

Fluxes of Nitrogen in Chaliyar River Estuary, India

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ABSTRACT

The Chaliyar river estuary is a positive coastal plain estuary with total drainage area of 2923 km². We investigated the estuary's functions as sink and transformer of nutrients (uptake and release, retaining and recycling of nutrients) and relative contribution of external nutrient supply, nutrient budget, geo-chemical and biochemical pathways. The major source of nitrogen in the estuary is the river discharge. During pre-monsoon period, the percentage of inorganic nitrogen to total nitrogen pool is at the minimum and the major form is organic nitrogen. During the post-monsoon period, the contributions from both these components are almost equal, with a predominance of inorganic form. The dissolved nitrogen components are present in one form or other through out the estuary in all seasons and so nitrogen is not a limiting nutrient for primary production. The urea-N fraction remains < 7% with the lowest levels in pre monsoon. The contribution of Ammonia-N to total nitrogen pool is < 10% during monsoon and pre monsoon seasons. The maximum contribution > 25% is in the post monsoon season. When the monsoon discharges are maximum, 80 -90% contribution to the total nitrogen pool is by nitrate-N alone and in the pre-monsoon months, 75-85% of total nitrogen pool is from the organic -N. The net fluxes of inorganic nutrients in monsoon and post monsoon season are very large- with very small positive or negative fluxes for the pre-monsoon months. The average net fluxes are 4.97 to 9.61 mg m⁻² s⁻¹ for the monsoon months and 7.22 to 8.01 mg m⁻² s⁻¹ for the post monsoon months. During pre monsoon period, ammonia is transported towards the river (-0.47 to 0.03 mg m⁻² s⁻¹). The net fluxes of nitrite-N are very small and directed upstream during the pre monsoon months. The average flux of nitrate is of the order of 81.09 to 134 mg m⁻² s⁻¹ for the monsoon months and 4.87 to 33.23 mg m⁻² s⁻¹ in the post monsoon months. During the pre monsoon months, negative net flux is towards the river and the magnitude decreases upstream. The net flux of phosphate increases from marine end towards riverine end with the monsoon month's net flux of 3.52 to 4.63 mg m⁻² s⁻¹. During the post monsoon months, fluxes vary from 1.87 to 2.82 mg m⁻² s⁻¹. The net fluxes are very small and directed towards the river in pre monsoon months**. Except in the pre monsoon, there is net transfer of nutrients to sea. The mean annual fluxes for nitrate-N, Ammonia-N and phosphate-P are 31.01 mg m⁻² s⁻¹, +3.9 mg m⁻² s⁻¹ and +2.39 mg m⁻² s⁻¹ respectively. The average peak southwest monsoon transport of nitrate, ammonia and phosphate to sea are 13.7 Mg d⁻², 1.2 Mg d⁻¹ and 0.61 Mg d⁻¹ respectively.

Key Words: Tropical Estuary, Nutrient Fluxes, Nitrogen, Seasonal Variation

INTRODUCTION

The estuarine ecological environments are complex and highly variable compared to other marine environments. The dominant controlling factor behind the distribution, speciation and reactivity of chemical components within estuaries is the mixing of fresh and saline waters. In an estuary, mixing occurs between

natural waters of very different chemical composition and physico-chemical properties. The dissolved plant nutrient elements nitrogen, phosphorous and silicon are usually higher in estuarine system than in the marine waters. Estuaries are generally regarded as one of the most productive aquatic systems and the nutrient supply from fresh water inputs is important in sustaining their high rates of primary production.

Nitrogen and phosphorus are described as bio-limiting elements as its concentration limits biological growth. The processes that govern the fate of these elements in estuaries differ and consequently the ratios of inorganic nitrogen to phosphorus in estuaries may vary widely with time and space. Estuaries function as important sinks and transformers of nutrients, thus altering the quantity and quality of nutrients transported from land to the sea. The elevated nutrients levels can lead to elevated phytoplankton productivity and can lead to hypoxia and eutrophication. The great concern over this problem has stimulated much research on the chemistry and geochemistry of nutrients in aquatic systems, the quantification of the sources and sinks of nutrients, and the dynamics of nutrient uptake and release. Perhaps, one of the most pivotal questions concerning nutrients in estuaries is the degree to which estuaries behave as traps, retaining and re-cycling nutrients within the system and the relative contributions of external nutrient supply.

A successful understanding of the role of estuaries as nutrient traps, filters or exporters requires a knowledge of the distribution of dissolved and particulate nutrient species as well as their rates of input, loss, and accumulation in coastal waters. The nutrient budget or mass balance can be a useful tool in describing the fate of nutrients in estuaries. Potentially the largest term in most estuarine nutrient budgets is the exchange of nutrients with offshore waters, which is usually determined by the difference or ignored due to difficulties involved in measuring small nutrient exchange differences in relatively larger tidal volumes (Kjerfve et al. 1982). In addition, the nutrient accumulation rates in estuarine sediments are difficult to measure against the large background of C, N, or P already present, and are complicated by suspension, bioturbation, and deposition rates that vary widely over time and space (Nowicki and Oviatt 1990).

MATERIALS AND METHODS.

The Chaliyar River is one of the major west flowing rivers of the Kerala state (South India). The river has a length of 169 km and the total drainage of 2923 Km². The maximum river discharge occur during the south-west monsoon months (June - August), and during this period, the tidal limit comes down to a distance of 5 Km from the river mouth. The lowest discharges are found to occur during April- May and the tidal incursions of seawater extends up to 25 Km from the river mouth (James and Sreedharan 1983). The

Chaliyar estuary is a typical positive estuary. The estuarine area considered for the investigation is shown in Figure 1. The eight stations along the four transects across the estuary were sampled for nutrient studies. The section 1 was near to the river mouth and the upstream sections were at distances of 5, 10 and 15 Km respectively, from the river mouth. The two sampling stations on each transect were almost equidistant from the river shore, one each on the northern and southern side. The physical dimensions of the sections are given in the Table 1.

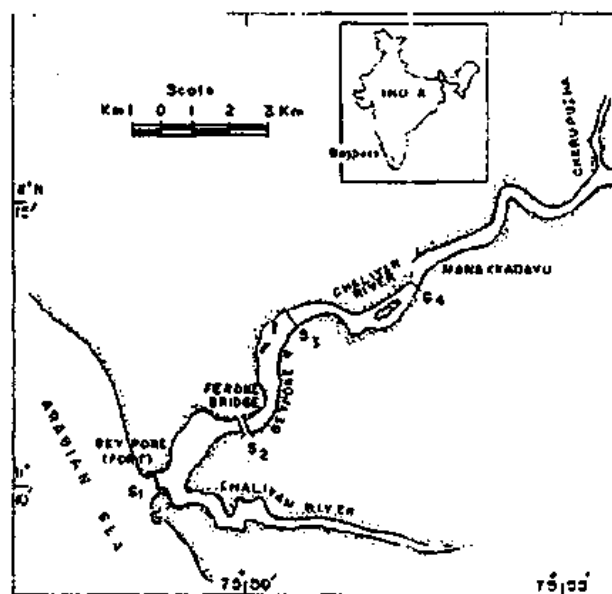


Figure 1. Sampling sites, S1 -S4, on River Chaliyar.

Table 1. Details of river cross-section at which fluxes were estimated

Section	Width (m)	Depth range- (m)
S1	390	2.45 - 2.95
S2	294	2.99 - 3.50
S3	200	4.00 - 4.54
S4	243	2.52 - 3.06

Monthly surveys were conducted in the estuary for a period of one year and the water samples were collected from three depth levels at two hour intervals. The sediment samples were collected from all stations at the time of high and low water using a hand-operated Van Veen grab. The undisturbed middle portions of the grab samples were used for the determination of grain size, nitrogen and phosphorus content.

The nutrient fluxes were calculated from velocity and nutrient concentration as given in Stern et al. (1986), with some modifications. Instead of the central point observation in Stern et al. (1986), the present samplings were done at two stations in a cross section and at three depth levels. The seaward and landward vectors of river flow at each sampling depth was multiplied by the respective nutrient concentration and averaged for the water column to get the instantaneous nutrient fluxes. The net fluxes are the algebraic sums of the instantaneous fluxes over the tidal cycle sampled divided by the number of observations in the tidal cycle. Net fluxes for all the stations with its cross sectional averages for each of the four sections were represented as flux per m^2 of cross sectional area per second.

The present investigation has the objective of studying the nutrient chemistry of this estuary and to have an estimate of the nutrient fluxes. The studies considered the identification of the sources and sinks of nutrients and defining the important geochemical and biochemical pathways of nutrients in the estuary. The distribution of nutrients in the estuary have been reported by Saraladevi et al., (1983) and their studies were confined to the river mouth. The fluxes of inorganic nutrients through various cross sections of the estuary were estimated. The material transport through a particular cross section was obtained by multiplying the averages of the net fluxes by the mean cross sectional area. The Fluxes of particulate and dissolved nutrients were not measured separately, so the fluxes discussed here represented the sum of particulate and dissolved fractions. The positive sign indicates transport towards the sea and the negative sign for transport towards the river.

RESULTS AND DISCUSSION

Nitrogen is supplied in elemental and chemically combined forms to estuaries. The main form of combined nitrogen is dissolved nitrate and has been identified as the growth-limiting nutrient. Natural levels of nitrate reported in most estuarine waters range

from 10 to 40 $\mu g/l$ and decreases to very low values in the marine end (De Souza et al. 1981, Sharp 1983). Other Important forms of nitrogen for bio- geochemical processes in estuaries are nitrite, ammonia and dissolved and particulate organic nitrogen compounds. Nitrite is present in estuarine waters in generally low concentrations as an intermediate product of microbial reduction of nitrate or oxidation of ammonia and as excretory product of plankton. In most estuaries, nitrite concentration seldom account for more than 10% of total oxidized nitrogen (Head 1985).

Physical, chemical and biological processes can affect the seasonal distribution of various nitrogenous nutrients in the estuary. The contribution of various nitrogen fractions to the total nitrogen pool of the estuarine waters was found to vary spatially and temporally. Several factors including external environmental conditions and physiological state of the phytoplankton ultimately regulate the rate of nitrogen uptake in the estuary. The effects of these uptake processes on ambient nitrogen distributions are determined by the physical features such as flushing rate and circulation in the estuary (Pennock 1987). Microbial transformation of nitrogen may be as important as phytoplankton uptake of inorganic nitrogen in determining the distributions of nitrogen among the major dissolved forms (Horrigan et al. 1990).

The major sources of inorganic nitrogen was through the river discharge as indicated by their maximum concentrations during the monsoon season (Tables 2 and 3). During the premonsoon months, when the riverine contribution was very small, percentage of inorganic nitrogen in the estuarine waters was the minimum and the major form of nitrogen was organic. During the post monsoon season, the contributions of both these components were almost equal in the estuarine waters even though there existed a predominance of the inorganic form. Generally, dissolved nitrogen compounds were present through out the estuary during all seasons in one form or other and so nitrogen was not a limiting nutrient in the estuary.

The contribution of Urea N to the total N pool of the estuary was found to be minimum during premonsoon (1.8 to 3.7%). The contribution of urea N was maximum in the upstream sections during monsoon months (3.7 to 5.3%) while it was maximum in the river mouth region during the post- monsoon period (6.2 to 7.3%). Trends in the urea-N distribution was similar to that reported by Verlenkar (1985) for the Mandovi estuary. The concentration was highest during the monsoon when physical processes like

Table 2. Percentage of different nitrogen fractions at various sections

Sections	NO ₃ + NO ₂	NH ₄ -N	Urea-N	Org-N
Pre- Monsoon				
S-1	13.80	4.80	3.70	77.70
S-2	10.60	7.60	3.30	78.50
S-3	18.80	9.80	1.80	69.50
S-4	10.00	1.50	2.60	85.90
Monsoon				
S-1	65.90	10.00	5.70	18.40
S-2	72.30	8.20	6.10	13.40
S-3	85.00	7.10	3.70	4.20
S-4	85.70	6.10	5.30	2.90
Post- Monsoon				
S-1	32.00	27.20	7.30	33.50
S-2	38.60	18.60	6.20	36.60
S-3	54.40	28.90	1.70	15.00
S-4	48.80	26.60	2.60	22.00

Table 3. Percentage of inorganic and organic nitrogen in the Chaliyar estuary.

Month	Inorg-N	Org-N	Month	Inorg -N	Org-N
January	54.5	45.5	July	80.4	19.6
February	19.5	80.5	August	82.4	17.6
March	13.9	86.1	September	63.4	36.6
April	19.2	80.8	October	67.9	32.1
May	28.9	71.1	November	86.5	13.5
June	93.9	6.1	December	67.9	32.1

precipitation and land drainage were active. The Urea-N in the estuary decreased to minimum values during the pre-monsoon season and this might be due to the utilization by phytoplankton. A high phytoplankton population was also reported during that period. The occurrences of urea in significant quantities in the estuary indicated the important contribution of this compound to regenerated production.

The contribution of ammonia-N to the total nitrogen pool of the estuary was < 10% during the monsoon and pre-monsoon periods. Maximum accumulation of ammonia-N >25% of total nitrogen occurred during the post monsoon period when the

opposing forces, viz. river runoff and tidal incursion were moderate. Ammonia distribution in the estuary clearly indicated the process of ammonification in the estuarine and riverine part, which is the ultimate step in the autopurification of organic matter.

The nitrite-N concentration was significantly high only in the post monsoon season. A close look at the tidal variations during this period showed the sequence of a peak concentration of ammonia followed by an increase in nitrite at all stations. This was indicative of nitrification in the water column. The nitrifying bacteria can play a key role, as they are able to oxidize ammonium to nitrate with nitrite as an intermediate. Nitrite may also be formed in the reduction of nitrate and denitrification.

Heavy rainfall and consequent land drainage was observed to be the main sources of nitrate in the estuary. High nitrate concentration in the run off waters can be related to the large amount of nitrogenous fertilizers used in agriculture. Since the nitrates are highly water-soluble, most of it may be leached away during the initial runoff period and this could be the reason for the decrease in nitrate concentration during July and August, even though the river discharge was high. A second nitrate peak observed during November was due to the influence of river discharge during the northeast monsoon. Much of the nitrate was washed out of the estuary during the period of high run off without being assimilated, due to short residence time and slow uptake of nitrate by phytoplankton. Nitrate concentration decreased during December and January due to the decrease in contribution from the land sources and increased uptake by primary producers. During the pre-monsoon months, the entire estuary was marine dominated and the contribution of nitrate from fresh water was practically absent. This together with the high biological activity brought nitrate concentration to a minimum. But during this period, there was an increase in organic-N concentration and this indicated that the major source of organic-N in this system is not the river runoff.

During the monsoon period, when the land drainage and river discharge were maximum, 80 - 90% of the total nitrogen pool in the estuary was contributed by nitrate alone. On the other hand, in the pre-monsoon period, when the estuary was marine dominated, 75-85% of the total nitrogen pool was organic-N. A sharp rise in organic-N accompanied by a depletion of inorganic-N during the pre- and post-monsoon seasons indicate phytoplankton productivity and nutrient enrichment due to favorable physico chemical conditions.

Nutrient Flux

Measurements of fluxes of biologically important elements such as carbon, nitrogen and phosphorus have begun with the realization that the biological productivity of estuaries and near-shore waters are determined by the river addition of nutrients. Nutrient fluxes depend on the vertical profiles of nutrient concentration and velocity, and on the location of the nutrient sources. Park and James (1990) have reported a method for estimating the flux of solutes in a cross-section based on the hourly contours of salinity and velocity and for explaining the mass transport mechanism in estuaries. Jordan et al. (1991) have estimated the fluxes of nutrients between the upper and lower parts of the Rhode river estuary using a mixing model with chloride as a conservative tracer.

The nutrient fluxes through four cross sections in the Chaliyar estuary were estimated to determine the relative influences of riverine and tidal forcing on the fluxes. Net fluxes are represented as mgperm^2 of cross sectional area (Table 4).

Table 4. Seasonal averages of fluxes ($\text{mg m}^{-2} \text{s}^{-1}$) of three forms of nitrogen through various cross sections of Chaliyar River

Sections	Nitrite-N	Nitrate-N	Ammonia-N
Pre -Monsoon			
S-1	-0.24	-2.92	-0.09
S-2	-0.19	-0.65	-0.35
S-3	-0.08	-0.97	-0.08
S-4	-0.13	-0.16	0.10
Monsoon			
S-1	2.21	81.09	4.97
S-2	1.57	79.60	5.67
S-3	2.61	122.46	8.20
S-4	2.49	134.31	9.61
Post-Monsoon			
S-1	0.64	14.87	7.22
S-2	0.79	17.55	4.08
S-3	0.77	8.01	7.61
S-4	0.91	33.23	

Ammonia Flux

Large net fluxes of ammonia-N were observed during the monsoon and postmonsoon seasons and very small positive or negative net fluxes were found during the

pre-monsoon season. During the month of September, an exceptionally high negative flux ($-7.60 \text{ mg mm}^{-2} \text{ s}^{-1}$) estimated at section 1. This can be explained as a result of the tidal input from the coastal region. High amounts of organic matter produced in the coastal areas due to the bloom conditions as a result of upwelling (Venugopal et al. 1979) might be transported into the estuary with the tide, the decay and decomposition of which resulted in high concentration of ammonia.

Average value of net fluxes during monsoon increased from $4.97 \text{ mg m}^{-2} \text{ s}^{-1}$ at section 1 to $9.61 \text{ mg m}^{-2} \text{ s}^{-1}$ at section 4 and the quantity varied from 7.22 to $5.01 \text{ mg m}^{-2} \text{ s}^{-1}$ during the post-monsoon season. An increased input from the coastal waters can be observed as an increase in the flux rate at section 1 compared to section 2. During the post monsoon period, ammonia-N was transported towards the river by tidal action and average values of net fluxes varied from $-0.47 \text{ mg m}^{-2} \text{ s}^{-1}$ at section 1 to $0.08 \text{ mg m}^{-2} \text{ s}^{-1}$ at section 3. At section 4, the net flux was directed downward with an average of $0.10 \text{ mg m}^{-2} \text{ s}^{-1}$.

Nitrite Flux

The net fluxes of nitrite-N were very small except during June and the maximum value was $8.50 \text{ mg m}^{-2} \text{ s}^{-1}$, which decreased after the peak monsoon period, and the net fluxes were directed towards upstream during the pre-monsoon months. Seasonal averages showed generally higher positive values in the upstream sections which indicated the source of this nutrient to be land derived and its magnitude was found very low and varying due to its unstable oxidation state.

Nitrate Flux

The seasonal variations in the magnitude of net fluxes were exactly similar to that of variation in concentration of nitrate-N. A gradual decrease in the net fluxes from the riverine end towards the marine end of the estuary was observed and the directions of the net fluxes were always towards the sea during the monsoon and post monsoon seasons. This clearly indicated the riverine source of nitrate-N as evidenced from other observations. Average net flux as high as $134.31 \text{ mg m}^{-2} \text{ s}^{-1}$ was found at section 4 whereas it was $81.09 \text{ mg m}^{-2} \text{ s}^{-1}$ at section 1 during the monsoon. During the post monsoon season it was 33.23 and $14.87 \text{ mg m}^{-2} \text{ s}^{-1}$ respectively. The reverse was the trend during pre-monsoon. The net fluxes were directed towards the river and their magnitude decreased towards upstream.

A change in the direction of the net fluxes was also observed in the upstream sections showing small positive values. Average net fluxes varied from $-2.92 \text{ mg m}^{-2} \text{ s}^{-1}$ at section 1 to $-0.16 \text{ mg m}^{-2} \text{ s}^{-1}$ at section 4.

DISCUSSION.

Nutrient flux studies indicated that except during the pre-monsoon period there was a net transport of inorganic nutrients into the sea and the rate of this transport were mainly controlled by the river flow. The tidal action is opposing the riverine influence that is reflected in the magnitude and direction of net fluxes studies at four sections of the estuary. Due to the greater tidal influence and mixing and diffusion processes, net fluxes in the down stream sections were less than that of the upstream sections. Other possible mechanisms that reduce the net fluxes towards the marine end are biological uptake, adsorption to sediment and incorporation into the interstitial waters.

Table 5 . Mean annual net flux of nutrients ($\text{mg m}^{-2} \text{ s}^{-1}$) at the river mouth (S-1) and upstream section S-4 of Chaliyar estuary.

Nutrient	Section 1	Section 4
Nitrate-N	31.01	55.79
Ammonia-N	3.98	5.90

The net annual fluxes of nutrients increases as riverine influence increases. In Chaliyar river estuary, tidal forcing is more at section 1. The transport of nitrate-N, and ammonia-N through various cross sections in the estuary are presented in Table 5. Since the values were considerably low, nitrite-N was ignored. Transports of nutrients were directed towards sea during monsoon and postmonsoon months, and were directed towards river during pre-monsoon. Considerable quantities of nutrients are transported through the estuary during October and November, which was the period of northeast monsoon. The quantity decreased during December and was minimum during January. Transport was directed towards the river during the pre-monsoon months (February to May) and maximum upstream transport was observed during May. Negative transport was comparably higher at

section 1 due to greater tidal forcing there. Maximum river transport of nutrients occurred during June - July, which was also the period of heavy rainfall and maximum river discharge. Transport decreased during August and September due to decrease in riverine forcing. The increased transport through section 1 compared to section 2 during the high runoff periods could be attributed to the influence of Chaliyar River, which enters into the estuary near section 1.

A comparison of nutrient transport rates through the upstream and down stream cross sections of the estuary indicated some amount of utilization or retention by the estuarine system. This has resulted from number of physical, chemical and biological processes taking place in the estuary. Even though there is some utilization of dissolved nutrients within the estuary, very large quantities of these are transported to the sea. During the peak southwest monsoon period, the amount of nitrate-N flushed out into the Arabian Sea through the Chaliyar river estuary after utilization is estimated to be 13.7 Mg per day and the corresponding values for ammonia-N is 1.2 Mg per day.

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