

**DEPARTMENT OF OCEANOGRAPHY  
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**DUIWENHOKS RIVER  
FIELD REPORT AND LOICZ BUDGET**



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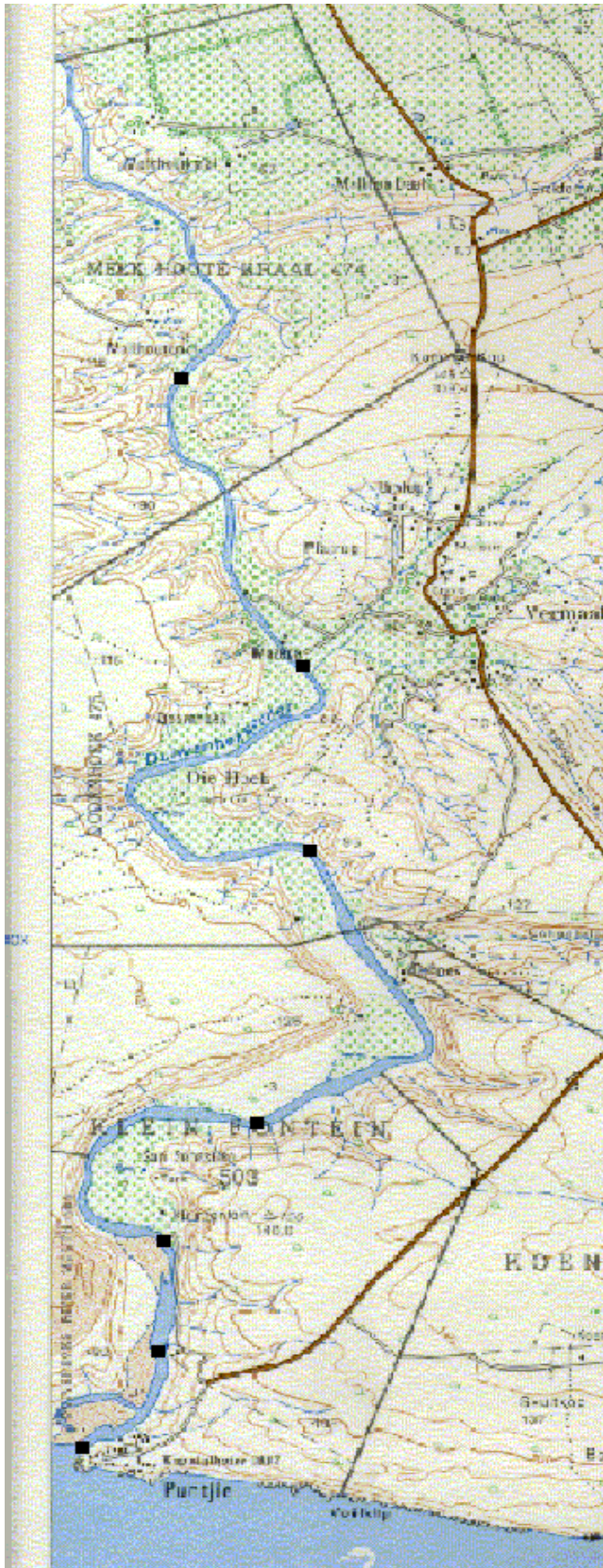
# **DUIWENHOKS FIELD REPORT**

## 1.1 INTRODUCTION

The Duiwenhoks River estuary was investigated during May 2002, it is located on the south-east coast of South Africa at 34°22'S, 21°00'E (see figure 1). The river originates on the southern slopes of the Langeberg Mountains and meanders for 82.7km until it reaches the coast at Vermaaklikheid, where it cuts through calcarenite, a highly erosive limestone, forming a steep canyon-like valley, which then opens into a steep sided basin at the coast. The only major town the Duiwenhoks River passes through is Heidelberg, roughly 40km upstream of the mouth.

The catchment (790km<sup>2</sup>) of the Duiwenhoks is an area that receives rainfall almost equally each season, with minor peaks in autumn and spring. For this study therefore, we have described the Duiwenhoks system as consisting of only one season. The mean annual precipitation in the region is about 774mm, calculated over a period of three years (1999-2002) and the mean annual evaporation, calculated over the same period is 1 104mm. The average flow rate of the river is 211 392 m<sup>3</sup>.day<sup>-1</sup>, ranging from 1.6416 x 10<sup>6</sup>m<sup>3</sup>s<sup>-1</sup> in March to 2.45376 x 10<sup>4</sup>m<sup>3</sup>s<sup>-1</sup> in June. These flow rates are proportional to the monthly rainfall averages. Average daily maximum temperatures range from 22°C in January to 16°C in July, while the daily average minimum temperatures are 15°C and 7°C respectively.

Most of the catchment area consists of privately owned farms: citrus and dairy farming dominate the upper catchment, while wheat is the major crop on the lower catchment. In the upper catchment, about 8kms upstream of Heidelberg, is the Duiwenhoks Dam. It was constructed in 1965 and has a capacity of 5.76 x 10<sup>6</sup> m<sup>3</sup>. The dam supplies water for irrigation and potable water for man, sheep and cattle in the regions of Heidelberg, Askraal, Witsands and a farming community that covers an area of 147 000ha. Many private dams exist on farms in the catchment area, but the construction of such dams is difficult to monitor. The increasing number of dams in the



**Figure 1.** The Duiwenhoks River Estuary (left) and its position on the South African coastline (below). The stations are marked with black bullets. The northernmost station marked on this map is 'Glory-be'. 5 stations are situated to the north of this position at approximately 1km intervals.



catchment area is likely to affect the mean annual runoff and therefore fresh- water input into the river and estuary.

The estuary is approximately 11km long and the surface area is 0.889km<sup>2</sup>, it is a fairly shallow estuary with an average depth of 1.89m. The average flushing time of the estuary, based on a volume of 1.68021 x 10<sup>6</sup>m<sup>3</sup> and an average flow rate of 211 392 m<sup>3</sup>.day<sup>-1</sup> is 7.95 days. The estuary basin is dominated by sandbanks, which are highly variable due to the longshore currents, tidal currents, river floods and aeolian sand movement.

The Duiwenhoks estuary is a permanently open system with a constricted tidal inlet. A rocky promontory with a heavily eroded subtidal platform characterizes the eastern bank of the estuary. The western bank is a narrow, sandy beach at the foot of the steep limestone plateau that extends from Witsands to the mouth of the Duiwenhoks. Partly vegetated hummock dunes are present, ranging from 5-10m in height in the backshore and 20- 30m in the upper backshore region.

Westerly to south- westerly winds are prevalent in the region of study, particularly between winter and spring. Wind velocities are typically high, with observed daily average maximums of 15m.s<sup>-1</sup>. Second in order of frequency, but with maximum average speeds of 18m.s<sup>-1</sup> are the easterly to south- easterly winds, which predominate during the summer. These winds have an integral role in the aeolian transport of sediment (and beach dynamics) due to their strength, and the fact that they occur most frequently in summer when the sands are dry. These winds blow sand from a sparsely- vegetated dune-field 1km upstream of the mouth into the estuary. The volume of dune-sand entering the estuary can be as much as 22 500m<sup>2</sup> and its removal relies on the ebb- tide and flash-floods.

From studies carried out on 1985, it has been shown that the outgoing tide has only about 60% of the speed of the incoming tide. The outgoing tide therefore lasts for 7 hours as opposed to the 5.5 hours for the incoming tide, as a result there is a net ingress of marine sediment. The system is in approximate sedimentary equilibrium though, as bank erosion during each ebb- tide partially counters the influx of marine sediment. The tidal range is 1.46m at the sea and 0.9m inside the mouth. Deep- sea waves approach the Duiwenhoks mouth primarily from the south south- west, this is consistent with the predominant south- westerly winds. The angle of approach of the deep-sea waves has resulted in a net

eastward longshore transport of marine sediment. Consequently, the beach has widened, the dunes have been built-up and a blunt sandspit west of the mouth has been formed.

There is a sewage outlet into the river at Heidelberg, but the effluent levels are well within the constraints given by the water quality guidelines.

The Duiwenhoks estuary is thus a relatively pristine system. Studies carried out by Turpie *et al.*, 2002 rated the Duiwenhoks as one of the top 50 South African estuaries, ranked in terms of conservation importance, which is calculated on the basis of size, type rarity and biodiversity.

The purpose of this study is to analyse certain physico-chemical properties of the estuary in order to gain an understanding of the physical and biological processes that occur within the system. Sources of anthropogenic inputs were considered and the extent to which these inputs may impede the natural processes of the estuary was also investigated. A budget describing the rate of material delivery to the system, the rate of material removal from the system and the rate of change of the material mass within the system was implemented, following the LOICZ (Land -Ocean Interactions in the Coastal Zone) Biogeochemical Modelling Guidelines.

## **1.2 METHODS**

A small craft was used to collect water samples along the estuary. Surface samples were taken by hand using a small bucket. Bottom layer samples were obtained using a Niskin bottle. Water was sampled at 1km intervals for 4 km upstream from “Glory Be” and at 2km intervals for 10km downstream to the river mouth.

Samples were taken for dissolved oxygen, nitrates, nitrites, phosphates and urea. Temperature and salinity were also recorded at each station and at each depth.

Dissolved oxygen samples were immediately spiked with MnCl and KI/KOH. Concentrations of dissolved oxygen were determined by the manual titrations during the field trip. Concentrations of phosphates were also determined on site using a spectrophotometer. Samples of nitrite, nitrate and urea were frozen and analysed back at the lab.

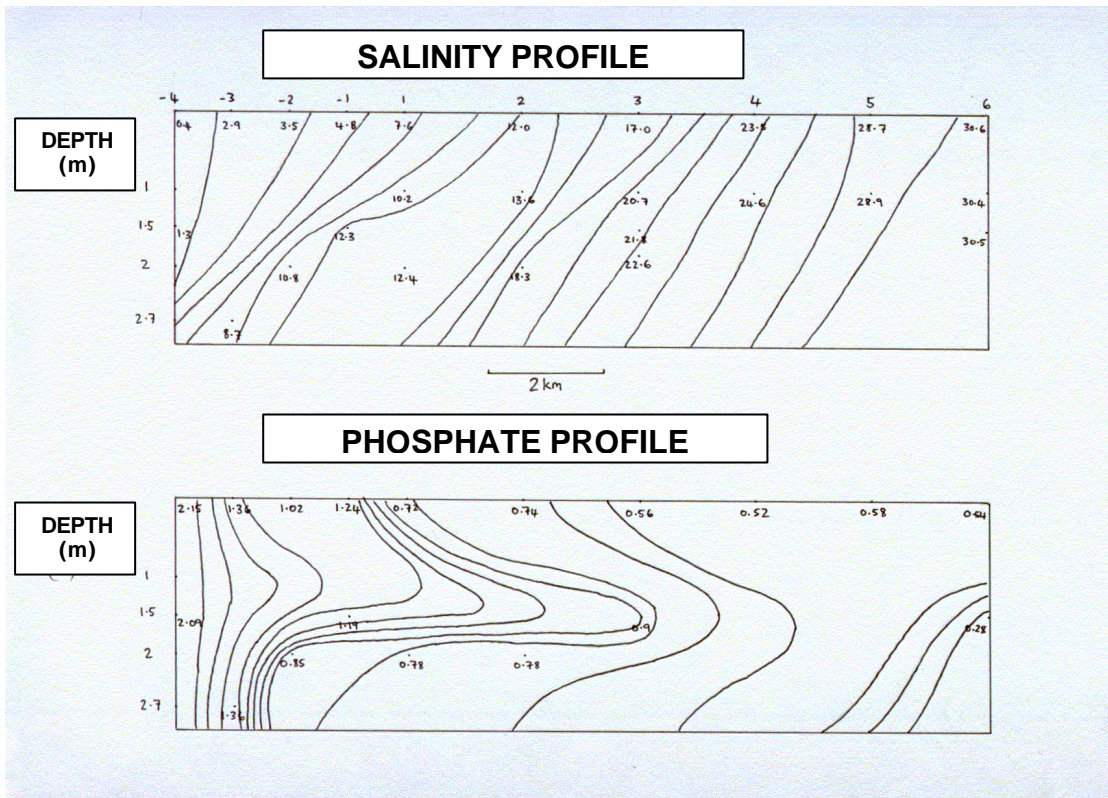
### 1.3 RESULTS

The results of the survey can be found as Appendix 1 at the back of the report. As expected, a salt wedge was found to exist extending from the mouth to about 14km upstream, where the salinity was found to be negligible. Figure 1a shows the salinity profile for the estuary 'box', the most striking feature being the slanting nature of the isohalines. This is due to the denser, more saline water flowing into the estuary from the sea sitting below the fresher, less dense river water flowing in at the head of the estuary.

Figure 2 shows the phosphate profile of the estuary. A gradient exists through the sampling area with the water at the top of the estuary having a higher phosphate content than the more saline water closer to the mouth. The profile shows a sub-surface tongue of phosphate rich water pushing out at around 1.5m, decreasing as it gets further away from the source of the phosphate and mixes with the more saline water.

Other variables sampled and analysed included temperature, nitrate-nitrite concentrations, urea and dissolved oxygen content. The average temperature of the estuary was 17.7°C, midway between the values of 16°C and 19.2°C recorded in the river and sea respectively. The nitrate-nitrite concentrations generally decreased from the river (24.97µg.at.l<sup>-1</sup>) to the sea (2.00 µg.at.l<sup>-1</sup>), with the average value of the estuary being 11.22 µg.at.l<sup>-1</sup>. The values were generally higher on the surface than lower down (1.5m to 2.7m), except for nitrate-nitrite rich areas of water found at depth close to the head of the estuary. The results of the dissolved oxygen analysis showed, as expected, higher dissolved oxygen contents found at the surface than at depth. The average for the whole estuary was 5.24ml.l<sup>-1</sup>, lower than both the more turbulent river (6.77ml.l<sup>-1</sup>) and high wave action zone of the sea (5.51ml.l<sup>-1</sup>). The average urea concentration for the estuary was 1.79µmol.l<sup>-1</sup>, less than both the river and sea water. An interesting point was that the urea values decreased noticeably (in the results) from the first day of sampling (17<sup>th</sup>), when the river water was sampled, until the last (20<sup>th</sup>), where very low concentrations were recorded near the head of the estuary.



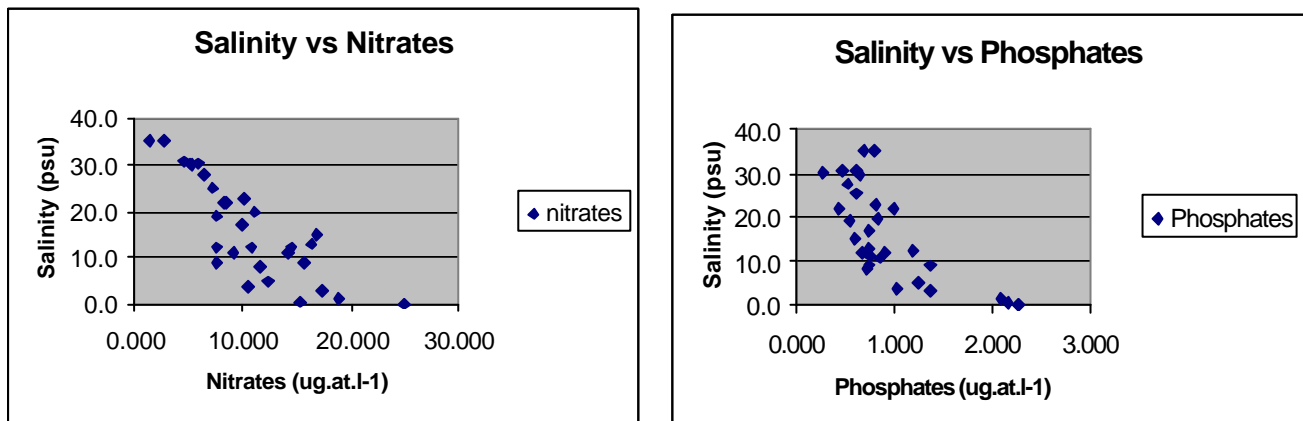


**Figure 2.** Salinity and Phosphate profiles of the estuary. The mouth is on the right-hand side.

## 1.4 DISCUSSION

The water entering the estuarine system from the Duiwenhoks river is fairly healthy and according to the water Quality Guidelines for Aquatic Ecosystems the values of Nitrate are indicative of oligotrophic conditions and low productivity systems with rapid nutrient cycling. The Phosphorous values however are somewhat higher and are at the sort of levels, which support high productivity and possibly even eutrophic conditions. These higher phosphorous values are possibly due to drainage from fertilised agricultural land or point source discharges such as domestic and industrial effluents. The ratio of inorganic nitrogen to inorganic phosphorous is less than 10:1 and characteristic of eutrophic and hypertrophic systems. Dissolved oxygen value for the river system is within target range for an aquatic ecosystem of high conservation value (Water Quality Guidelines,1996).

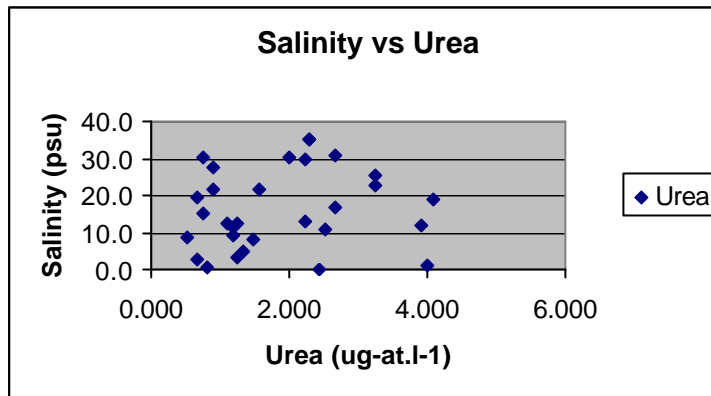
The concentrations of Nitrate and Phosphate are highest in the river and drop as one moves towards the sea, with lowest concentrations in the sea. The following graphs of salinity against the above mentioned nutrients were made to assess whether the decrease in nutrient concentrations, approaching the sea, are directly related to dilution by nutrient poor sea water.



**Figure 3.** Graph of Salinity vs. Nitrates and Salinity vs. Phosphates, showing the variation in the concentration of these nutrients as one approaches more saline water at the mouth.

These graphs show a fairly linear relationship between salinity and the nutrients, nitrates and phosphates, with some of the variation probably ascribed to different sampling times on 17 and 18 May and associated different tidal phases.

The following graph of salinity against urea shows no distinguishable trend, with variable results at the surface and bottom along the estuary system.



**Figure 4.** Graph of Salinity vs. urea, showing no obvious trend.

some curious results were obtained with a large variation between the days of sampling, could be related to input of urea into the system or the different tidal states on the different days of sampling.

Comparing the data from this study with data collected in 1985 (CSIR, No.34, 1990) certain differences are evident in the physico-chemical characteristics. The phosphate levels are higher, further up the estuary, but overall not markedly different to concentrations in 1985. Nitrates are higher throughout the system, by over  $10 \mu\text{g.at.l}^{-1}$  10 km from the mouth and by about  $4 \mu\text{g.at.l}^{-1}$  near the mouth.

Comparing the nutrient concentrations of the Duiwenhoks river and estuary system with a system known to have a higher nutrient loading could be a useful way to obtain an appreciation of the state and health of the above mentioned system. For example the Zeekoe system, which flows into False Bay east 8km east of Muizenberg (CSIR, No.15, 1982), receives a high nutrient load from the sewage works located on it's banks. As expected values of phosphate differs enormously between the two estuaries, with average values of phosphate 100 times higher in Zeekoe estuary. This helps illustrates that the sewage and nutrient input into the Duiwenhoks is insignificant and the system is a healthy one.

## **LOICZ BUDGET**

## 2. LOICZ BUDGET

Once a preliminary study of the estuary had been done we were able to decide on a modeling approach, adopted from the LOICZ Biogeochemical Guidelines, that would best suit this system.

Salinity profiles showed that the system is vertically stratified and has features indicative of a salt-wedge estuary. Surface waters were less saline and therefore more buoyant than the dense, more saline bottom water. This is characteristic of systems that have relatively weak tidal currents, inhibiting vertical mixing and resulting in a sharp and stable halocline between the two layers. The salty bottom layer becomes thinner upstream and eventually terminates at approximately 11 km from the mouth. It is this stratification that justifies the use of a one box, two-layer model.

From monthly averages of rainfall over a twenty year period peaks occur in spring and in autumn, but are insignificant and do not have a considerable effect on the fresh-water input into the system. For this study therefore, we regarded the system to be one-seasonal, receiving an equal amount of rainfall throughout the year.

Fresh-water inputs into the system included river discharge and precipitation. There was no sewage input directly into the system, though there was input into the Duiwenhoks River at Heidelberg. The volume of sewage input into the system is included in the rate of river discharge. The volume of groundwater input was unfortunately not available therefore our total input value will be underestimated.

**Table 1. Physical characteristics of the Duiwenhoks River estuary.**

<b>Characteristic</b>	<b>Value</b>
Catchment (km <sup>2</sup> )	790
Length of estuary (km)	11
Surface area (km <sup>2</sup> )	0.889
Average depth (m)	1.89
Average system volume (10 <sup>6</sup> m <sup>3</sup> )	1.68

## 2.1 Water and Salt Balance

**Table 2. Physical properties, water budgets and water exchange times in the Duiwenhoks River estuary for 2002**

Freshwater input ( $10^3\text{m}^3\cdot\text{d}^{-1}$ )			Residual Flow ( $10^3\text{m}^3\cdot\text{d}^{-1}$ )	River Salinity (psu)	Ocean Salinity (psu)	Estuary Salinity (psu)	Exchange Volume ( $10^6\text{m}^3$ )	t (day)
$V_q$	$V_p$	$V_e$						
211.4	1.9	2.7	-210.6	0.2	35.2	17.2	1.378	6.52

Refer to appendix 2 for the manual budgeting calculations

Water and salt budgets for the Duiwenhoks River estuary are summarized in Table 2. The system was divided into two layers to accommodate the salinity gradient existing vertically through the water column. The top layer was defined as being from the surface to about 0.5m and the lower layer extending from there to the bottom of the estuary.

Evaporation rates were found to be almost double that of precipitation rates, but these are both significantly lower than the river flow rate of the fresh water entering at the top of the estuary.

A small craft was used to collect water samples along the estuary. Surface samples were taken by hand using a small bucket. Bottom layer samples were obtained using a Niskin bottle. Water was sampled at 1km intervals for 4 km upstream from “Glory Be” and at 2km intervals for 10km downstream to the river mouth.

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## **2.2 Budgets of non-conservative materials**

**Table 3. Nonconservative fluxes of C, N and P in the Duiwenhoks River estuary for 2002**

<b>DDIP</b> (mol.d <sup>-1</sup> )	<b>DDIN</b> (mol.d <sup>-1</sup> )	<b>(p-r)</b> (mol.d <sup>-1</sup> )	<b>(nfix-denit)</b> (mol.d <sup>-1</sup> )	<b>(p-r)</b> (mmol.m <sup>-2</sup> d <sup>-1</sup> )	<b>(nfix-denit)</b> (mmol.m <sup>-2</sup> d <sup>-1</sup> )
-205.198	-400.00	+2.175x10 <sup>4</sup>	+2.88x10 <sup>3</sup>	+24.5	+3.2

Refer to appendix 2 for the manual budgeting calculations

Concentrations of NO<sub>2</sub>, NO<sub>3</sub> (DIN) and PO<sub>4</sub> (DIP) were determined from samples taken at stations along the Duiwenhoks River. The eight stations were spaced approximately 1 km apart upstream and 2 km apart downstream along the estuary, sampled quasi-synoptically.

The nutrient concentrations were averaged across the 8 stations to obtain a single representative value for the estuary, giving a value for DIN and DIP respectively. Nutrient concentrations were also determined for the fresh river input and the adjacent ocean. No point sources of nutrient input were located.

### DIP Balance

The results indicate that there is a net removal of PO<sub>4</sub> in the surface layer and a net production in the bottom layer. The non-conservative flux ( $\Delta$ DIP) of  $-205.197 \times 10^3 \text{ mmol.d}^{-1}$ , shows that the estuary has a net removal of PO<sub>4</sub>.

### DIN Balance

A net production of DIN occurs in the surface and bottom layer of the estuary. Hence non-conservative flux ( $\Delta$ DIN) of  $-0.4 \times 10^6 \text{ mmol.d}^{-1}$  is a nitrogen producing estuarine system.

## **2.3 Stoichiometric estimates of the net system metabolism**

Non-conservative behaviour is assumed to be of biological origin, and for the purpose of this LOICZ budgeting exercise, the Redfield ratio applies to the system. The observed DIP values in the Duiwenhoks system can be used to estimate the net production of organic matter. In order to express the net ecosystem metabolism (NEM) in terms of carbon, we make the assumption that NEM is the result of organic matter production - respiration (p-r) and that the Redfield Ratio between carbon and DIP is 106:1.

$$\text{NEM} = (p-r) = -106(D \text{ DIP})$$

A NEM value of  $+24.5 \text{ mmol.m}^{-2}\text{d}^{-1}$  was obtained, showing that the estuary is net autotrophic, with photosynthesis exceeding respiration. The estuary is therefore a net producer of organic matter.

Using the Redfield Ratio, the non-conservative flux can be calculated using the formula:

$$(nfix - denit) = D \text{ DIN} - D \text{ DIP}(N:P)$$

The denitrification can be determined using the Redfield ratio of 16:1 for N:P, and the observed value for  $\Delta$ DIP, this allows the  $\Delta$  DIN to be expressed as  $16(\Delta$ DIP), yielding a value of  $+3.24 \text{ mmol m}^{-2} \text{ d}^{-1}$ . This indicates that the estuary is fixing nitrogen.

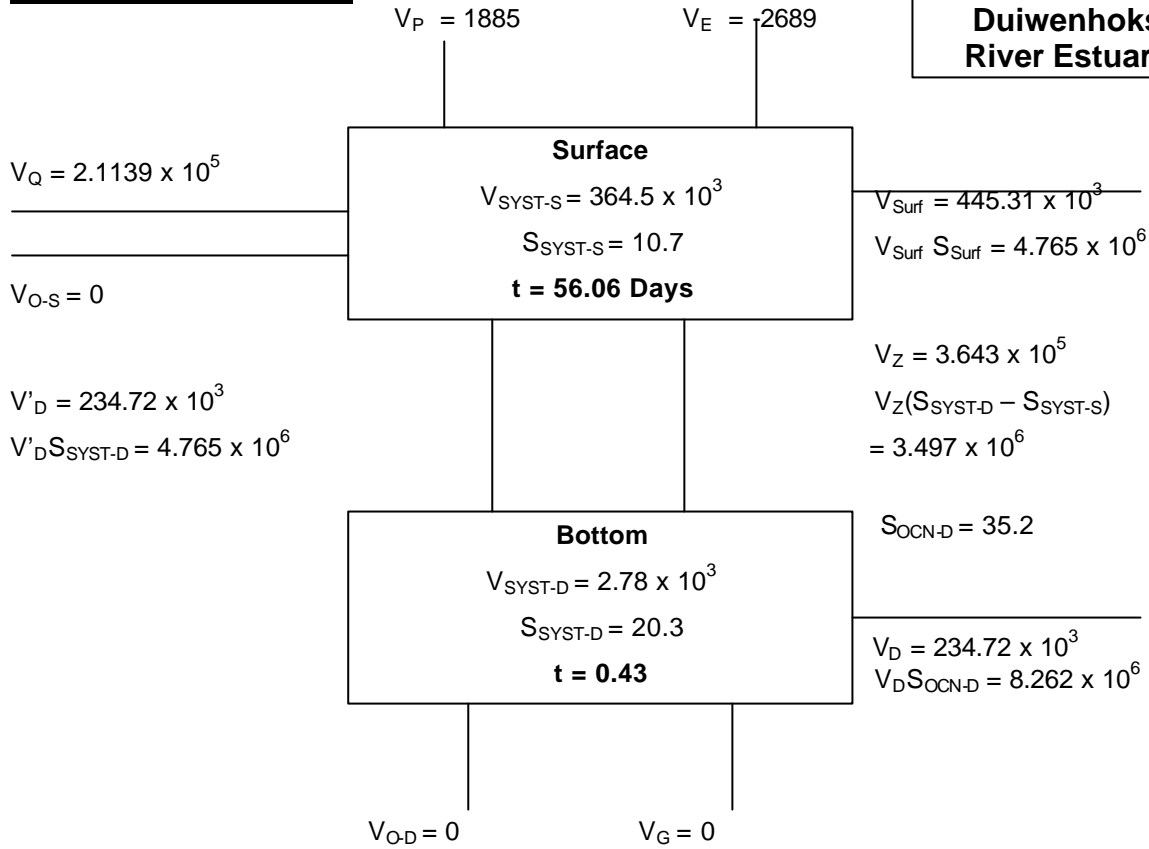
## **2.4 Schematics of budgets**

Please refer to the Water and Salt, Nitrate and Phosphate 'boxes' over the page.



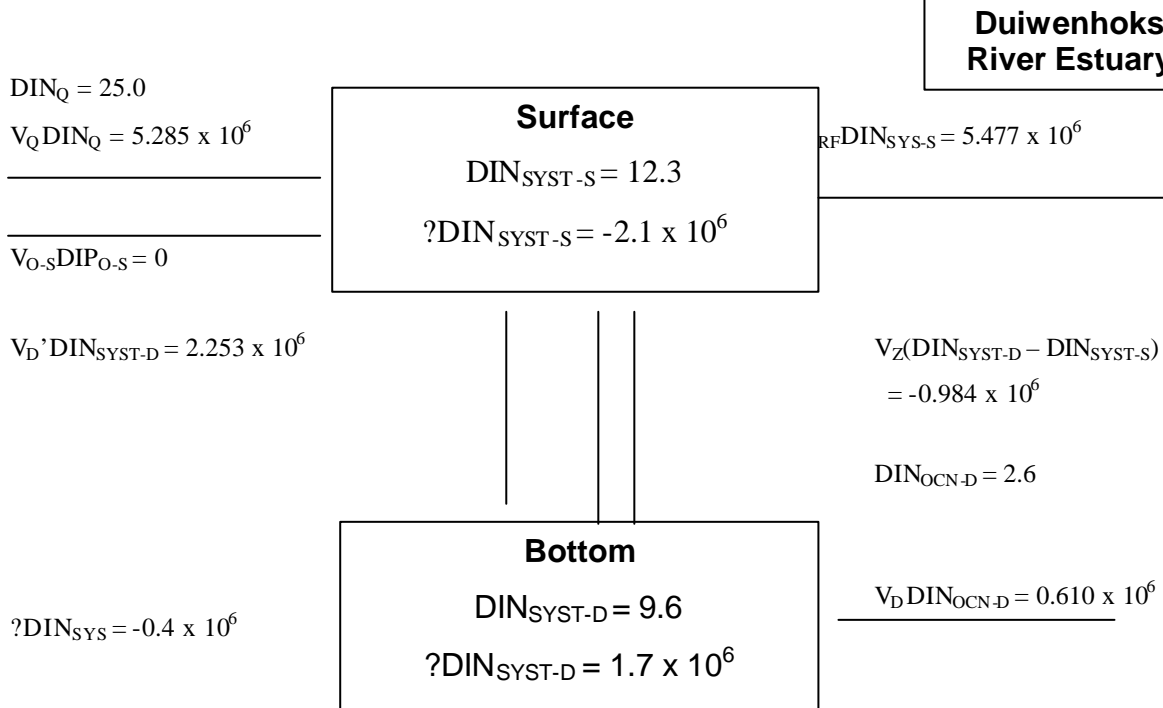
## Water and Salt Budget

### Duiwenhoks River Estuary



## Nitrogen Budget

### Duiwenhoks River Estuary



**Phosphate budget**

**Duiwenhoks  
River Estuary**

$DIP_Q = 2.3$

$V_Q DIP_Q = 486.20 \times 10^3$

$445.31 \times 10^3$

$V_{O-S} DIP_{O-S} = 0$

$V_D' DIP_{SYST-D} = 211.25 \times 10^3$

$DIP_{SYST-S}$

**Surface**

$DIP_{SYST-S} = 1.0$

$?DIP_{SYST-S} = -252.14 \times 10^3$

**Bottom**

$DIP_{SYST-D} = 0.9$

$?DIP_{SYST-D} = 46.944 \times 10^3$

$V_{SURF} DIP_{SYST-S} = -$

$V_Z (DIP_{SYST-D} -$

$= -36.430 \times 10^3$

$DIP_{OCN-D} = 0.7$

# **APPENDICES**

**APPENDIX ONE**  
**1. WATER BUDGET**

$$\begin{aligned} V_Q &= 211\,392 \text{ m}^3\text{day}^{-1} \\ V_E &= 2\,688.9 \text{ m}^3\text{day}^{-1} \\ V_P &= 1\,885.2 \text{ m}^3\text{day}^{-1} \end{aligned}$$

$$\begin{aligned} S_{\text{sys-s}} &= 10.7 \text{ psu} \\ S_{\text{sys-d}} &= 20.3 \text{ psu} \end{aligned}$$

**Residual Flux ( $V_R$ )**

$$\begin{aligned} V_R &= V_{\text{out}} - V_{\text{in}} \\ &= V_E - (V_Q + V_P) \\ &= 2\,688.9 - (211\,392 + 1\,885.2) \\ &= \underline{-210\,588.3 \text{ m}^3\text{day}^{-1}} \end{aligned}$$

**Deep Water Input ( $V_D'$ )**

$$\begin{aligned} V_D' &= V_R (S_{\text{sys-s}}) / (S_{\text{sys-s}} - S_{\text{sys-d}}) \\ &= -210\,588.3 (10.7) / (10.7 - 20.3) \\ &= \underline{234\,718.2 \text{ m}^3\text{day}^{-1}} \end{aligned}$$

$$\begin{aligned} V_{\text{surf}} &= -(V_R - V_D) \\ &= -(-210\,588.3 - 234\,718.2) \\ &= \underline{445\,306.5 \text{ m}^3\text{day}^{-1}} \end{aligned}$$

**2. SALT BUDGET**

$$\begin{aligned} S_{\text{sys-s}} &= 10.7 \text{ psu} \\ S_{\text{sys-d}} &= 20.3 \text{ psu} \\ S_{\text{ocn-d}} &= 35.20 \text{ psu} \end{aligned}$$

**Vertical Mixing ( $V_Z$ )**

$$\begin{aligned} V_Z &= V_D (S_{\text{ocn-d}} - S_{\text{sys-d}}) / (S_{\text{sys-d}} - S_{\text{sys-s}}) \\ &= 234\,718.2 (35.2 - 20.3) / (20.3 - 10.7) \\ &= \underline{364\,302.2 \text{ m}^3\text{day}^{-1}} \end{aligned}$$

Ocean Salt Flux

$$\begin{aligned} &= V_D S_{\text{ocn-d}} \\ &= 234\,718.2 (35.2) \\ &= \underline{8\,262\,080.6 \text{ m}^3\text{day}^{-1}} \end{aligned}$$

Entrainment Salt Flux

$$\begin{aligned} &= V_D S_{\text{sys-d}} \\ &= 234\,718.2 (20.3) \\ &= \underline{4\,746\,779.5 \text{ m}^3\text{day}^{-1}} \end{aligned}$$

Total Surface Salt Flux

$$\begin{aligned} &= V_{\text{surf}} S_{\text{sys-s}} \\ &= 445\,306.5 (10.7) \\ &= \underline{4\,746\,779.5 \text{ m}^3\text{day}^{-1}} \end{aligned}$$

### 3. N AND P BUDGETS

#### NITROGEN

$$\begin{aligned} \text{DIN}_{\text{sys-s}} &= 12.3 \text{ mmol.m}^3 \\ \text{DIN}_{\text{sys-D}} &= 9.6 \text{ mmol.m}^3 \\ \text{DIN}_{\text{ocn-D}} &= 2.6 \text{ mmol.m}^3 \\ \text{DIN}_Q &= 25.0 \text{ mmol.m}^3 \end{aligned}$$

#### Riverine DIN Flux

$$\begin{aligned} &= V_Q \text{DIN}_Q \\ &= \underline{5.2848 \times 10^6 \text{ mmol day}^{-1}} \end{aligned}$$

#### Deep Ocean water DIN Flux

$$\begin{aligned} &= V_D \text{DIN}_{\text{ocn-D}} \\ &= \underline{0.610267 \times 10^6 \text{ mmol day}^{-1}} \end{aligned}$$

#### Total Surface DIN Flux

$$\begin{aligned} &= V_{\text{surf}} \text{DIN}_{\text{sys-D}} \\ &= \underline{5.47727 \times 10^6 \text{ mmol day}^{-1}} \end{aligned}$$

#### Deep water DIN Flux

$$\begin{aligned} &= V_D \text{DIN}_{\text{sys-D}} \\ &= \underline{2.2532947 \times 10^6 \text{ mmol day}^{-1}} \end{aligned}$$

#### Vertical Mixing DIN Flux

$$\begin{aligned} &= V_Z (\text{DIN}_{\text{sys-d}} - \text{DIN}_{\text{sys-s}}) \\ &= \underline{-983\,615.9 \text{ mmol day}^{-1}} \end{aligned}$$

$$\text{DDIN} = \text{Flux}_{\text{out}} - \text{Flux}_{\text{in}}$$

$$\begin{aligned} \text{DDIN}_{\text{sys-s}} &= -(-V_{\text{surf}} \text{DIN}_{\text{sys-s}} + V_Q \text{DIN}_Q + V_D' \text{DIN}_{\text{sys-D}}) \\ &= \underline{-2.1 \times 10^6 \text{ mmol.day}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{DDIN}_{\text{sys-D}} &= -(-V_D \text{DIN}_{\text{sys-D}} + V_D \text{DIN}_{\text{ocn-D}}) \\ &= \underline{1.7 \times 10^6 \text{ mmol.day}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{DDIN}_{\text{sys}} &= \Delta \text{DIN}_{\text{sys-S}} + \Delta \text{DIN}_{\text{sys-D}} \\ &= \underline{-0.4 \times 10^6 \text{ mmol.day}^{-1}} \end{aligned}$$

## PHOSPHATES

$$\begin{aligned} \text{DIP}_{\text{sys-S}} &= 1 \text{ mmol.m}^3 \\ \text{DIP}_{\text{sys-D}} &= 0.9 \text{ mmol.m}^3 \\ \text{DIP}_{\text{ocn-D}} &= 0.7 \text{ mmol.m}^3 \\ \text{DIP}_Q &= 2.3 \text{ mmol.m}^3 \end{aligned}$$

### Riverine DIP Flux

$$\begin{aligned} &= V_Q \text{DIP}_Q \\ &= \underline{486\,201.6 \text{ mmol.day}^{-1}} \end{aligned}$$

### Deep Ocean water DIP Flux

$$\begin{aligned} &= V_D \text{DIP}_{\text{ocn-D}} \\ &= \underline{164\,302.7 \text{ mmol.day}^{-1}} \end{aligned}$$

### Total Surface DIP Flux

$$\begin{aligned} &= V_{\text{surf}} \text{DIP}_{\text{sys-S}} \\ &= \underline{445\,306.5 \text{ mmol.day}^{-1}} \end{aligned}$$

### Deep water DIP Flux

$$\begin{aligned} &= V_D \text{DIP}_{\text{sys-D}} \\ &= \underline{211\,246.38 \text{ mmol.day}^{-1}} \end{aligned}$$

### Vertical Mixing DIP Flux

$$\begin{aligned} &= V_Z (\text{DIP}_{\text{sys-d}} - \text{DIP}_{\text{sys-S}}) \\ &= \underline{-36\,430 \text{ mmol.day}^{-1}} \end{aligned}$$

$$\text{DDIP} = \text{Flux}_{\text{out}} - \text{Flux}_{\text{in}}$$

$$\begin{aligned} \text{DDIP}_{\text{sys-S}} &= -(-V_{\text{surf}} \text{DIP}_{\text{sys-S}} + V_Q \text{DIP}_Q + V_D \text{DIP}_{\text{sys-D}}) \\ &= \underline{-252\,141.5 \text{ mmol.day}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{DDIP}_{\text{sys-D}} &= -(-V_D \text{DIP}_{\text{sys-D}} + V_D \text{DIP}_{\text{ocn-D}}) \\ &= \underline{46\,943.7 \text{ mmol.day}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{DDIP}_{\text{sys}} &= \Delta \text{DIP}_{\text{sys-S}} + \Delta \text{DIP}_{\text{sys-D}} \\ &= \underline{-205\,197.8 \text{ mmol.day}^{-1}} \end{aligned}$$

#### 4. STOICHIOMETRIC RELATIONS

Approximation of net metabolism: photosynthesis minus respiration (p-r)

$$\begin{aligned}(\mathbf{p-r}) &= -\Delta\text{DIP}(\text{C:P}) && (\text{C:P} = 106:1) \\ &= -\Delta\text{DIP}(106)\end{aligned}$$

$$\begin{aligned}(\mathbf{p-r})_{\text{sys-s}} &= -(-252\,141.5)106 \\ &= 26.73 \times 10^6 \text{ mmol.d}^{-1} \\ &= \mathbf{+30.06 \text{ mmol.m}^{-2}\text{d}^{-1}}\end{aligned}$$

$$\begin{aligned}(\mathbf{p-r})_{\text{sys-D}} &= -(46\,943.7)106 \\ &= -4.98 \times 10^6 \text{ mmol.d}^{-1} \\ &= \mathbf{-5.6 \text{ mmol.m}^{-2}\text{d}^{-1}}\end{aligned}$$

$$\begin{aligned}(\mathbf{p-r})_{\text{sys}} &= -(-205\,197.8)106 \\ &= 21.75 \times 10^6 \text{ mmol.d}^{-1} \\ &= \mathbf{+24.5 \text{ mmol.m}^{-2}\text{d}^{-1}}\end{aligned}$$

The positive (p-r) results show that the surface and the system in general is **net autotrophic**, while the bottom of the system is **heterotrophic**.

**Approximation of net denitrification and nitrogen fixation (Nfix – denit)**

$$\begin{aligned}(\mathbf{Nfix - denit}) &= \Delta\text{DIN} - \Delta\text{DIP}(\text{N:P}) && (\text{N:P} = 16:1) \\ &= \Delta\text{DIN} - \Delta\text{DIP}(16)\end{aligned}$$

$$\begin{aligned}(\mathbf{Nfix - denit})_{\text{sys-s}} &= -2.1 \times 10^6 - (-252\,141.5 \times 16) \\ &= 1.9 \times 10^6 \text{ mmol.d}^{-1} \\ &= \mathbf{2.2 \text{ mmol.m}^{-2}\text{d}^{-1}}\end{aligned}$$

$$\begin{aligned}(\mathbf{Nfix - denit})_{\text{sys-D}} &= 1.7 \times 10^6 - (46\,943.7 \times 16) \\ &= 0.95 \times 10^6 \text{ mmol.d}^{-1} \\ &= \mathbf{1.07 \text{ mmol.m}^{-2}\text{d}^{-1}}\end{aligned}$$

$$\begin{aligned}(\mathbf{Nfix - denit})_{\text{sys}} &= 0.4 \times 10^6 - (-205\,197.8 \times 16) \\ &= 2.89 \times 10^6 \text{ mmol.d}^{-1} \\ &= \mathbf{3.24 \text{ mmol.m}^{-2}\text{d}^{-1}}\end{aligned}$$

The positive values indicate that the system is **net nitrogen fixing**.

## APPENDIX TWO

Station No.	Temperature ( C)	Salinity	Nitrate	Nitrate	Urea	Phosphate	Dissolved O2	Depth m	
		(psu)	(ug/l)	umol-N/l	(umol-N/l)	ug.at.l-1	ml.l-1		
<b><u>River Water:</u></b>		16.0	0.2	349.625	24.973	2.444	2.270	6.770	0.0
<b><u>Estuary : Surface</u></b>									
20/-4/S		0.4	215.377	15.384	0.815	2.150	5.492	0.0	
20/-3/S		2.9	243.210	17.372	0.667	1.360	5.083	0.0	
20/-2/S		3.5	146.775	10.484	1.259	1.020	5.376	0.0	
20/-1/S		4.8	171.222	12.230	1.333	1.240	5.457	0.0	
17/1/S	16.9	9.0	218.604	15.615	1.185	0.730	4.990	0.0	
18/1/S	17.1	7.9	162.877	11.634	1.481	0.710	5.372	0.0	
17/2/S	17.3	12.9	228.768	16.341	2.222	0.730	4.640	0.0	
18/2/S	18.6	11.1	126.380	9.027	1.185	0.750	5.590	0.0	
17/3/S	17.7	18.9	105.085	7.506	4.074	0.530	5.290	0.0	
18/3/S	18.9	15.1	237.084	16.935	0.741	0.592	5.426	0.0	
17/4/S	17.5	25.2	102.160	7.297	3.259	0.610	5.190	0.0	
18/4/S	18.8	21.8	116.071	8.291	1.556	0.434	5.618	0.0	
<b><u>Estuary : Bottom</u></b>									
<b>Bottom and Intermediate</b>									
20/-4/B		1.3	263.159	18.797	4.000	2.090	5.450	1.5	
20/-3/B		8.7	105.411	7.529	0.519	1.360	4.531	2.7	
20/-2/B		10.8	198.879	14.206	2.519	0.850	4.457	2.0	
20/-1/B		12.3	202.033	14.431	1.259	1.190	4.721	1.5	
17/1/I	17.1	10.2						1.0	
17/1/B	17.3	12.1	151.478	10.820	3.926	0.890	5.890	2.0	
18/1/B	17.4	12.2	106.957	7.640	1.111	0.671		2.0	
17/2/I	17.2	14.2						1.0	
17/2/B	17.2	17.0	138.514	9.894	2.667	0.730	3.910	2.0	
18/2/I	18.1	13.0						1.0	
18/2/B	17.7	19.6	155.198	11.086	0.667	0.829	4.906	2.0	
17/3/I	17.5	19.8						1.0	
17/3/B	17.3	22.6	140.929	10.066	3.259	0.810	5.000	1.7	
18/3/I	17.8	21.6						1.0	
18/3/B	17.7	21.8	117.614	8.401	0.889	0.987		1.5	
17/4/B	17.4	26.0						1.0	
18/4/B	18.2	23.8						1.0	



17/5/S	17.5	29.8	73.198	5.228	2.222	0.650	5.590	0.0
18/5/S	18.2	27.7	90.288	6.449	0.889	0.513	6.731	0.0
17/5/B	17.6	30.0						1.0
18/5/B	18.2	27.7						1.0
17/6/S	17.8	30.7	63.873	4.562	2.667	0.610	6.340	0.0
18/6/S	18.0	30.5	83.144	5.939	0.741	0.474	5.753	0.0
18/6/l	18.0	30.4						1.0
17/6/B	17.8	30.7						1.5
18/6/B	18.0	30.4	71.384	5.099	2.000	0.276	5.123	1.5

**Sea Water:**

Mouth	19.2	35.2	37.058	2.647	2.296	0.690	5.510	0.0
Stilbaai	19.0	35.2	17.736	1.267	2.296	0.790		0.0

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