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## Nitrogen dynamics in the sediments of a wetland coastal ecosystem of southern India

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The study area, Kuttanad Waters is a part of the Cochin estuarine system on the west coast of India. Kuttanad is well known for its agricultural activity and so the major contribution to the inorganic ions of nitrogen will be from fertilisers applied in agriculture. Based on observed salinity the stations have been divided into three zones. The fresh water zones had higher quantities of silt and clay whereas the estuarine zone was more sandy. The chemical speciation scheme applied here distinguishes three forms of ammoniacal nitrogen species: exchangeable, fixed, and organic ammoniacal nitrogen. No significant trends were observed in the seasonal distribution of total, exchangeable, fixed and organic nitrogen. A significant concentration of exchangeable ammonia was observed in the sediment due to their predominantly reducing environment, which restricts nitrification. High  $\text{NH}_4\text{-N}$  concentrations in the pore waters, along with the sedimentary composition leads to a significantly high quantity of fixed  $\text{NH}_4\text{-N}$ . The low values for N org is due to high mineralisation or deamination of organic nitrogen

*Keywords:* Sediment; Nitrogen; Chemical speciation; Seasonal variations; Monsoon

### 1. Introduction

The source of nitrogen (N) and phosphorus (P) in most aquatic environments is from discharges off the land, where synthetic fertilizers and detergents are major contributors. Although concentrations of nutrients in aquatic systems are governed by the biological uptake and regeneration, sedimentary processes are also important [1]. The Kuttanad region is well known for its agricultural activity and the major contribution to the inorganic ions of nitrogen will be from fertilisers applied in agriculture. The dynamicity of this water body is considered to be maximum during the post-monsoon season. In the case of nitrogen, the inorganic species nitrite, nitrate and  $\text{NH}_4^+$  ions are considered as the major sources of bio-available-N. A major portion of the recycled nitrogen released to the water from the sediments is in the form of  $\text{NH}_4^+$ . The availability of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  depends on the concentration of dissolved oxygen, and so generally in estuarine sediments, due to the reducing conditions,  $\text{NH}_4^+$  is the major product.

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Though sediments are considered to be an active media in the diagenesis of organic matter, its actual contribution towards the N cycle is still not completely clear. The significant differences between the properties of phosphorus species and nitrogen species resulted in diverting more attention towards the phosphorus cycles. The inorganic phosphorus species, which acts as the primary source of bio-available-P are the ions of ortho-phosphoric acid. These are capable of forming a wide variety of soluble and insoluble salts, leading to considerable dynamicity to the system. In the case of nitrogen the inorganic species nitrite, nitrate and  $\text{NH}_4^+$  ions, which are considered as the major sources of nitrogen to the biota, gives only soluble inorganic nitrogen compounds. This restricts the contribution of sedimentary bound inorganic nitrogen species in the N cycle. Generally the reducing environment available with the sediment will favour for the decomposition of the organic nitrogen to  $\text{NH}_4^+$ , and is not favourable for the formation of nitrite or nitrate. In many cases the situation may even lead to the denitrification of any available nitrite or nitrate [2, 3]. In many cases the tendency of inorganic nitrogen species either generated or available by some other processes will tend to get transferred or dissolved in the bulk waters. The actual transfer from the sediment to the water takes place through sediment-water boundary interface, with transport and diffusion occurring through the pore water. In any case, a reverse movement of inorganic nitrogen species from water to the sediment is not possible. So the sediment can have only three forms of the nitrogen exchangeable ammonia, fixed ammonia and organic nitrogen. As the movement of inorganic nitrogen species can take place only in a direction towards the water column, the amount of exchangeable ammonia present in the sediment will be very low.

The distribution pattern of sediments in an estuary depends on several factors such as sediment sources, the texture of the sedimentary material supplied, the bottom topography of the basin and general hydrographical factors [4]. In estuarine and wetland ecosystem, the in situ production and land runoff brings in comparatively high organic content into the sedimentary compartment. The diagenetic character of these systems will have high contribution to the diagenesis also. The previous studies on the nitrogen dynamics in the estuarine system mainly concentrate on the distribution of oxides of nitrogen, fractionation of organic nitrogen forms [5–9]. The attempt towards the chemical speciation of the ammoniacal species is only very scarce [10, 11]. Previously, no serious effort had been directed towards the assessment and characterization of the nitrogen species in this system. These studies are significant because this wetland ecosystem is an extension of the tropical Cochin Estuary and receives inflow from five rivers.

## 2. Material and methods

### 2.1 Study area

The Kuttanad area is rightly called the “Rice Bowl of Kerala”. This wetland system contributes nearly 20% of the total rice production of the State of Kerala. The aquatic system is highly productive and also contains substantial fishery resources. The total agricultural area is ~54,935 ha. The amount of artificial fertilizers used in this area is about 8409 tonnes per year.

The area of study, Kuttanad Waters, is a part of the Cochin Estuarine system and forms the southern part of Vembanad Lake. The lake is connected to the Arabian Sea at Cochin, India (figure 1). This is the only source for tidal intrusion to the lake. The area of study, extends from  $9^\circ 28'$  to  $10^\circ 10'N$  (Lat) and  $76^\circ 13'$  to  $76^\circ 31'E$  (Long) and runs parallel to the southern part of the west coast of India. The hydrographic features of this part of the estuary are controlled mainly by discharges from five rivers (Manimala, Meenachil, Pamba, Achenkoil and

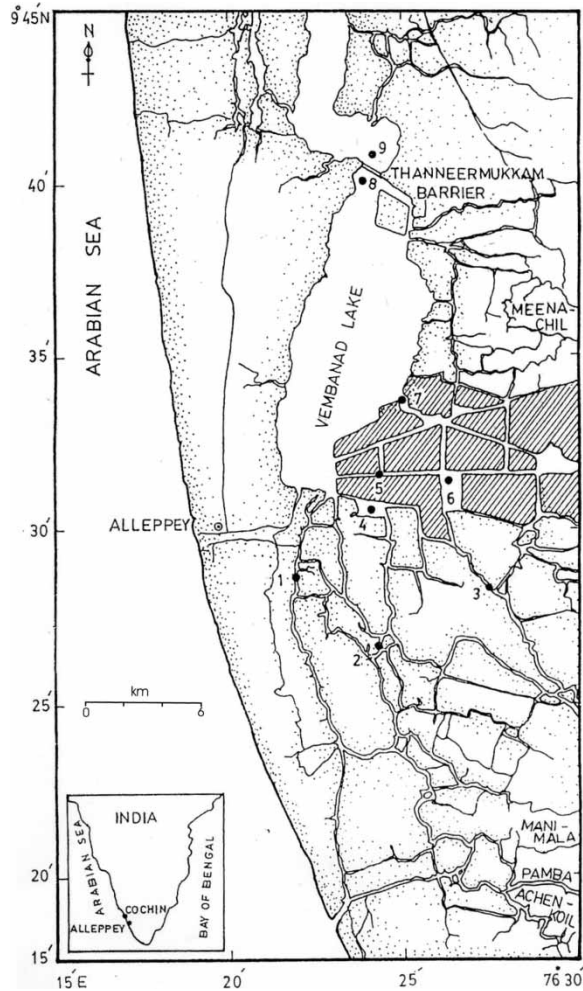


Figure 1. Location of the study area (sampling stations indicated by numbers from 1–9).

Muvattupuzha) and also by tidal intrusions of saline waters from the Cochin Estuarine system. The average depth of all the rivers varies between 1.5–10 meters.

Thanneermukkam barrier, a type of hydraulic control (figure 1), was commissioned in 1976 to help prevent the intrusion of saline water into Kuttanad paddy fields during December to March and thereby protect the ‘Punja’ crop. This barrier was originally envisaged to be closed for a period of three months (15 December to 15 March) every year while control gates remained open during monsoon months to facilitate the evacuation of floodwater. The deterioration of the water quality, after the construction of Thanneermukkam barrier, is suspected to be one of the reasons for the massive spread of fish diseases and fish mortality during recent years. Furthermore, the zone of salinity gradient shifted towards the north end of the lake.

The areas of investigation and station locations are given in figure 1. The region lying between the Thanneermukkam barrier and the coastal town of Alleppey was subdivided into three zones within which nine stations were selected for sampling. The first zone contains Stations 1 to 4, the second zone Stations 5 to 7 and the third zone Stations 8 to 9. All the zones exhibit a riverine character during the monsoon season. Zone 1 is completely riverine in nature during both the pre-monsoon and post-monsoon seasons. The main cultural activity

in this area is agriculture. During the pre-monsoon season, the second zone shows estuarine characteristics but is dominated by fresh water during the other two seasons. Stations in the third zone are estuarine in nature during both pre- and post-monsoon seasons.

## 2.2 Sampling

Sediment samples were taken at monthly intervals during the period May 1996 to May 1997 at each station. Sediment was collected using a van Veen grab (0.032 m<sup>2</sup>) and put in well-labelled polythene bags. The procedure was done three times to form three replicates and then frozen at -4 °C until analysed.

## 2.3 Laboratory analysis

Organic Carbon (OC) was determined by following the wet oxidation method (Gaudett and 1974) [12]. Textural analysis of the sediments was determined by the method of Carvar 1971 [13]. The classification of sediments as prepared by [14] is made use of in the present study.

**2.3.1 Speciation of nitrogen.** The speciation of nitrogen was done using the scheme proposed by [15] Keeney and Bremner (1966) and [16] Silva and Bremner (1966). This scheme is not capable of identifying and estimating the nitrate and nitrite species, if any, associated with the sediment.

Exchangeable nitrogen (N ex) is defined here as the amount of NH<sub>4</sub><sup>+</sup> extracted by 2N KCl solution; fixed ammonium (N fix) is the fraction liberated by HCl solution after destruction of the organic matter with a hypobromite solution and removal of N ex. Organic nitrogen (N org) is defined here as the difference between total nitrogen (N tot) and inorganic nitrogen (N fix + N ex):

$$N \text{ org} = N \text{ tot} - (N \text{ fix} + N \text{ ex})$$

Total nitrogen was estimated using Kjeldhal method and the distilled ammonia was determined by back titration with 0.01N HCl.

Exchangeable nitrogen (N ex) was estimated after shaking 6 g sediment with 10 ml 2N KCl solution, 0.1 g MgO was added which was followed by flushing with a few ml of Milli-Q water [15]. The extracts were transferred to the Kjeldahl steam distillation unit, 10 ml 10N KOH was added and the ammonia distilled as those described for N tot.

Fixed nitrogen (N fix) was estimated after the addition of 20 ml of KOBBr/KOH (6 ml of Br<sub>2</sub> in 200 ml of 2N KOH, freshly prepared every day) solution to 2 g of sediment sample and mixed [16]. After 2 hours the solution was boiled for 1 min with 20 ml 0.5N KCl solution. The mixture was then flushed into a 50 ml centrifuge tube, which was centrifuged for 10 min. The liquid was decanted and the sediment was mixed again with 20 ml 0.5N KCl solution followed by centrifuging and decanting. Approximately 20 ml of 1N HCl solution was added to the remaining sediment, which was subsequently shaken for 24 h. The suspension was then transferred into a Kjeldahl flask and after the addition of 20 ml 10N KOH solution the ammonia was distilled as described previously for N tot.

All extractions for the speciation were performed on the wet sediment. All data is expressed in terms of the dry weight, using the dry-to-wet ratio, for effective comparison with earlier works. Dry-to-wet ratios were determined by drying the samples at 105° C for 24 hours and taking the weight before and after drying.

## 2.4 Data analysis

Basic statistical analysis was carried out in all parameters to check the validity of the data. Pearson correlations analysis was carried out to test correlation among the three fractions of nitrogen during three seasons. The significance of seasonal variations of different forms of nitrogen was analysed statistically using student's t-test.

## 3. Results and discussion

The speciation scheme applied here distinguishes three forms of ammoniacal nitrogen species: exchangeable, fixed, and organic ammoniacal nitrogen. The percentage of different forms of nitrogen to the total nitrogen is given in table 1 and the distribution of total nitrogen is shown in figure 2.

In zone I the percentage of exchangeable nitrogen varied between 3.99 and 16.16 of the total nitrogen during the pre-monsoon, whereas, the same during monsoon and post-monsoon were in the range of 0.66–8.07 and 2.96–11.02 respectively. In zone II the maxima and minima during pre-monsoon, monsoon and post-monsoon were 19.84 and 3.89, 7.07 and 1.55 and 14.19 and 5.93 respectively. In zone III the corresponding ranges were 7.31–9.54, 14.78–20.23 and 4.84–5.38 in the respective order of the seasons.

In zone I the percentage composition of fixed nitrogen to the total nitrogen content was found to be in the ranges 7.27–54.84 during the pre-monsoon, 20.70–36.26 for monsoon and 26.12–31.46 during post-monsoon seasons. In zone II a maximum of 40.25 and minimum of 14.94 was reported during the pre-monsoon. During the monsoon and post-monsoon seasons the percentage of the above was in the range of 9.29–15.29 and 12.31–26.24 respectively. In zone III a maximum of 23.78, 43.07 and 21.71 and a minimum of 20.57, 29.41 and 8.84 corresponding to pre-monsoon, monsoon and post-monsoon seasons respectively was observed.

From the recorded values it is evident that organic nitrogen constitutes the major share of the total nitrogen content. During the pre-monsoon the percentage of organic nitrogen to the total nitrogen rose up to a maximum of 81.04 while the minimum is 38.66 in zone I. The same was found to vary between 51.21 and 73.11 during the monsoon and 59.31 to 70.92 during the post-monsoon. In zone II, organic nitrogen contributed to the total nitrogen a maximum of 79.96% and a minimum of 55.36% during the pre-monsoon. During monsoon and the

Table 1. Seasonal variations of different fractions of nitrogen (%) in sediments.

Fractions of N	Seasons	Stations								
		1	2	3	4	5	6	7	8	9
N ex	pre mon	16.16	9.65	6.50	3.99	19.84	3.89	5.10	9.54	7.34
N fix		7.27	9.31	54.84	24.79	24.75	40.25	14.94	20.57	23.78
N org		76.57	81.40	38.66	71.21	55.36	55.86	79.96	69.89	68.91
N ex	mon	0.66	6.19	6.11	8.70	7.70	1.55	6.73	14.78	20.23
N fix		28.47	20.70	36.26	22.87	15.29	14.18	9.29	43.70	29.41
N org		70.87	73.11	57.63	51.21	77.65	83.65	83.98	42.15	50.36
N ex	post mon	7.99	2.96	4.80	11.20	14.19	5.93	7.37	4.84	5.38
N fix		29.66	26.12	31.46	29.68	17.66	12.31	26.24	21.71	8.84
N org		62.34	70.92	63.74	59.31	68.15	81.75	66.39	73.45	85.78

Note: mon: monsoon; N: nitrogen; N ex: exchangeable nitrogen; N fix: fixed nitrogen; N org: organic nitrogen.

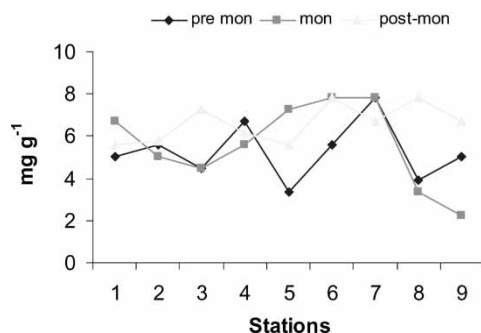


Figure 2. Seasonal variations in concentrations ( $\text{mg g}^{-1}$ ) of Total Nitrogen in sediments from different sampling stations and zones within the Kuttanad Waters of southern India.

post-monsoon this ranged between 77.65–83.98 and 66.39–81.75 respectively. In zone III the range of percentage contribution of organic nitrogen to the total nitrogen were 68.91–69.89, 42.15–50.36 and 73.45–85.78 for the pre-monsoon, monsoon and post-monsoon respectively.

A significant concentration of exchangeable ammonia was observed in this study, which is quite unexpected. It is to be stated that the speciation was done on the wet samples, which contained pore water also. As described above the  $\text{NH}_4^+$  formed by the mineralisation of the organic matter in the sediments gets rapidly dissolved in the pore waters. In the pore water this ammonia will be available until it gets diffused into the water column [2]. So it can be considered that the concentration observed is a reflection of the formation and residence time of  $\text{NH}_4^+$  in the pore water. The contribution of pore water towards the estimated exchangeable ammonium is not worked out here mainly because the intention of the study was to quantify the availability of different nitrogen species in the sedimentary compartment. The present observation indicates significant contribution from the sediment towards  $\text{NH}_4^+$  concentration in the water column. It is reported that in most coastal environments the vast majority of recycled nitrogen released to the water from sediments is in the form of  $\text{NH}_4^+$  [17]. Further, it is suggested that this  $\text{NH}_4^+$  is regenerated by the decomposition and deamination of organic matter with subsequent diffusion to the overlying water. It is also observed that the relative influence of sediment nitrogen cycling on the water column processes tends to decrease with increasing depth [18]. The amount of  $\text{NH}_4^+$  can also be influenced by the nitrification process and it is suggested that nitrification rates are regulated generally by availabilities of oxygen or  $\text{NH}_4^+$  [19]. Anoxic metabolism in sediments is observed to build up dissolved ammonia in the interstitial waters of near shore sediments [20, 21].

Lange [10] has reported that no detectable differences in the various N fractions between wet freeze-dried and oven-dried samples were observed. He has also observed that the pore water ammonium concentration is also considerably low and so its contribution is considered as insignificant.

### 3.1 N fix

The fixed nitrogen represents the  $\text{NH}_4^+$ -N fixed to the clay minerals and so its percentage depends on the sediment characteristics. It is reported that the clay minerals illite and kaolinite etc. are capable of fixing ammoniacal nitrogen. Stevenan and Kemp [22, 11] have observed that this fixation is more or less governed by the depth of the sediment. Lange [10] pointed out that the fixed nitrogen has a definite correlation with aluminium.

In the present study the N fix ranged between 36.24–54.84% of the total nitrogen. The observed range is in tune with the earlier reports. The sediments of the Kuttanad have showed

silty clay characteristics in zone I and II. The studies on the chemical characteristic of the sediments of these back water systems have shown that the clayey fraction contains significantly high Aluminium. The reducing environment prevailing in the sedimentary compartment restricts the nitrification processes and the significantly high  $\text{NH}_4^+$ -N in the pore waters, along with the sedimentary composition leads to a markedly high fixed  $\text{NH}_4^+$ -N. The sediment nitrification rates are observed to be governed by the availabilities of oxygen or  $\text{NH}_4^+$  [19]. The observed  $\text{NH}_4^+$  concentration can also be due to the decrease in the oxygen availability to the sediments. Anoxic sediments are observed to contribute  $\text{NH}_4^+$  significantly to the overlying water [2].

### 3.2 N org

Generally the N org is the major constituent of the total nitrogen in the sediments, which may even represent more than 90% of the total nitrogen. In the sediment where the organic matter is less, a lower percentage of organic nitrogen is observed. In the present study the observed percentage of N org, which varies between 38.66–85.98, indicates a significantly low percentage in these sediments. The possibilities for such a low organic N content can be due to:

1. High mineralisation or deamination of N org, which can substantially decrease the percentage of organic nitrogen. The sedimentary environment plays a significant role here. Organic matter has a high affinity for a fine-grained sediment because it adsorbs onto mineral surfaces. Zone III, because of the slight estuarine character, behaved in a different way. The sediment in this zone had a considerably higher sandy character and the amount of organic carbon was significantly low. Suthhof *et al.* [23] reported that sediments which have comparatively more sand content, are relatively poor in organic matter preservation. Sandy soils are well aerated and tend to have low soil moisture content, which environmental conditions favour low organic matter content. Silt- and clay-sized fractions are responsible for the greatest changes occurring in most of the organic matter present in the system. It is reported that in sediments having low organic carbon content the percentage of organic nitrogen is also less.
2. Significant input of anthropogenic organic matter with low nitrogen content can be another reason. But the C/N ratios indicated higher nitrogen content in the sediments [1].

The significance of seasonal variations of different forms of nitrogen was analysed statistically using student's t-test. Seasonal variations of all the three forms were insignificant at 0.05 levels. Variations of N tot during different seasons were also insignificant at 0.05 level. The summary statistics of organic carbon and the texture of the sediment were given in table 2.

Table 2. Stationwise summary statistics of organic carbon (OC) and texture of the sediments.

		1	2	3	4	5	6	7	8	9
OC mg g <sup>-1</sup>	Mean	20.68	20.01	22.92	19.24	17.29	17.79	16.53	12.82	6.84
	SD	13.39	13.21	12.85	12.07	10.16	10.48	11.3	11.05	3.42
Sand (%)	Mean	39.26	40.35	29.17	19.83	44.11	42.79	62.03	87.85	89.28
	SD	7.61	33.60	27.14	20.35	26.72	5.48	25.82	7.56	4.99
Silt (%)	Mean	18.20	32.93	46.81	46.32	34.58	41.14	28.37	8.19	6.68
	SD	11.67	15.93	15.55	4.60	25.52	15.78	13.98	7.83	0.96
Clay (%)	Mean	27.84	26.70	24.00	33.82	21.28	16.04	9.51	3.94	4.01
	SD	7.34	17.79	16.81	15.90	12.65	10.44	11.92	3.75	4.54



Pearson correlations analysis revealed a negative correlation between exchangeable and organic fractions of Nitrogen during pre-monsoon and post-monsoon ( $P < 0.05$ ). But there is significant negative correlation between the three fractions during monsoon ( $P < 0.05$ ).

In conclusion the presence of high N ex and comparable N fix in the sedimentary compartment suggests mixed possibilities. The distribution of N ex, N fix and N org in the sedimentary compartment is indicative of significant contribution from the sediment to the nitrogen cycle in the system.

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