Fractionation and bioavailability of phosphorus in a tropical estuary, Southwest India

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Abstract Phosphorus fractionation was employed to find the bioavailability of phosphorus and its seasonal variations in the Panangad region of Cochin estuary, the largest estuarine system in the southwest coast of India. Sequential extraction of the surficial sediments using chelating agents was taken as a tool for this. Phosphate in the water column showed seasonal variations, with high values during the monsoon months, suggesting external runoff. Sediment texture was found to be the main factor influencing the spatial distribution of the geochemical parameters in the study region. Similarly, total phosphorus also showed granulometric dependence and it ranged between 319.54 and 2,938.83 µg/g. Calcium-bound fraction was the main phosphorus pool in the estuary. Significant spatial variations were observed for all bioavailable fractions; iron-bound inorganic phosphorus (5.04–474.24 µg/g), calcium-bound inorganic phosphorus (11.16–826.09 µg/g), and acid-soluble organic phosphorus (22.22–365.86 µg/g). Among the non-bioavailable phosphorus, alkali-soluble organic fraction was the major one (51.92–1,002.45 µg/g). Residual organic phosphorus was comparatively smaller fraction (3.25–14.64% of total). The sandy and muddy stations showed distinct fractional composition and the speciation study could endorse the overall geochemical character. There could be buffering of phosphorus, suggested by the increase in the percentage of bioavailable fractions during the lean premonsoon period, counteracting the decreases in the external loads. Principal component analysis was employed to find the possible processes influencing the speciation of phosphorus in the study region.

Keywords Phosphorus · Fractionation ·
Bioavailability · Geochemistry · Nutrients ·
Tropical estuary

Introduction

Estuaries are generally regarded as highly eutrophic systems as a result of anthropogenic nutrient inputs. Phosphorus (P) is the key element of eutrophication processes as it tends to accumulate in wetland systems and can function as an internal load to the overlying water column for a long period (Reddy et al. 1996). Because of its influence on the productivity (Caraco et al. 1990), identification of P compounds in estuarine sediments and the knowledge of changes in the makeup of the P pool in space and time are highly relevant

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(Morton and Edwards 2005; Hou et al. 2009). P cycling and bioavailability in estuaries depend upon its speciation (Paludan and Morris 1999; Andrieux-Loyer and Aminot 2001; Coelho et al. 2004). A useful tool to estimate the stock of potentially accessible forms is to fractionate P based on the extractability by leaching reagents of increasing aggressiveness (Golterman 1996; Perkins and Underwood 2001; Tiyapongpattana et al. 2004).

However, the complexity of the physicochemical and biological processes found in these transition zones, pose challenges for investigating the estuarine nutrient dynamics. There is a conspicuous lack of information about the concentration, turnover rates, transport, and fate of P in the estuarine systems. Also there are distinct variations from one estuary to another, defying generalization. The main objective of the present study is to quantify different P fractions in the surficial sediments of Cochin estuary using sequential extraction. It is intended to understand the association of P with various sedimentary parameters and to estimate its mobility, biological availability, and the diagenesis.

Materials and methods

Study area

Cochin estuary (09°30′–10°12′ N; 76°10′–76°30′ E) is a part of Vembanad-Kol wetlands and it is the largest estuarine system in the southwest coast of India. It is very peculiar and complex in the sense that it lies parallel to the coastline with several islands and small arms. Unlike many other estuaries in the world, six rivers with their tributaries along with several canals bring large volumes of freshwater into the estuary. It is one of the highly productive estuarine systems (Qasim 2003) and has been designated as a 'Ramsar site' (No. 1214). Tides at Cochin are of a mixed semi-diurnal type, with the maximum spring tide range of about 1 m (Srinivas 1999). Because of the low tidal amplitudes, incomplete flushing often results.

This estuary is under the profound influence of monsoon. About 71% of annual rainfall is contributed by monsoon (Jayaprakash 2002). Accordingly, there are three seasonal conditions prevailing viz. monsoon (June–September), post-monsoon (October–January), and pre-monsoon (February–May). Hydrobiological studies of the estuary (Menon et al. 2000) showed that the high flushing during monsoon completely transforms the estuary into a freshwater habitat. Post-monsoon is generally the stabilization period and during pre-monsoon, when the runoff is least, the estuary is predominantly marine in nature.

The studies on Cochin estuary were mainly confined to the main arm or near the barmouth; narrow inner regions were not seriously considered. Detailed studies on the nutrient geochemistry of the estuary including the inner areas are imperative to derive a long-term sustainable management scheme for this important ecosystem. Panangad region, situated about 10 km away from the barmouth, in the southern arm of the estuary, is selected as a representative study area (Fig. 1). It includes the narrow inner part of the estuary as well as the main arm. It is surrounded by Nettoor and Panangad islands and generally shallow in nature with an average depth of 2.5 m and a maximum of about 5 m.

Sampling and analysis

Monthly observations were carried out from six sampling stations in the Panangad region from January to December 2003, except May (Fig. 1). Data collections were organized on days of higher tidal range (near spring tide). Water samples were collected using Van Dorn water sampler and the surficial sediments (0–5 cm) were sampled using a Van Veen grab (0.042 m^2).

Phosphate in the water samples was estimated with the phosphomolybdate blue method (Grasshoff et al. 1983). The textural characteristics of the sediments were determined by pipette analysis (Folk 1980), after removing the inorganic carbonates using 10% HCl and organic matter using H_2O_2. Sediment was wet sieved through a 63-μ sieve to collect the sand fraction. The mud fraction was divided into silt (63–4 μ) and clay (<4 μ) fractions by timed gravimetric extraction of the dispersed sediments. Folk (1980) classification scheme was followed to assess the nature of the sediments. Finely powdered air-dried sediment samples were used for the analyses
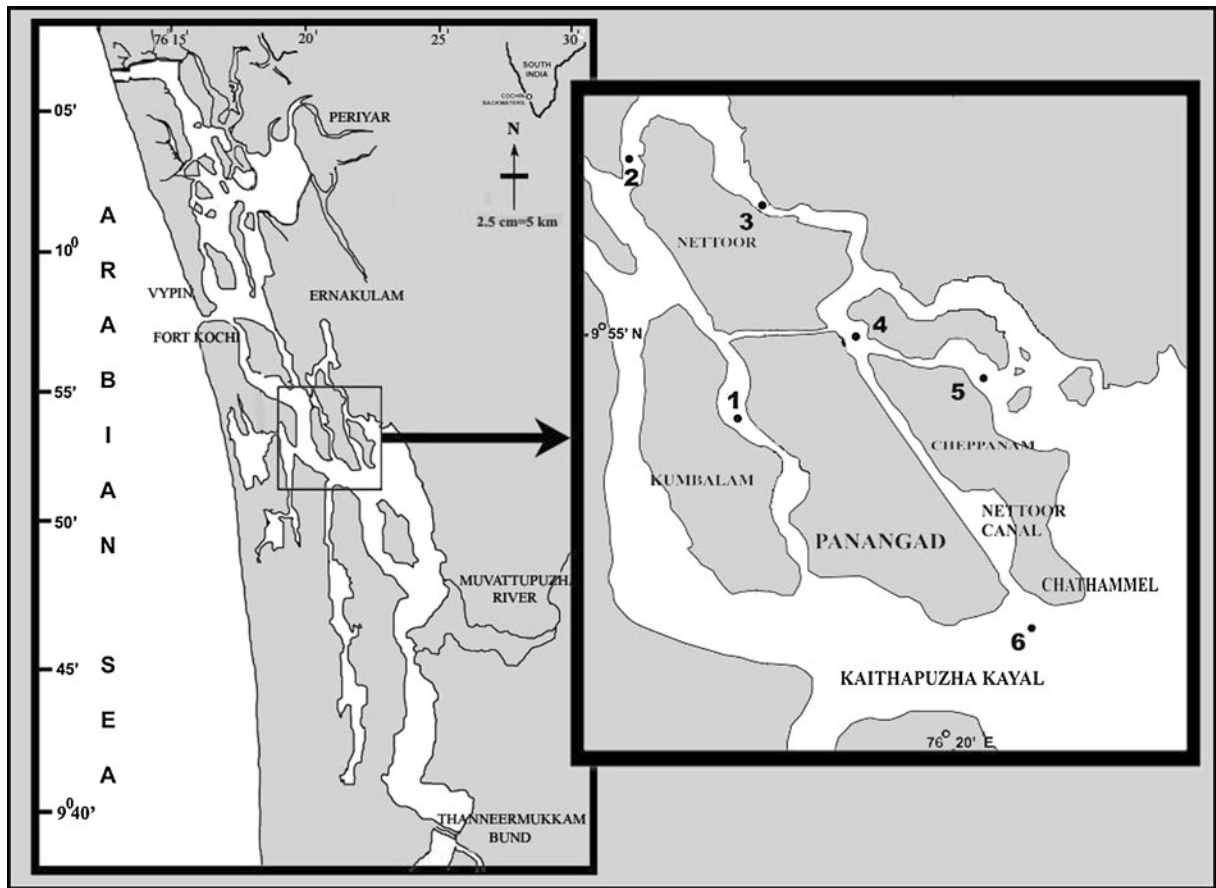
Fig. 1 Cochin estuary showing sampling locations

of the rest of the parameters, and the values are expressed on dry weight basis. Total carbon, nitrogen, and sulfur of the surficial sediments were analyzed using CHN analyzer (VarioEL lll CHNS). Organic carbon was also determined using CHN analyzer by removing the inorganic carbon with dilute HCl (Tung and Tanner 2003). About 1 g of the sediment was carefully digested with a triacid mixture ($HClO_4$, HNO_3, and HCl in the ratio 1:1:3) and the total iron concentration was determined by atomic absorption spectrophotometry (Perkin-Elmer 3110). Analysis of certified reference standards (BCSS-1, Canadian National Research Council) showed the accuracy and precision of the Fe analysis to be 6% and 3%, respectively. For benthic analysis, the sediment samples were sieved on a mesh size of 0.5 mm and the organisms retained were preserved in 5% buffered formalin containing Rose Bengal stain. All the organisms were sorted, identified, and counted in the laboratory.

P fractionation of approximately 0.8 g of the sediment portions was performed in replicates by sequential extraction with chelating compounds (Golterman 1996), with the modification of Diaz-Espejo et al. (1999). In this method, the iron-bound P (Fe–P) was first extracted with Ca–EDTA/dithionite with constant shaking for 1 h. Secondly, 0.1 M Na_2–EDTA was added to the previous pellet and constantly shaken for 1.5 h to get calcium-bound P (Ca–P). In the next step, acid hydrolysable organic P (acid–OP) was extracted with 0.5 M H_2SO_4 by shaking constantly for half an hour. 2M NaOH was added to the previous pellet and kept at 90°C for 2 h to yield alkali-soluble P (alkali–OP). The residue was digested with 0.5 M H_2SO_4 and 2 g $K_2S_2O_8$ for the residual organic fraction (R–OP). The Ca–EDTA/dithionite

and the Na$_2$–EDTA extractions were repeated twice to ensure a complete P extraction. Phosphate in the extracts was estimated with the phosphomolybdate blue method (Grasshoff et al. 1983). Additionally, total P from the first two extracts was also measured by digesting with 0.5 M H$_2$SO$_4$ and 2 g K$_2$S$_2$O$_8$ in order to include their organic fractions (Fe–OP and Ca–OP). The EDTA method allows a specific extraction of inorganic P with less destruction of organic P (Golterman 2001; Kassila and Hussenot 2004). Fe–IP, Ca–IP, and acid–OP were considered as a source of

bioavailable P for phytoplankton (Diaz-Espejo et al. 1999).

Results

Phosphate in the water column showed seasonal variations, with high values during the monsoon months and very low values during the pre-monsoon months (Fig. 2). In the pre-monsoon season, the surface range was between zero and 3.96 μmol/l and at the bottom; the range was
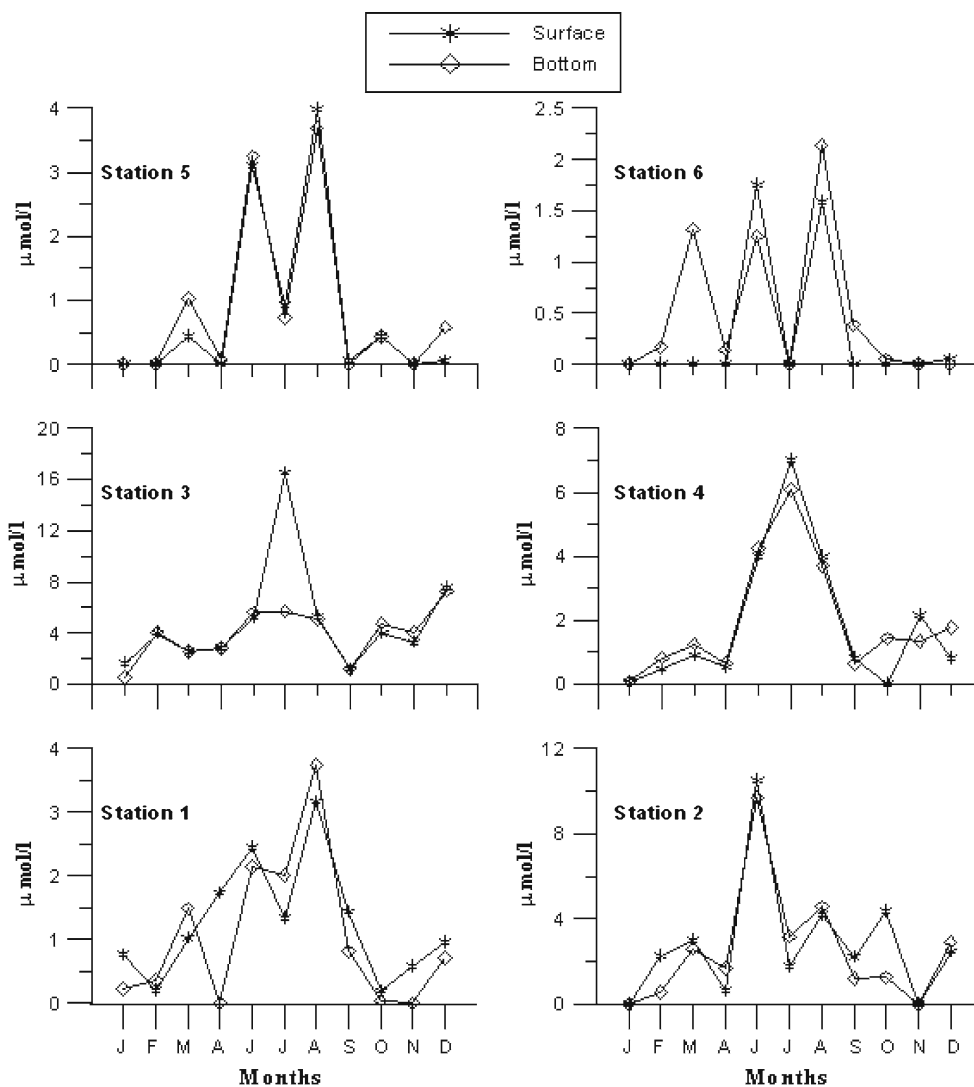

Fig. 2 Monthly variation of phosphate in the water column

Table 1 Seasonal averages of geochemical parameters in the study region (% weight ± SD)

Parameters	Station 1			Station 2			Station 3		
	Pre	Mon	Post	Pre	Mon	Post	Pre	Mon	Post
Sand	82.50 ± 1.20	82.70 ± 1.20	81.90 ± 0.90	92.40 ± 4.20	93.90 ± 4.20	90.10 ± 1.30	97.60 ± 0.70	98.10 ± 0.70	97.20 ± 0.20
Silt	7.30 ± 1.90	6.60 ± 1.30	8.20 ± 1.30	1.40 ± 0.60	1.20 ± 0.70	1.70 ± 0.20	0.60 ± 0.20	0.40 ± 0.30	0.80 ± 0.10
Clay	10.20 ± 0.70	10.80 ± 0.5	9.90 ± 0.50	6.20 ± 3.50	4.80 ± 3.70	8.20 ± 1.10	1.80 ± 0.40	1.50 ± 0.40	2.00 ± 0.20
Total carbon	0.68 ± 0.10	0.69 ± 0.05	0.81 ± 0.24	0.10 ± 0.03	0.07 ± 0.01	2.53 ± 1.87	0.21 ± 0.17	0.09 ± 0.02	0.10 ± 0.04
Organic carbon	0.54 ± 0.12	0.50 ± 0.03	0.59 ± 0.19	0.08 ± 0.05	0.06 ± 0.02	1.87 ± 1.61	0.16 ± 0.12	0.07 ± 0.03	0.06 ± 0.03
Total nitrogen	0.12 ± 0.02	0.10 ± 0.06	0.15 ± 0.09	0.06 ± 0.03	0.09 ± 0.04	0.26 ± 0.24	0.08 ± 0.02	0.09 ± 0.01	0.03 ± 0.05
Total sulfur	0.27 ± 0.01	0.26 ± 0.09	0.32 ± 0.08	0.04 ± 0.03	0.03 ± 0.00	0.92 ± 0.74	0.09 ± 0.06	0.04 ± 0.02	0.02 ± 0.01
Total iron	2.40 ± 0.23	2.34 ± 0.32	2.33 ± 0.52	0.45 ± 0.15	0.34 ± 0.14	2.08 ± 1.15	0.72 ± 0.39	0.28 ± 0.08	0.68 ± 0.65

Parameters	Station 4			Station 5			Station 6		
	Pre	Mon	Post	Pre	Mon	Post	Pre	Mon	Post
Sand	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	26.40 ± 6.00	27.00 ± 7.00	30.90 ± 0.90	0.40 ± 0.10	0.40 ± 0.10	0.40 ± 0.00
Silt	54.00 ± 1.90	53.10 ± 1.30	55.00 ± 1.40	51.50 ± 6.20	52.10 ± 4.40	47.90 ± 4.40	67.20 ± 2.70	68.50 ± 1.90	65.90 ± 1.70
Clay	46.00 ± 1.90	46.90 ± 1.30	45.00 ± 1.40	22.10 ± 0.80	20.90 ± 0.50	21.20 ± 0.60	32.40 ± 2.60	31.10 ± 1.80	33.70 ± 1.80
Total carbon	2.83 ± 0.91	3.50 ± 0.14	3.37 ± 0.12	2.65 ± 0.83	2.68 ± 0.20	2.35 ± 0.21	3.61 ± 0.08	3.86 ± 0.13	3.74 ± 0.03
Organic carbon	2.00 ± 0.88	2.48 ± 0.29	1.99 ± 0.22	1.72 ± 0.66	1.86 ± 0.26	1.62 ± 0.24	2.51 ± 0.15	2.47 ± 0.10	2.36 ± 0.08
Total nitrogen	0.27 ± 0.18	0.42 ± 0.03	0.46 ± 0.09	0.32 ± 0.10	0.29 ± 0.05	0.30 ± 0.06	0.33 ± 0.02	0.35 ± 0.04	0.36 ± 0.08
Total sulfur	0.88 ± 0.27	1.13 ± 0.06	1.09 ± 0.08	0.82 ± 0.18	0.79 ± 0.12	0.83 ± 0.07	1.17 ± 0.22	1.14 ± 0.24	1.52 ± 0.20
Total iron	5.91 ± 2.17	7.19 ± 0.27	7.54 ± 0.79	4.80 ± 1.08	5.29 ± 0.53	5.12 ± 0.99	7.52 ± 0.12	7.37 ± 0.29	6.98 ± 0.21

Pre pre-monsoon, *Mon* monsoon, *post* post-monsoon

Table 2 Benthic population of the study region

Groups	Station 1			Station 2			Station 3		
	Pre	Mon	Post	Pre	Mon	Post	Pre	Mon	Post
Polychaetes	897.1 ± 131.5	261.6 ± 85.0	1,345.3 ± 633.5	817.5 ± 184.9	129.1 ± 67.6	940.4 ± 470.0	253.7 ± 72.8	101.2 ± 22.8	294.0 ± 51.9
Molluscs	31.7 ± 55.0	29.8 ± 59.5	113.0 ± 52.6	23.8 ± 41.2	53.6 ± 40.7	389.3 ± 190.0	–	65.5 ± 22.8	178.4 ± 112.3
Amphipods	476.3 ± 519.1	65.5 ± 52.8	432.9 ± 171.2	134.9 ± 131.1	71.4 ± 27.5	59.5 ± 68.7	111.1 ± 112.5	17.9 ± 22.8	101.2 ± 94.0
Tanaids	238.1 ± 148.7	273.7 ± 211.6	496.2 ± 302.6	95.2 ± 85.8	101.2 ± 22.8	53.6 ± 68.4	142.9 ± 41.2	41.7 ± 29.9	154.6 ± 142.0
Crabs	–	6.0 ± 11.9	36.3 ± 62.9	15.9 ± 27.5	6.0 ± 11.9	53.6 ± 49.1	47.6 ± 47.6	–	6.0 ± 11.9
Others	83.3 ± 16.9	11.9 ± 13.7	29.8 ± 45.1	55.6 ± 27.5	–	11.9 ± 13.7	7.9 ± 13.7	23.8 ± 0.0	23.8 ± 19.4
Total	1,698.8 ± 573.6	573.6 ± 237.1	2,444.3 ± 1,124.3	1,142.8 ± 304.0	361.2 ± 69.4	1,508.3 ± 607.0	563.2 ± 169.0	249.9 ± 41.2	757.8 ± 354.9

Groups	Station 4			Station 5			Station 6		
	Pre	Mon	Post	Pre	Mon	Post	Pre	Mon	Post
Polychaetes	404.6 ± 103.9	136.9 ± 99.8	601.2 ± 182.8	333.3 ± 85.9	107.1 ± 90.1	350.5 ± 145.3	285.7 ± 148.8	152.1 ± 44.2	319.0 ± 115.3
Molluscs	–	23.8 ± 47.6	107.1 ± 16.8	23.8 ± 41.2	–	–	31.7 ± 55.0	47.6 ± 55.0	440.4 ± 307.7
Amphipods	365.1 ± 36.4	65.5 ± 22.8	261.8 ± 180.9	55.5 ± 13.7	65.5 ± 11.9	119.0 ± 47.6	87.1 ± 49.7	53.6 ± 35.7	72.7 ± 71.8
Tanaids	777.7 ± 469.8	77.4 ± 35.7	280.0 ± 91.9	111.1 ± 153.1	89.3 ± 11.9	181.7 ± 94.1	214.1 ± 63.1	89.3 ± 52.8	23.8 ± 27.5
Crabs	–	–	59.5 ± 119.0	–	–	23.8 ± 47.6	71.5 ± 86.0	6.0 ± 11.9	71.4 ± 41.2
Others	23.8 ± 23.8	6.0 ± 11.9	31.7 ± 36.4	23.8 ± 41.2	11.9 ± 13.7	23.8 ± 0.0	63.5 ± 55.0	23.8 ± 33.7	6.0 ± 11.9
Total	1,571.2 ± 509.1	309.5 ± 101.0	1,279.8 ± 435.1	547.5 ± 166.7	273.7 ± 90.1	692.9 ± 253.5	753.7 ± 96.9	372.3 ± 76.8	915.4 ± 349.4

Others include penaeid prawns, benthic fishes, isopods, and cumaceans

Table 3 Seasonal variations of different phosphorus fractions in the study region (μg/g dry weight $\pm$ SD)

Stations	Season	Fe–IP	Fe–OP	Ca–IP	Ca–OP	Acid–OP	Alkali–OP	ROP	Total P
1	Pre-monsoon	80.48 (4.54)	26.27 (33.95)	238.06 (75.74)	11.79 (0.29)	164.68 (57.20)	175.11 (2.75)	85.25 (17.32)	781.61 (147.49)
2		5.04 (2.18)	20.61 (1.67)	11.16 (2.08)	159.87 (44.88)	22.22 (4.71)	57.65 (5.14)	43.00 (5.43)	319.54 (34.75)
3		66.59 (26.72)	11.15 (1.90)	51.46 (1.95)	94.28 (42.85)	45.83 (16.14)	90.51 (28.31)	49.00 (10.00)	408.81 (18.35)
4		474.24 (33.12)	20.24 (4.86)	481.58 (170.99)	178.10 (66.05)	217.19 (41.13)	286.58 (69.43)	161.25 (24.75)	1,819.14 (410.31)
5		340.79 (18.88)	14.91 (3.29)	463.44 (101.09)	73.22 (37.96)	276.47 (38.71)	317.07 (49.96)	146.25 (3.75)	1,632.12 (132.45)
6		324.42 (0.84)	27.85 (3.22)	826.09 (87.19)	52.92 (5.89)	242.37 (24.27)	486.95 (39.98)	117.13 (24.88)	2,027.72 (87.72)
1	Monsoon	26.60 (2.18)	33.72 (9.38)	140.09 (99.03)	278.92 (227.82)	158.55 (45.16)	181.79 (46.03)	58.58 (24.91)	878.24 (206.63)
2		14.53 (1.87)	29.64 (6.24)	33.01 (5.18)	35.69 (7.89)	29.65 (4.88)	602.49 (41.06)	53.41 (7.16)	798.42 (45.14)
3		16.29 (2.33)	34.92 (4.67)	23.4 (3.56)	25.78 (4.85)	43.06 (9.14)	424.67 (36.16)	52.3 (4.88)	620.42 (39.86)
4		120.31 (17.43)	92.30 (4.78)	325.60 (127.67)	319.62 (3.37)	262.60 (46.66)	579.57 (46.84)	177.36 (6.56)	1,877.35 (102.44)
5		65.63 (5.41)	56.05 (5.56)	190.58 (76.04)	317.45 (140.45)	298.04 (35.19)	703.47 (28.29)	279.83 (24.21)	1,911.04 (12.32)
6		118.63 (32.40)	39.00 (11.35)	702.22 (76.97)	471.50 (176.67)	365.86 (45.09)	1,002.45 (97.93)	239.18 (0.04)	2,938.83 (286.43)
1	Post-monsoon	32.63 (3.32)	152.68 (52.85)	160.12 (48.90)	210.49 (147.95)	170.95 (68.66)	144.53 (79.13)	29.27 (4.02)	900.66 (3.24)
2		114.66 (46.18)	156.62 (67.26)	106.42 (2.36)	436.13 (224.53)	132.87 (43.63)	51.92 (7.83)	43.49 (16.40)	1,042.10 (392.55)
3		8.55 (2.34)	20.27 (3.16)	83.34 (4.89)	11.4 (5.79)	55.04 (5.97)	783.38 (57.44)	33.3 (7.47)	995.28 (58.91)
4		281.79 (84.86)	116.22 (83.73)	549.66 (81.08)	181.37 (143.81)	272.37 (19.41)	340.08 (123.73)	69.63 (9.61)	1,811.10 (33.09)
5		73.48 (9.93)	110.98 (17.61)	174.75 (85.12)	194.16 (69.74)	313.37 (37.00)	273.22 (1.84)	123.11 (8.59)	1,263.06 (70.48)
6		120.70 (18.06)	466.91 (113.10)	574.23 (102.46)	600.96 (364.76)	300.38 (10.53)	217.22 (0.00)	110.42 (8.67)	2,390.80 (374.26)

between zero and 4.14 μmol/l. During monsoon, surface water showed a variation from zero to 16.46 μmol/l and the bottom varied from zero to 9.70 μmol/l. Surface values ranged between zero and 7.58 μmol/l during post-monsoon and at bottom the range was between zero and 7.30 μmol/l.

The textural composition of the sediment (Table 1) showed distinct spatial variation. But seasonal variations were absent. Coarser fractions (>63 μ) were dominant at stations 1, 2, and 3 while stations 4, 5, and 6 were mainly consisted of finer fractions. As per the classification by Folk (1980), sediments at stations 2 and 3 were sandy in nature, whereas at stations 5 and 6 were muddy. Sandy mud nature was found at station 1 and sandy silt at station 4. Total carbon content showed a wide variation, ranging from 0.10% to 3.61% during pre-monsoon and from 0.07% to 3.86% during monsoon. It ranged between 0.10% and 3.74% during post-monsoon. Organic carbon content showed similar distributional characteristics to that of total carbon. It varied from 0.08% to 2.51% during pre-monsoon. The monsoon and post-monsoon variations were from 0.06% to 2.48% and from 0.06% to 2.36%, respectively. Total nitrogen content in the sediment ranged from 0.06% to 0.33% during pre-monsoon and from 0.09% to 0.42% during monsoon. It varied between 0.03% and 0.46% during post-monsoon. Sulfur content varied from 0.04% to 1.17% during pre-monsoon and between 0.03% and 1.14% during monsoon. Post-monsoon range was from 0.02% to 1.52%. Iron content ranged between 0.45% and 7.52% during pre-monsoon and between 0.28% and 7.37% during monsoon. During post-monsoon, the range was from 0.68% to 7.54%. All the geochemical parameters were found to be higher at the muddy stations. Macrobenthic community in the study region was dominated by polychaetes, mollusks, and crustaceans (Table 2). Seasonal distribution of the benthic density showed that post-monsoon season was the most productive one. A sharp decline in number was noticed during monsoon. Muddy stations did not show any significant enrichment in the benthic density.

Total phosphorus (TP) in the surficial sediments ranged between 319.54 and 2,938.83 μg/g (Table 3). In general, higher concentrations were found at muddy station (station 6) and lower at sandy stations (stations 2 and 3). Monsoon season recorded comparatively higher concentration.

Among the bioavailable P fractions, Fe–IP ranged between 5.04 and 474.24 μg/g in the study region and constituted about 1.6% to 26.07% of TP during pre-monsoon. It was lower during monsoon and post-monsoon seasons, contributing to 1.82% to 6.4% and 0.86% to 15.6%, respectively. Ca–IP, the major fraction, varied widely in the study region and it ranged from 11.16 to 826.09 μg/g. It constituted to about 3.49% to 40.74% of TP during pre-monsoon. During monsoon its contribution was from 3.77% to 23.89% and during post-monsoon from 8.37% to 24.02%. Acid–OP varied between 22.22 and 365.86 μg/g in the study region. It ranged between 6.95% and 16.94% of TP during pre-monsoon and between 3.71% and 12.45% during monsoon. The post-monsoon variation was from 5.53% to 24.81% of TP.

Among the non-bioavailable fractions, Fe–OP ranged between 11.15 and 466.91 μg/g in the study region. Ca–OP varied between 11.4 and 600.96 μg/g. One of the major fractions was alkali–OP and it varied between 51.92 and 1,002.45 μg/g. R–OP was comparatively smaller fraction and ranged between 29.27 and 279.83 μg/g.

Discussion

Phosphate concentration in the water column followed marked seasonal rhythm. During pre-monsoon period, when the system is predominantly saline, low nutrient concentration was observed. The monsoon season, with the maximum influx of freshwater, showed a conspicuous increase in the concentration. It is evident from its significant positive correlations with river runoff, current and TSS and the negative correlation with salinity (Renjith et al. 2004). This also indicates the significant role of the sediments and suspended particles in the P dynamics. Phosphate is associated with and liberated by sediment particles, through a complex series of absorption and disassociation reactions (Millero and Sohn 1992). The transformation of dissolved P into particulate form is a critical process influencing its concentrations in natural waters (Benitez-Nelson

2000; Reynolds and Davies 2001). Phosphate also showed significant spatial variation ($p < 0.001$) with higher concentrations in sandy stations 2 and 3. The concentration of phosphate in the overlying water depends on the ability of the sediments to retain or release phosphate. Nair et al. (1993) also reported the influence of sediment activity in the distribution of nutrient pool in Cochin estuary.

ANOVA (two-way without replication) showed significant spatial variations ($p < 0.001$) for all the geochemical parameters analyzed with higher values at the muddy stations and lower values at the sandy stations. Seasonal variations of all the geochemical parameters were not statistically significant. Correlation analysis (Table 4) revealed that silt and clay fractions have high positive correlations with most of the analyzed sedimentary parameters. Sand fractions showed similar negative behavior. These indicate that the main factor influencing the geochemistry of the surficial sediments in the study region could be the sediment texture. It is very well established that organic carbon, nutrients, and metals are enriched in silt and clay fractions than in sand (Krishna Prasad and Ramanathan 2008; Wen et al. 2008).

Stoichiometric ratios of nutrients have been utilized in many estuarine studies to determine the origin and transformations of organic matter (Yamamuro 2000). The C:P ratio varied widely in the study region (~1–28) and was lower in the muddy stations than in the sandy ones. The total organic carbon: organic phosphorus (TOC:OP) ratio was also less at the sandy stations, indicating good preservation of organic P compounds in these sediments. However, the N:P ratio did not show considerable variations among stations and ranged between 0.3 and 2.7. Both these ratios did not show any seasonal variation and were far below the Redfield ratio (Hecky et al. 1993), indicating the possibility of P enrichment in this estuary. The lower N:P ratios also suggest that there might be higher benthic nitrogen recycling, and denitrification, and the benthic release of nitrogen could play a role in sustaining the productivity of the system.

Unlike the geochemical parameters, significant seasonal variations were observed in the case of benthos. There was significant spatial vari-

ation ($p < 0.05$) also, but the benthic density was lower at the muddy stations. Correlation analysis also reflects this anomaly, showing no significant relationship with any of the other sedimentary parameters. The detrimental effects of the heavy metals, like Ni and Pb, found enriched at the muddy stations (Renjith and Chandramohanakumar 2009) might be the reason for lower benthic abundance, despite being organic rich. It is also established that the nature of the sediment did not fully explain the substantial spatial and temporal variability in the benthos (Ysebaert et al. 2005). It is still unclear how functional changes could alter rates of nutrient regeneration and bioturbation in benthic systems (Weston 1990).

TP, like the other geochemical parameters, was significantly higher ($p < 0.001$) at the muddy stations. Significant spatial ($p = 0.008$) and temporal variations ($p = 0.014$) were observed for Fe–IP. Other bioavailable fractions Ca–IP and acid–OP exhibited highly significant spatial variations ($p < 0.001$) with higher values at the muddy stations. Alkali–OP was significantly higher ($p = 0.05$) during monsoon. Significant spatial ($p = 0.005$) and seasonal ($p = 0.024$) variations were observed for R–OP also. Correlation analysis (Table 4) confirmed the significant interrelations among the bioavailable fractions. These fractions also showed significant correlation with other sediment components. R–OP showed significant positive correlations with all the parameters except Fe–IP and benthos. Alkali–OP showed significant negative correlation with benthos.

P chemistry in sediments is largely influenced by redox conditions, and the redox cycle of Fe greatly affects P geochemistry after burial (Slomp et al. 1996; Cha et al. 2005). Total organic carbon: total sulfur (TOC:TS) ratio gives a qualitative indication of the redox status of the environment of deposition, when TS concentrations are high (Raiswell et al. 1987). TOC:TS > 5 are considered as oxic sediment with oxygenated bottom water, TOC:TS = 1.5–5 indicates deposited under periodic anoxia and TOC:TS < 1.5 represents anoxic sediment with anoxic water. The TOC:TS values in the study region lie in the second category suggesting that these sediments undergo sulfate reduction below an oxygenated water

Table 4 Correlations between seasonal averages of different fractions of phosphorus and other sedimentary parameters ($n = 18$)

	Fe–IP	Fe–OP	Ca–IP	Ca–OP	Acid–OP	Alkali–OP	ROP	Sand	Silt	Clay	TC	TOC	TN	TS	Fe	Benthic density
Fe–IP	1															
Fe–OP	−0.05	1														
Ca–IP	0.72[a]	0.23	1													
Ca–OP	−0.03	0.70[a]	0.31	1												
Acid–OP	0.47[b]	0.34	0.75[a]	0.55[b]	1											
Alkali–OP	−0.03	−0.23	0.30	0.04	0.30	1										
ROP	0.34	−0.03	0.50	0.40	0.75[a]	0.57[b]	1									
Sand	−0.57[b]	−0.28	−0.78[a]	−0.41	−0.92[a]	−0.34	−0.79[a]	1								
Silt	0.60[a]	0.22	0.71[a]	0.35	0.90[a]	0.33	0.80[a]	−0.98[a]	1							
Clay	0.49[b]	0.36	0.85[a]	0.49	0.89[a]	0.34	0.71[a]	−0.95[a]	0.88[a]	1						
TC	0.54[b]	0.34	0.67[a]	0.56	0.92[a]	0.24	0.77[a]	−0.93[a]	0.92[a]	0.87[a]	1					
TOC	0.56[b]	0.29	0.68[a]	0.54	0.91[a]	0.25	0.76[a]	−0.91[a]	0.91[a]	0.86[a]	0.99[a]	1				
TN	0.52[b]	0.50[b]	0.72[a]	0.67	0.92[a]	0.23	0.72[a]	−0.91[a]	0.89[a]	0.88[a]	0.96[a]	0.94[a]	1			
TS	0.49[b]	0.36	0.61[a]	0.54	0.91[a]	0.16	0.68[a]	−0.90[a]	0.89[a]	0.84[a]	0.98[a]	0.98[a]	0.94[a]	1		
Fe	0.52[b]	0.35	0.75[a]	0.50	0.96[a]	0.29	0.78[a]	−0.98[a]	0.97[a]	0.93[a]	0.95[a]	0.94[a]	0.94[a]	0.93[a]	1	
Benthic density	0.16	0.21	0.00	0.00	−0.07	−0.56[b]	−0.40	0.23	−0.24	−0.20	−0.15	−0.14	−0.10	−0.10	−0.18	1

[a] Correlation is significant at the 0.01 level
[b] Correlation is significant at the 0.05 level

column (Hedges and Keil 1995). The degree of pyritization in these types of sediments generally lies in the range between 0.46 and 0.80, corresponding to poorly laminated sediments with sparse bioturbation (Raiswell et al. 1987). These conditions suggest that the pyrite formation could be Fe limited.

The Fe:P ratio is also considered to be a measure of free sorption sites for phosphate ions on iron oxyhydroxide surfaces and the total Fe:P ratio above 15 (*w:w*) is enough for Fe to control the benthic flux of P from sediment to oxic water (Jensen et al. 1992). Rydin and Brunberg (1998) also described the formation of an effective oxic barrier with the above Fe:P ratio. In the study region, Fe:P ratio was less in the sandy stations 2 and 3 during monsoon and post-monsoon seasons, resulting in lower concentration of Fe:P. However, Fe:P ratio was about double of the critical value for the muddy stations throughout the year. Therefore, there seems to be enough Fe in surface sediments to bind P along the estuarine gradient at the muddy stations. These resulted in the spatial variability of Fe–IP in the study region.

Calcium-bound fraction was found to be the main P pool in the estuary. Carbonate-adsorbed P has been identified as an important and potentially dominant phase of P in shallow-water tropical carbonate-rich sediments, due to the high adsorption capacity of carbonates (Short et al. 1990; Millero et al. 2001). The high concentration of calcium-bound P in the study region might be interpreted by the favorable accumulation of calcium in estuarine environment under higher salinity and pH conditions (Huanxin et al. 1994). The study region is renowned for black clam (*Villorita cyprinoids*) fisheries of Cochin estuary (Lakshmilatha and Appukuttan 2002), and their shell is thick and rich (93.3% to 95.8%) in calcium carbonate (Kripa et al. 2004). Apart from live clam beds, the estuary has extensive subfossil deposits also.

Acid–OP includes apatite-bound phosphate and biochemical components such as nucleic acids, lipids, and sugars that bound to phosphate (De Groot 1990). The main component of alkali–OP is humic substances (Golterman 2001). P associated with humic acids has been considered either to be an integral part of humic acids or as a phos-

phate/metal/organic matter complex (Stevens and Stewart 1982). This fraction may to some unknown extent contain phytate, an organic phosphate that is common in plants and sediments (De Groot and Golterman 1993; Dvorakova 1998).

Total organic fraction ranged between 44.63% and 94.93% in the study region and higher percentage was noticed at the sandy stations. Also, this fraction was higher during monsoon. The high organic P content in the sediments might be the result of flocculation and precipitation processes involving humic acids from advective mixing of seawater with the nutrient-rich freshwater input from the river (Paludan and Jensen 1995; Paludan and Morris 1999). Salinity also plays a role in the seasonal variations of P fractions as it controls the flocculation and sedimentation mechanisms in estuarine environments, changing the availability of elements (Kautsky 1998). During the monsoon season, when the system changes to a freshwater condition, Ca–IP is found to be lower. It might be due to the lower availability of solid calcium carbonates, which is governed by salinity and pH (Huanxin et al. 1994; Zwolsman 1994). The higher amount of alkali–OP during monsoon might be the runoff of humic-associated P and the lower salinity might have prevented the flocculation in the upper reaches.

The percentage of bioavailable fractions ranged between 12.02 and 61.82 during pre-monsoon at the sandy stations and between 64.48 and 67.04 at the muddy stations. These fractions varied from 9.67% to 37.03% and from 29.0% to 40.38%, respectively, at these stations during monsoon. During post-monsoon, the sandy stations showed a variation between 14.76% and 40.38% and the muddy stations between 41.63% and 60.95%. It could be noted that the Fe–OP and Ca–OP fractions, which were higher during post-monsoon season are converted to their inorganic fractions during pre-monsoon. This actually resulted in the increase of the bioavailable fractions during pre-monsoon season. Hence, it could be concluded that there could be buffering of P during this lean period, when there is no run-off, which might act as an additional potential reservoir for primary production.

As a result of the diagenetic reorganization of P within sediments, organic P concentrations

usually decrease with time as it is ultimately transformed to bioavailable forms. Bacteria are generally considered to be the catalysts that accelerate the solubilization of P (Gatcher and Meyer 1993) and the processes of anoxic mineralization of phytate (Golterman et al. 1998) could release organic P buried during monsoon season. Microbially induced changes in pH and redox potential affect the ability of sediments to retain inorganic P (Roden and Edmonds 1997; Gachter and Muller 2003).

Principal component analysis (PCA) was carried out for establishing the plausible processes influencing the speciation of P in the study region. PCA using varimax rotation method extracted three components, which explained 87.4% of the total variance (Table 5). The first factor, which showed 60.6% of the variance, includes TP, all the bioavailable forms and R–OP along with the granulometry and the organic content. This indicates that P distribution is primarily associated with the fine sediment fraction. The absence of any significant loadings on alkali–OP suggested external input. Factor 2 (13.8% of total variance) includes only Fe–OP and Ca–OP, signifying that

neither the granulometric composition nor the organic content have any influence on these two fractions. This factor might be the mineralization of sedimentary organic matter by bacterial activity, which ultimately results in the increase in their respective inorganic fractions. Factor 3 accounted for 13% of the total variance and shows significant positive loadings on alkali–OP and R–OP and an opposite loading on benthic density. This factor could be attributed to external input through monsoon flushing.

Conclusion

TP, like the other geochemical parameters, showed granulometric dependence and the seasonal variations were also absent. Fractionation analysis established similar spatial trends for all bioavailable fractions. Significant seasonal variations could also be noticed for Fe–IP and alkali–OP. The sandy and muddy stations showed distinct fractional composition and the speciation study could endorse the overall geochemical character. There could be buffering of P, seen by the increase in the percentage of bioavailable fractions during the lean pre-monsoon period, compensating the reduction in external loads. This study underlines the role of chemical speciation of P as an indicative of the processes controlling the pathways of P in the estuarine environment and its importance in maintaining the fertility of the system. The fractionation studies are also helpful in understanding the diagenetic transformations of organic P in sediments. It is essential to take into account of the redox-sensitive P pool while considering management strategies for the estuary, particularly in fine-textured substratum.

Table 5 Results of principal component analysis showing the loading pattern

Parameters	Component		
	1	2	3
Fe–IP	0.771	−0.407	−0.332
Fe–OP	0.198	0.847	−0.288
Ca–IP	0.857	−0.039	−0.030
Ca–OP	0.346	0.855	0.053
Acid–OP	0.903	0.287	0.135
Alkali–OP	0.241	−0.125	0.832
R–OP	0.717	0.076	0.547
TP	0.853	0.243	0.282
Sand	−0.947	−0.147	−0.204
Silt	0.935	0.090	0.206
Clay	0.893	0.237	0.184
TC	0.915	0.289	0.129
TOC	0.919	0.246	0.125
TN	0.892	0.413	0.079
TS	0.884	0.316	0.065
Fe	0.935	0.249	0.164
Benthic density	−0.037	0.040	−0.852

Rotation method, Varimax with Kaiser Normalization; rotation converged in six iterations

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