Indian Journal of Geo-Marine Sciences
Vol. 41 (2), April 2012, pp. 180-187

Water quality variation and nutrient characteristics of Kodungallur-Azhikode Estuary, Kerala, India

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Received 25 February 2011; revised 24 June 2011

Present study focussed on the water quality status in relation to various anthropogenic activities in the Kodungallur-Azhikode Estuary (KAE). Average depth of the estuary was 3.6 ± 0.2 m with maximum of 4.3 ± 0.4 m in the estuarine mouth. Dissolved oxygen showed an average of 5.1±1 mg/l in the water column, whereas the highest BOD value was noticed during monsoon period (3.1 ± 0.8 mg/l) which could be due to high organic enrichment in the water column. pH displayed slightly alkaline condition in most of the stations and it varied from 7.2 ± 0.5 in Station 7 to 7.5 ± 0.5 in Station 1. Salinity in the estuary displayed mixo-mesohaline nature with clear vertical stratification. High river discharge could have resulted in nutrients and silt loading into the estuary, which makes a highly turbid water column particularly during the monsoon period, which limits light penetration and subsequent primary productivity. Turbidity in the water column showed an average of 20.2 ± 15.8 NTU. Estuary was nitrogen limited during post and pre monsoon periods. Nitrate-nitrogen content in the estuarine water gave negative correlation with ammonia.

[**Keywords:** water quality, eutrophication, nutrients, estuary]

Introduction

Estuaries are fragile habitats, experiencing declining water quality and eutrophication. Anthropogenic inputs associated with agriculture, aquaculture, urbanization, coastal development and industrial expansion are a primary cause for the decline in the quality of natural habitats in these sensitive waters[1,2]. Estuaries receive substantial amount of nutrients as well as anthropogenic wastes from land and transferred toward inshore seas; estuaries also receive nutrients and organic matter from wetlands[3,4]. Phytoplankton production in estuaries is controlled by macronutrients[5,6] specifically nitrate-nitrogen (NO_3-N), phosphate-phosphorous (PO_4-P) and silicate-silicon (SiO_3-S). Nitrogen limited phytoplankton production is a common occurrence in tropical waters such as Mandovi-Zuari[7], Cochin estuary[8,9], Godavari estuary[10&11] and Hoogly estuary[12]. However, seasonal phosphorous limitation has been found in several estuaries[13]. Higher rates of nutrient inputs[14] lead to higher organic carbon production[15] in estuarine ecosystems where the active biological pump transfers significant amounts of organic carbon to the sediments[16&17]. Nevertheless, the fate of the organic carbon in a coastal ecosystem depends on its origin, composition and stability of the water column. The nutrient concentrations were two to three times higher during peak monsoon period compared to the pre monsoon and post monsoon periods in the Mandovi-Zuari estuarine ecosystem; however primary production was lower during former than latter period due to high suspended load[18]. Similar observations were found in the Cochin back-waters where river discharge controls the nutrients flux to the estuary during monsoon period whereas anthropogenic activities and sediment re-suspension alters the nutrient stoichiometry during less river discharge[15]. It is noticed that out of the total transport of nutrients, major part of the dissolved inorganic nitrogen (DIN), dissolved reactive phosphate and silicate were transported during peak monsoon period in the Hoogly estuary[12]. Therefore, the present study aims to understand the processes controlling nutrient abundances in a tropical microtidal estuary and its stoichiometry.

Materials and Methods

The Kodungallur-Azhikode Estuary (KAE) is a tropical microtidal estuary (10°11'-10°12' N and 76°10'-76°13' E) having an area of 700 ha. It supply substantial amount of nutrients into nearby

Lakshadweep Sea mainly during south west monsoon season. The Karuvannur River and Chalakkudy River are the major rivers emptying into the KAE. Monthly field sampling was conducted at the KAE for twelve months (July 2009 to June 2010). Seven stations (Fig. 1) with varied ecological characteristics were selected in the estuary for monthly field sampling. Water samples were collected using *Niskin water sampler*. The water transparency measured by *Secchi disc* in the field. Samples for dissolved oxygen (DO) were fixed onboard and the remaining water samples were collected in 1-L plastic bottles kept in ice boxes and brought to the laboratory at the earliest possible time. DO was estimated according to Winkler's method[19]. pH was determined using an *Systronics* pH meter (No. 335 [accuracy ± 0.01]). Samples for nutrients DIN (ammonia-nitrogen + nitrite-nitrogen + nitrate-nitrogen), DIP (dissolved inorganic phosphate) and DISi (dissolved inorganic silicate) were analyzed following the standard methods[19,20,21&22]. Conductivity was measured by *Systronics* digital potentiometer (No. 318), turbidity, total dissolved solids (TDS) by *Systronics* water analyser (No. 317), salinity by *Systronics* water analyser (Model no. 317 [Accuracy ± 0.01]) calibrated with standard seawater and values periodically checked against $AgNO_3$ titration[23]. Carbon dioxide, alkalinity, hardness and Biological Oxygen Demand (BOD) were determined by standard procedures[23]. One-way analysis of variance (ANOVA) was used to calculate the month wise variation in different physicochemical and biological parameters. *PRIMER v6.1* was employed for *Bray-Curtis* similarity index analysis for measuring the similarity of dissolved nutrients among stations[24].

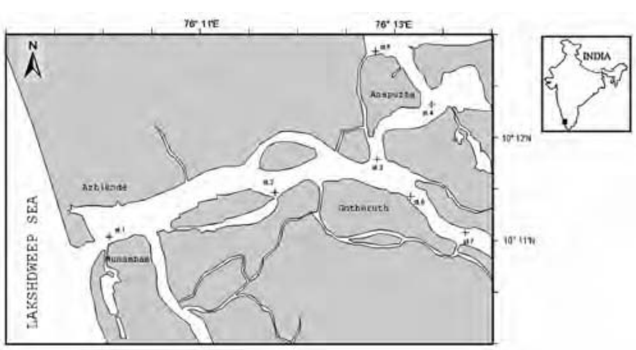

Fig. 1—Map of Kodungallur-Azhikode estuary (KAE) showing study sites (St.1- Munambam, St.2 - Moothakunnam, St.3 - Kottapuram, St.4 - Anapuzha, St.5 - Krishnankotta, St.6 - Gothuruth, St.7 - Puthanvelikkara)

Results and Discussion

Estuarine wetlands are known to contribute to the maintenance of water quality[25]. Because wetlands have a high rate of biological activity, they are effective in transforming many of the common pollutants found in coastal and estuarine waters into harmless by-products or essential nutrients which can be utilized for additional biological activity[26]. Mean depth of the Kodungallur-Azhikode estuary (KAE) was increased[27] from 2 m to 3.6 m with maximum of 4.3 ± 0.4 m at Station 1 could be due to extensive sand mining. It would be reduce natural river flow and natural material flux in the estuary. An average water temperature of 28.9 ± 2°C was observed during the study period (Fig. 2A) with clear vertical stratification; predominantly during post monsoon period. It was moderately low in the water column during monsoon (av: 27.5 ± 2.6°C), compared to pre monsoon (30.4 ± 0.8°C) and post monsoon (av: 28.7 ± 1.3°C) seasons. It was noticed that lowest water temperature observed during the month of July (av: 23.9 ± 0.5°C) and highest in March (31.3 ± 0.8°C). Slightly higher surface temperature (av: 29 ± 2.1°C) was observed in the estuary than that of bottom waters (av: 28.7 ± 2.1°C). The ANOVA of the water temperature showed overall significant at 1% level (F = 83.346). Transparency values were generally low (av: 0.6 ± 0.3 m) in the KAE especially during monsoon season. In the spatial scale, it was lowest in Station 5 (av: 0.8 ± 3 m) and highest in Station 6 (1.1 ± 0.5 m). Transparency of water column negatively correlated with BOD values at 5 % level (r^2 = -0.158). Turbidity level in the estuary was enormously increased particularly during monsoon season due to high influx of silt content, agricultural runoff, sewages and other allochthonous organic matters (Fig. 2B), it could have altered the trophic status of KAE. Apparently high turbidity values were observed in the KAE with an average of 9.8 ± 11.8 NTU; whereas, the peak concentration was recorded during monsoon season (av: 20.2 ± 15.8 NTU) compared to other seasons. The turbidity values tended to show wide variation in the surface and bottom waters in the seven stations of KAE. Highest mean turbidity value was observed at mouth of the estuary represented by Station 1 (av: 13.1 ± 16.4 NTU). Turbidity values showed positive correlation with nitrate-nitrogen, TDS and Eh at 1% level (r^2 = 0.07). Mean TDS value noticed in the KAE was14.7 ± 16.4 ppt. Peak values were observed during monsoon season (av: 18.6 ± 28.8 ppt) followed by pre monsoon (av: 13.4 ± 3.9 ppt) and post monsoon (av: 11.4 ± 4.1 ppt).

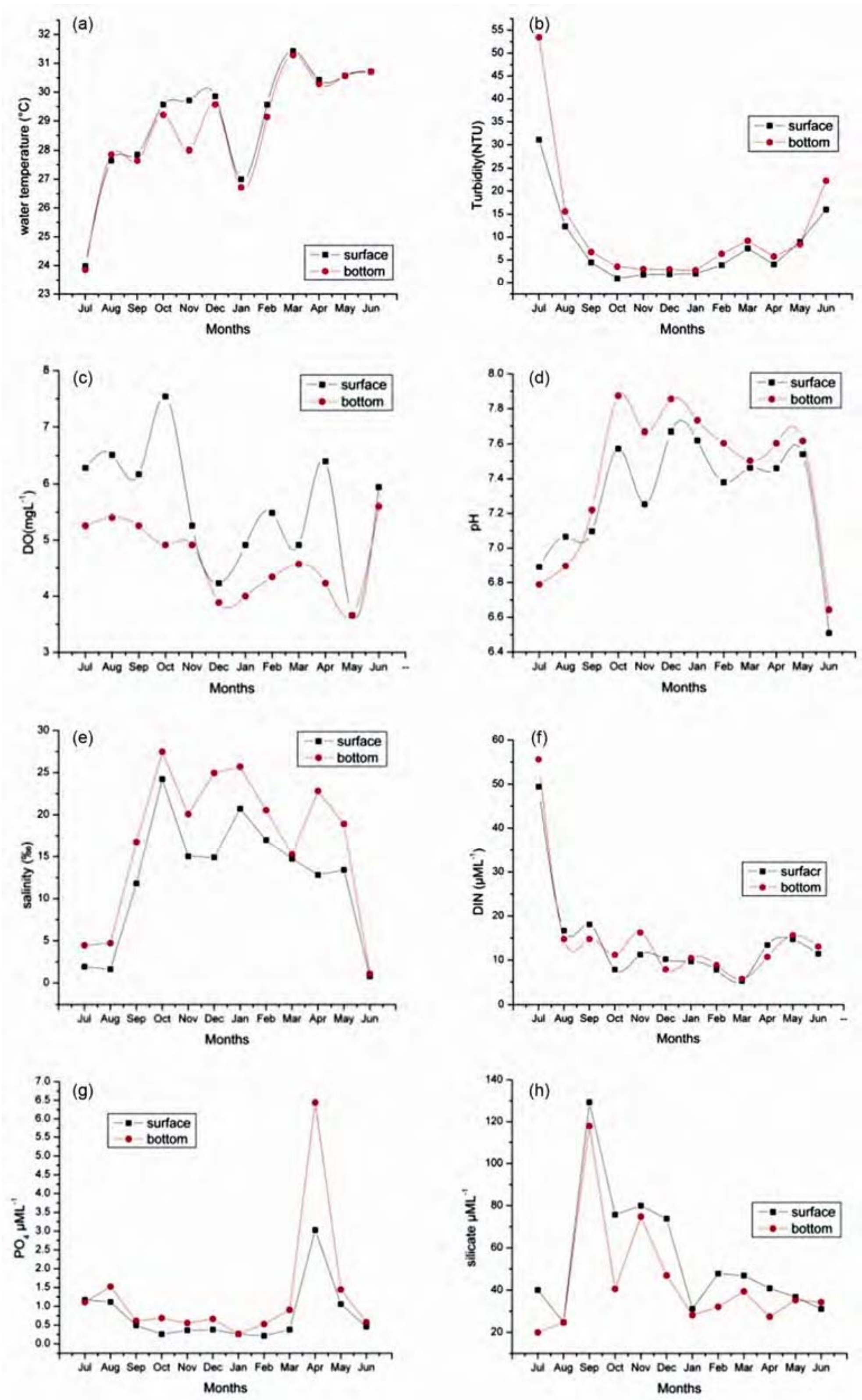

Fig. 2—Distribution of (A) temperature, (B) turbidity, (C) dissolved oxygen, (D) pH, (E) salinity, (F) DIN, (G) DIP and (H) DISi in the Kodungallur-Azhikode estuary during July 2009 - June 2010

The discernible spatio-temporal variation was observed in the pH values (Fig. 2D). It was generally on alkaline side (av: 7.4 ± 0.4) in most of the months. But during peak monsoon marked by heavy rain, values were tended to fell in all the stations of KAE (av: 6. 9 ± 0.2) due to high fresh water discharge. Higher pH values were observed in estuarine mouth (av: 7.5 ± 0.5) when compared to the estuarine head (Station 7; av: 7.2 ± 0.5). Estuarine water showed an average redox potential (Eh) of -1.9 ± 36.6 mV. Significant Eh variation was observed in the water column, bottom water showed highly reduced condition (av: -4.8 ± 38.4 mV) when compared to surface water (av: 1 ± 36.2 mV). Observed reduction in water column Eh values immediately after south west monsoon could be due to organic enrichment and its degradation. The average dissolved oxygen (DO) concentration of 5.1 ± 1 mg/l was observed for the KAE (Fig. 2C). The mean DO values ranged from 4.7 ± 1.3mg/l in Station 1 to 5.9 ± 1.4 mg/l in Station 6. Monsoon season showed highest DO content (av. 5.8 ± 0.5 mg/l) as compared to post monsoon period (av: 5 ± 1.2 mg/l) and pre monsoon period (av: 5 ± 0.9 mg/l). The oxygen rich river discharge could be the reason for comparatively high DO values noticed in the estuarine head region (station 6 and station 7), as compared to other stations. A discernible trend was observed in the DO regime in the estuary, where surface water was higher than bottom waters. Surface water DO (av: 5.6 ± 1.1 mg/l) displayed comparatively higher values than bottom waters (av: 4.7 ± 0.6 mg/l). High river influx and tidal mixing could be the reason for comparatively high DO level as observed during the south west monsoon. The ANOVA of the DO showed overall significant at 1% level (F = 7.113). A positive correlation significant at 1% level emerged between DO and Eh (r^2 = 0.295). CO_2 values in the estuary showed comparatively high values due to the various human activities in the region and this could lead to ecosystem stress[28]. Carbon dioxide (CO_2) values showed highest mean in Station 5 (av: 7.1 ± 2.1 mg/l) and minimum observed in Station 7 (av: 5.3 ±1.8 mg/l); The CO_2 values were high in post monsoon (av: 6.9 ± 1.8 mg/l) as compared to monsoon period (av: 6 ± 1.1 mg/l) and pre monsoon period (av: 6.3 ± 2.5 mg/l) in the KAE. A remarkably high CO_2 value of 14 mg/l was recorded in the bottom water in Station 2 during September. The high CO_2 values observed in the most of the stations particularly in the Station 1 (av: 7 ± 3 mg/l) and Station 5 (av: 7.1 ± 2.1 mg/l). The ANOVA of alkalinity showed overall significant at 1% level (F = 22.490). The average Biological Oxygen Demand (BOD) during the present study was 2.6 ± 0.9 mg/l; it was high in the Station 1 (av: 3.1 ± 1.5 mg/l). BOD level comparatively increased during monsoon period (av: 3.1 ± 0.8 mg/l) as compared to the post monsoon (av: 2.2 ± 1.1 mg/l) and pre monsoon (av: 2.3 ± 0.6 mg/l). The alkalinity showed a moderate trend in all the seven stations of KAE with an average of 35.1 ± 18.4 mg/l. Comparatively high alkalinity was observed during pre monsoon period (av: 43.7 ± 20.4 mg/l) when compared to monsoon (av: 24.4 ± 6 mg/l) and post monsoon (av: 36.9 ± 20.9 mg/l) seasons. Highest mean alkalinity value recorded at station 1 (av: 40.3 ± 29 mg/l). The mean calcium hardness of KAE was 750 ± 870.3 mg/l and it showed portends to increase from monsoon (av: 490.2 ± 838.3 mg/l) to pre monsoon period (av: 1294 ± 1070.9 mg/l).

Average salinity of estuary showed mesohaline nature. The maximum average salinity was recorded at mouth region (Station 1; av: 18.9 ±10.5‰) and minimum at estuarine head (Station 7; av: 10.2 ± 8.6‰). Clear vertical stratification and seasonality (Fig. 2E) were observed in salinity pattern. Bottom water salinity showed higher values (av: 16.9 ± 8.9‰) compared to surface water salinity (av: 12.4 ± 7.4‰); however, well mixed water column was observed in the Station 6. The salinity values showed a definite trend, where it decreased from estuarine mouth to head. During the monsoon period (June to September) salinity values were comparatively low (av: 5.4 ± 5.8‰); however, salinity enormously increased (av: 21.6 ± 4.8‰) during post monsoon period (October to January) could be due to sea water incursion and less river discharge. But, salinity tends to decreased (16.1 ± 3.6‰) during pre monsoon period (February-May) as a result of commencement of south-west monsoon. The ANOVA of salinity showed the variation between months and were significant at 1% level (F = 33.433).

In estuarine ecosystems, the major sources of nutrients are from rivers, ground water, atmosphere and sediments[29]. The nutrient load from river influx was extreme depending on the allochthonous and autochthonous precipitations in the basins. All nutrient peaks harmonized with each other. Rapid nutrient inputs are of considerable importance since they can modify the phytoplankton community structure[30]. Nutrients and other suspended solids brought into the estuary those results in decreased light penetration and high flushing time lead to subsequent decrease in primary production. In the KAE, the major source of macro nutrients input was associated with river discharge during south-west monsoon. Estuaries receive nutrients also from rain water[11]. During the study period, the average nutrient concentrations were 15.0 ± 12.1 µmol/L for dissolved inorganic nitrogen (DIN; nitrate-nitrogen + nitrite-nitrogen + ammonia nitrogen), 49.1 ± 28.7 µML for dissolved inorganic silicate (DISi), and 1 ± 1.3 µmol/L for dissolved inorganic phosphate (DIP). The average nitrate-nitrogen (NO_3-N) of KAE water was 10.2 ± 12.8 µML. The average NO_3-N values ranged from 7.9 ± 9.9 µML in Station 2 to 13.6 ± 19.8 µML in station 7. Comparatively high NO_3-N was observed during monsoon period (av: 19.1 ± 19.4 µmol/L), whereas relatively low NO_3-N content was observed in post monsoon (av: 7.4 ± 3.6 µmol/L) and pre monsoon periods (av: 3.8 ± 3.3 µmol/L). The average nitrite-nitrogen (NO_2-N) content of KAE water was 0.3 ± 0.2 µML and highest value recorded during pre monsoon period (0.4 ± 0.3 µML). Nitrate-nitrogen showed significant correlation between turbidity and TDS at the 0.01 level (r^2 = 0.612). The mean ammonia-nitrogen varied from 3 ± 2.8 µmol/L in Station 7 to 5.6 ± 5.5 µmol/L in Station 3. Ammonia value shows monthly average of 4.5 ± 2.9 µML in the KAE. *Bray-Curtis* similarity index of DIN content in the water column (Fig. 3A) showed overall similarity of >34% with highest between surface DIN content between months August and September (>92%). Phosphate-phosphorous (PO_4-P) values showed an average of 1 ± 1.3 µML in the seven stations with highest during pre monsoon season (av: 2 ± 2.1 µmol/L). Comparatively high content of PO_4-P was observed in bottom water (av: 1.3 ± 1.7 µML) when compared to surface water (av: 0.8 ± 0.8 µML). However, DIP showed overall similarity of >24% between the stations, with highest observed (Fig. 3B) between bottom water DIP content of months October and December (>93%). Silicate-silicon (SiO_3-S) values highly varied during the study (av: 49.1 ± 28.7 µML). Considering the seasonal average, a slight increase in SiO_3-S content was observed in the water column during post monsoon period (av: 56.4 ± 21.9 µmol/L). DISi showed overall similarity of >55% with highest (Fig. 3C) between surface and bottom water (>98%) during the month of August (Fig. 3C); this could be due to well mixing of water column during south west monsoon. Estuarine primary production, size, depth, volume, influx rate, water residence time, tidal exchange, vertical mixing and stratification could also affect the nutrient transport and cycling in the estuary; however, average nutrient concentrations of the KAE was well below those of the San Francisco Bay[31], Chesapeake Bay[32], Pearl River estuary[33] and the Guadiana estuary[34]. DIP showed negative correlation with BOD; whereas, DISi showed positive correlation with CO_2 at 5% level (r^2 = 0.171). The ANOVA of the nitrate-nitrogen showed overall significant at 1% level (F = 50.537). Among the three major macronutrients, DIP concentrations were comparatively low in the KAE. The ANOVA of DIP showed the variations between months were significant at 1% level (F = 10.897).

It is noted that inorganic phosphate in the Godavari estuary was lowest compared to that in the other Indian estuaries[35]. But in this study DIP in the KAE was slightly lower than Godavari estuary (1.5 ± 3.8 µML); phosphorous limitation was also observed in the estuary during south west monsoon period. The ANOVA of DISi showed overall significant at 1% level (F = 38.965). The maximum DIN and DISi concentrations in the downstream and upstream occurred in the south west monsoon. DIN (Fig. 2F) and DIP (Fig. 2G) were the primary limiting macronutrients especially as regulators of phytoplankton. The average N: P ratio of the KAE (Table 1) was well above *Redfield ratio* during south west monsoon season (27.9 ± 14.2) then it was decreased to 7.4 ± 3.4 (post monsoon); which indicates that KAE was phosphorous limited during monsoon season and nitrogen limited during post and pre monsoon periods. Nitrogen imitated conditions were similarly observed in the various estuaries of India such as Cochin backwaters[8], Godavari estuary[11], Mandovi - Zuari estuarine ecosystem[7], Hoogly estuary[12], Ashtamudi estuary[36]. Higher values of the *Redfield ratio* are interpreted as indicative of phosphorous limitation and on the other hand, low ratios suggest nitrogen limitation[37]. The inorganic nitrate constituted the major fraction of total DIN (av: 58%) in the surface and bottom waters of the estuary. Comparatively high concentration of allochthonous as well as autochthonous nutrient levels in the KAE is an indicator of

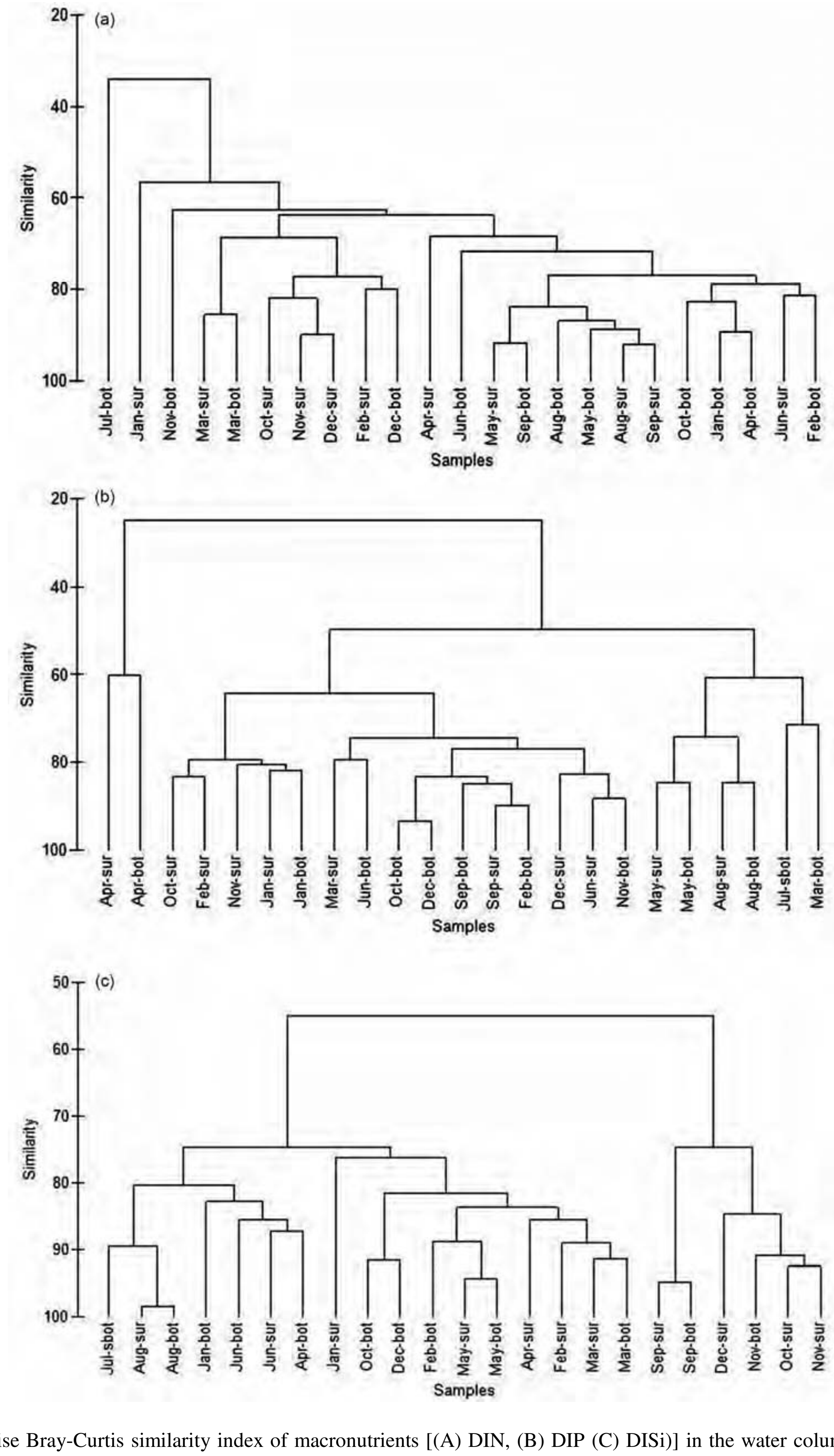

Fig. 3—Month wise Bray-Curtis similarity index of macronutrients [(A) DIN, (B) DIP (C) DISi)] in the water column of Kodungallur-Azhikode estuary during July 2009 - June 2010

Table 1—Seasonal variability (standard deviation) of DIN and the nutrient ratio in the Kodungallur-Azhikode estuary during July 2009 - June2010

	Monsoon	Post-monsoon	Pre-monsoon
NO_2-N (μML^{-1})	0.3 ± 0.2	0.2 ± 0	0.4 ± 0.3
NO_3-N (μML^{-1})	19.1 ± 19.4	7.4 ± 3.6	3.8 ± 3.3
NH_4+ (μML^{-1})	4.9 ± 3.6	3.0 ± 2	6.6 ± 2.4
N : P	27.9 ± 14.2	7.4 ± 3.4	4.2 ± 3.6
Si : N	3.1 ± 3.1	26.5 ± 9.6	11.4 ± 8.3
Si : P	83.2 ± 96.2	5.3 ± 1.7	4.5 ± 2.5

anthropogenic eutrophication. Intensive sand mining, poor agricultural practices and failures in urban planning resulted in excessive allochthonous and autochthonous nutrients and sediment transfer in to the KAE waters; could be accelerate eutrophication process in the estuary. Perhaps, its appropriately scaled and parameterized regulations are the only realistic options for controlling eutrophication in this estuarine system.

Acknowledgements

Authors are thankful to the Kerala State Council for Science, Technology and Environment (KSCSTE) for financial assistance and to the Head, Dept. of Marine Biology, Microbiology and Biochemistry, School of Marine Sciences, Cochin University of Science and Technology for providing necessary facilities.

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