:N ratios (Skov and Hartnoll, 2002) – probably the result of nitrogen immobilization (see earlier text box).

Mangroves generally act as exporters of organic and inorganic nutrients to coastal ecosystems and outwelling of dissolved organic nutrients (N & C) is often underestimated. However, there are reports documenting mangroves as net importers of organic carbon, retaining large proportions of litter production for *in situ* consumption, mainly as a result of restricted inundation regimes. Again, factors such as geomorphology and the strength and frequency of tidal inundation will affect the behaviour of mangroves in relation to their potential to export production (Lee, 1995). For example, Wolanski (1992) found that stable coastal boundary layer water can form in shorelines fringed by straight mangroves sheltered by headlands. This coastal boundary layer will effectively reduce the extent of outwelling from mangroves to the offshore areas. Under such conditions, outwelling effects will only be present over restricted distances.

A.3 NUTRIENT CYCLING AND TRANSFORMATION IN ESTUARIES

Different approaches used internationally to assess the influence of catchment flows on nutrient dynamics in estuaries have been discussed by Ferguson *et al*. (2004).

Although first order nutrient budgets (e.g. mass balance budgets), which account for external sources of nutrient inputs to estuaries, are fairly straightforward and have been applied by Eyre (1995), Nixon *et al.* (1995) and others, it was concluded that nutrient export (or exchange) across the estuarine-ocean boundary was often more difficult to quantify (Ferguson *et al*., 2004). At this boundary there is typically a low signal-to-noise ratio that increases potential errors in budget estimates. Problems encountered in the direct measurements of estuarine-ocean fluxes include:

- High spatial and temporal variability in velocities and nutrient concentrations across this boundary
- Small net exchange relative to peak ebb and floods discharges.

Estuarine-ocean fluxes are therefore more commonly estimated from parameters that can be quantified more readily, such as inputs to estuaries and nutrient cycling within estuaries, where the exchange is estimated as the difference between these two components (Nixon *et al*, 1995; Ferguson *et al*., 2004).

An approach that is being applied to assess nutrient cycling in estuaries is the individual rate measurements of processes within the water column and sediments (e.g. O'Donohue *et al*., 2000). However, such processes usually show large spatial and temporal variability and inaccuracies can be encountered when extrapolating results from individual rate measurement experiments to the ecosystem scales (Ferguson *et al*., 2004).

Another approach that is widely used to assess nutrient cycling in estuaries is mixing diagrams (or property-salinity plots) (Church, 1986; Fisher *et al*., 1988; Balls, 1994; Regnier *et al*., 1997; Eyre, 1994; Eyre, 1997; Eyre, 1998; Eyre, 2000; Eyre & Balls, 1999; Hydes *et al*., 1999; Ferguson *et al*., 2004). The concept of assessing nutrient processes by comparison to a theoretical line representing conservative mixing of river and seawater was also applied earlier by Liss (1976), Boyle *et al*. (1974), Head (1985) and others. The mixing diagram approach plots nutrient concentrations against salinity along the estuarine gradient. Mixing diagrams provides a convenient method for displaying the net effect of nutrient processes within estuaries, whereby deviation from the conservative mixing line is used to interpret results. For example, downward curvature in the mixing diagram implies nutrient uptake, while upward curvature implies nutrient release (Eyre, 2000; Ferguson *et al*., 2004). The mixing diagram is schematically illustrated in Figure A.6.

An advantage of the mixing diagram approach is that it uses measurements from the water column, thus integrating the net effect of nutrient cycling within the estuary. In doing so, problems of spatial variability encountered in the scaling up of rate measurements can be overcome. It has even been argued that estimations based on an integrated net effect (as with the mixing diagram approach) are quantitatively far more accurate than the extrapolation of individual rate measurements due to the potential errors encountered in each of the steps of the latter (Ferguson *et al*., 2004). Another advantage of the mixing diagram approach versus the rate measurement approach is that the former requires far fewer intense data collection programmes and is therefore considered more suitable for routine assessments (Eyre, 2000) or in instances where resources are limited.

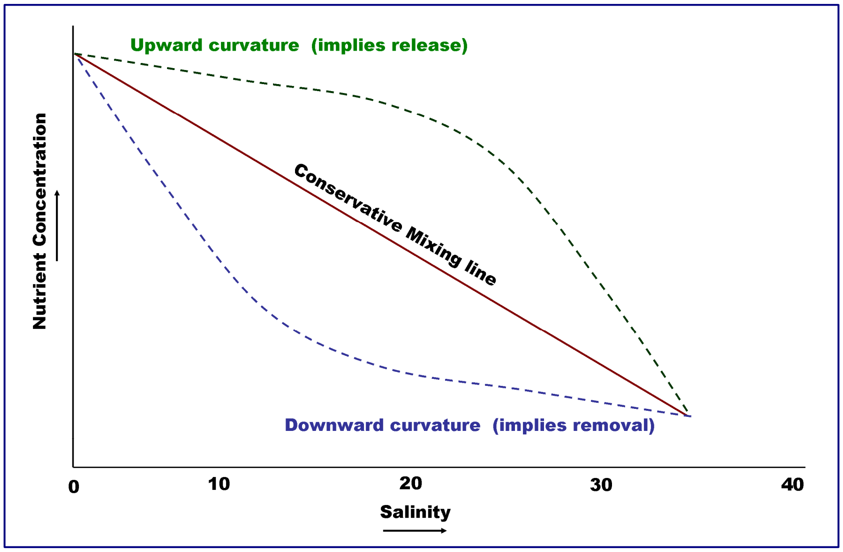


Figure A.6: Schematic illustration of a mixing diagram (or property-salinity plot)

Mixing diagrams have also been used effectively to give indications of dominant biogeochemical processes influencing nutrient cycling and transformation in estuaries. For example, mixing diagrams showing downward curvature for nutrients such as DIN and DIP, but upward curvature for chlorophyll a, most likely suggest uptake of nutrients by phytoplankton as the major removal mechanism (Eyre, 2000).

However, the mixing diagram approach has also received criticism in the literature, mainly related to its steady state assumptions (Eyre, 2000). For example, if nutrient concentrations entering the estuary through river inflow or through tidal intrusion vary on a temporal scale shorter than the flushing time of the estuary, the mixing diagram may falsely indicate non-linear distribution. Eyre (2000) suggested that such problems can be overcome by including measurements on variation in river/seawater concentrations and flushing times in the data collection programmes. In this way, conservative mixing lines in the mixing diagrams are calculated rather than using the usual theoretical mixing lines. Calculation of conservative mixing lines is discussed in more detail by Eyre (2000) and requires measured cross-section data and volume of the estuary, salinity distribution on the sampling day/s, daily river discharges, measured daily river concentrations and seawater salinity and nutrient concentrations.

The mixing diagram approach usually assumes a single freshwater source for the calculation of the conservative mixing line (Hydes *et al*., 1999). Where there are other tributaries or external water sources (e.g. sewage run-off) running into the estuary, it will be important to consider these in the interpretation of the mixing diagram. For example, it was found that small steps of downward curvature in the mixing curve of nitrate, which was superimposed on the general removal curve, corresponded to the dilution from a tributary that entered an estuary but that had lower concentrations than the main river (Eyre, 1994). This concept is illustrated in Figure A.7.

Based on the above, mixing diagrams appear to be a more robust and convenient method for routine (or first level) assessments of nutrient cycling and transformation within estuaries, particularly where resources for data collection programmes are limited.

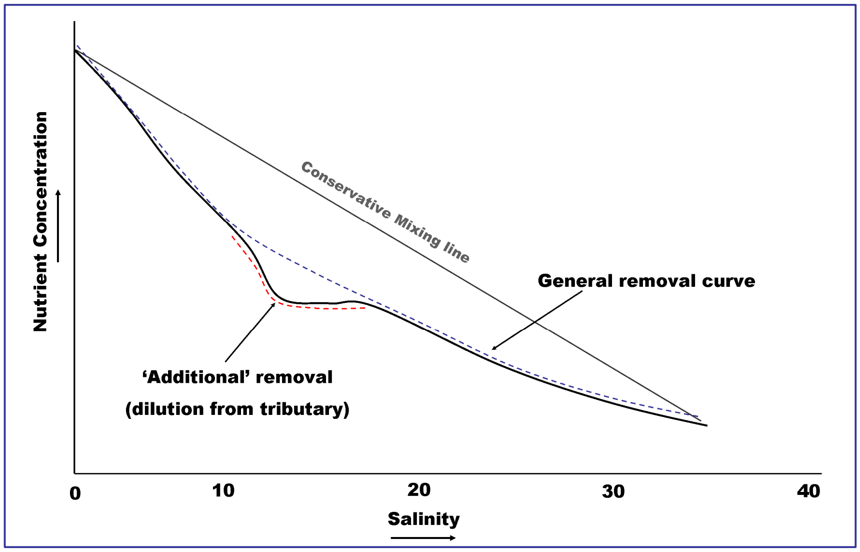


Figure A.7: Schematic illustration of potential effect of other external sources on a mixing diagram

Another important (physical) control that determines the degree to which nutrients are transformed within a specific coastal domain is flushing time or retention time (i.e. the time it takes to replace water or that water remains within a specific area) (Eyre and Balls, 1999).

In estuaries, flushing times are primarily controlled by three factors (R van Ballegooyen, CSIR, pers comm.), namely:

- Hydrology (river inflow patterns, strongly influenced by climate)
- Tidal exchange (as influenced by the state of the tide and mouth status)
- Bathymetry (i.e. size and shape of estuary).

Hydrology is therefore important both in terms of defining spatial and temporal variation in catchment fluxes (e.g. nutrient and sediment loads) and spatial and temporal variation in flushing times (or water circulation patterns) in estuaries. Flushing times, in turn, control the extent to which *in situ* (physical, chemical, bacterial or biological) processes influence nutrient cycling and transformation. For example, in rapidly flushed systems, nutrients tend to behave conservatively, while *in situ* processes have a much larger effect on nutrient cycling in systems with longer flushing times (Balls, 1994).

Across the world there are marked differences in hydrological regimes (or river flow patterns) (Peel *et al*., 2004). For example, Peel *et al*. (2004) found that the variability in annual run-off of systems in temperate Australia and in temperate/arid regions in southern Africa are consistently higher than on other continents, supporting earlier findings that southern hemisphere continents have higher variability in run-off than northern hemisphere continents. Two main factors were suggested for the distinct difference between the hemispheres, namely:

- Variability in annual precipitation (higher variability in the southern hemisphere continents)
- Continental distribution of evergreen and deciduous vegetation in temperate regions – temperate forests in the northern hemisphere consist largely of deciduous trees, while temperate forests in the southern hemisphere are largely evergreen.

> As a result of the low fertility of soils in Australia and southern Africa (due to their extreme age), these areas do not supply sufficient nutrients to support deciduous trees that develop new foliage every season. Evergreen trees are therefore more adapted to these low nutrient conditions. However, to maintain foliage, evergreens need to transpire moisture, even when it is present in only small amounts. These trees are therefore able to completely eliminate the run-off component of a moisture budget unless rainfall is unusually abundant for extended periods (i.e. they are very effective in utilising water when present in small quantities) (Epinions, 2005).

Other factors that could potentially also contribute to variability in run-off between the southern and northern hemisphere continents include: continental differences in the percentage of forested catchment area and continental differences in mean annual daily temperature range (Peel *et al*., 2004).

Variability in annual run-off is expressed as the coefficient of variation (C_v), which is much higher for Australian rivers ($C_v = 0.7$) than for European ($C_v = 0.29$) and North American r($C_v = 0.35$) rivers (Eyre, 1994). A typical coefficient of variation reported for South African rivers is 0.8, similar to that of Australian systems (www.waterandclimate.org/data/Documents/storage.doc).

Variability in run-off in further reflected in peak and annual floods (relative to mean annual run-off), defined by the ratio between the average volume of the 1:100 year flood (Q_{100}) and mean annual flood discharges (Q). The high variability in run-off of Australian rivers results in high ratios ($Q_{100}/Q = 5.08$) compared with European ($Q_{100}/Q = 2.2$) and North American ($Q_{100}/Q = 3.6$) systems where run-off is less variable (Eyre, 1994).

Catchment dimensions and rainfall patterns have a significant influence on run-off patterns. For example, Australian rivers are usually short with relatively small catchments and as a result run-off to estuaries is delivered as short-lived high energy events (on the scale of days), separated by long periods of dry spells (on the scale of months or years) (Eyre, 1994).

Run-off patterns also determine the characteristics of sediment loads. In the case of Australia, run-off patterns (short-lived events, separated by long periods of dry spells) favour accumulation of material in catchments. As a result, sediment loads are dominated by fine, suspended particles rather than coarser sediment, which also influence the manner in which nutrients are transported from the catchments to the estuaries. For instance, the majority of phosphorous (P) is transported from catchments in particulate forms (through adsorption onto the finer, suspended particles) rather than in its dissolved forms (Eyre, 1994).

Taking these differences into account, together with differences in tidal exchange and bathymetrical characteristics (e.g. European systems are often deeper that those in Australia and South Africa), it is likely that conceptual models describing nutrient cycling in northern hemisphere estuaries may not necessarily be relevant to systems in southern hemisphere continents. To illustrate these differences, examples of systems studied in North America (illustrating the influence of less variable and more consistent hydrological regimes) and Australia (illustrating the influence of highly variable and less consistent hydrological regimes) are briefly discussed below.

A.3.1 North American systems (Northern hemisphere)

A typical example of river inflow into the larger estuaries of the temperate northern hemisphere regions is provided in Figure A.8 (Potomac River inflow to Chesapeake River Estuary).

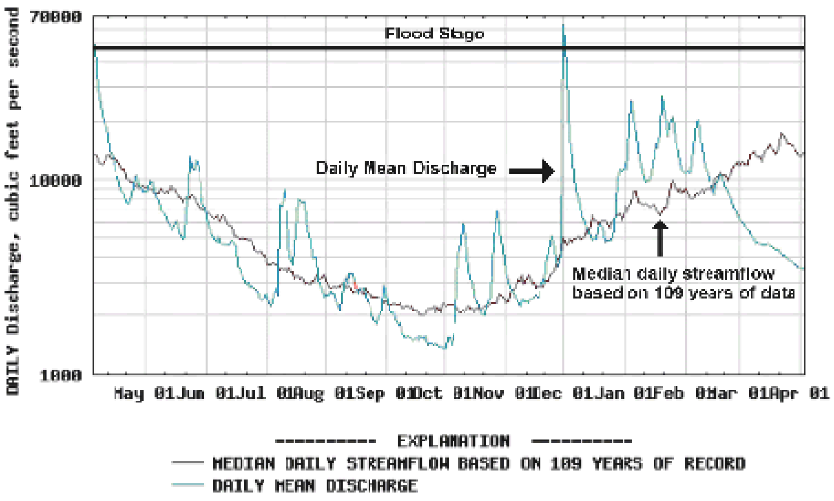


Figure A.8: River inflow into Chesapeake Bay from Potomac River (http://md.water.usgs.gov/publications/press_release/current/)

A number of conceptual models have been developed for temperate northern hemisphere estuaries, including that of Fisher *et al*. (1988), based on results obtained from the Chesapeake, Delaware and Hudson River estuaries in North America (Figure A.9) (Note that this is a general model and site-specific variability needs to be considered when applied to specific systems).

Large tidal estuaries of temperate regions in the northern hemisphere range from well mixed to partly-stratified with a well-defined two-layered circulation developing for part of the year following freshwater inputs, usually in spring (Eyre, 1998). These systems are characterised by a horizontal salinity gradient, spatially ranging over scales of kilometres to hundreds of kilometres. The scale of the gradient depends on river inflow from the catchment and coastal geomorphology. The low salinity (or oligohaline) regions are characterised by a turbidity maximum, resulting from flocculation of freshwater-derived material (geochemical processes) and the two-layered circulation of estuaries that promote retention of particles (Fisher *et al*., 1988). Degradation of deposited organic material (heterotrophic bacterial activity) is also active in this area (biochemical processes). As a result of low light availability, primary production is suppressed in this region, but a chlorophyll a maximum, associated with the uptake of river-derived nutrients (i.e. biological uptake), typically develops further downstream as waters become clearer (a subsequent zooplankton maximum developing downstream of the chlorophyll a maximum has also been observed, but this needs further testing) (Fisher *et al*., 1988). These systems usually demonstrate estuarine outwelling, which intensifies along with stratification during spring run-off (Eyre, 1998).

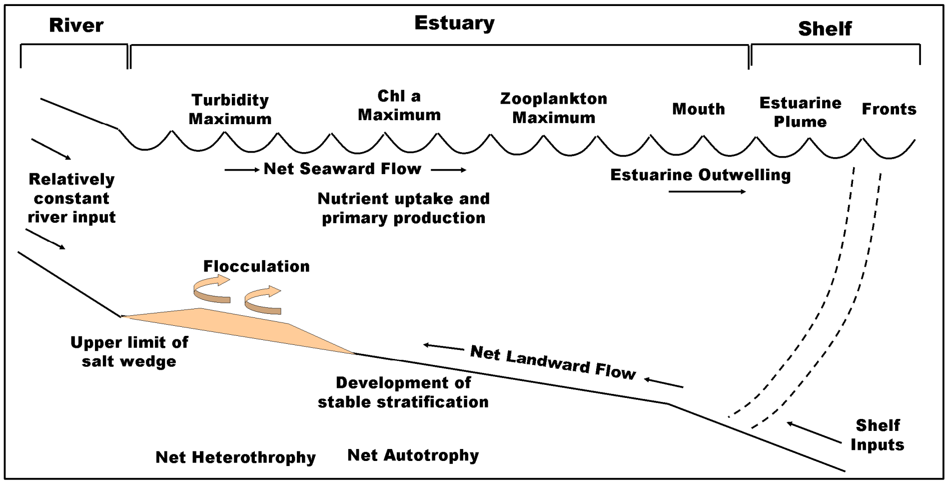


Figure A.9: ***General conceptual model for temperate northern hemisphere estuaries (after Fisher et al., 1988 and Eyre, 1998)***

Key to the development of the different zones in large temperate systems in the northern hemisphere is stable stratification (or two-layered circulation), characteristic of larger tidal estuaries with relatively constant river inflow. This mechanism firstly retains particles, resulting in the turbidity maximum, and secondly provides stratified conditions that are suitable habitats for phytoplankton production (Fisher *et al*., 1988; Eyre, 1998).

The generic conceptual model (Figure A.9) suggests that temperate northern hemisphere estuaries display a nutrient maximum (where nutrient-rich water enters the estuary), turbidity maximum (oligohaline region), chlorophyll a maximum and zooplankton maximum along the salinity gradient. The distribution and extent of these zones depend on factors such as flushing times and volumes (physical processes) (Fisher *et al*., 1988). These large estuaries are thus important geochemical (e.g. flocculation), biochemical (e.g. organic degradation) and biological (e.g. primary production) ‘reactors’ that transform trace elements (including nutrients) en route from the catchment (river) to coastal shelf waters (Church, 1986). The composition of estuarine outwelling (i.e. that which is delivered to the coastal shelf) is the result of these different processes.

A.3.2 Australian systems (Southern hemisphere)

In his studies, Eyre (1998) found that Australian estuaries can be subdivided into five broad categories, based on their hydrological and meteorological regimes, namely:

- *Mediterranean* (10% of systems – mainly south-western Australia). These estuaries receive episodic freshwater input during winter and experience summer droughts. Eight percent are bar-built estuaries which are closed seasonally. Winter floods produce intense stratification but are usually not sufficient to flush saline water completely, although some of the shallower systems can be flushed completely.
- *Temperate* (12% of Australian systems - Tasmania, Victoria, South Australia and southern New South Wales). There are no well-defined seasonal variations in flow although flow generally increases during late winter and spring. Systems are usually stratified for much of the year, with conditions intensifying during spring (associated with increased inflow). Generally, flooding does not result in complete flushing (hydrologically these are similar to temperate northern hemisphere systems).

- *Transitional* (5% of systems). These are the drowned river valleys with no well-defined seasonal variations in flow, although winter storms can be significant (geomorphologically similar to temperate northern hemisphere systems). Short-lived winter storms generate a surface freshwater plume that may extend offshore, but does not persist for long due to large tidal ranges.
- *Arid tropical and subtropical* (6% of systems – mainly Western Australia). These systems receive very little inflow, usually only during storms and cyclones which may only occur every few years. Due to high evaporation rates, these systems often develop inverse salinity gradients.
- *Wet and dry tropical and subtropical* (68% of Australian estuaries – NSW, Queensland, Northern Territory and northern Western Australia). These systems are dominated by short lived, but large freshwater inputs during summer and very little or no flow during winter. They are usually shallow due to tectonic stability and relatively low coastal relief. As a result, high summer flows usually flush saline water completely from the estuary. Following a high flow event, these estuaries usually rapidly re-establish strong salinity gradients due to large tidal ranges, progressively moving from highly stratified salt wedge systems to becoming vertically well-mixed.

Generic models for nutrient cycling in southern hemisphere systems are largely limited to those developed for Australian subtropical systems (Eyre and Twigg, 1997; Eyre, 1998; Eyre and Ferguson, 2006) (subtropical systems making up the bulk of their systems). A typical example of river inflow patterns to subtropical estuaries of Australia (southern hemisphere) is provided in Figure A.10.

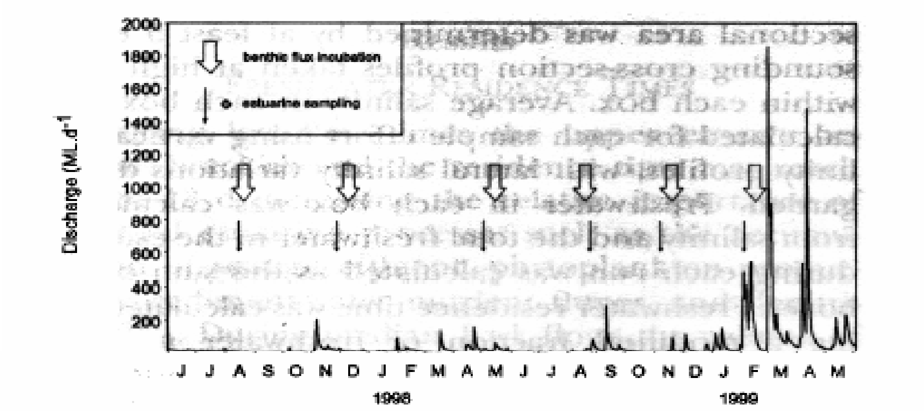


Figure A.10: **Brunswick Estuary: Example of river inflow patterns (hydrology) of subtropical systems in Australia (southern hemisphere) (taken from Ferguson et al., 2004)**

A simplified conceptual model, based on the results of a number of Australian studies (see earlier), is provided in Figure A.11.

Although nutrient processes are generally much more complex, this simplified conceptual model provides an overview of the key processes that govern nutrient cycling and transformation during different (hydrological) phases. These phases are summarised below:

- *Floods/High flow phase*. During this phase nutrient cycling and transformation in the estuary are largely governed by physical processes, i.e. flushing and scouring. Nutrients (and sediment) entering the estuary from the river are flushed through the system into coastal shelf waters, without any significant transformation happening in the estuary. Nutrient concentrations in the water column typically show conservative behaviour (as illustrated by mixing diagrams). Depending on the size of the flood, sediment and nutrients can also be scoured from the estuary and transported into the coastal shelf. Except for the latter, pelagic-benthic recycling processes are mostly decoupled.

Due to rapid flushing and low light availability (high turbidity), biological uptake of nutrients (e.g. phytoplankton production) within the estuary is insignificant.

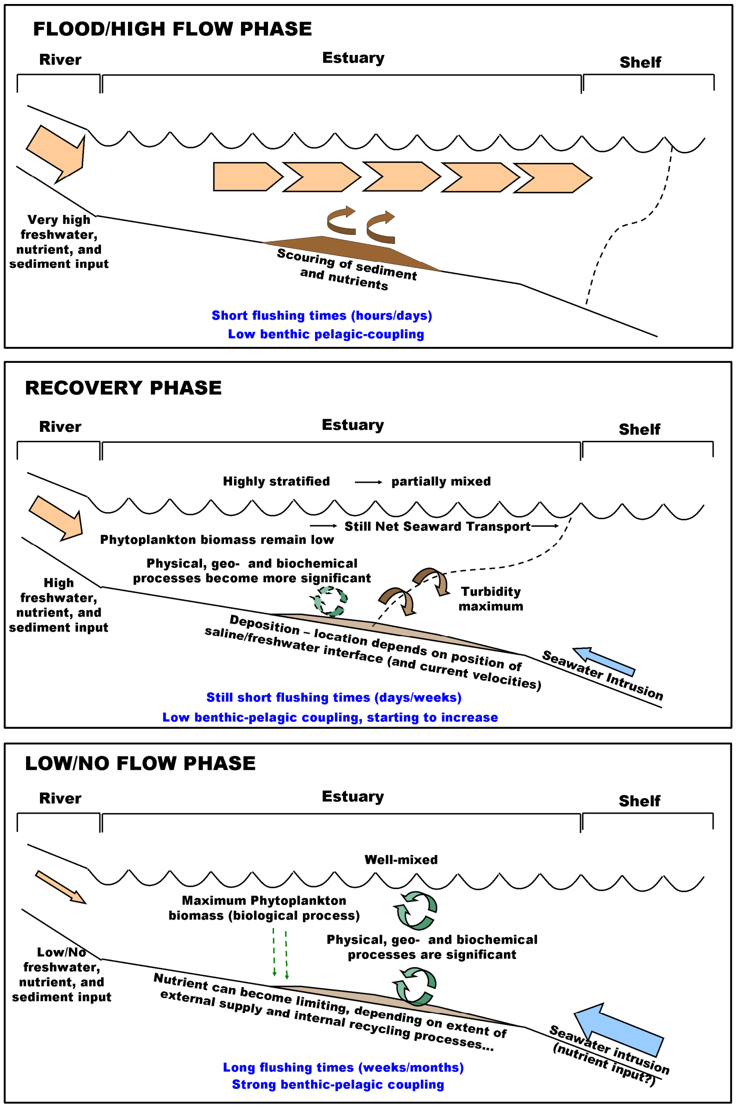


Figure A.11: ***General conceptual model of nutrient cycling in subtropical estuaries in Australia (southern hemisphere) (adapted from Eyre, 1998; Eyre, 2000)***

- *Recovery phase*. This phase can also be referred to as the 'depositional phase', as river-derived suspended material gets deposited in the estuary. The extent of deposition (both in terms of volume and spatial distribution) depends on factors such as the timing and size of the preceding flow event (which determines suspended material loads), current velocities within the estuary and the location of the freshwater/saline interface. The recovery phase is therefore important in that it determines the potential nutrient supply (food store) available to the estuary in the subsequent low/no flow phase.

  At the onset of this phase, the estuary is strongly stratified as a result of significant saline intrusion along the bottom (due to a large tidal range), gradually becoming partially mixed.

Phytoplankton biomass is still low as flushing times are still relatively short. Geochemical (e.g. adsorption/desorption and flocculation) and biochemical processes (nitrification and denitrification) become more significant, initiating benthic-pelagic coupling.

- *Low/no flow phase*. During this phase, the effect of geochemical and biochemical processes on nutrient cycling and transformation is significant, usually resulting in strong benthic-pelagic coupling. Physical processes (e.g. wind mixing) remain important in term of re-suspension of deposited material, particularly in shallower areas.

  Due to long flushing times, phytoplankton biomass typically reaches its maximum during this phase. Inorganic nutrients introduced from the river during the flood/high flow phase are usually rapidly depleted. Thereafter, phytoplankton (and benthic microalgae) biomass is dependent on the extent of external nutrient supply (either from river or sea) and recycling processes within the estuary.

A.4 NUTRIENT CYCLING AND TRANSFORMATION ON COASTAL SHELVES INFLUENCED BY CATCHMENT FLOWS

Estuaries typically act as the transition zone between rivers and the sea, in which complex nutrient cycling and transformation processes can modify catchment fluxes prior to exchange across the estuary-nearshore boundary (refer to Section A.3). However, there are also instances (e.g. during floods or high flow periods) where estuaries merely act as a conduit for catchment flows to the sea. In such instances, the transformation of catchment-derived material that would typically occur within the confines of an estuary, occurs in the adjacent nearshore and coastal shelf. This influences the magnitude and type of transformation processes, which may differ from those occurring in estuaries.

The dynamics of plumes from large rivers, such as the Zaire, Zambezi and many Northern American, Canadian and Asian systems, have been well documented. These were recently also the topic of a review article (Dagg *et al.*, 2004). However, research on the plume dynamics of smaller rivers, typical of Australian and South African systems, appears to be more limited (Gaston *et al*., 2006).

Although many of South Africa’s river systems fall within the ‘smaller estuaries’ category, there are systems like the Gariep (Orange), Umzimvubu and Thukela that, during high flows and floods, may exhibit plume dynamics in the nearshore and coastal shelf that are similar to those of the larger river systems.

During high flows, rivers can effectively acts as a point source of dissolved and organic matter to coastal shelves, as these constituents are typically present in lower concentrations in seawater. There are, however, large variations amongst systems.

Numerous physical factors influence the transport and dispersion of river plumes in the nearshore and coastal shelf environment, including:

- Hydrology (river inflow patterns which are strongly influenced by the climate)
- Wind patterns
- Tides
- Currents
- Bathymetry of the estuary.

The physical transformation of river plumes on coastal shelves is therefore governed by a number of complex processes that occur on different temporal and spatial scales but that are typically much smaller than traditional oceanic scales (Dagg *et al*., 2004).

Studies in the southern Californian Bight showed that, in the case of the Santa Clara River plume, inertia (i.e. tendency of river flow to continue in motion at the same speed and direction) and coastal winds and current forcing were important to the dispersal of river plumes (Warrick *et al*., 2004). As inertia dissipated (largely due to turbulence mixing), the plume became more subject to buoyancy and rotational forcing. However, transport and dispersion of the surface plume were dramatically altered by local wind stresses and coastal currents (Geyer *et al*., 2000; Warrick *et al*., 2004). Similar dispersal mechanisms were observed in a northern Californian system (Eel River) (Geyer *et al*., 2000).

Inertia dominated systems have been classified as 'Case 1' or large-scale discharges according to Garvine (1995), representing large-scale or fast flowing river plumes for which strong boundary fronts and significant across-shore fluxes are expected. These river plumes are usually markedly different to the 'Case 2' or small-scale discharges where advection is largely alongshore due to geostrophic momentum balances (Gaston *et al*., 2006).

In conjunction with field measurement programmes, remote sensing has been used successfully to study the transport and dispersion of river plumes, although these techniques could not be used effectively to calculate mass outputs from coastal rivers, e.g. Sea-Viewing Wide Field-of-View (SeaWiFS) satellite sensor (Mertes and Warrick, 2001; Warrick *et al*., 2004; Otero and Siegel, 2004). Otero and Siegel (2004) also applied specific techniques to distinguish between effects of river input and upwelling in sediment plumes and phytoplankton blooms in the Santa Barbara Channel (along the northernmost edge of the Southern Californian Bight).

Although physical transformation of plumes is quite variable, largely depending on local physical forcing mechanisms, there are a number of geochemical and biological processes that are more consistent within river plumes (Dagg *et al*., 2004). When (fresh) river water is discharged into the sea (saline water), density differences result in the development of a buoyant plume, that causes a decrease in turbulence. This reduced turbulence also reduces the plume's ability to transport suspended lithogenic matter, resulting in large quantities of suspended matter settling from the plume. Along the edges of the plume, coloured dissolved organic matter (e.g. humic substances), introduced by rivers, is diluted with clearer seawater, thus enhancing light penetration. These changes in the physical and optical regimes markedly influence geo- and biochemical and biological processes within plumes. Temporal and spatial scales, over which transformation processes occur, vary greatly, depending on factors such as discharge volume, suspended sediment loads, light and temperature. Some of the documented processes observed in river plumes are briefly discussed below.

As river water mixes with seawater, flocculation occurs (typically at the low salinity ranges). Sorption of inorganic P and organic constituents to suspended particles also occurs during this mixing phase. Conversely, at higher salinities, adsorbed inorganic P, introduced by rivers, is released from suspended particles. It is known that large portions of total P, entering coastal margins from rivers, are associated with suspended sediments (Nixon *et al*., 1996).

In the low salinity mixing zone, aggregation of dissolved and colloidal matter also occurs, enhancing the settling of particulate matter. Dissolved organic matter (C, N and P) can have significant colloidal fractions, resulting in such compounds also settling rapidly from the plume. For example, in the Mississippi's river plume, aggregation and settling reduced the suspended matter concentration in the plume by more than 90% within 5-10 km from the river mouth (Dagg *et al*., 2004). Because different types of aggregates are influenced differently by, for example, salinity, this selective removal creates a mechanism whereby river-derived constituents settle out at different locations along the plume pathway.

River plumes usually introduce high inorganic nutrient concentrations to coastal shelves, which provides favourable conditions for primary production, particularly in zones where settling of suspended matter[s?] (e.g. through flocculation and aggregation) improves light availability. In large river plumes, maximum phytoplankton production is often observed at intermediate salinities, attributed to declined turbidity in the presence of reasonably high nutrient concentrations. What is interesting is that the location of the phytoplankton maxima along the salinity gradient differs from one system to another, linked to differences in salinities at which suspended matter settles out. Suspended solid concentration <10 mg/ℓ has been reported to favour phytoplankton production in these plumes. However, factors other than light availability can also influence the distribution and extent of primary production, such as the depth of the surface mixed layer and mixing rates. As mixing with nutrient poor seawater increases along the plume pathway, certain nutrients can become limiting, resulting in a decline of phytoplankton production. Here factors such as dilution, grazing and sinking also start to have a more significant influence on phytoplankton biomass (Dagg *et al*., 2004).

Eyre & Balls (1999) also found rapid biological uptake of phosphate and nitrate (and a marked increase in chlorophyll a) at the seaward edge of a tropical system's plume in Australia (Annan), where the settling of river-derived suspended matter from the plume reduced turbidity and provided sufficient light penetration to support primary production. A similar effect was also observed in other large tropical systems (e.g. Zaire, Mississippi, Grijalva-Usumacinta) (Cadee, 1984; Wysocki *et al*., 2006; Signoret *et al*., 2006).

Evidence of nutrient remineralisation within river plumes is also well documented (review by Dagg *et al*. 2004; Eyre and Balls, 1999) and is an important nutrient source for primary production when river-borne inorganic nutrients become depleted. For example, a conceptual model for N recycling in the Mississippi River plume showed that (Dagg *et al*., 2004):

- At low salinities, recycling rates of ammonium by bacteria were low, as liable dissolved organic matter (N) sources were low, i.e. most river DOM was refractory, while *in situ* phytoplankton production was also still low
- At intermediate salinities, recycling rates of ammonium were highest as high phytoplankton production and biomass provided ample liable organic matter
- At high salinities, recycling rates of ammonium decreased again as phytoplankton production dropped due to nutrient limitations.

Eyre & Balls (1999) also found high ammonium concentrations in the offshore plume of the Annan system (Australia), which they attributed to recycling of particulate and dissolved organic matter (N) in the plume (whether the organic matter was from river origin or phytoplankton production at sea was not revealed). Strong density differences limited mixing of the plume with deeper water, which allowed a much longer residence time for material in the plume (days to a week) to undergo biogeochemical processing.

Although river-derived organic matter is often refractory (i.e. resistant to biodegradation), there is surprisingly little evidence indicating accumulation of such matter in the ocean. In this regard, photochemical transformation has been identified as a potentially important process through which even refractory river-derived organic matter can be regenerated at sea (Dagg *et al*., 2004).

It is also known for zooplankton to directly consume river-derived particulate organic matter (e.g. detritus) in plume areas, representing an alternative route for remineralisation of nutrients (generating ammonium through excretion) (Dagg *et al*., 2004).

River plumes can also influence nutrient cycling in the bottom sediments (or benthic boundary layer [BBL]) on coastal shelves, either directly or indirectly (Wysocki *et al*., 2006; Gaston *et al*., 2006; McKee *et al*, 2004). As discussed earlier, a number of processes (e.g. flocculation, aggregation, sorption/desorption, mineralization, grazing and settling) alter the characteristics of suspended particles (both lithogenic and biogenic) in river plumes. These processes, in turn, affect the flux and composition of river-derived matter that settles to the BBL (McKee *et al*., 2004), in this way affecting the BBL directly. In deeper waters, for example, the liable fraction of river-derived particulate organic matter often undergoes pre-depositional degradation (e.g. through mineralization and grazing), with mostly refractory organic matter reaching the BBL. This process is usually less efficient in nearshore environments as a result of shallower waters in combination with sedimentation processes.

Settling of marine-derived phytoplankton (phytodetritus) and faecal pellets from organisms that utilized river-derived nutrients and detritus as food sources accounts for indirect ways in which catchment flow can influence nutrient processes in the BBL (Wysocki *et al*., 2006).

Biogeochemical processes are important in the BBL of river-dominated coastal margins because of the large quantities of particulate organic matter deposited in these areas. However, the transport (deposition and subsequent resuspension/redistribution) and transformation (e.g. biogeochemical cycling) of matter in the BBL are highly variable, making the measurement and modelling of such (site-specific) processes very challenging. McKee *et al*. (2004) highlighted the following aspects (concerns) when studying biogeochemical cycling in the BBL of river dominated coastal margins:

- Particulate fractions in catchment fluxes (lithogenic and biogenic), typically ending up in the BBL, are usually very poorly quantified on both event and seasonal scales. Strong temporal variation in particulate loads from catchments (as reflected in measurements taken in some rivers) emphasizes the need to resolve temporal scales of these fluxes.
- Transport rates (deposition and subsequent resuspension/redistribution) of matter in the BBL are controlled by a complex combination of factors, such as river fluxes, physical forcing (tides, currents, waves and wind), depth and morphology of the coastal shelf and biogeochemical processes. Temporal and spatial differences in transport and biogeochemical process rates in the BBL can therefore be significant.
- Because of large temporal and spatial variability, the BBL of river dominated coastal margins is often wrongly characterised as ‘one system’, when in fact it is comprised of several sedimentary features and sub-environments (e.g. traditional seabed in ‘depocentres’, fluid and ephemeral muds, shore-face deposits and coarse grain deposits). For example, the shorter time scales (days) and sediment depth scales (cm) associated with the ‘ephemeral layer’ are probably more important to nutrient cycling and transformation than the longer-term sedimentation rates that are often used. Temporal and spatial dynamics (site-specific) in the BBL of river dominated coastal margins therefore need to be recognised and accommodated if useful insight is to be gained into the significance these zones have on nutrient processes and production in the coastal ecosystem.

SECTION B

NUTRIENT CYCLING AND TRANSFORMATION IN SOUTH AFRICAN ESTUARIES

B.1 OVERVIEW OF KEY INFLUENCING FACTORS

Based on the overview on nutrient cycling and transformation (Section A), a number of important factors were highlighted as having a marked influence on such processes in estuaries, namely:

- Flushing time, primarily influenced by the hydrological regime (river inflow patterns), tidal exchange and the size and shape of an estuary
- Size of intertidal zones, an important factor that influences the extent of possible nutrient exchange between intertidal areas and open waters
- Estuarine aquatic vegetation, important in establishing key nutrient cycling and transformation processes that could occur within a system.

A brief overview of some of these characteristics relevant to South African systems is discussed below.

B.1.1 Hydrological Regime of South Africa

The hydrological regime (or river flow patterns) within a catchment depends largely on climate (or rainfall) and the catchment size and relief. South Africa has a highly variable climate and therefore highly variable rainfall patterns. Along the coast, the climate ranges from semi-arid on the west coast, to Mediterranean (winter rainfall areas) along most of the south-western Cape coast to subtropical (summer rainfall areas) along the Kwazulu-Natal east coast. Rainfall patterns along the south coast are bi-modal, with peaks in spring and autumn (Figure B.1).

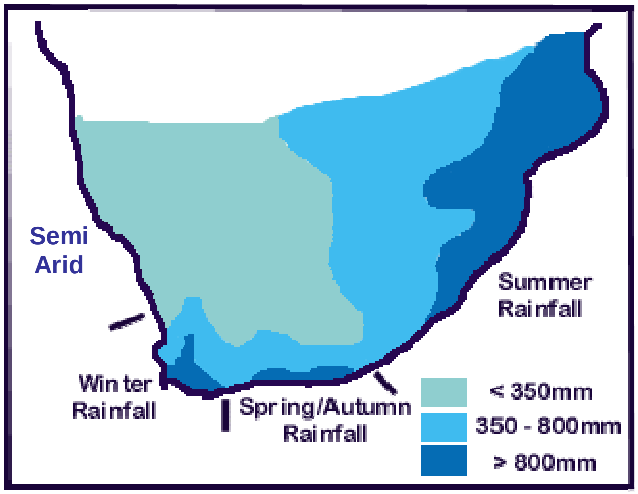


Figure B.1: ***Rainfall distribution patterns along the South African coast (Source: http://sacoast.uwc.ac.za/education/resources/sacoast/)***

Catchment size is important as it controls the magnitude and flow distribution of river run-off (Reddering and Rust, 1990) and, as with rainfall, it shows large variability with southern African systems, ranging from very small (<1 km^2) to very large catchments (>10 000 km^2).

Systems receiving run-off from large catchments in the winter and summer rainfall areas, for example, tend to display strong seasonal flow distribution patterns, with high and low flow periods extending over weeks to months (e.g. Thukela and Olifants estuaries), where the seasonal distribution of low and high flow periods is determined by rainfall patterns within the catchment (Figures B.2). In contrast, in systems receiving run-off from relatively small catchments, low flow periods are typically 'interrupted' by high flow <u>events</u> (lasting from hours to days) (e.g. Siyaya Estuary) (Figure B.3), where the distribution of these events is driven by rainfall patterns within the catchment (the latter are characteristic of Australian systems where rivers are usually short with relatively small catchments - Eyre, 1994).

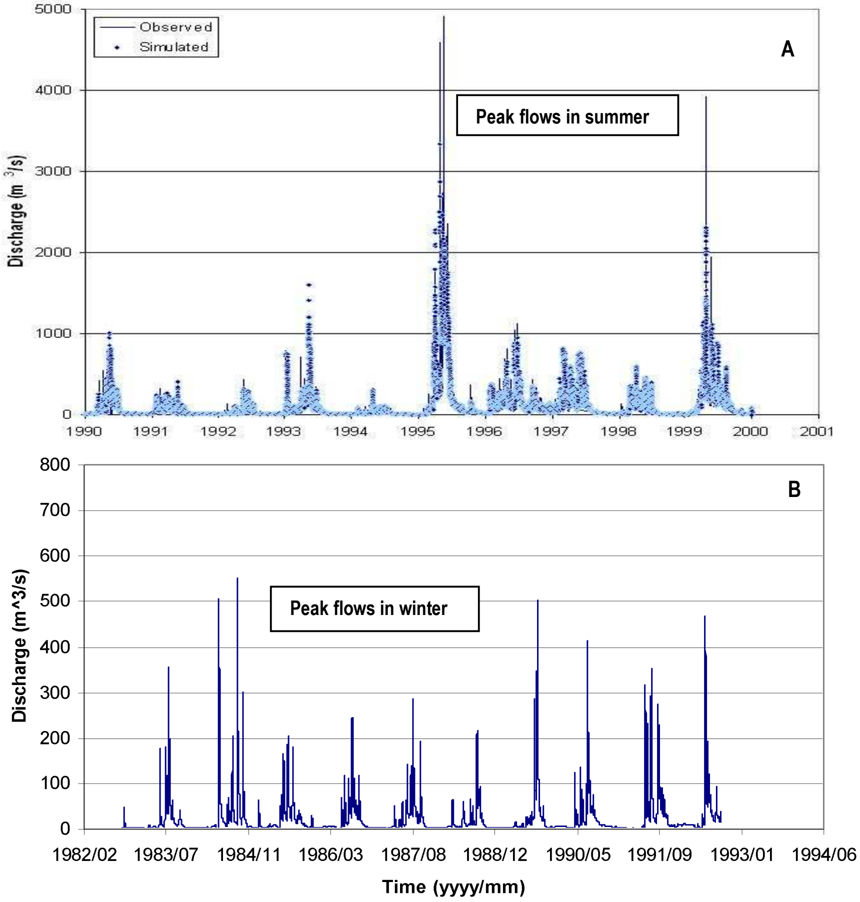


Figure B.2: ***Typical seasonal river inflow patterns of systems draining large catchments: (A) Thukela Estuary (catchment 29 000 km^2 draining a summer rainfall area) and (B) the Olifants Estuary (catchment 49 000 km^2 draining a winter rainfall area) (DWAF 2004b; Taljaard et al., 2006)***

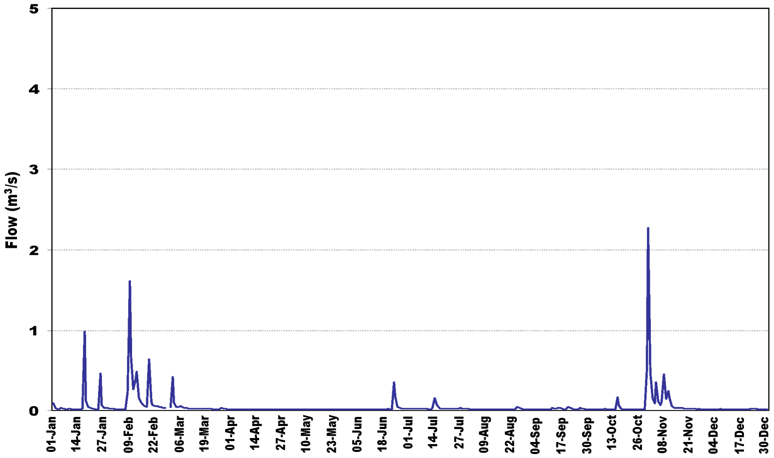


Figure B.3: ***Typical seasonal river inflow patterns of systems draining small catchments – Siyaya Estuary (catchment 18 km^2 draining a summer rainfall area) (<u>www.dwaf.gov.za/hydrology</u>)***

Taking the above into account, it can generally be assumed that:

- Systems receiving run-off from the semi-arid regions are subject to extended periods of low to no river inflow interspersed with short flash flood events that last from hours to days.
- Systems receiving run-off from winter rainfall areas are subject to extended low flow periods during the dry summer months, receiving highest run-off during the wet winter months. During winter, run-off from smaller catchments typically occurs as specific events, i.e. high run-off (indicative of short flushing times) is separated by periods of low run-off (indicative of longer flushing times). However, in the case of larger catchments, average winter run-off is maintained at higher levels compared to that of smaller catchments, although peak flows are still quite variable.
- Systems receiving run-off from summer rainfall areas are typically subject to extended periods of low run-off (indicative of long flushing times) during winter, with highest run-off (indicative of short flushing times) during summer. During summer, run-off from smaller catchments tends to occur as specific events, i.e. high run-off (indicative of short flushing times) is separated by periods of low run-off (indicative of longer flushing times). However, in the case of the larger catchments, average run-off is maintained at higher levels during summer (indicative of low flushing times), although peak flows are still quite variable.
- Systems receiving run-off from bimodal rainfall areas usually receive freshwater inflow throughout the year with no well-defined seasonal trends although rainfall in autumn and spring tends to be slightly higher. For smaller catchments, run-off occurs as short-lived flushing events (or freshettes) separated by distinct periods of low flow. In the case of larger catchments, a similar pattern is expected, except that base flows may be slightly higher and separation between freshettes and low flow periods less pronounced.

This variability in rainfall patterns also played an important role in the long-term development of South Africa's estuaries. For example, along the arid regions of the west coast, the development of estuaries is stunted by low average river inflow and infrequent flooding, while systems on the south coast are better developed as a result of more rain and more frequent flooding. The characteristics of catchments (or drainage basins) have a major influence on the behaviour of estuaries. Catchments draining along the east coast of South Africa (Kwazulu-Natal), with comparatively high relief coupled with high discharge, supply rivers that tend to deliver substantial volumes of sediment to estuaries. As a result, most east coast estuaries are dominated by river-borne sediments and flood tide deltas are rare. These estuaries are the result of effective flushing of sediment from these systems through regular flooding. Although the high sediment yield of east coast (KZN) systems could be expected to support the development of ebb-tidal deltas in the nearshore, this is not common as a result of the high energy coastline and the narrow continental shelf (Reddering and Rust, 1990).

B.1.2 Physical Characteristics of South African Estuaries

Although the hydrological regime is a key controlling factor of the flushing time (or retention time) of water in estuaries, other physical characteristics are also important in this regards, such as:

- Tidal exchange
- State of the mouth (e.g. unrestricted, restricted or closed)
- Size and shape (bathymetry) of the estuary
- Size of intertidal areas (particularly those vegetated by saltmarsh or mangrove swamps), as these, together with tidal range (determining the extent of tidal flushing of intertidal areas), and the energy of tidal flows are particularly important in terms of nutrient exchange across the intertidal/open water boundary (either the estuarine channel or adjacent coastal waters) (Valiela *et al*., 1978; Lee, 1995).

A brief overview describing some of these key characteristics in South African systems is provided below.

South Africa has about 250 functional estuaries draining into three coastal biogeographical regions (Figure B.3), namely:

- Cool temperate region (10 estuaries)
- Warm temperate region (128 estuaries)
- Sub-tropical region (121 estuaries).

The maximum tidal range of the South African coast is about 2 m between successive high and low spring tides, classifying South African systems as microtidal estuaries (Whitfield, 1992). Whitfield (1992) classified South Africa's estuaries into five types, based on a variety of criteria such as mouth characteristics, tidal prism and mixing processes (Table B.1).

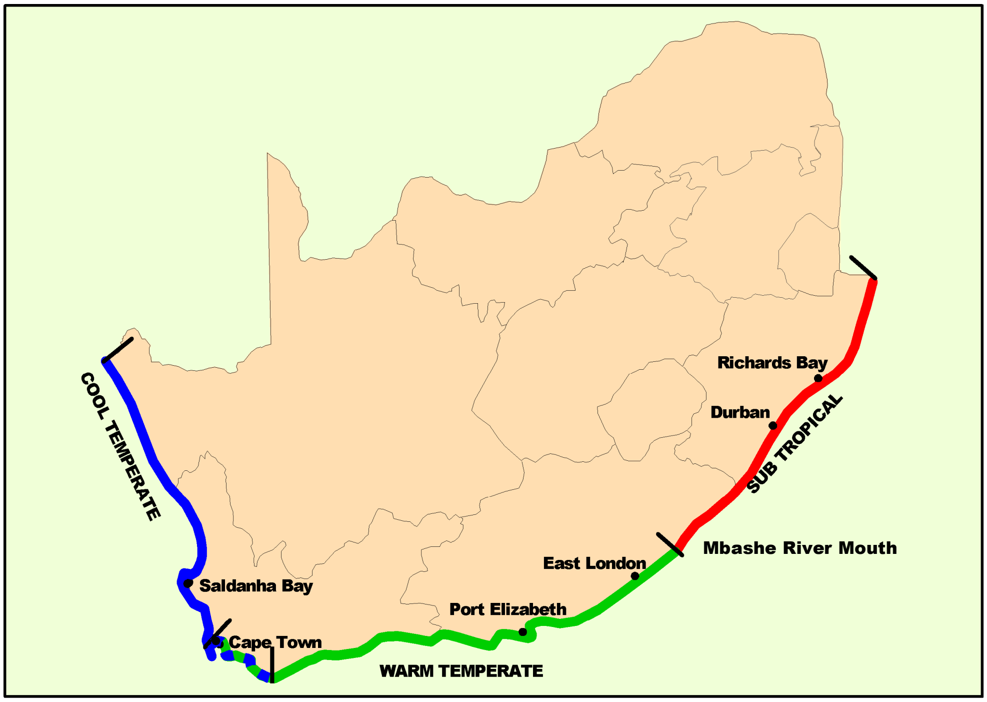


Figure B.3: Distribution of biogeographical regions along the South African coast

TABLE B.1 Distribution of estuary types in the three biogeographical regions of South Africa (Whitfield, 1992)

ESTUARY TYPE	*BIOGEOGRAPHICAL REGION*		
	COOL TEMPERATE	*WARM TEMPERATE*	*SUB-TROPICAL*
Temporarily open/closed estuary	5	86	94
Permanently open estuary	2	29	16
River mouth	2	6	4
Estuarine bay	0	1	3
Estuarine lake	0	4	4
Modified or canalised estuary	1	2	0

Temporarily open/closed estuaries, such as the Palmiet, Groot Brak and Mhlanga systems, are blocked off for varying periods of time by a sand bar that forms across the mouth. Closure is determined by a range of factors such as low river flow, high wave action and the availability of sediment in the vicinity of the mouth. Most of these systems have relatively small catchments (<50 km^2) and extended low flow periods (often for several months). The tidal prism is usually small (<10^6 m^3) when the mouth is open and absent under closed conditions. About 75 % of South Africa's estuaries fall within this category.

Permanently open estuaries, such as the Olifants, Breede and Mzimkulu systems, are permanently open to the sea with a horizontal salinity gradient and sometimes vertical stratification, depending on factors such as river inflow, state of the tide and bathymetry. Moderate tidal prisms (10^6-10^7 m^3) provide sufficient energy to keep the mouth open even during periods of low river inflow. The catchments of permanently open systems are usually >500 km^2 and often >10 000 km^2. Generally, there is a wetland (intertidal) area in the lower to middle reaches occupied by saltmarsh in the temperate regions and mangroves in the sub-tropical region. Submerged macrophytes (e.g. *Zostera*) are also characteristic of the middle and lower reaches (more saline areas) of permanently open estuaries.

River mouths, such as the Orange and Thukela estuaries, are usually fairly small estuaries, backed by large catchments (>10 000 km^2). River inflow is often characterised by heavy silt loads. Consequently, these estuaries are usually shallow (<2 m water depth) despite the large seasonal river inflow. Scouring during episodic floods can however deepen these systems to reach depths >10 m. The tidal prism is small (<10^6 m^3), with saline intrusion seldom occurring any significant distances upstream during moderate and high flows. These systems are usually open to the sea, although mouth closure does occur during extended low flow periods (Whitfield, 1992).

Estuarine bays, such as Knysna and Durban Bay have large tidal prisms (>10^7 m^3) and are permanently open to the sea. The mouth area is usually deep (>3 m), resulting in strong tidal fluctuation in the lower reaches of the estuary, similar to tidal variation at sea. These estuaries are generally large (> 1 200 ha) and marine dominated, due to the strong tidal exchange and relatively small catchments (compared to their size). Estuarine bays are characterised by extensive (intertidal) marsh and/or mangrove areas.

Estuarine lakes, such as St Lucia and Kosi Bay are separated from the sea by sand dune systems, with either a permanent or temporary link to the sea. These systems are large (> 1 200 ha) but, due to the restricted connection to the sea, the tidal prism is usually small to negligible. When cut off from the sea, these systems function as coastal lakes.

In summary, Reddering and Rust (1990) noted the following general physical forces influencing the behaviour of southern Africa estuaries:

- The majority of estuaries are small with tidal prisms of less than 10^6 m^3
- Most estuaries occupy drowned river valleys (ria-type estuaries) with only a few that have developed on coastal plains
- Most estuary mouths are restricted or periodically closed off from the sea by a sand bar
- Flood tidal deltas are common in west and south coast systems (Cape), but mostly absent in east coast systems (Kwazulu-Natal)
- Ebb-tidal deltas are poorly developed throughout
- Not all estuaries have well-developed intertidal areas.

B.1.3 Typical Aquatic Vegetation in South African Estuaries

Estuarine plant community types can also have a marked influence on nutrient cycling and transformation within a particular estuary (see Section A.2.5). Knowledge of the distribution of estuarine aquatic vegetation within individual systems therefore provides valuable information on possible nutrient cycling and transformation processes.

An overview of the characteristics of aquatic vegetation in South African estuaries has been provided by Adams *et al*. (1999) and Steinke (1999). In these studies estuarine vegetation was grouped into:

- microalgae (phytoplankton and benthic microalgae)
- macroalgae
- submerged and floating macrophytes
- reeds and sedges
- saltmarsh
- mangroves

i. Microalgae (phytoplankton and benthic microalgae)

Phytoplankton distribution patterns in South African estuaries are extremely variable. Using chlorophyll a as an estimate of biomass, this variability is shown in the minimum and maximum concentrations measured in a range of South African systems (Table B.2).

Based on these results, the phytoplankton chlorophyll a concentrations appear to be generally low in most South African estuaries. However, although phytoplankton productivity per unit area might be low, the area available for phytoplankton production (water column) can sometimes be so large that its contribution to overall system primary productivity can be significant, as was observed in the Swartkops Estuary (Adams *et al*., 1999).

TABLE B.2: Range of chlorophyll a concentrations measured in South African estuaries (after Adams et al., 1999)

ESTUARY	*CHLOROPHYLL A (µg/ℓ)*	
	Minimum	*Maximum*
Palmiet	*2*	*8*
Bot	*0*	*6*
Sundays	*12*	*23 (>100 during bloom)*
Kariega	*1*	*8*
Great Fish	*0 (106 during bloom)*	*52 (210 during bloom*
Keiskamma	*0*	*19*
Nahoon	*1*	*6*
Gqunube	*5*	*15*
Kwelera	*0*	*10*
St Lucia	*0*	*16*

Major factors found to influence phytoplankton production in estuaries included nutrient availability, retention time and light availability (turbidity). Water residence time is particularly important in terms of nutrient utilisation, where too short residence time (hours to days) does not allow for effective trapping of nutrients by phytoplankton. Studies in the Swartkops Estuary showed that phytoplankton blooms developed when the residence time of water was longer than the doubling time requirements of a bloom (Adams *et al*., 1999). Although high turbidity is usually a limiting factor for phytoplankton production in larger, deeper systems, this does not seem to be an issue in the shallower, well-mixed systems of South Africa, such as the St Lucia Estuary, where chlorophyll a was present in the water column even under extreme turbidity (Fielding *et al*., 1991).

Similar to phytoplankton, benthic microalgae production in South African estuaries shows large variability. Studies conducted along the south coast of South Africa (Adams *et al*., 1999) found that, in systems where river flow introduced low nutrient concentrations, benthic microalgae biomass far exceeded phytoplankton biomass, while in systems where river flow introduced high nutrients (e.g. through fertilizer enrichment), phytoplankton biomass was highest (Table B.3).

TABLE B.3: Benthic microalgae and phytoplankton biomass (as chlorophyll a) calculated for a number of estuaries on the South African south coast, linked to the nutrient status of river inflow (after Adams et al., 1999)

ESTUARY	*NUTRIENT STATUS OF RIVER INFLOW*	*BIOMASS (kg chlorophyll a/estuary)*	
		Phytoplankton	*Benthic microalgae*
Goukou	*Low*	*0.07*	*23*
Gourits	*Low*	*0.04*	*16*
Great Brak	*Low*	*0.40*	*62*
Keurbooms	*Low*	*0.06*	*20*
Gamtoos	*High*	*17.00*	*14*
Sundays	*High*	*86.00*	*14*

ii. Macroalgae

Although Day (1981) suggested that macroalgae were not well represented in South African estuaries, more recent studies seem to show a different picture. For examples, in the Kromme, Kowie and Kariega estuaries, marine dominated systems in the warm temperate region (Eastern Cape), macroalgae were found to make up a substantial proportion of primary production biomass. Also, opportunistic species such as *Chladophora* and *Enteromorph* (able to tolerate fluctuating salinity) have been encountered in closed or temporarily closed estuaries characterised by long residence times (Adams *et al*., 1999).

iii. Submerged and Floating Macrophytes

Submerged macrophyte communities in South African estuaries are highly variable both on temporal and spatial scales. For example, the seagrass *Zostera capensis*, a species that prefers more saline water, occupies the intertidal mud banks of most of the permanently open estuaries in the cool and warm temperate (Cape) estuaries. Due to its strong morphological structure and ability to tolerate daily periods of exposure, this seagrass can withstand strong currents and tidal fluctuation. *Ruppia cirrhosa* is more common to temporarily open/closed estuaries, characterised by fluctuating salinities. However, this submerged macrophyte is also found in the calm brackish upper reaches of permanently open estuaries (Adams *et al*., 1999).

Studies investigating nutrient cycling in submerged macrophyte beds in South African systems include those of Howard-Williams and Allanson (1981) on P cycling in *Potamogeton pectinatus* beds in Swartvlei, and Tibbles *et al*. (1994) on N fixation associated with *Zostera* beds in the Langebaan Lagoon.

Results from Swartvlei found that exchange of soluble P between *Potamogeton* beds in the littoral zone and the open waters was low, attributed to effective cycling of the nutrient within the beds (by components such as periphyton, *Chladophora*, filter-feeders and sediment). Slow exchange between the littoral zone and the open water was considered an important physical factor contributing to this 'closed' cycling of P in the *Potamogeton* beds (Howard-Williams & Allanson, 1981).

N fixation studies on Z*ostera* beds of the Langebaan Lagoon showed that the highest rate of N-fixation was associated with beds with the highest organic matter content. Overall, the study showed that fine muddy sediments supported significantly higher nitrogenase activity compared with sandy sediments, largely controlled by the organic matter concentrations - muddy sediment having higher organic content than sandy sediments. Studies by Mazure and Branch (1979) also showed that macrophyte litter produced in the Langebaan Lagoon (mainly during seasonal die-back) was low in N. However, due to bacterial colonisation, this litter was N-enriched (through bacterial N-fixation), becoming more nutritional to other heterotrophs (e.g. detritivores). In the Langebaan Lagoon, bacterial N-fixation was considered an important source of new N through this enrichment process.

iv. Reeds and Sedges

Reeds, sedges and rushes are important plants found in the fresh and brackish part of South African estuaries, usually along the banks (emergent plants). *Schoenoplectus triqueter* and *Phragmites australis* (common reed) typically grow in brackish areas (<15 ppt). In more saline systems, tidally inundated by sea water (35 ppt), such as the Kromme and Keurbooms estuaries, *Phragmites* beds survive as a result of ground water seepage creating fresh or brackish zones around the root systems (Adams *et al*., 1999).

Studies on the Mhlanga Estuary showed that litter (detritus) from both *Phragmites australis* and *Scoenoplectus triqueter* beds supplied about 90% of the organic nutrient demand of the fish community of the estuary, particularly during die back in late summer (Whitfield, 1980).

Floating macrophytes, such as *Azolla filiculoides*, do occur in South African estuaries and are usually restricted to the less saline (< 5ppt), calmer areas of estuaries. However, the typical species encountered are all exotic to South Africa (Adams *et al*., 1999).

v. Saltmarsh

Saltmarsh only occurs in certain estuaries along the South African coast, mostly in the cool and warm temperate regions. To the north of the Kei Estuary, the sub-tropical climate tends to favour mangrove swamps (Adams *et al*., 1999). Interestingly, more than 75% of South Africa's estimated 17 000 ha of estuarine saltmarsh vegetation is confined to five estuaries, namely, the Langebaan Lagoon (where freshwater inflow is primarily through groundwater), Knysna, Swartkops, Berg and Olifants estuaries. Saltmarsh vegetation in estuaries shows a distinct zonation linked to tidal inundation and salinity distribution patterns. Saltmarsh species that are common to South African estuaries include:

- *Spartina maritime,* found in 18 of the larger, permanently open systems in the cold and warm temperate regions, usually occurring in the zone between mean sea level (MSL) and mean high water neap (MHWN)
- *Sarcocornia perennis* characteristic of the zone between MHWN to mean high water spring (MHWS)
- *Sarcocornia pillansii*, typical of the zone above MHWS, only occasionally flooded by sea water
- *Juncus kraussi,* also typical of the zone around MHWS but only where salinities are usually below 20 ppt.

The effects of intertidal saltmarsh on nutrient cycling and transformation have been studied in a number of South African systems, including:

- Swartkops Estuary (e.g. Winter and Baird, 1991; Baird and Winter, 1992)
- Kariega Estuary (e.g. Taylor, 1992; Taylor and Allanson, 1995)

In the Swartkops Estuary, the exchange of nutrients between intertidal saltmarsh (*Spartina maritime*) and open waters in the lower reaches of the system was studied during a low flow period (Baird and Winter, 1992). Results showed that (inorganic and organic) nutrient fluxes between the intertidal marsh and the estuary, mainly driven by tidal exchange, were small as the marsh retained and utilised most of its own production, virtually functioning as an independent ecosystem. Earlier studies on the Swartkops Estuary did, however, report a net export of nutrients (carbon, DIN & DIP) from the estuary to the nearshore, based on flux measurements across the mouth (Winter, 1990). Contrary to later findings, this was largely attributed to export from saltmarsh areas.

Studies on the Kariega Estuary, during a marine dominated state, also found that fluxes from (high) intertidal marsh areas (colonised by *Sarcocornia perennis* and *Chenolea diffusa*) played a small role in the nutrient cycling in the estuary, compared with tidal inputs, even though the intertidal marshes comprised 24% of the estuary's area. However, tidal inputs had a marked impact on the fluxes of DIN (nitrate) to the marsh, where high nitrate inputs (linked to upwelling) resulted in a marked increase in the biological uptake rate in the marsh (Taylor, 1992). It was also speculated that the high elevation of these marsh types and the degree of water exchange with adjoining areas limited export of organic nutrients - in the case of the Kariega, the high marsh areas were mostly exposed to the atmosphere, facilitating exchange of gaseous carbon with the atmosphere rather than organic carbon with the estuary (Taylor and Allanson, 1995).

vi. Mangroves

In South Africa, mangrove swamps extend from the Nahoon Estuary in the south to Kosi Bay in the north. South Africa has relatively few mangrove species, with the dominant ones being (Steinke, 1999):

- *Avicennia marina* (white or grey mangrove)
- *Bruguiera gymnorrhiza* (black mangrove)
- *Rhizophora mucronata* (red mangrove)

A distribution map of mangroves in South Africa (including approximate areas) has been provided by Steinke (1999). More recently, the distribution and areas of mangroves swamps in the former Transkei were updated by Adams *et al*. (2004). Zonation patterns of mangrove species in estuaries are considered to be a function of factors such as (Steinke, 1999):

- Physiological adaptability to salinity gradients
- Physiological adaptability to the frequencies of tidal inundation across the intertidal zones
- Tidal sorting of propagules based on differences in their size
- Predation on propagules (e.g. by crabs).

Nutrient related studies on mangrove swamps in South African estuaries primarily focused on the role of these plant communities as organic nutrient sources to estuarine and coastal food webs (Steinke, 1999). The importance of mangroves as a source of organic carbon (also referred to as reduced carbon), mainly through litter production, has been studied extensively by Steinke and others (overview provided in Steinke, 1999). Their studies showed that, when litter falls, there is an initial rapid loss of mass, followed by a steady decrease in mass for the remainder of the decomposition period. They also found that, during decomposition, the N concentration in leaf litter increased due to the colonisation by microorganisms and associated N-fixation, increasing the nutritional value of the leaf litter (although P concentrations decreased sharply). This emphasised the important role of mangroves as a (organic) nutrient source, as well as a substratum for (inorganic) nutrient release (e.g. through leaching).

Animals in mangrove swamps (e.g. crabs) are also known to play a significant role in biodegradative processes. Through their action, these animals contribute to breaking down leaf litter to finely particulated detritus, which further stimulates bacterial decomposition, while also becoming a valuable food source to detritus feeders (e.g. certain fish species) (Steinke *et al*., 1993).

B.2 PROPOSED CONCEPTUAL MODELS FOR SOUTH AFRICAN ESTUARIES

B.2.1 Hydrodynamic States

The hydrological regime (as determined by climate and catchment size and relief) is a key driver in determining the hydrodynamic status (and subsequently the nutrient cycling and transformation processes) within estuaries, influencing important aspects such as flushing times and the location of the freshwater front (or freshwater/saline interface).

Over the past years, correlations between river flow and hydrodynamic states within estuaries have been developed for a number of South African estuaries as part of ecological water requirement studies (e.g. DWAF, 2004a, DWAF, 2004b, Taljaard *et al.*, 2005 & Taljaard *et al*., 2006). Based on the outcome of those studies, as well as new learning gained through this study, four hydrodynamic states appear to be typical of South African estuaries, namely (Figure B.4):

- *Freshwater-dominated (high flow) State,* referring to periods when river inflow to an estuary is such that the system is either completely fresh (e.g. during floods) or freshwater dominated (e.g. seasonal high flows), with the freshwater front located outside the estuary in the nearshore or coastal shelf environment, occasionally moving into the estuary (e.g. during spring flood tides). During this state, flushing times are short, typically ranging between hours to days. Under flood conditions, tidal variation is small, with limited water exchange between intertidal areas and open waters. In large catchments, this limited tidal variation can last for days to weeks (e.g. Orange Estuary).
- *Transition (freshette) State,* referring to periods when river inflow to an estuary is still significant so as to create a freshwater front well beyond the head of the estuary, but which is 'halted' by tidal intrusion of saline water usually along the middle reaches. As reflected in the name, this state occurs for relatively short periods at a time ('pulse' effect), either in the transition period between the Marine-dominated and Freshwater-dominated states or when a pulse of freshwater (freshette) is introduced to an estuary. Density differences at the freshwater front usually result in strong (longitudinal and/or vertical) stratification, as well as a decrease in turbulence. As a result, a 'lingering' freshwater plug or plume forms within the estuary, with flushing times ranging between days to weeks, depending on the size and shape of the estuary. Water exchange between intertidal areas and open waters can be significant during this state, depending on the extent of tidal exchange (as determined by the state of the tide and mouth status) and the relative size of the intertidal zone. However, freshettes may well restrict tidal exchange in the higher flow ranges, thus reducing potential water exchange between intertidal areas and open waters.

  Although tidal intrusion does occur, it is not considered to be on a scale that would result in significant water exchange between intertidal areas and open waters. The Transition State usually reverts into either the Marine-dominated State or the Closed Mouth State (see below), although it can also move into the Freshwater-dominated State (e.g. if it occurs in the transition period between the dry and wet seasons).
- *Marine-dominated (low flow) State,* referring to periods when an estuary is marine-dominated, due to low/no river inflow. During this state, tidal exchange is usually most significant, although largely a function of the state of the tide and mouth dimensions (width and depth). Water exchange between intertidal areas and open waters can thus be significant, depending on the extent of tidal exchange and the relative size of the intertidal zone. The freshwater front, if present, is usually confined to the upper reaches of the estuary.

  In larger systems, flushing times in the middle and upper reaches can be fairly long (weeks to months), while strong tidal exchange in the lower reaches may account for much shorter flushing times (hours to days). In smaller systems, tidal flushing may well be able to maintain fairly short flushing times throughout the system.

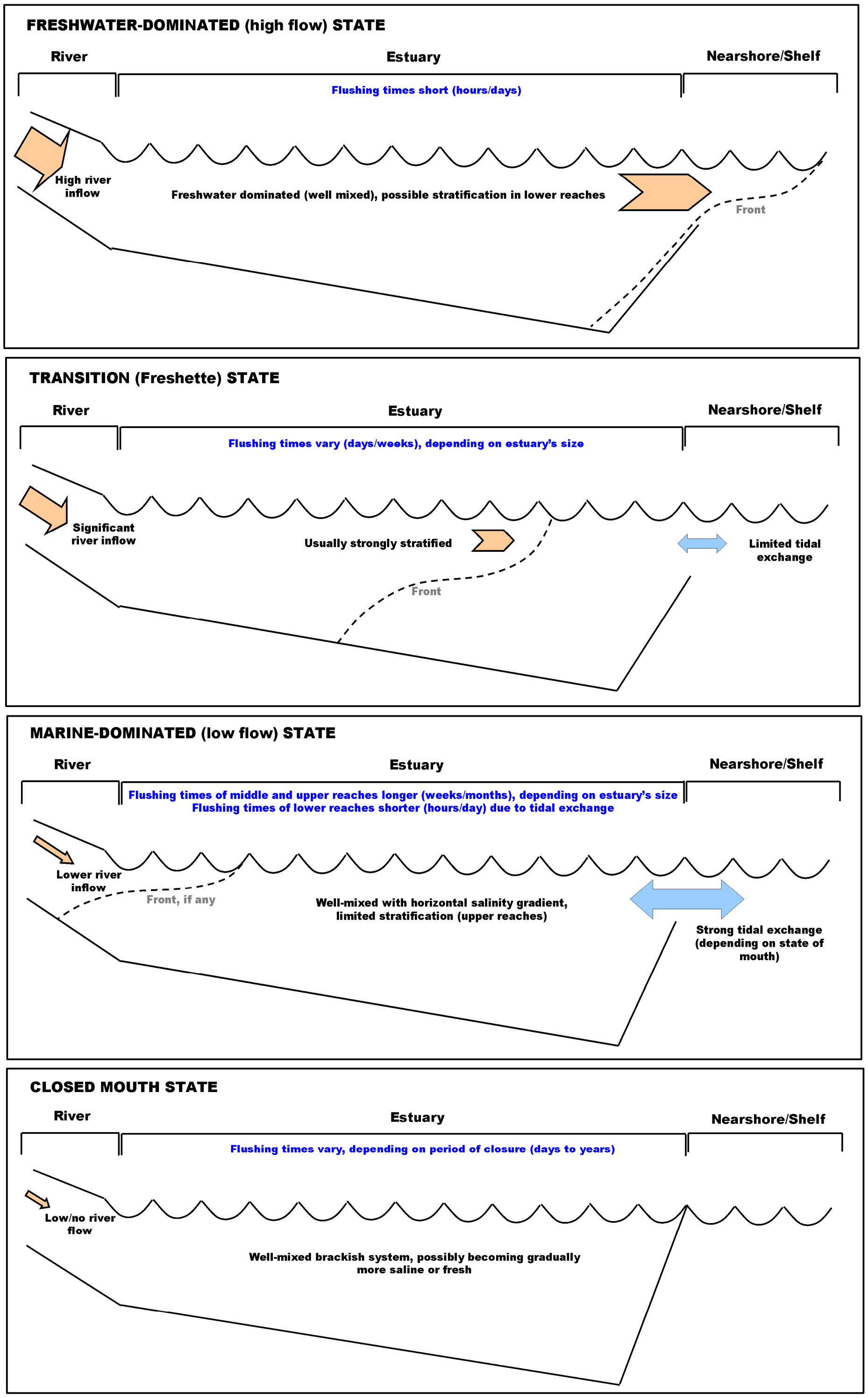
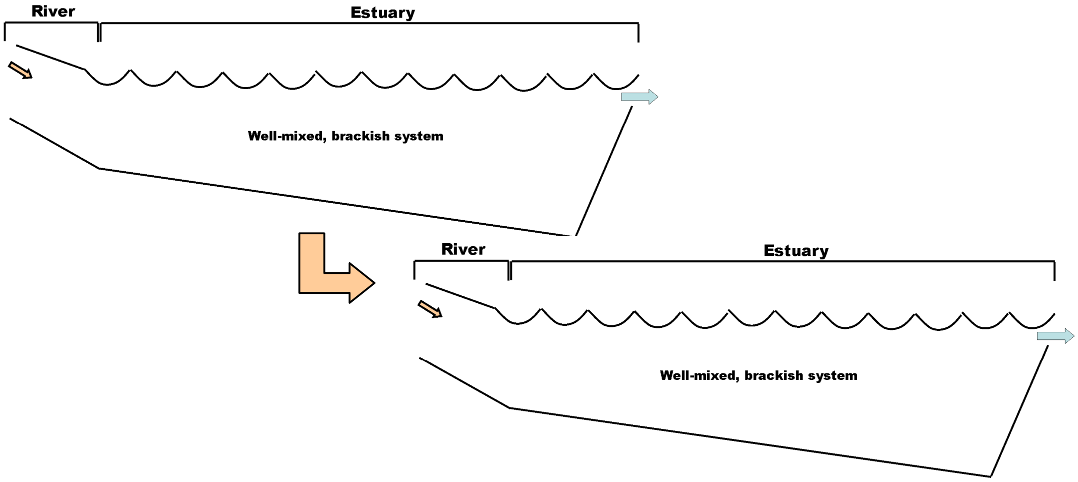


Figure B.4: Conceptual models of the different hydrodynamic states typical of South African estuaries

- *Closed Mouth State,* referring to periods when an estuary is closed off from the nearshore due to the formation of a sand bar across the mouth. Flushing times (or lack thereof) depend on the period of closure, which can range from days to years. For shallower systems, typical of South Africa, this state eventually reverts to a well-mixed system (due to wind turbulence) with no distinct stratification. Systems located in areas with high evaporation rates during low flow periods usually become more saline, even hypersaline, during this state (e.g. in the cool and warm temperate regions). On the other hand, systems where river inflow is balanced by seepage through the berm become increasingly fresh during this state (e.g. systems along the east coast of South Africa, also characterised by lower evaporation rates during the low flow periods) (Perissinotto *et al*., 2004; Snow and Taljaard, in prep).

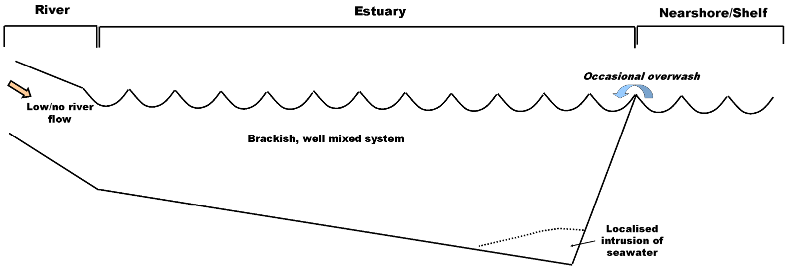
Initial conditions during this state can vary considerably. For example, in larger estuaries, such as Great Brak, the closed state is typically preceded by a Marine-dominated State (CSIR, 1998), while in the smaller systems along the Kwazulu-Natal coast (e.g. Mdloti Estuary), a Transition-type State can still be present at closure. These estuaries usually require much larger river flows to keep the mouth open (because of high sediment supplies and strong wave action) creating a strong freshwater front within the estuary even during the Closed Mouth State, which is more representative of the typical transition state. As there is no significant tidal variation during the closed mouth state, water exchange between intertidal areas and open waters is limited.

A number of the temporarily open/closed systems along the South African coast also show variations within the closed mouth state, namely the 'semi-closed state' and occasional 'overwash of seawater'. In the semi-closed state, reduced river inflow (and high wave action) result in equilibrium between the increase in berm height (the sand bar across the mouth) and the water level in the estuary. This allows water to drain from the estuary, but limits tidal intrusion only to spring high tides At the onset of this state, vertical stratification usually develops as a result of low density freshwater flowing across higher density saline waters. Through entrainment of freshwater into the more saline bottom layer, as well as wind mixing forces, the estuary gradually changes into a homogenous brackish water body:



The duration of the stratified conditions depends on river inflow, the strength of wind mixing forces and the depth of the estuary. For example, a shallow system, subject to strong wind mixing forces, will become a homogenous water body much faster than a deep, wind protected system.

During overwash, seawater spills into the estuary over the berm (e.g. during spring high tides), but without any water exchange through the mouth:



In the case of small estuaries, overwash can result in a significant increase near the mouth.

The hydrodynamic states described above are obviously a simplified representation of the real situation, but are considered to be representative of the general situation encountered in South African estuaries. There may therefore be systems that show some degree of deviation from this conceptual model.

River inflow ranges corresponding to each of the above-mentioned hydrodynamic states are site-specific and will depend on characteristics such as the size and shape (bathymetry) of an estuary, tidal exchange and other physical dynamics controlling the dimensions (depth and width) of the mouth. Therefore, to establish typical seasonal frequency distributions of hydrodynamic states within a particular system, based on seasonal river inflow patterns, it will be necessary to first define the relationship between river inflow and each of these hydrodynamic states, taking into account site-specific physical characteristics.

B.2.2 Nutrient Cycling and Transformation

Since the hydrodynamic status (in terms of flushing times and location of the freshwater front) is a key driver in determining nutrient cycling and transformation processes within estuaries, it should be possible to link dominant nutrient cycling and transformation processes to hydrodynamic states.

The aim here is to propose generic conceptual models of dominant nutrient cycling and transformation processes for different hydrodynamic states. It is recognised that there are systems that may behave differently (exceptions), as a result of site specific features. Also, shifts between states and dominant nutrient processes may be ‘fuzzy’. The aim here is therefore to provide a simple, first phase approach to predicting key nutrient cycling and transformation processes within estuaries, based on hydrodynamic status, and taking into account vegetation types, to assist in identifying focal areas for more detailed scientific assessment.

Conceptual models for dominant nutrient cycling and transformation processes, under each of the (hydrodynamic) states, are discussed below (for details on specific processes refer to Section A).

i. Freshwater-dominated (high flow) State

During this state, nutrient cycling and transformation within an estuary are largely controlled by physical processes, such as <u>flushing and re-suspension</u> (Figure B.5a). Nutrients (both organic and inorganic) entering the estuary from the catchment are flushed out into the nearshore and coastal shelf environments, without any significant transformation happening in the estuary. Depending on the size of the flow event, sediment and (organic) nutrients may be scoured (re-suspended) from the estuary and transported into the nearshore and coastal shelf.

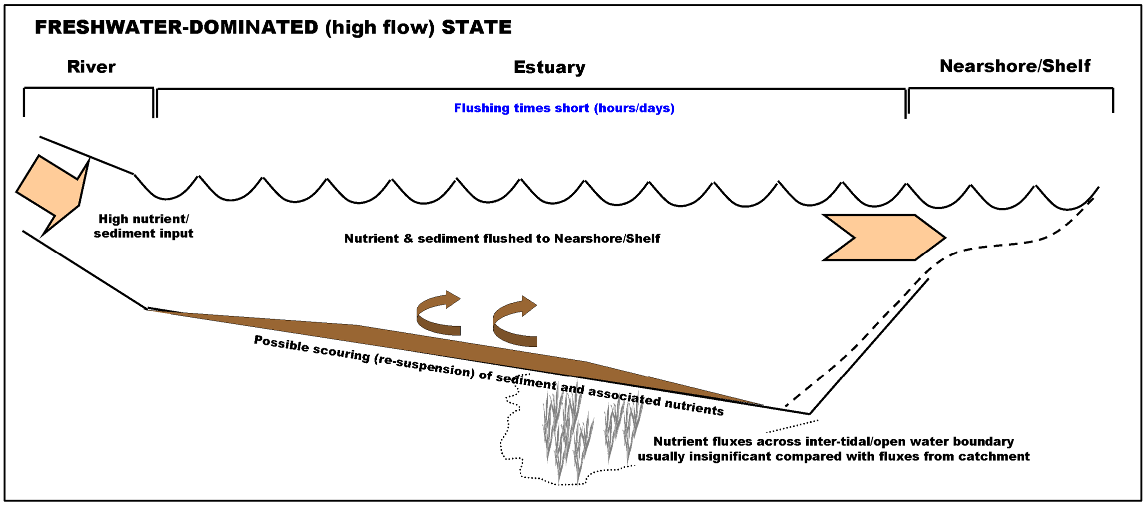


Figure B.5a: Conceptual model of dominant nutrient cycling and transformation processes during Freshwater-dominated State

Biochemical and biological processing usually have little influence on nutrient transformation in the water column, due to rapid flushing times. In addition, high turbidity (low light availability) and strong flows inhibit primary production, both water column (phytoplankton) and benthic (e.g. benthic microalgae and submerged macrophytes) production.

During this state, (nutrient) fluxes across the inter-tidal/open water boundary are probably insignificant compared with those being introduced from the catchment. However, in the case of major floods, large quantities of accumulated organic material (e.g. plant litter) can be washed from intertidal areas into the nearshore and coastal shelf.

Water column nutrient concentrations in the estuary will largely resemble those of the inflowing river water, following a conservative mixing line.

ii. Transition (freshette) State

Although this state may only occur for relatively short periods at a time (i.e. pulse effect), it has important implications for nutrient cycling and transformation within estuaries (Figure B.5b).

Firstly, as a result of decreased turbulence in the vicinity of the freshwater front, catchment-derived sediment and organic material are typically deposited in the estuary (sedimentation). The extent of deposition (both in terms of volume and spatial distribution) will depend on factors such as the timing and size of the flow event (determining suspended and organic material loads), particle size, current velocities within the estuary and the position of the freshwater front. Therefore, although the duration of this state may be relatively short, it is important in determining the potential nutrient supply ('food store') available to the estuary in subsequent states, e.g. Marine-dominated State.

Secondly, salinity, pH and other physico-chemical gradients near the freshwater front increase the potential effect of geochemical processes (e.g. adsorption/ desorption and flocculation) on nutrient transformation.

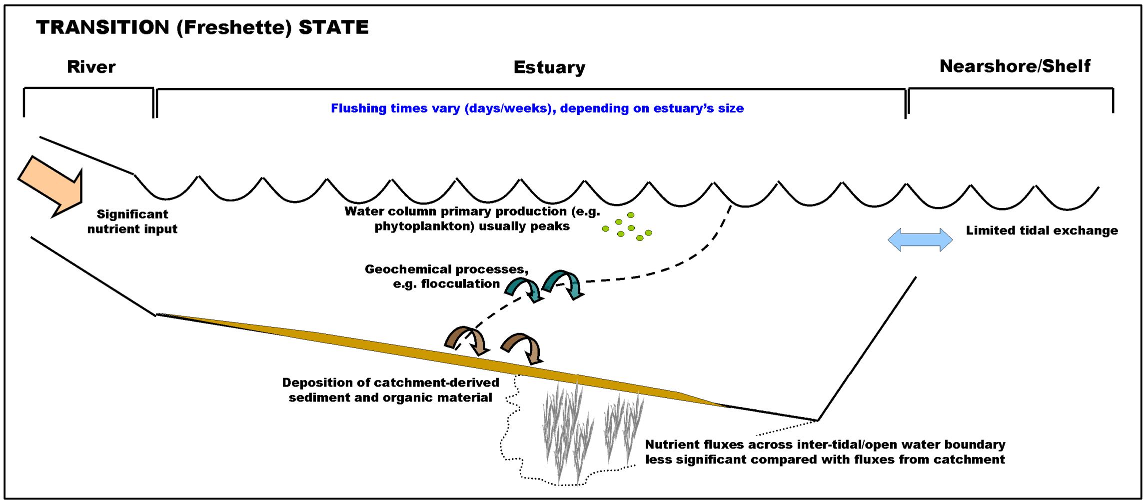
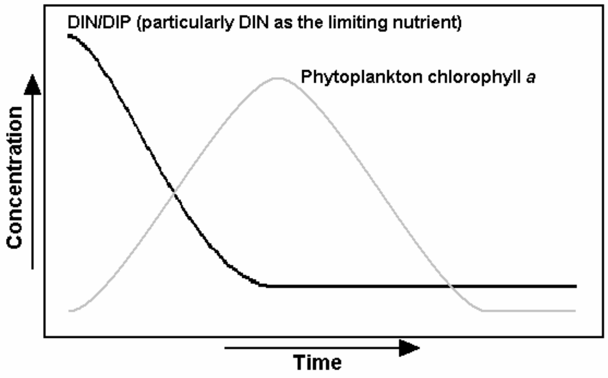


Figure B.5b: ***Conceptual model of dominant nutrient cycling and transformation processes during the Transition State***

Thirdly, many of South Africa's estuaries rely on catchment-derived nutrients to stimulate water column primary production (phytoplankton) (Snow *et al*., 2000a; Gama *et al*., 2005) (Figure B.5b). With the freshwater front being retained within the estuary, a plug of ('lingering') higher nutrient freshwater develops and conditions become conducive to water column primary production. In this regard, Allanson and Read (1995) argued that the salinity gradient at the (freshwater) front, coupled with the phenomenon of hydrodynamic trapping, the flocculation of suspended matter and the availability of nutrients, provide the stimulus for pelagic (phytoplankton) production, and ultimately define the richness of phytoplankton and zooplankton stocks (pelagic production) in estuaries.

Although benthic production and biogeochemical processes may well be significant in terms of nutrient cycling and transformation in sediments during this state, this state is not considered to have a marked influence on water column nutrients due to fairly short flushing times.

During the Transition State, water column nutrient distribution patterns (a proxy of the extent of transformation occurring within the estuary) can vary considerably. For example, at the onset of the Transition State, during the initial freshwater pulse, nutrient distribution patterns may follow a conservative mixing line (i.e. concentrations are mainly determined by the mixing between the fresh and seawater), except nutrients that may be removed from the water column through geochemical process at the freshwater front (e.g. organic nutrients and inorganic phosphorous) (Figure A.6). However, as the state prevails, marked removal of inorganic nutrients (particularly limiting nutrients) is expected with an increase in water column organic matter (as phytoplankton biomass increases) particularly in the vicinity of the freshwater front (Snow and Taljaard, in prep):



Exchange across the estuary-nearshore boundary mainly constitutes seawater moving back and forth with the tide. Tidal exchange may introduce nutrients to the estuary (e.g. upwelling). Inundation of intertidal areas may result in exchange of nutrients across the intertidal/open water boundary. However, during this state, the influence of intertidal areas on open water nutrient dynamics may well be masked by the influence of the freshette (i.e. the catchment).

The Transition State usually reverts into either the Marine-dominated or the Closed Mouth state, although it can move into the Freshwater-dominated State, e.g. in the transition period between the dry and wet seasons. In doing so, nutrient cycling and transformation processes also change towards those of the new state.

iii. Marine-dominated (low flow) State

During this state, a freshwater front may still exist within the estuary, but is usually constrained to the upper reaches. As a result, a 'mini' Transition State may be present, but is not expected to have any wide-scale effects on nutrient cycling and transformation (Figure B.5c).

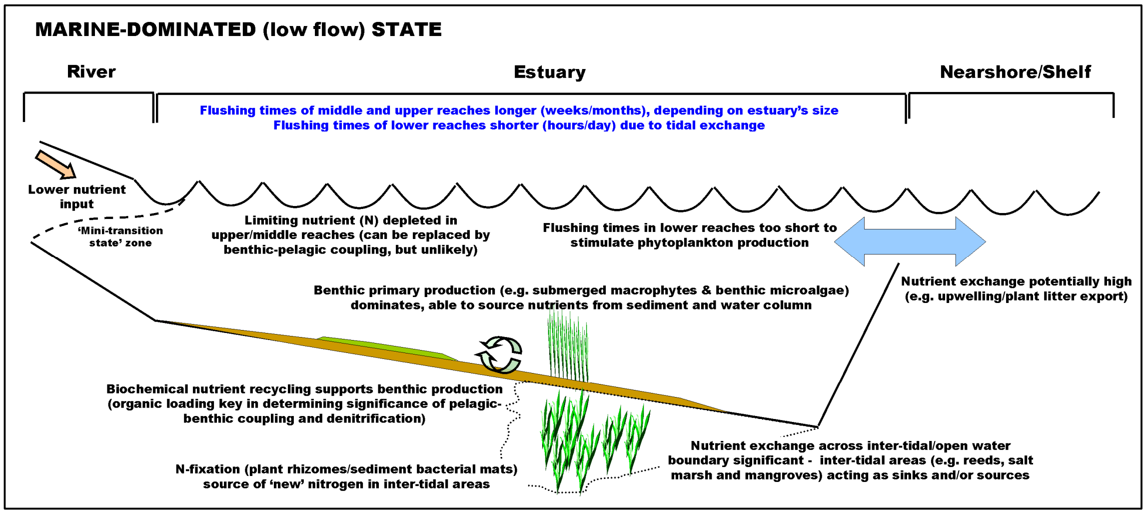


Figure B.5c: Conceptual model of dominant nutrient cycling and transformation processes during Marine-dominated State

More stable sediments (and longer flushing times) favour conditions for benthic activity (e.g. formation of bacterial and microalgal mats), where *in situ* biochemical processes (e.g. remineralisation and N-fixation) become important sources of nutrients for benthic production.

Benthic-pelagic coupling (e.g. sediment remineralisation providing nutrients for water column primary production) can occur, but is largely determined by organic loads at the sediment-water interface (e.g. high organic loads favour strong benthic-pelagic coupling). However, in South African estuaries, primary productivity is usually dominated by benthic producers (e.g. benthic macroalgae and rooted macrophyte) during Marine-dominated States, as was observed in the Kariega Estuary (Allanson and Read, 1995). It is therefore argued that, in most South African systems, sediment organic nutrient stocks (or food stores) are generally insufficient to support large-scale benthic-pelagic coupling through remineralisation. Therefore, when river inflow is low and external water column nutrient supplies are limited, most systems are unable to support significant water column primary production once water column nutrient stocks have been depleted, as during a Marine-dominated State. Exceptions are systems that are artificially enriched. For example, in the Gamtoos Estuary, agricultural return flow was found to maintain fairly high phytoplankton production, even during low flow periods (Snow *et al*., 2000a).

During the Marine-dominated State, tidal exchange is usually strongest and most favourable for (nutrient) exchange across the intertidal-open water boundary. Intertidal primary production (e.g. benthic microalgae, reeds, saltmarsh , mangroves) can thus have a marked influence on nutrient cycling and transformation, also in open waters. Microorganisms colonising intertidal sediments (e.g. bacterial mats) or those associated with the rhizome zones of intertidal vegetation (e.g. reed-beds, saltmarsh and mangroves) can also introduce 'new' nitrogen through fixing atmospheric N into ammonium (N-fixation). During the Marine-dominated State, intertidal areas can therefore act as significant sinks (e.g. reeds) or sources (e.g. leaf litter introduced by mangroves) of nutrients to estuaries and nearshore environments. In a particular estuary, the magnitude of nutrient exchange across the intertidal-open water boundary would largely depend on factors such as the size of the intertidal area, the extent and energy of tidal intrusion and vegetation type.

Certain geochemical processes (e.g. dissolution of Si) may also contribute significantly to nutrient transformation during a marine dominated state. For example, increases in water column DRS concentrations have been observed in a number of South African estuaries (e.g. Kariega and Olifants estuaries) and systems elsewhere during marine dominated states, attributed to dissolution of diatom debris (Allanson and Winter, 1999; Taljaard *et al*., 2006; Eyre and Balls, 1999).

Large submerged macrophyte beds (e.g. *Potomageton*) are also known to release significant amounts of DIP to estuarine waters through foliar release, such as observed in the Swartvlei and Olifants estuaries (Howard-Williams and Allanson, 1981; Taljaard et al., 2006).

Loss of nutrients from estuaries through, for example, denitrification or coupled nitrification-denitrification can also occur, but again this is largely determined by organic loading, where processes may be inhibited by low concentrations (too little fuel) and by very high organic loading (due to anoxia).

During the Marine-dominated State, physical processes (e.g. wind mixing) remain important in terms of re-suspension of deposited material, particularly in shallower areas.

Due to significant tidal exchanges during the Marine-dominated State (depending on mouth status), upwelling may also be an important source of new inorganic nutrients (particularly DIN) to estuaries adjacent to coastal upwelling cells. However, rapid water exchange (short flushing times) in the lower reaches probably prevents this nutrient source from being effectively utilised by water column primary producers (e.g. phytoplankton) and it is largely submerged macrophytes and intertidal communities (e.g. salt marsh) that benefit (Taylor, 1992).

NOTE:

Similar to the freshwater front, a seawater front may also develop within an estuary (along the seaward end) during the Marine–dominated State. In the vicinity of this front, higher nutrient seawater (e.g. introduced during upwelling) may be retained for a long enough time to stimulate water column productivity. Although such production is expected to be limited to a fairly small section of the water column and therefore not to have a marked influence on overall estuarine productivity, this needs to be confirmed through appropriate field measurement programmes.

As proposed above, geochemical, biochemical and biological processes within estuaries can have a marked influence on nutrient cycling and transformation during the marine–dominated state and it is expected that nutrient concentrations in the water column will largely deviate from the conservative mixing line (Figure A.6), either showing removal (e.g. due to biological uptake or denitrification) or release/addition (e.g. remineralisation, desorption, foliage release or dissolution).

The extent to which these processes will influence nutrient cycling and transformation within a particular estuary is strongly linked to site specific flushing times. For example, in smaller systems where tidal flushing is able to maintain fairly short flushing times throughout the estuary, processes requiring longer flushing times may not be as effective. This aspect should therefore be considered when assessing the significance of the above-mentioned nutrient cycling and transformation processes on a particular estuary in the Marine-dominated State.

iv. Closed Mouth State

Similar to the Marine-dominated State, more stable sediments (and longer flushing times) favour conditions for benthic activity (e.g. formation of bacterial and microalgal mats), where *in situ* biochemical processes (e.g. remineralisation and N-fixation) become important sources of nutrients for benthic production (Figure B.5d).

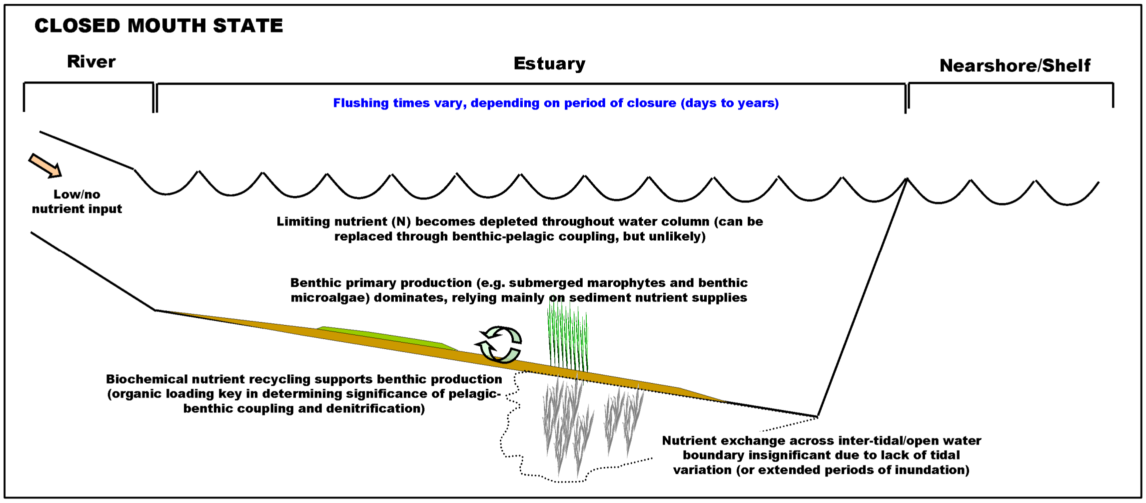


Figure B.5d: ***Conceptual model of dominant nutrient cycling and transformation processes during Closed Mouth State***

Benthic-pelagic coupling (e.g. sediment remineralisation providing nutrients for water column primary production) can occur, but is largely determined by organic loads at the sediment-water interface. However, it is argued that in most South African systems sediment organic nutrient stocks are generally insufficient to support large-scale water column primary productivity through benthic-pelagic coupling, except maybe in artificially enriched estuaries.

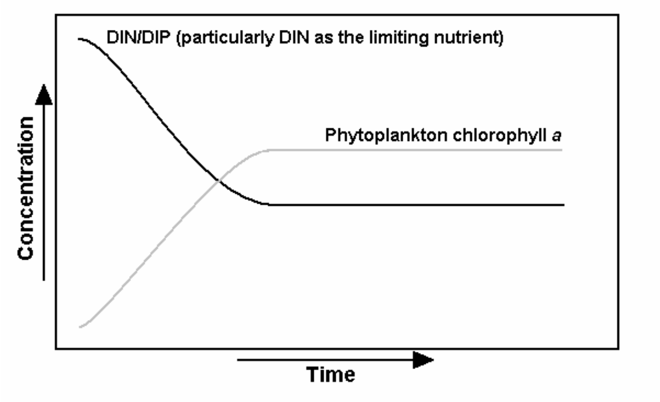
Although intertidal primary production may still be significant, exchange between intertidal areas and open waters is probably insignificant due to a lack of tidal variation. Extended periods of inundation can result in die-back of intertidal vegetation (which may subsequently be a significant source of organic material to the estuary and adjacent coastal ecosystems when tidal exchange is re-established or when the system is flushed).

When the mouth of an estuary closed for an extended period, extensive beds of submerged macrophytes (such as **Ruppia cirrhosa*****) have been known to develop, e.g. Weskleinemonde Estuary, Eastern Cape (Prof J B Adams, NMMU, pers comm.). When the mouth opens and the system becomes tidal again, these extensive beds die back due to a reduction in water level, exposure and subsequent dessication. Through tidal exchange, large quantities of organic matter are then exported to coastal ecosystems. A similar phenomenon was observed in the Bot Estuary, Western Cape (Branch et al., 1985).***

During the closed mouth state, physical processes (e.g. wind mixing) remain important in terms of re-suspension of deposited material, particularly in shallower areas.

The extent to which processes affect nutrient cycling and transformation during a closed mouth state can vary considerably, depending on the period of closure. Also, as discussed earlier, in smaller systems (e.g. those along the Kwazulu-Natal coast), a strong freshwater front can still be present after closure. In such instances, the dominant nutrient cycling and transformation processes usually show a stronger resemblance to those of a transition state.

If a system is in a perched, semi-closed state (i.e. when there is an outflow, but no tidal exchange), water column productivity may also become significant. Flow velocities are usually not very high, with the result that a continuous supply of (river-derived) inorganic nutrients is retained in the estuary for long enough to maintain water column production, as illustrated below (Snow and Taljaard, in prep):



During ‘overwash’, upwelling may also influence nutrient cycling, albeit limited to the lower reaches near the mouth. Here higher nutrient availability, together with sufficient residence time, can stimulate water column primary production in the form of phytoplankton or macroalgal blooms. For example, a peak in phytoplankton production was observed in the Van Stadens Estuary after an overwash event (Gama *et al*., 2005).

It can therefore be expected that, during the Closed Mouth State, nutrient concentrations in the water column are likely to deviate from the conservative mixing line (Figure A.6), either showing removal (e.g. due to biological uptake or denitrification) or release/addition (e.g. remineralisation and nitrogen fixation).

B.3 APPLICATION TO SELECTED CASE STUDIES

Studies addressing the temporal and spatial variation in the nutrient status of South African estuaries, linked to river inflow patterns, were fairly limited up to about 1999 (see review by Allanson and Winter, 1999). However, in 1998 the National Water Act (Act 36 of 1989) was promulgated, which established the concept of aquatic ecosystems having a right to water and that such ecological water requirements had to be determined for South Africa’s water resources, which includes estuaries.

Therefore, since 1999, a number of studies assessing the nutrient status of South African systems in relation to river inflow increased markedly (mostly commissioned by DWAF or the Water Research Commission).

These included studies on the:

- Olifants Estuary (Taljaard *et al.*, 2006)
- Palmiet Estuary (CSIR, 2000)
- Breede River Estuary (DWAF, 2004a)
- Great Brak (CSIR, 1998)
- Gamtoos Estuary (Snow *et al.*, 2000a; Scharler and Baird, 2003; Whitfield and Wood, 2002)
- Kromme Estuary (Scharler and Baird, 2000; Snow *et al*., 2000b; Taljaard *et al*., 2005)
- Mngazana Estuary (0?, 2005)
- Mhlanga and Mdloti estuaries (Perissinotto *et al*., 2004)
- Thukela River Estuary (DWAF, 2004b)
- Maitlands and Van Stadens estuaries (Gama *et al*., 2005).

Most of these studies focussed on the effect of reduced freshwater inflow (i.e. water circulation), but did not necessarily provide quantitative information on the influence of *in situ* geochemical and biochemical processes on nutrient cycling and transformation. A number of studies, however, did investigate links between inorganic nutrients and primary (microalgal) production (Snow *et al.*, 2000a, 2000b; Gama *et al*., 2005).

As a first phase verification of the applicability of the proposed conceptual models for nutrient cycling and transformation, four South African systems (from different biogeographical regions) were selected as case studies, namely, the Olifants (cool temperate), Kromme (warm temperate), Mdloti (sub-tropical) and Thukela (sub-tropical) estuaries.

i. Olifants Estuary (Cool Temperate Region)

The Olifants Estuary is a large, permanently open, linear system (36 km long and covering an area of about 400 ha), receiving river inflow from the Olifants/Doring catchment, one of the largest catchments in South Africa (approximately 49 000 km^2) that falls within a winter rainfall area (Figure B.6). The mouth is situated between a large sand spit on the southern and a rocky bluff on the northern side. The position is fixed in the north by a reef (Morant, 1984). Just upstream of the mouth, the estuary widens to about 400 m, with water depths typically ranging between 3 – 5 m. From about 15 km upstream of the mouth, the estuary becomes narrower (100 – 200 m) and shallower with water depths around 2–3 m. The head of tidal intrusion is approximately 36 km from the mouth at a low-water bridge near Lutzville.

As the Olifants Estuary receives run-off from a large catchment in a winter rainfall area, river inflow usually displays strong <u>seasonal flow distributions</u>. High and low flow periods extend over weeks to months, high flows occurring during winter and low flows during summer (Figure B.2). The marine-dominated (low flow) state is therefore characteristic of the summer months, while the freshwater-dominated (high flow) state typically occurs during the wet winter months. The transition state is usually present only for short periods between the marine-dominated and freshwater-dominated states.

Inorganic nutrient data were collected from the Olifants Estuary during a Transition State (June 1999) when winter rains had just commenced, which introduced a significant pulse of freshwater into the system, as well as during a Marine-dominated State (March 2004) when inflow had been very low (<2 m^3/s) for several months (Figure B.7a).

Salinity-property plots (mixing diagrams) for inorganic nutrients (DIN, DIP and DRS), measured during these surveys, are presented in Figure B.7b.

During June 1999, mixing diagrams show that inorganic nutrient concentrations in the water column tend to follow a conservative mixing line. This is expected at the onset of a Transition State, where biochemical and biological processes may not have had sufficient time to alter concentrations.

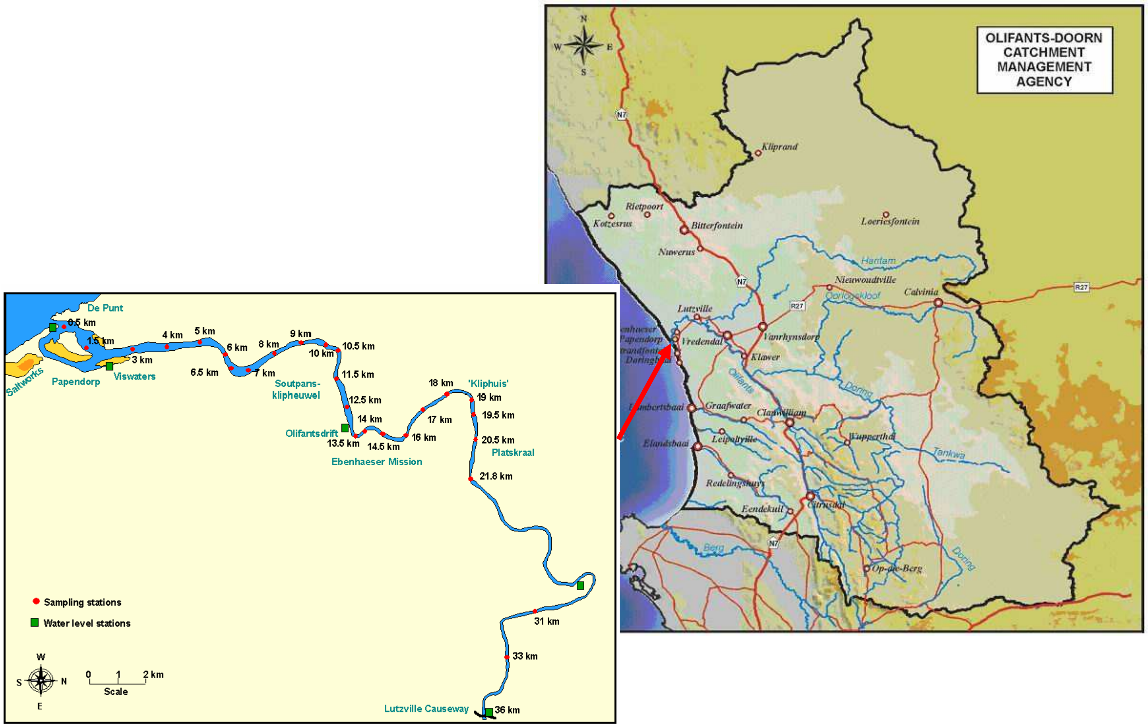


Figure B.6: Map of the Olifants Estuary and catchment

However, in the March 2004 survey, when the systems had been in a Marine-dominated State for several months, inorganic nutrient concentrations deviated markedly from the conservative mixing line, mainly attributed to the longer flushing times when *in situ* (chemical, biochemical and biological) processes can markedly transform nutrients. Although the lower reaches of the system[s?] experienced strong tidal exchange (thus fairly short flushing times), residence time of water in the middle and upper reaches was much longer. Water in the estuary became depleted of DIN with evidence of only limited replenishment through river inflow in the upper reaches (salinity <5 ppt) and tidal intrusion near the mouth (salinity >30 ppt). Dense beds of submerged macrophytes (*Potamogeton*) developed in the upper middle reaches. Low flow velocities and improved light availability, associated with an extended low flow period, created this favourable habitat for plant growth. Biological uptake in this region of the estuary probably contributed to the depleted DIN status in the water column, acting as a nutrient sink.

Where DIN concentrations clearly indicated nutrient removal during the March 2004 survey, the opposite was observed for DIP (Figure B.7b). Although reasons for the introduction of DIP to the water column were inconclusive, it is likely that geochemical processes (e.g. desorption of P from particulate phases) and/or foliar release (associated with the dense *Potamogeton* beds) were contributing factors.

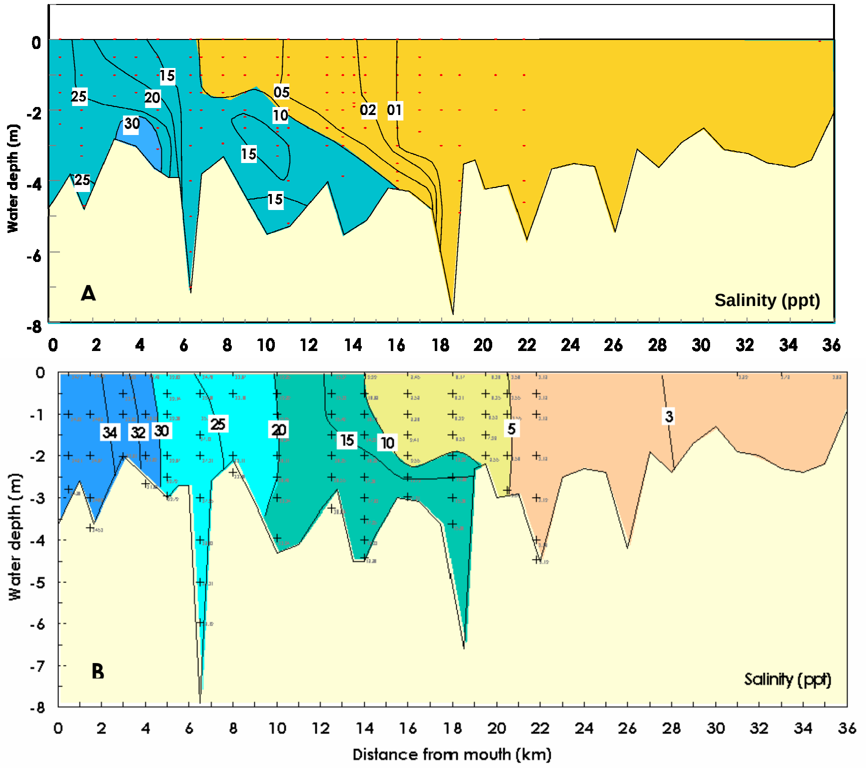


Figure B.7a: ***Salinity distribution patterns measured in the Olifants Estuary during A) Transition State (June 1999) and B) Marine-dominated State (March 2004)***

DRS also diplayed non-conservative behaviour, with a maximum concentration at around 15–20 ppt. Similar features have been observed in three Australian (tropical) and three Scottish (temperate) estuaries, but in the low salinity range (Eyre and Balls, 1999). These maxima were mainly attributed to dissolution of diatom skeletons at the sediment/water surface.

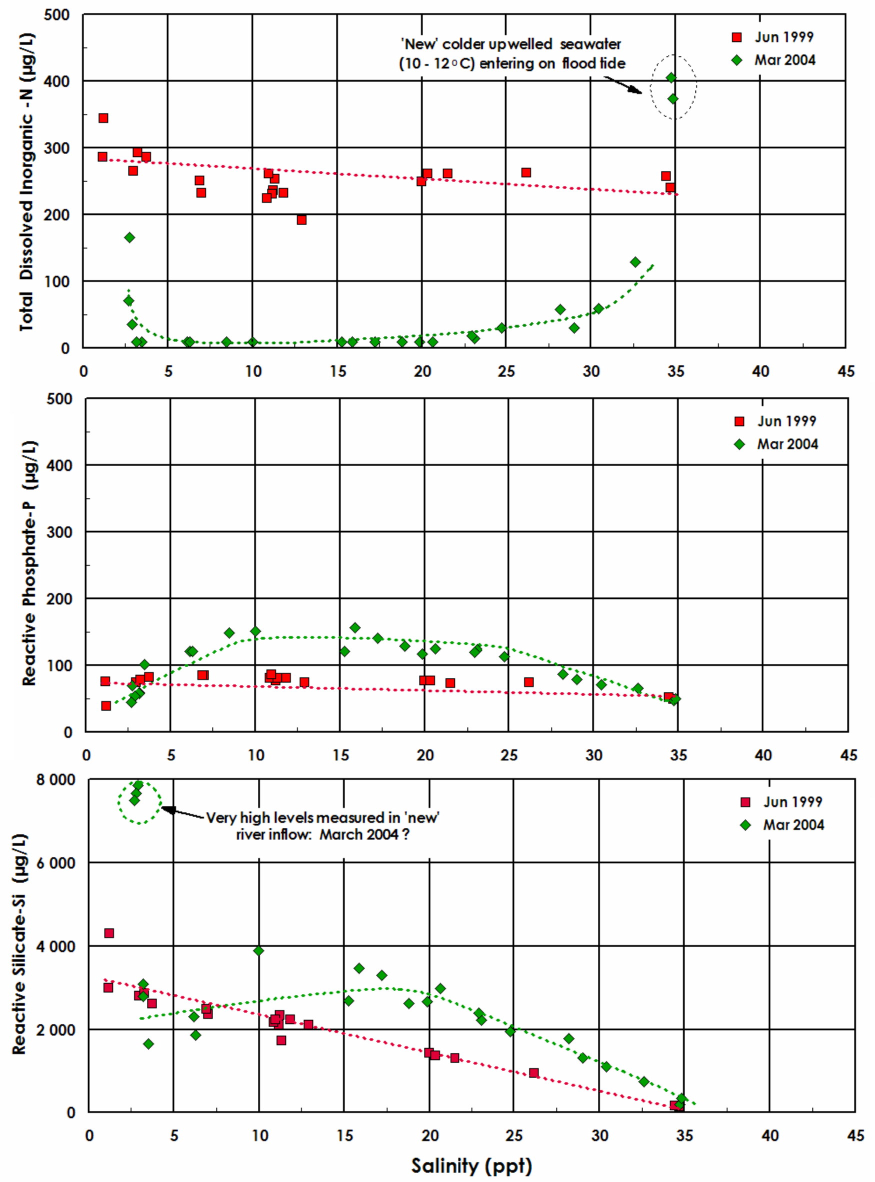


Figure B.7b: Mixing diagrams for inorganic nutrients measured in the Olifants Estuary (taken from Taljaard et al., 2006)

ii. Kromme Estuary

The Kromme Estuary is a permanently open system, relatively narrow (average width of approximately 80 m) that extends 14 km upstream of the mouth to a rocky sill forming the tidal head (Figure B.8). The Kromme drains a fairly small catchment, approximately 936 km^2. The estuary also receives run-off from tributaries such as the Geelhoutboom River some 7 km upstream, but these are not considered to be significant freshwater contributors to the system (Scharler & Baird, 2000).

The lower reaches of the estuary (up to about 5 km from the mouth) are relatively shallow (water depth about 1.5 m) with a sandy bottom substrate. Upstream of this, the estuary deepens to between 3-5 m with current velocities being generally lower than 0.3 m/s (values of the order of 1 m/s are common in the mouth area). Extensive saltmarsh covers the banks of the estuary in the middle and lower reaches, while the channel meanders between vegetated cliffs in the upper reaches. A marina has been developed on the west bank near the mouth.

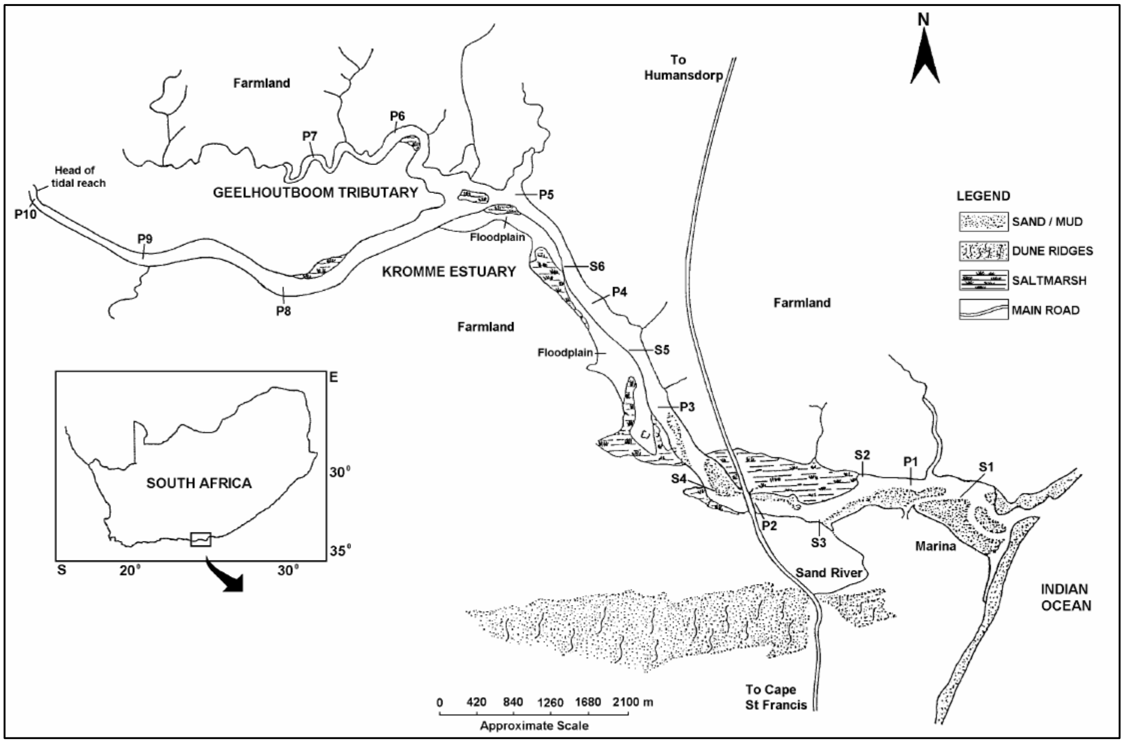


Figure B.8: Map of the Kromme Estuary (after Wooldridge and Callahan, 2000)

The Kromme catchment falls within a bi-modal rainfall area, peaking in autumn and spring. As a result of its fairly small catchment size, high flows occur as high flow events, rather than seasonal high flow periods, even under the Reference (natural) Condition. Two large dams (Churchill and Mpofu dams) on the Kromme River have largely modified river inflow to the estuary, which now only receives freshwater pulses when the dam overflows or when water (2 x 10^6 m^3) allocated for ecological purposes is released. The Kromme Estuary therefore mostly exists in a Marine-dominated State, occasionally shifting into the Transition State (triggered by a freshwater pulse). The system seldom reaches Freshwater-dominated state (even under the Reference condition), the combined effect of the hydrological regime and the size and shape of the estuary (deep upper reaches).

Studies conducted by Scharler and Baird (2000) and others found that, during a freshwater release (2 x 10^6 m^3), a pulse of freshwater was introduced to the estuary, mimicking a Transition State. However, due to the initial condition (salinities being 35 ppt throughout), as well as the shape of the estuary (deep basin near the head), the freshwater front took the shape of a freshwater surface layer overlying saline bottom waters (Figure B.9a).

The pulse of freshwater introduced slightly higher DIN concentrations to the estuary, but DIP concentrations remained low, resulting in N:P ratios being persistently higher than the Redfield ratio (16:1) Because the Kromme catchment consists of Table Mountain Sandstone, nutrient concentrations in river inflow are not expected to be high (Reddering, 1980), although the low DIP concentrations were probably also linked to DIP being trapped in upstream dams (e.g. adsorption onto settled sediment particles).

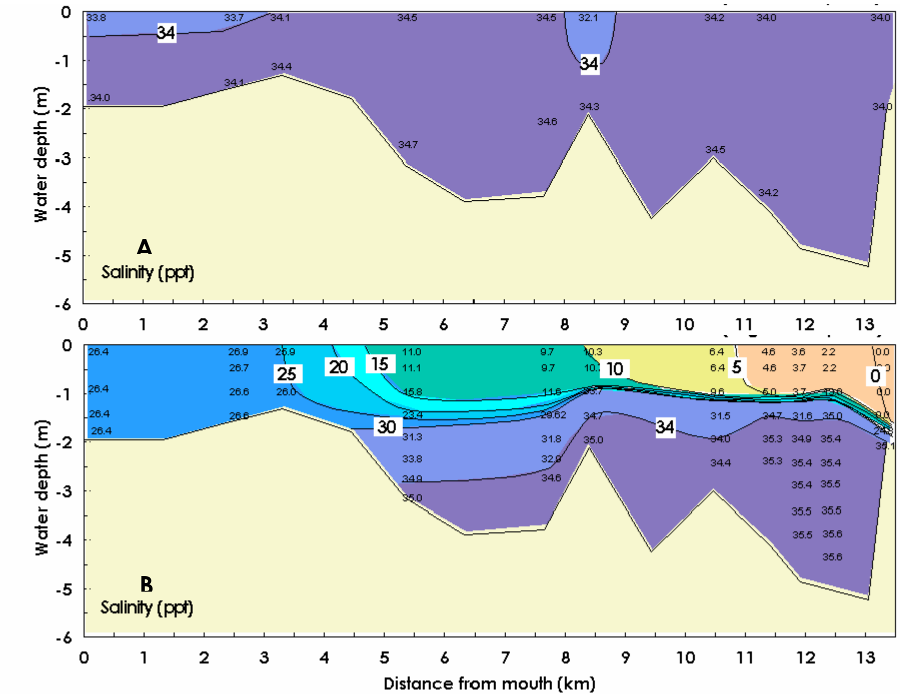


Figure B.9a: Salinity distribution patterns measured in the Kromme estuary during A) Marine-dominated State and B) Transition State (mimicked by a freshwater release in November 1998

Just after the release, rapid removal of DIN from the estuary's water column was attributed to phytoplankton production, but because the event was short-lived, the increase in water column primary production was much less than expected. Interestingly, the response was detected in terms of significant increases in diatom and flagellate numbers and not as a marked increase in chlorophyll a concentrations (Snow *et al*., 2000b). Other possible factors contributing to the limited production included: P limitation (N:P ratios were consistently lower than the Redfield ratio for optimal growth – 16:1) and nutrient starvation of primary producers (marked reductions in 'new' nutrient inputs – through river inflow - diminished estuarine standing stocks) (Scharler and Baird, 2000). Interestingly, intertidal benthic microalgal production also increased (although not significantly) in response to the freshwater pulse, but not the subtidal production. The latter was attributed to strong stratification that prevented higher nutrient surface water from reaching the sediments (Snow *et al*., 2000b; Snow and Adams, 2006).

During its Marine-dominated state (no or very low river inflow), the Kromme Estuary changes into a near homogenous water body, where salinities typically range between 35 and 39 ppt (depending on the duration of low/no flow conditions and evaporation rates, hypersaline condition can develop in the middle and upper reaches). Studies showed that, during this state, water column DIN and DIP concentrations become depleted (< 50 µg/ℓ and <10 µg/ℓ, respectively) (Taljaard *et al*., 2005). These depleted nutrient concentrations support the suggestion by Scharler and Baird (2000) that the standing stock of bacteria and micro-zooplankton in this estuary is probably too low (possibly also low organic loading) to provide sufficient quantities of recycled nutrients during periods when the main nutrient supplier (the Kromme River) is 'switched off'. This suggestion is also supported by low water column primary productivity, measured during Marine-dominated States on other occasions (Baird and Heymans, 1996; Snow *et al*., 2000b).

The role of other benthic primary producers, e.g. submerged macrophytes (*Zostera capensis*), saltmarsh and reed-beds, in nutrient cycling and transformation in the Kromme Estuary has not yet been investigated.

Likewise, the role of upwelling in nutrient cycling and transformation has also not been investigated for the system. Although the sea gains an importance as a nutrient source when freshwater inflows are restricted, Scharler and Baird (2000) do not believe that such input would sustain viable plankton populations in the Kromme Estuary. Tidal flushing in the lower reaches of the system is probably also too strong to sustain significant phytoplankton populations. However, the sea may well be a significant nutrient source for submerged macrophytes and intertidal saltmarsh , particularly during the Marine-dominated State, as was observed in the Kariega Estuary (Taylor, 1992).

iii. Mdloti Estuary (Sub-tropical Region)

The Mdloti Estuary is a small, temporarily open/closed estuary along the Kwazulu Natal east coast. The catchment is relatively small (about 484 km^2) and falls within a summer rainfall area (Figure B.10). River flows to the estuary have been substantially modified by the Hazelmere Dam and effluent from two wastewater treatment works discharges (Perissinotto *et al*., 2004).

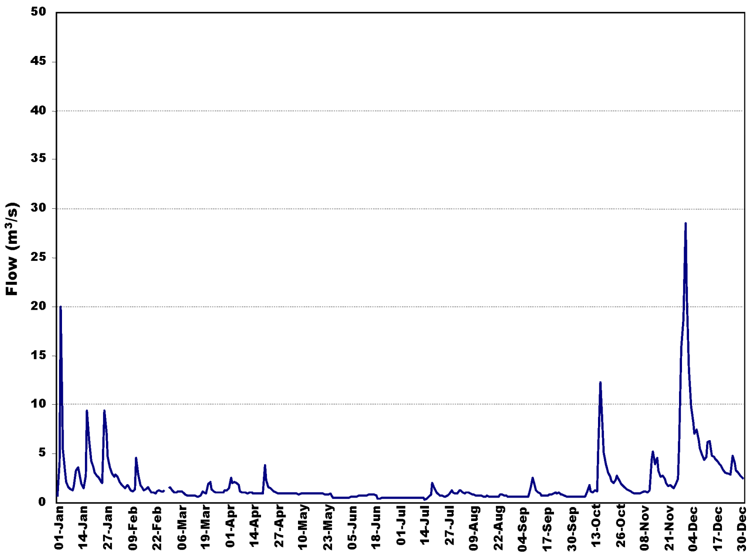


Figure B.10: ***Illustration of typical seasonal river inflow patterns to Mdloti Estuary (Daily flow of 1997) (www.dwaf.gov.za/hydrology)***

The estuary is a small and shallow system (about 2 km long covering an area of about 80 ha) with a perched mouth, resulting in relatively small tidal exchange during the open phases (Figure B.11).

During the low flow season (in this case winter), the system is generally in a Closed Mouth State, while during the wet season (summer), the system fluctuates between a Freshwater-dominated State and Closed Mouth/Transition State. Because the mouth is perched (limiting tidal exchange) and wave action along the coast is strong (requiring significant river inflow to maintain an open mouth), the Marine-dominated State generally does not occur in this system. For these same reasons, the estuary is in a Transition-type State (a strong freshwater presence is evident in the system) even after closure. The Mdloti Estuary also functions in the semi-closed state and receives occasional overwash during the Closed Mouth State (CSIR, 2002).

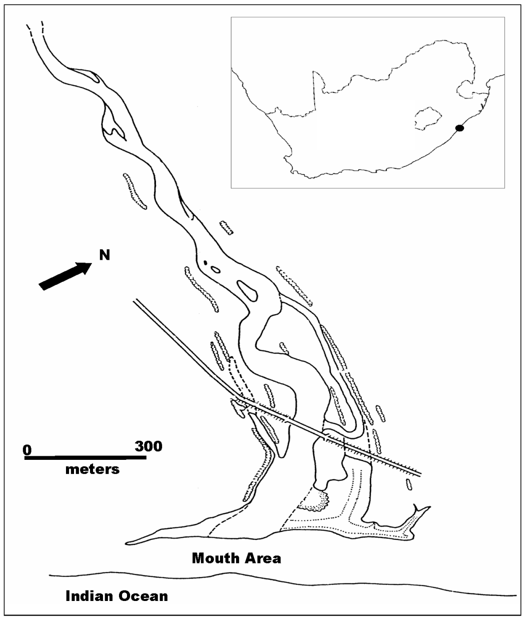


Figure B.11: Map of the Mdloti Estuary (Source: R Perissinotto)

Studies conducted in the Mdloti Estuary during 2002/2003 showed a marked difference in DIN and DIP concentrations between open (Freshwater-dominated) and closed (Closed Mouth/Transition) states, where concentrations were normally 1.5-10 times higher during the open state than the closed state (Perissinotto *et al*., 2004). In contrast, lowest water column productivity (phytoplankton production) was measured during open states and peaked during closed states. Water column production is expected to be low during Freshwater-dominated States, particularly in these small systems, due to short flushing times. Because the estuary usually closes whilst still in a Transition State, river nutrients are retained for long enough periods to stimulate significant water column primary production during this state. Although lowest DIN & DIP concentrations were measured during closed states, it is likely that this was the result of phytoplankton production depleting water column nutrients that may well have been present at the time of closure.

Higher DIN and DIP concentrations measured in the sediments of the Mdloti Estuary during the Closed Mouth State (compared to periods when the mouth was open) were attributed to remineralisation within the sediments that became more important after closure (Perissinotto *et al*., 2004). Benthic microalgal production was also greater during the Closed Mouth State, probably the result of more stable sediment conditions and nutrient availability.

iv. Thukela Estuary (Sub-tropical Region)

The Thukela Estuary is a small (about 6 km long, covering an area of about 60 ha during low flow periods) and shallow (average depth <1.5 m) system (Figure B.12), but with a large catchment area (approximately 29 000 km^2) (DWAF, 2004b). River inflow usually displays strong <u>seasonal flow distribution</u>, with high and low flow periods extending over weeks to months, high flows occurring during summer (Figure B.2).

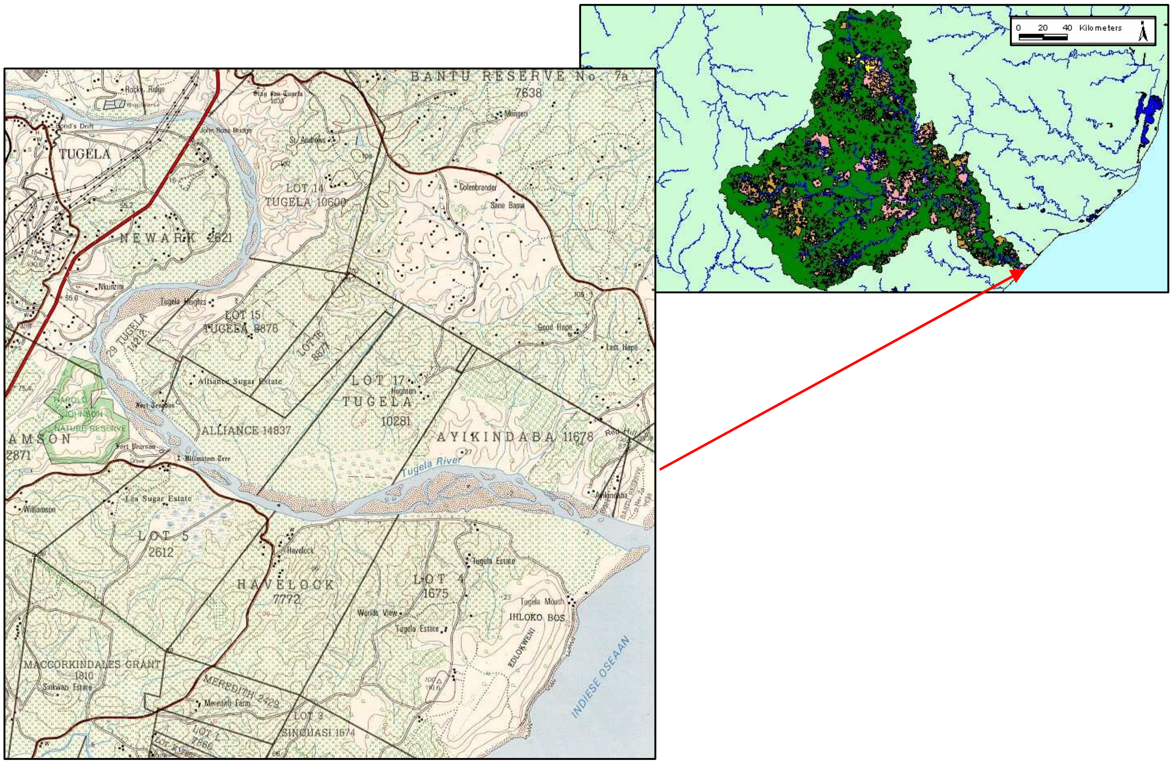


Figure B.12: Map of the Thukela Estuary and its catchment (DWAF, 2004b; www.environment.gov.za/soer/estuary)

Strong wave action and high sediment availability require a significant river flow to maintain an open mouth (~ 5 m^3/s) and the Thukela, being a small system, therefore seldom (if ever) experiences the Marine–dominated State. In the open phases, the estuary is mainly in a Freshwater-dominated (high flow periods, e.g. summer) or Transition State (lower flow periods, e.g. winter). The estuary closes occasionally during low flow periods, but probably remains in a Transition-type State when the mouth closes, similar to the Mdloti Estuary.

During the Freshwater-dominated State, flushing times are very short and the estuary primarily becomes a conduit for river-derived nutrients and suspended matter to the nearshore and coastal shelf (Figure B.13).

In August 2001, inorganic nutrients and primary production measurements were taken in the Thukela Estuary, when the system was in a Transition State (open) (Figure B.14a). During this study, DIN concentrations were low (<100 µg/ℓ and mostly present as Ammonium-N). DIP and DRS concentrations seemed to follow a conservative mixing line, although data in the middle salinity ranges were limited (Figure B.14b).

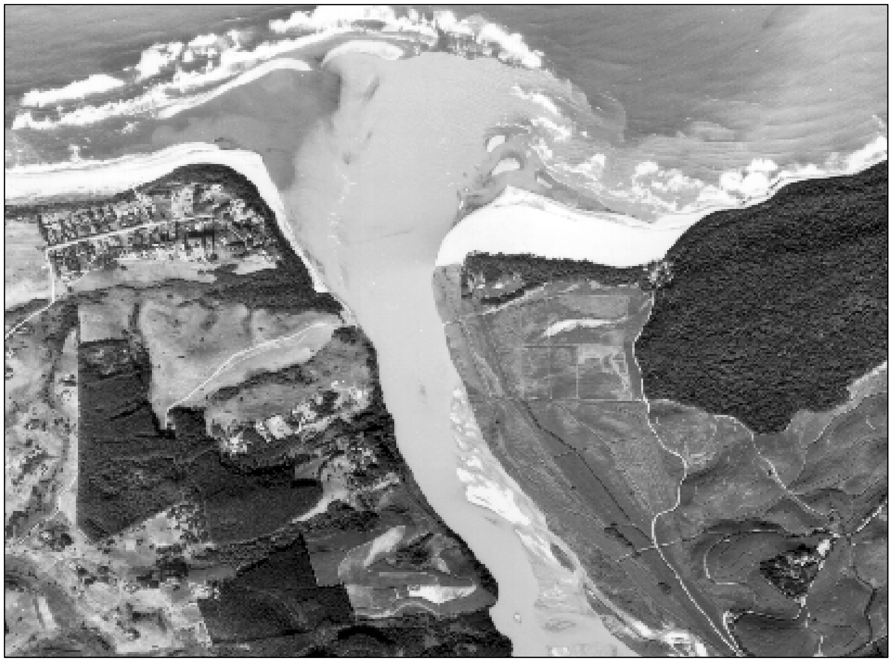


Figure B.13: Thukela Estuary in a Freshwater-dominated State (May 1976) (taken from DWAF, 2004b)

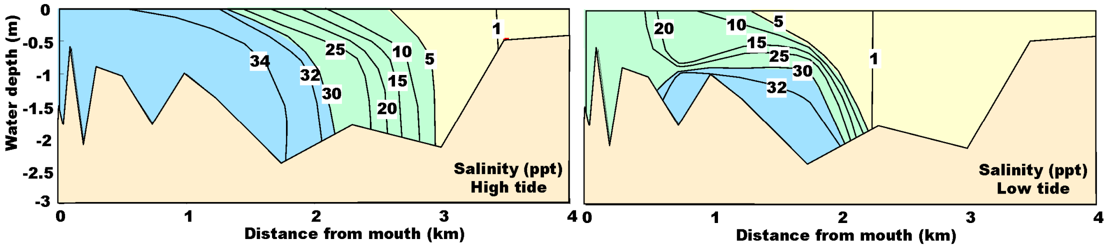


Figure B.14a: Salinity distribution patterns measured in the Thukela Estuary in August 2001 (Transition State)

Water column primary production (phytoplankton) showed peak concentrations in the middle reaches (between 1.25 and 3 km upstream of the mouth), coinciding with the position of the freshwater front at this time (Figure B.14a), with highest concentrations being measured at water depths between 0.5 and 2 m (~120 µg/ℓ chlorophyll a) (DWAF, 2004b). Flushing times were sufficiently long, even in this fairly small system, to stimulate water column production.

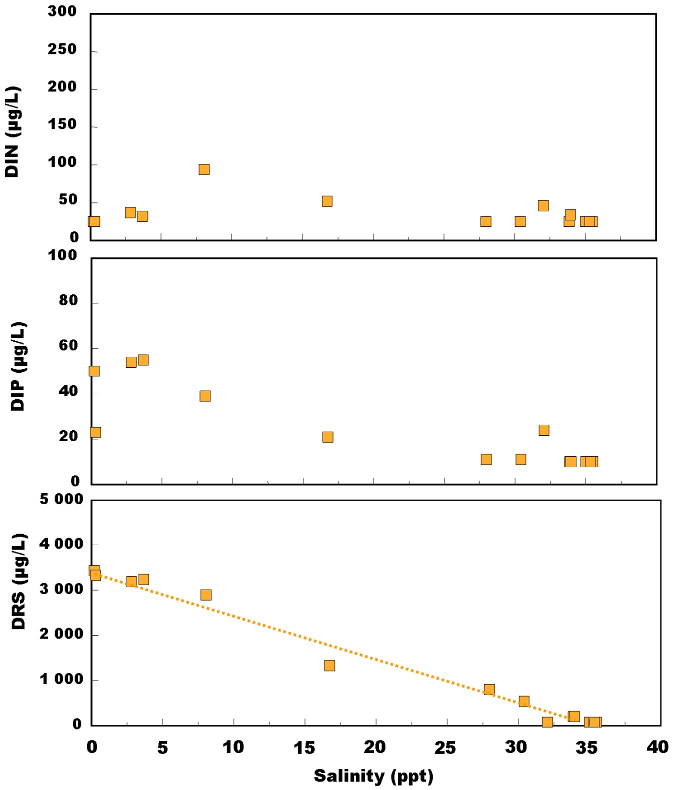


Figure B.14b: Salinity-property plots for inorganic nutrients measured in Thukela Estuary (August 2001)

Based on this preliminary verification, using four South African estuaries from different geographical regions as case studies, it appears as if most of these systems generally fit within the conceptual models proposed for nutrient cycling and transformation under different hydrodynamic states.

However, the measurement programmes undertaken in the case study estuaries were not necessarily designed to properly verify these types of models. A measurement programme is therefore proposed in Section C, specifically aimed at verifying these models, using the Kwazulu Natal region (east coast) as study area.

SECTION C

RECOMMENDATIONS FOR FUTURE RESEARCH

Key components that are required to quantify (and predict) the influence of catchment fluxes on nutrient cycling and transformation and primary productivity in coastal ecosystems can be summarised as:

i. Temporal variation of catchment fluxes across the river-estuary boundary, including river flow distribution patterns, as well as material fluxes such as sediments, organic matter and inorganic nutrients

ii. Temporal (and spatial) variation in nutrient cycling and transformation processes (including primary production) within estuaries that potentially influences fluxes across the estuary-nearshore and coastal shelf boundary

iii. Nutrient cycling and transformation processes (including primary production) within river fronts (or plumes) in nearshore or coastal shelf systems, and the ripple effect on primary productivity of these systems, focusing on a regional scale.

This report primarily addressed (ii), providing a review of the key processes, as well as conceptual models on dominant nutrient cycling and transformation processes in South African estuaries under different hydrodynamic states (that are, in turn, linked to different river inflows). In doing so, it provided a first phase (qualitative) mechanism to predict dominant nutrient cycling and transformation processes within estuaries, as well as the scales of nutrient fluxes across the estuary-nearshore and coastal shelf boundary.

Estuarine vegetation also plays an important role in nutrient cycling and transformation, in addition to a number of other *in situ* physical and geo- and biochemical processes. Although there have been studies on the role of estuarine vegetation types on nutrient cycling and transformation in South African estuaries, these have only been conducted on selected systems and vegetation types (see Section B). However, to be able to confidently extrapolate (quantitatively) those results to other South African estuaries requires further verification. In undertaking such investigations, the CSIR needs to collaborate with other centres of expertise (e.g. Nelson Mandela Metropolitan University, Universities of Stellenbosch and Natal, and the Oceanographic Research Institute) to further develop and explore research questions that would provide improved understanding of such matters.

This report also touched on (iii), providing a brief introduction to nutrient cycling and transformation processes studied in offshore river plumes worldwide. This aspect has, however, not received much attention in South Africa and is an area that needs further research to be able to assess the importance of catchment fluxes to coastal ecosystem production.

To solve (i), what is basically required is routine long-term monitoring of river flow and biogeochemical variables, at appropriate time scales and as close as possible to the head of estuaries (i.e. where it would be best representative of fluxes to the estuary). DWAF, as part of its national water quality management programme, does have continuous flow recorders and water quality monitoring stations situated on a large number of rivers. However, few of these stations are located at the head of estuaries.

To accurately assess or predict temporal variation in such fluxes requires long-term data sets, which are not easily provided through short-term monitoring programmes. As a result, second best options are typically applied, such as extrapolating existing data (from stations further upstream) or simulating the data using hydrological models. It is therefore recommended that DWAF seriously consider extending continuous flow gauging and long-term water quality monitoring programmes to include sites representative of inflows to estuaries.

As part of a CSIR research project to evaluate the influence of catchment fluxes on regional functionality of coastal ecosystems (both in terms of the coastal-parallel and land-to-sea vectors) (using the KwaZulu Natal coast as study area), the following is recommended *re* addressing nutrient cycling and transformation processes:

- Assess the scale and magnitude of inorganic and organic nutrient fluxes across the river-estuary boundary of selected estuaries in the KZN study area, using existing data from DWAF's river gauging and water quality monitoring programme (www.dwaf.gov.za/hydrology). Based on the outcome of this evaluation, recommendations for future monitoring and research requirements will be proposed.
- A measurement programme needs to be designed and implemented to verify the conceptual models proposed for nutrient cycling and transformation (this report), focusing on systems within the KZN region. This will be explored as a separate sub-project.

  Ideally, measurement programmes should include a number of different systems (e.g. with varying catchment areas and different estuary types that support different vegetation types), sampled under different hydrodynamic states (e.g. Freshwater-dominated, Transition, Marine-dominated and Closed Mouth states). As this may be very costly (both in terms of time and money), it is recommended that at least the following scenarios be investigated:

  - High flow period (summer) when systems are likely to be Freshwater-dominated or in a Transition state
  - Low flow period (winter) when systems are likely to be either in a Marine-dominated or Closed Mouth State.
- A measurement programme to investigate actual nutrient and transformation processes (including primary production) linked to river fronts in nearshore and coastal shelf environments along the South African (east) coast needs to be designed and implemented so as to better understand these processes within the southern African system, as well as to calibrate and verify prediction tools.
- A (numerical) modelling approach needs to be developed to quantify and predict nutrient cycling and transformation processes and production in coastal systems (inclusive of estuarine, nearshore and coastal shelf ecosystems), capable of evaluating catchment flux scenarios on a regional scale (including multiple catchments). Important aspects that need to be explicitly addressed are the temporal and spatial scales of boundary conditions and input parameters to successfully apply such an approach (this aspect still needs further exploration)

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