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Biogeochemical Cycling of Phosphorus in the Cochin Backwaters: Southwest Coast of India

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Abstract

Here we studied total phosphorus and its fractions in sediments from the Cochin backwaters along with dissolved inorganic phosphate, tidal currents, pH, and salinity during the monsoon and pre-monsoon periods. During the monsoon, sediments function as a sink for phosphate derived from land-based pollutant sources, whereas, during the pre-monsoon, sediment re-suspension provides a source of phosphate to the overlying water column, both with the capacity to alter eutrophication events. The heavy river runoff during the monsoon lowers the pH and salinity of the water column, thereby enhancing adsorption of phosphorus from water to sediments. In contrast, seawater incursion during the pre-monsoon increases the pH and salinity of the water column to enhance the desorption of phosphorus from sediments to the water. Iron-bound inorganic (0.48-0.78 mg g^{-1}) and organic phosphorus (1.04-1.30 mg g^{-1}), calcium-bound inorganic (0.78-1.56 mg g^{-1}) and organic phosphorus (1.13-1.83 mg g^{-1}), acid-soluble organic phosphorus (0.07-0.21 mg g^{-1}), and alkali-soluble organic phosphorus (0.22-0.70 mg g^{-1}), were detected in sediments. The main sedimentary phosphorus pool was a calcium- and iron-bound phosphorus compound. Precipitation/flocculation of dissolved inorganic phosphate within the estuarine salinity gradients (~15-30), followed by its adsorption/desorption with iron oxy-hydroxides and calcium carbonate minerals that settle in the bottom sediments govern the phosphorus biogeochemistry of the Cochin backwaters.

Keywords: Biogeochemistry; Phosphorus; Tides; Currents; Sediment; Eutrophication

Introduction

Estuaries are regarded as highly eutrophic systems as a result of anthropogenic nutrient inputs [1,2]. They are biologically productive transition zones between land and sea that play a vital role in transforming, recycling, and sequestering nutrients (e.g., Nitrogen, Phosphorus and Silica), and organic matter, and thus influencing nutrient loading to coastal systems. Eutrophication caused by high concentrations of nutrients (Nitrogen and Phosphorus), is a major environmental problem for lakes and rivers on the southwest coast of India [2,3]. In recent decades, increased population growth and related activities, such as various agricultural practices, discharge of industrial effluents and sewage run-off from urban areas to water bodies, have increased nutrient inputs by many times to the levels that occur naturally [4,5]. Removal of the nitrogen and phosphorus contamination from the water body of lakes and rivers on the southwest coast of India has thus becomes an urgent need [6].

The dynamics of nutrients (e.g., Nitrogen and Phosphorus), and the primary production in estuaries are strongly dependent on their biogeochemical cycles. Estuaries transform phosphorus speciation through biogeochemical processes, which control P evolution and distribution of the land–sea interface. Phosphorus (P) is known to limit phytoplankton growth and primary productivity in many coastal waters worldwide [7-11]. Yet, the processes involved in phosphorus (P) transformation and cycling among inorganic and organic P forms are poorly known in estuaries. Therefore, it is important to know the processes that control phosphorus inputs and its biogeochemical cycling in the coastal environment.

Sediments are recognized as a principal reservoir which accumulates or releases pollutants (e.g., P), which plays a significant role in maintaining the trophic status of a water body [12]. Sediments in eutrophic waters act as a sink of P whereas those of oligotrophic systems act as a source of P to the overlying water [13,14]. Phosphorus entering the estuary in dissolved forms absorb to suspended particles and will subsequently sink to the sediment [9]. The concentration of dissolved inorganic phosphorus in the overlying water column of an estuary depends upon the ability of the surficial sediments to retain or release dissolved inorganic phosphate (DIP) [15]. Studies of phosphorus dynamics of the Cochin estuary are mainly restricted to dissolved inorganic phosphate (DIP) in water and total phosphorus content in sediments [1,16-19]. However, total phosphorus content in sediments does not provide an accurate assessment of phosphorus cycling or its bioavailability in the estuarine environment as it depends on speciation [20-22]. Since the amount of phosphorus released from sediments is called internal phosphorus loading which can enhance eutrophication, an estimation of sediment-bound phosphorus fractions in an estuary is necessary for predicting the ecological risks and in understanding the phosphorus biogeochemical cycling.

Phosphate is present in sediments in organic and inorganic forms. The sedimentary phosphorus cycle is characterized by the burial of inorganic phosphorus, degradation of organic phosphorus, and interaction of phosphate with metal oxides in the sediment. As these compounds have different chemical and biological properties, it is essential to establish the distribution of the different P-forms. Various extraction techniques can be used to determine the chemical speciation of sedimentary bound phosphates [20]. Specific chemical fractionation procedures involving sequential extractions, based on the differences in reactivity towards various solid phases, to different extraction solutions is used as a tool to characterize various inorganic and organic bound phosphorus forms that present in sediments [23-26]. Sequential leaching extraction schemes identify the compounds by using chelating agents which can be used to understand the association of phosphorus with iron and calcium and thereby determine its mobility, solubility, and bio-availability in the water column [27]. In this study, we evaluate the DIP concentrations in water, total phosphorus and its various fractions in sediments along with the hydrographic data (tides, currents, and salinity) during the monsoon and pre-monsoon periods in order to understand the phosphorus biogeochemical cycling in the Cochin backwaters. The main aim of the present study was to investigate the chemical speciation of phosphorus in sediments of the Cochin backwaters and its impact on biogeochemical cycling.

Materials and Methods

Description of the study area

The Cochin backwaters (Lat. 9°30 ' -10°10 ' N and Lon. 76°15'-76°25'E; Figure 1), is the largest tropical estuary on the west coast of India, with a total length of ~80 km and an area of ~230 km^2. The estuary is situated parallel between the Arabian Sea on the west and Western Ghats, a continuous mountain chain on the east [4]. The hydrology of the Cochin backwaters is governed by micro-tides (≤ 1.0 m) and the seven monsoons fed perennial rivers (Chalakkudi, Periyar, Muvattupuza, Meenachil, Manimala, Pamba, and Achenkovil) which originate in the Western Ghats and debouch into the Arabian Sea [1]. This estuary sustains high biological production due to surplus nutrients largely supplied by these rivers [3]. The estuarine system is connected to the Arabian Sea by two tidal inlets, one at the Cochin bar mouth (~450 m wide) and the other at Azheekkode (~250 m wide), which exchange water following the tidal cycle. The Cochin bar mouth forms the main entrance to the Arabian Sea. The estuary is generally wide (0.8-1.5 km) and deep (4-13 m) towards the south, but becomes narrow (0.05-0.5 km) and shallow (0.5-3.0 m) in its northern part.

Station locations

5 stations were selected within a stretch of ~5 km (with a distance of ~1 km between each station) in the northern part of the Cochin backwaters (Figure 1) for time-series measurements of environmental parameters during the monsoon (28 October 2003) and pre-monsoon (22 March 2004) seasons as a part of the project "Ecosystem modelling of Cochin backwaters". Station 1 at Bolgatty was located in the lower estuary (nearer to Cochin inlet) whereas station 5 at Vaduthala was located at the upper estuary (downstream area of the river Periyar). These stations were affected by varying concentrations of effluent discharges from industries, agricultural fields and urban areas through the river Periyar.

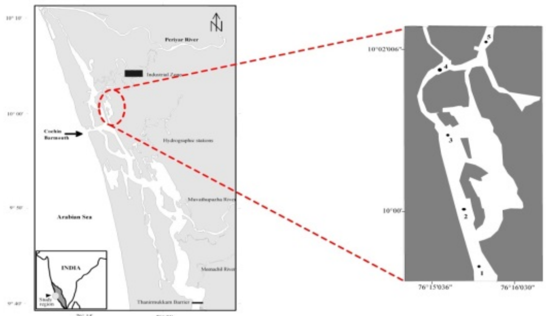

Figure 1: Sampling locations in the Cochin backwaters.

Sampling, data and analysis

Water samples were collected at each station using a Niskin sampler from a depth of 0.5 m below the surface and from 2 m depth at 3 hourly intervals for a 30 hour period on 4 occasions, during October 2003 and March 2004. The samples were subjected to various physic-chemical analyses within an hour of collection. Salinity was determined using a Salinometer (Digi Auto 3G, Tsurumi Seiki, Japan, accuracy ± 0.001psu) and pH was determined using an ELICO LI610 pH meter (accuracy ± 0.01). Samples for nutrient analysis (dissolved inorganic phosphate), were filtered through a Whatman No.1 filter paper and were analysed in a UV-VIS Spectrophotometer (1650 Shimadzsu), using the molybdenum blue/ascorbic acid method [28]. Precision of phosphate measurement was ± 0.04 µmol P l-1. Suspended particulate matter (SPM) was determined as the weight difference of material that retained on pre-weighed Millipore membrane filters (pore size, 0.45 µm), after filtering a known volume of water sample. Variation in water levels and flow were recorded from 2 Station locations (lower and upper estuary), of the northern estuary at every 10 minute interval, using tide gauges (Valeport) and current meters (RCM9) moored for 30 days continuously during the monsoon and pre-monsoon seasons.

Surface sediments (0-5 cm) were collected from all stations using a van Veen Grab. By using a Teflon-coated spatula the top 2 cm layer of surface sediments was carefully skimmed, excluding shells, and the collected sediments were packed in airtight polythene bags and kept frozen (−5°C) until analysis. Dried (at 70°C) sediment samples were used for texture analysis, organic carbon and phosphorus determination. Textural characteristics (sand, silt and clay) of sediments were determined by pipette analysis [29]. Organic carbon content in sediments was determined using the chromic acid digestion, which is followed by back titration with ferrous ammonium sulphate [30]. Total phosphorus (TP) in sediments was determined by molybdenum blue/ascorbic acid colorimetric method after pre-treating the powdered sample with potassium per sulphate ($K_2S_2O_8$) and digesting the mixture in an autoclave at 120°C, for 30 minutes [28].

Sequential extraction

Sequential extractions using chelating agents were used for estimating the different sediment phosphorus fractions [27]. Iron-bound and Ca-bound Phosphorus were extracted with buffered Ca–EDTA/dithionite and Na – EDTA/dithionite, respectively. These fractions were further analysed for inorganic and organic forms by acid per sulphate digestion, to obtain the total fraction. Acid-soluble organic phosphorus were extracted with 2M H_2SO_4 and alkali–soluble organic phosphorus were extracted with 2M NaOH. All these extractions were carried out under mild continuous shaking. Each phosphorus fraction was determined using the molybdenum blue/ascorbic acid colorimetric method [28]. The phosphorus concentrations in sediments are expressed in mg/g, dry weight. The chelating agents and the target phase are presented in Table 1.

Steps	Extractant	Form of phosphorus extracted
I	Ca–EDTA/dithionite (pH ≈ 9)	Iron-bound phosphorus
II	Na–EDTA/dithionite (pH ≈ 4.5)	Calcium bound phosphorus fraction
III	0.5 M H_2SO_4	Acid soluble organic phosphorus
IV	2 M NaOH at 90°C for 2 hours	Alkali soluble organic phosphorus
V	Digestion with $K_2S_2O_8$ for 1 hour in acid medium	Residual organic phosphorus

Table 1: Extraction scheme for the speciation of phosphorus in sediments.

Results

Tides and currents

In general, currents in the region are dominated by mixed semi-diurnal tides (Figure 2a-2d), than diurnal tides which will result in swift currents and hence two high or two low water levels of unequal heights are observed in every day. During the monsoon and pre-monsoon seasons, the downstream (Station 1 at Bolgatty) and upstream (Station 5 at Vaduthala) regions of the north estuary, exhibited large spring–neap tide phase variability.

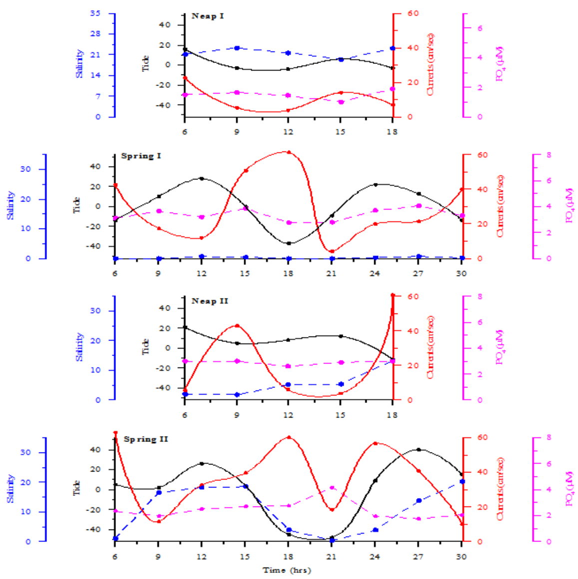

Figure 2a: Variations of salinity (psu), tide (cm), currents (cm/s) and phosphate (μM) at the spring and neap phases of tides at Bolghatty (Station1) during the monsoon.

Maximum tidal ranges (difference in amplitude between lowest low tide and highest high tide), were observed during the spring tide when compared to the neap tide at the downstream part (Station 1 at Bolgatty) when compared with the upstream part (Station 5 at Vaduthala) of north estuary. The amplitude of the tide is found to be more intense, during the pre-monsoon when compared to the monsoon and the tidal circulation (currents) decreases from the downstream station at Bolgatty to the upstream station at Vaduthala of north estuary due to heavy fresh water influxes from the Periyar river [31]. During both seasons, currents and tides were strong only during the spring phase, but are comparatively weaker during the neap phase. The high and low variation of water levels during the various phases of the tide indicates a net renewal of resident water mass transportation to and from the estuary probably due to swift currents [1].

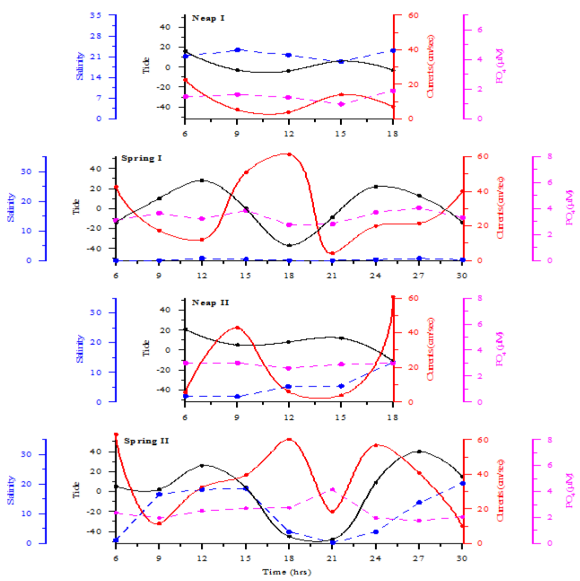

Figure 2b: Variations of salinity (psu), tide (cm), currents (cm/s) and phosphate (μM) at the spring and neap phases of tides at Bolghatty (Station1) during the pre-monsoon.

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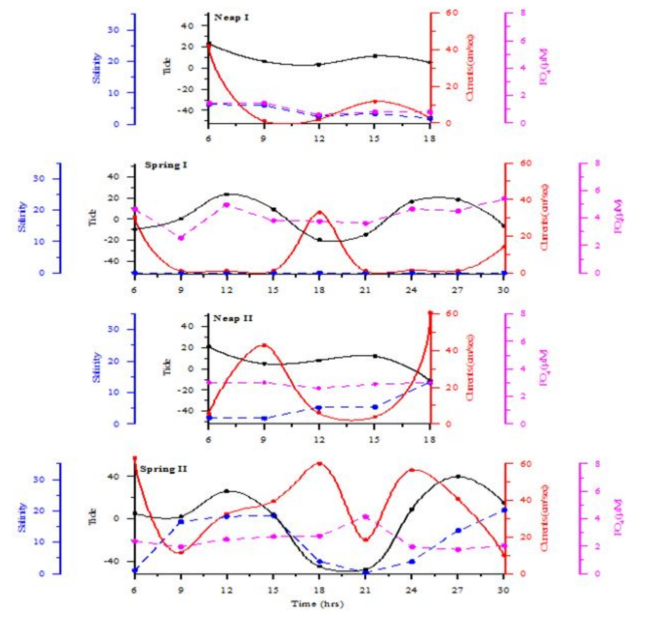

Figure 2c: Variations of salinity (psu), tide (cm), currents (cm/s) and phosphate (µM) at the spring and neap phases of tides at Vaduthala (Station 5) during the monsoon.

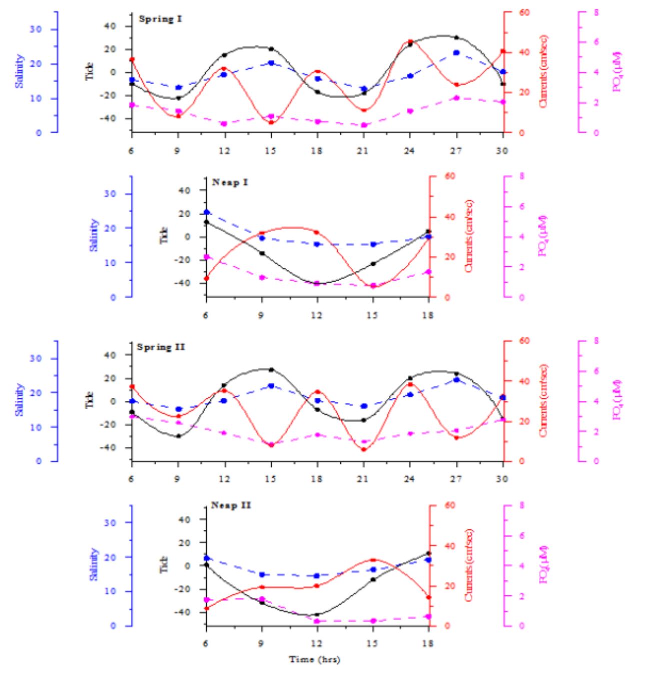

Figure 2d: Variations of salinity (psu), tide (cm), currents (cm/s) and phosphate (µM) in spring and neap tides at Vaduthala (Station 5) during the pre-monsoon.

Variation of hydrographical parameters with tides

The data for various hydrographical parameters shown in Figures 3-6 are presented in such a way that the X-axis represents the station locations which are of ~1 km apart and the Y-axis represents the time of water sampling which was always started at 06.00 hours on each day.

Variation of salinity with tides

The water column was found to be strongly stratified during the monsoon but only a weak stratification was found during the pre-monsoon. During the monsoon, at the neap1 and spring II phases of tide the surface and bottom waters was found to be low saline due to weak saline water incursion (8-20) during the high tide (Figure 3a). During the monsoon, at the neap II and spring 1 phase of tide a dominant fresh water inflow is noted on surface waters of the estuary as indicated by the zero salinity values towards the seaward end (Figure 3a). Hence, during the monsoon period due to the prevailing dominance of fresh water, the entire water column of the estuary was found to be low saline with strong stratification.

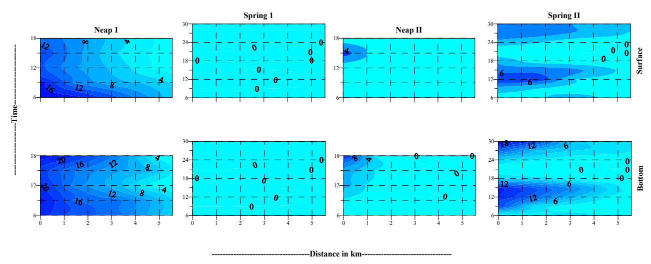

Figure 3a: Variations of salinity (psu) at different stations with respect to time (hours) at the spring and neap phases of tides during the monsoon.

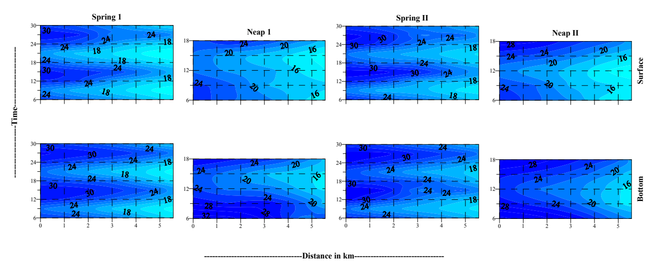

Figure 3b: Variations of salinity (psu) at different stations with respect to time (hours) at the spring and neap phases of tides during the pre-monsoon.

During the pre-monsoon period, the surface and bottom waters showed higher salinity values in the entire time intervals at the downstream region, while lower salinity values were prevalent towards the upstream region (Figure 3b). The increased tidal activity during the spring and neap phases of tides brought in a vertical mixing of the water column, which increases the salinity values during the pre-monsoon when compared to the monsoon (Figure 3b). During the pre-monsoon period, tides overwhelm the river runoff and the entire water column of the estuary was found to be high saline with weak stratification.

Variation of pH with tides

During the monsoon, at neap I phase of the tide, the pH value (range and average) in surface and bottom waters varied from 6.13 to 8.09 (6.99 ± 0.51) and 6.34 to 7.82 (7.27 ± 0.75), whereas at spring II phase of the tide, the pH values in surface and bottom waters varied from 5.70 to 7.70 (6.84 ± 0.52) and 5.77 to 7.81 (6.94 ± 0.59), respectively. Similarly, during the monsoon, at spring I phase of tide, the pH values (range and average) in surface and bottom waters varied from 5.96 to 6.78 (6.43 ± 0.16) and 6.04 to 6.88 (6.47 ± 0.17), whereas at neap II phase of the tide, the pH values in surface and bottom waters varied from 5.98 to 7.24 (6.61 ± 0.32) and 6.03 to 7.45 (6.68 ± 0.38), respectively. High pH values (range and average), were predominant at Neap I and Spring II phases of the tides, whereas low pH values were predominant at Spring I and Neap II phases of the tides (Figure 4a).

During the pre-monsoon, at spring I phase of the tide the pH values (range and average), in surface and bottom waters varied from 6.61 to 8.24 (7.48 ± 0.43) and 6.67 to 8.18 (7.62 ± 0.36), whereas at spring II phase of tide, the pH values in surface and bottom waters varied from 7.25 to 8.19 (7.72 ± 0.26) and 7.06 to 8.19 (7.77 ± 0.26), respectively. Similarly, during the pre-monsoon, at neap I phase of tide the pH values (range and average), in surface and bottom waters varied from 6.89 to 8.26 (7.42 ± 0.41) and 7.05 to 8.03 (7.48 ± 0.30), whereas at neap II phase of tide, the pH values in surface and bottom waters varied from 7.13 to 8.20 (7.58 ± 0.40) and 7.11 to 8.31 (7.66 ± 0.36), respectively. During the pre-monsoon, high pH values (range and average), were predominant at spring phases (spring I and II), whereas low pH values were predominant at neap phases (neap I and II). pH values were increased considerably during the pre-monsoon season when compared to the monsoon season (Figure 4b). During both seasons, increased pH values corresponds with high tides and pH values showed a decreasing trend from downstream region to the upstream region of north estuary due to discharge of industrial effluents through the river Periyar.

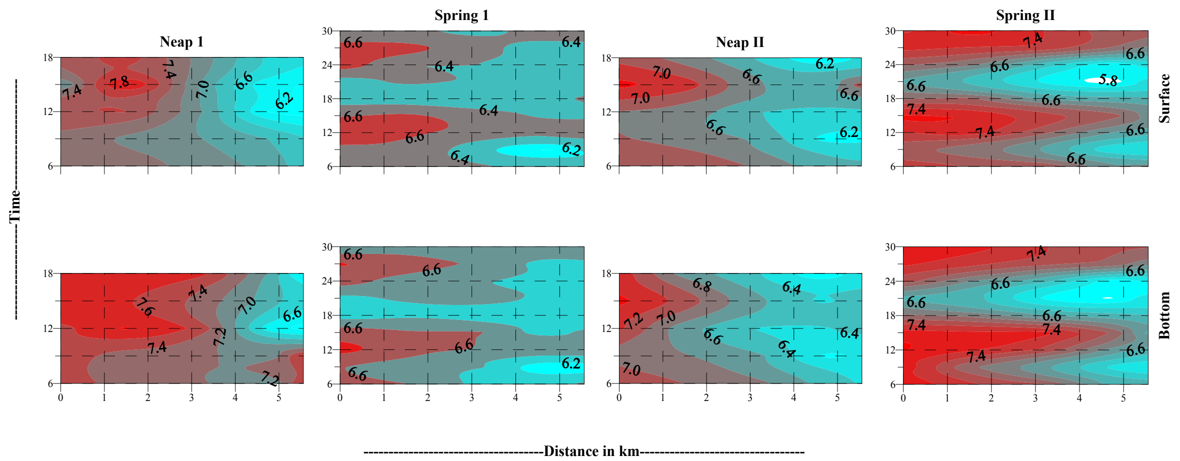

Figure 4a: Variations of pH at different stations with respect to time (hours) at the spring and neap phases of tides during the monsoon.

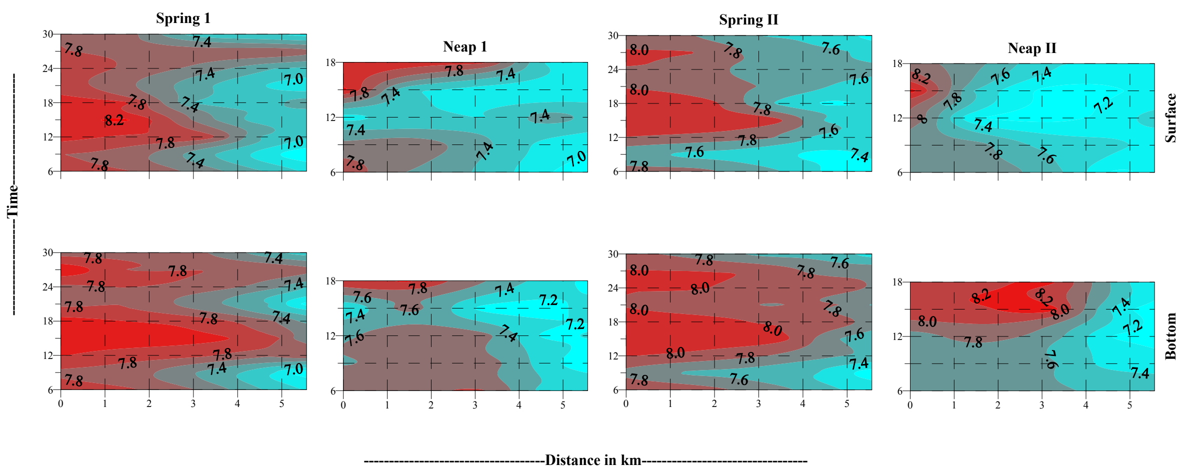

Figure 4b: Variations of pH at different stations with respect to time (hours) at the spring and neap phases of tides during the pre-monsoon.

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Variations of Suspended Particulate Matter (SPM) with tides

During the monsoon, at spring I phase of tide, the SPM concentrations (range and average) in surface and bottom waters varied from 32 to 122 mg/l (64 ± 23.66 mg/l) and 42 to 108 mg/l (78.73 ± 25.25 mg/l), whereas at neap II phase of tide, the SPM concentrations in surface and bottom waters varied from 52 to 98 mg/l (76.64 ± 19.07 mg/l) and 58 to 95 mg/l (75.84 ± 14.18 mg/l), respectively. High SPM concentrations, noted in upper estuary correspond with low tide and SPM concentrations showed a decreasing trend towards lower estuary (Figure 5a). In the neap I phase of tide, a high SPM concentration was observed along with high tide at the seaward end. The very high SPM concentrations (~100 mg/l), noted during the monsoon in the upper estuary in the spring I, spring II and neap II phases of tides is due to heavy freshwater influxes that carrying soil eroded particulate matter from the banks of the river Periyar.

During the pre-monsoon, at spring II phase of tide the SPM concentrations (range and average) in surface and bottom waters varied from 18 to 96 mg/l (53.27 ± 17.37 mg/l) and 18 to 95 mg/l (59.56 ± 16.90 mg/l), whereas at neap I phase of tide the SPM concentrations in surface and bottom waters varied from 36 to 79 mg/l (50.68 ± 11.12 mg/l) and 35 to 87 mg/l (58.76 ± 14.74 mg/l), respectively. High SPM concentrations noted in lower estuary corresponds with high tide and showed a decreasing trend towards the upper estuary (Figure 5b). High SPM concentrations were observed during the Spring II phase of tide whereas low SPM concentrations were observed during the Neap I phase of tide. The variation in SPM concentrations were marginal during the spring phases (Spring I and II) of tide, but are considerable during the neap phases (Neap I and II) of tide. SPM values were considerably higher during the monsoon season than the pre-monsoon season.

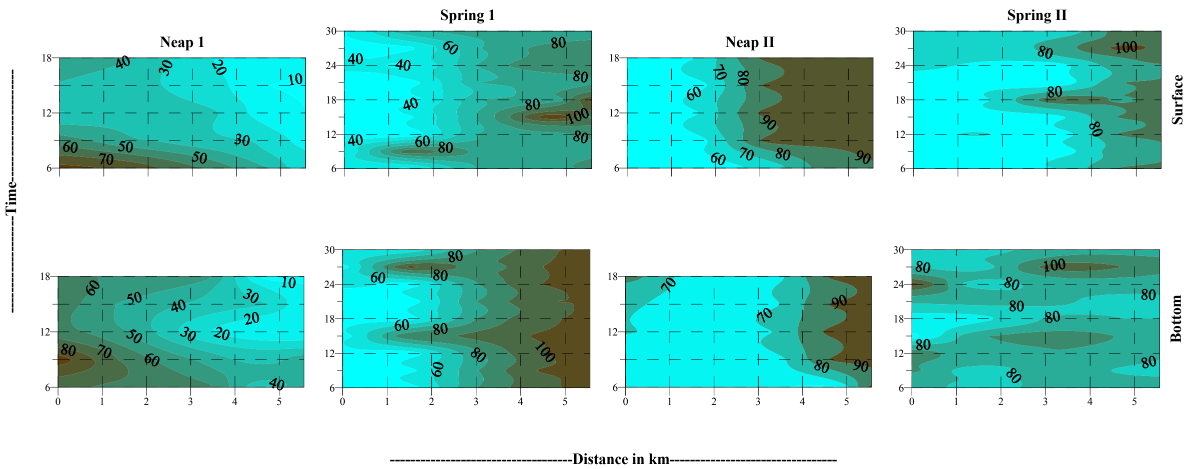

Figure 5a: Variations of suspended particulate matter (mg/l) at different stations with respect to time (hours) at the spring and neap phases of tides during the monsoon.

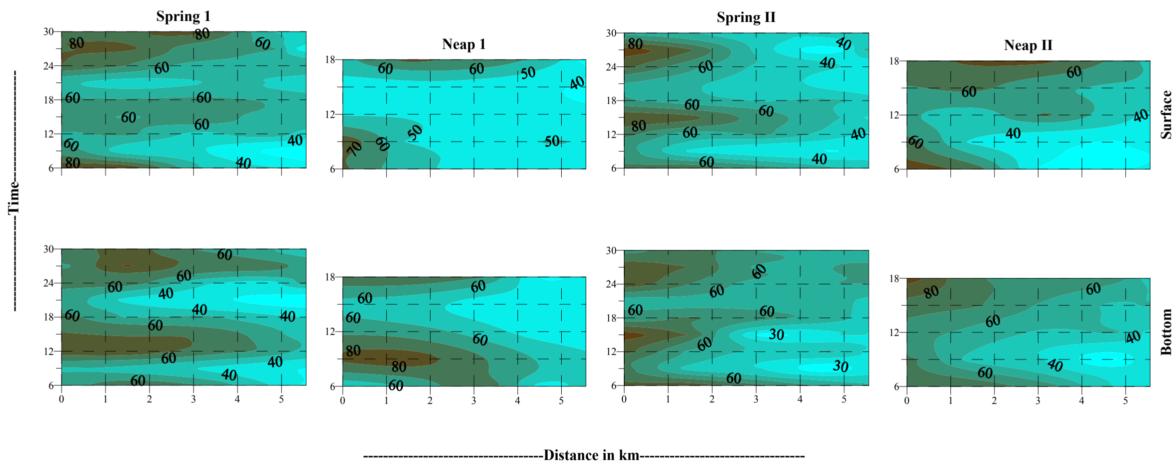

Figure 5b: Variations of suspended particulate matter (mg/l) at different stations with respect to time (hours) at the spring and neap phases of tides during the pre-monsoon.

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Variation of Dissolved Inorganic Phosphate (DIP) with tides

Dissolved inorganic phosphate (DIP) levels were considerably higher during the monsoon than the pre-monsoon season (Figure 6a). During the neap I phase of tide, phosphate concentrations (range and average), in surface and bottom waters ranged from 0.50 to 1.60 µM (0.95 ± 0.33 µM), and 0.55 to 1.90 µM (1.16 ± 0.39 µM), respectively. Similarly, during the neap II phase of tide, phosphate concentrations (range and average) in surface and bottom waters ranged from 1.60 to 3.45 µM (2.66 ± 0.47 µM), and 2.10 to 4.85 µM (2.81 ± 0.40 µM), respectively. During the spring I phase of tide, phosphate concentrations (range and average), in surface and bottom waters ranged from 0.50 to 5.55 µM (3.72 ± 0.91 µM), and 1.80 to 5.40 µM (3.7 ± 0.71 µM), respectively. Similarly, during the spring II phase of tide, phosphate concentrations (range and average) in surface and bottom waters ranged from 0.95 to 6.25 µM (2.38 ± 0.86 µM), and 0.35 to 6.45 µM (2.39 ± 1.10 µM), respectively. The high DIP values in the lower estuary in the spring I, spring II, and neap II phases of tides, corresponds with low salinity and low pH values suggest that the source of phosphates was from the riverine end of the upper estuary. Hence, during the monsoon, the wide range of DIP concentrations (0.35 to 6.45 µM), along with the higher value of ~6 µM, being encountered at the freshwater end implies its origin via. industrial, domestic and agricultural effluents that draining through the river Periyar.

DIP showed a contradictory behaviour during the pre-monsoon when compared to the monsoon (Figure 6b). During the pre-monsoon season, at the spring II phase of tide, phosphate concentrations (range and average), in surface and bottom waters ranged from 1.14 to 3.41 µM (2.22 ± 0.56 µM) and 1.16 to 3.33 µM (2.49 ± 0.57 µM), respectively. Similarly, during the Neap II phase of tide, phosphate concentrations (range and average), in surface and bottom waters ranged from 0.30 to 2.92 µM (1.21 ± 0.76) µM and 0.32 to 3.90 µM (1.93 ± 1.09 µM), respectively. The concentration of phosphates (range and average), was high at Spring II phase of tide, whereas it was low at Neap II phase of tide. High phosphate concentrations were observed along with high tide in the lower estuary whereas low phosphate concentrations were observed with low tide in the upper estuary. During the pre-monsoon, high DIP values observed in the lower estuary, corresponds with high pH and high salinity values.

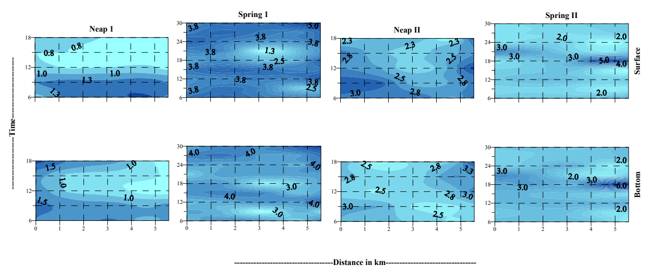

Figure 6a: Variations of dissolved inorganic phosphate (µM) at different stations with respect to time (hours) at the spring and neap phases of tides during the monsoon.

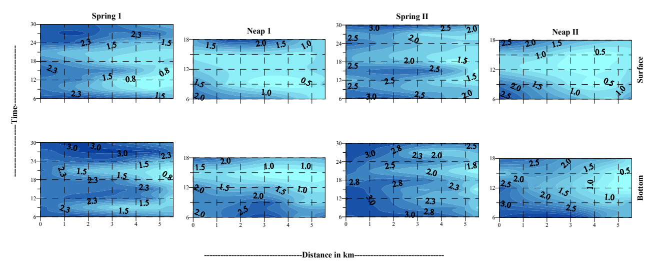

Figure 6b: Variations of dissolved inorganic phosphate (µM) at different stations with respect to time (hours) during the spring and neap tides of pre-monsoon season.

Correlation analysis

Significant positive correlations (n=90) were noted between salinity and pH both during the monsoon and pre-monsoon seasons (Figure 7a-7d). Because of extraneous input of DIP, during the monsoon (except at the neap I phase of the tide), DIP showed an insignificant correlation with salinity (Figure 7a). During the pre-monsoon and at the first observation during the monsoon (neap I), a significant positive correlation was observed between salinity and DIP (Figure 7c and 7d). Significant positive correlations were noted between salinity and suspended particulate matter only during the pre-monsoon season when compared with the monsoon season (Figures 7a-7d).

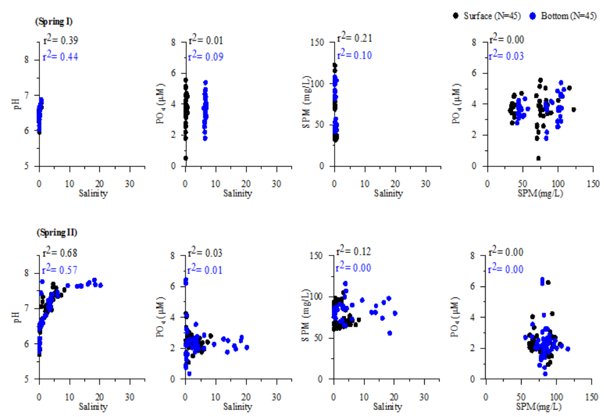

Figure 7a: Correlations between Salinity, pH, Phosphate and Suspended particulate matter at the spring tide during the monsoon.

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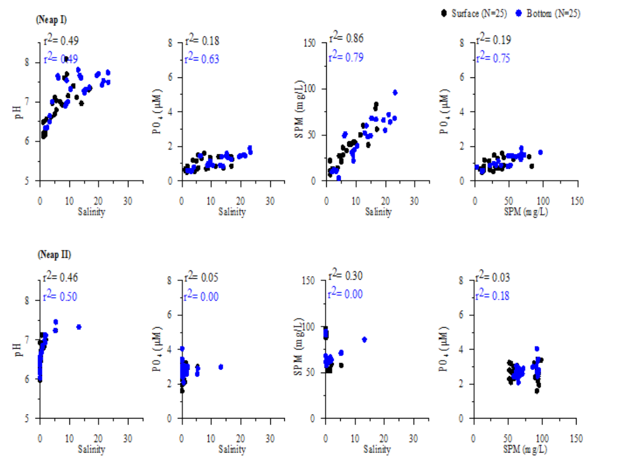

Figure 7b: Correlations between Salinity, pH, Phosphate and Suspended particulate matter at the neap tide during the monsoon.

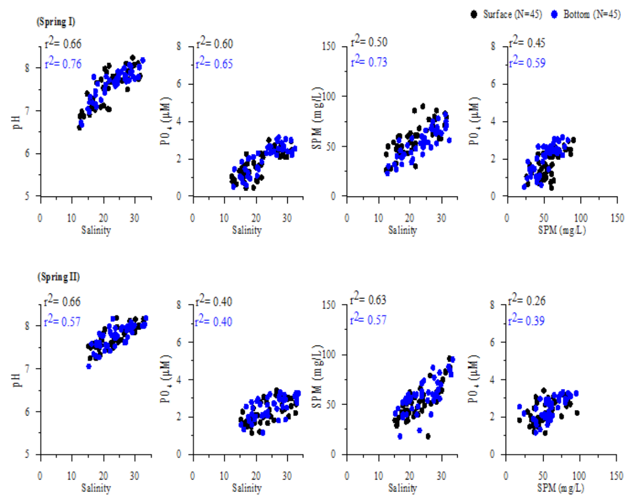

Figure 7c: Correlations between Salinity, pH, Phosphate and Suspended particulate matter at the spring tide during the pre-monsoon.

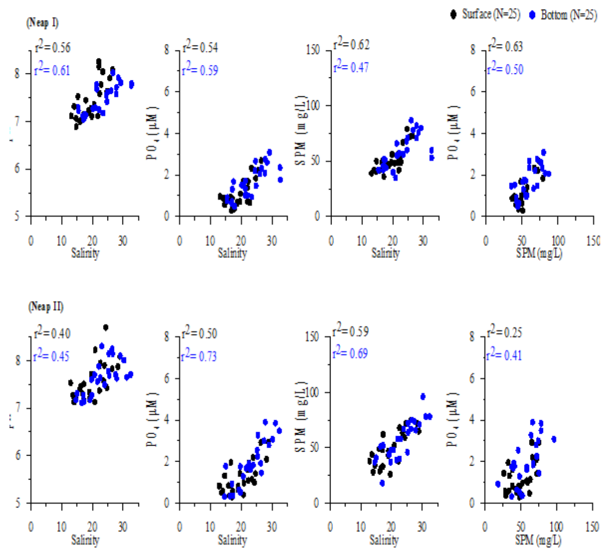

Figure 7d: Correlations between Salinity, pH, Phosphate and Suspended particulate matter at the neap tide during the pre-monsoon.

Texture and organic carbon content in sediments

The texture (sand, silt and clay), of bed sediments showed a wide range of variations and is indicative of severe stress in the shallow coastal environment of Cochin due to human activities (Table 2). During the monsoon, sand forms a major fraction in sediments at the upstream station 5, whereas silt forms a major fraction in sediments at the downstream station 1. But during the pre-monsoon, even if sand forms a major fraction in sediments at the upstream station 5, clay forms a major fraction in sediments at the downstream station 1. The heavy fresh water discharges through the river Periyar and bed-load movements associated with tidal currents enhances a downward transport of fine sediments (clayey and silty particles) towards the seaward regions (at Stations 1 and 2) whereas the sandy particles gets deposited at the riverine regions (at Stations 3, 4 and 5). Organic carbon content ranges in sediments were higher during the pre-monsoon (4.49 to 6.90 mg/g) when compared to the monsoon season (4.10 to 6.31 mg/g). Very high organic carbon content (>5.0 mg/g) noted in sediments is indicative of excessive organic pollution loads derived from domestic sewage entering the Cochin estuary.

Sediment texture and organic carbon	**Monsoon**					**Pre-monsoon**				
Stations	1	2	3	4	5	1	2	3	4	5
Sand (%)	16.93	42.86	85.44	64.15	85.13	3.26	40.51	84.41	88.41	82.04
Silt (%)	44.57	30.14	9.56	17.35	0.37	23.74	29.99	1.59	0.59	4.96
Clay (%)	38.50	27.00	5.00	18.50	14.50	73.00	29.50	14.00	11.00	13.00

Organic carbon (mg/g)	6.31	4.81	4.20	4.35	4.10	6.80	5.90	6.90	4.49	5.18

Table 2: Texture (%) and organic carbon content (mg/g) in sediments of the Cochin estuary.

Phosphorus fractionation in sediments

Total phosphorus (TP), iron bound inorganic phosphorus (Fe-IP), calcium bound inorganic phosphorus (Ca-IP), iron bound organic phosphorus (Fe-OP), calcium bound organic phosphorus (Ca-OP), alkali soluble organic phosphorus (alkali-OP), and acid soluble organic phosphorus (acid–OP) contents in sediments were shown in Table 3. Total phosphorus concentrations in sediments showed higher concentration ranges during the monsoon (5.42 to 5.78 mg/g), when compared to the pre-monsoon (4.35 to 5.22 mg/g), season. During the monsoon and pre-monsoon seasons, similar to the total phosphorus content in sediments, the different phosphorus fractions also showed seasonal variations in the lower estuary (at Stations 1 and 2) while in upstream regions it showed almost constant values (at Stations 4 and 5) due to continuous loading of phosphates by industrial and domestic effluent discharges through the river Periyar [1].

The calcium bound inorganic, iron bound inorganic and acid soluble organic fractions of phosphorus in sediments were considered as a source of bio-available phosphorus for phytoplankton growth [32]. Calcium bound inorganic phosphorus (Ca-IP) concentrations was high during the monsoon (1.44 to1.56 mg/g) whereas it was low during the pre-monsoon (0.78 to 1.31 mg/g). Iron bound inorganic phosphorus (Fe-IP) also exhibited an increase in concentrations during the monsoon (0.71-0.78 mg g^{-1}) when compared to pre-monsoon (0.48 to 0.71 mg/g) season. During both seasons, Ca and Fe inorganic fractions exhibited a decreasing trend towards the lower estuary. Similarly, acid soluble organic phosphorus (Acid – OP) in sediments varied from 0.16 to 0.21 mg/g and 0.07 to 0.17 mg/g during the monsoon and pre-monsoon seasons respectively. The sequence of various bio-available fractions of phosphorus in sediments during the monsoon and pre-monsoon periods follows an order: Ca-IP>Fe-IP>Acid – OP. Since considerable levels of bio-available fractions of phosphorus (Ca-IP~20-28%, Fe-IP~11-14%, Acid – OP~2-3%) is present during the monsoon and pre-monsoon periods which implies that sediments of Cochin estuary can act as an internal source of phosphorus [14].

Similar to inorganic fractions of phosphorus, organic fractions of phosphorus in sediments also exhibited seasonal variations (Table 3). Iron bound organic phosphorus content in sediments varied from 1.04 to 1.20 mg g^{-1} and 1.18 to 1.30 mg/g during the monsoon and premonsoon seasons. Similarly, calcium bound organic phosphorus concentrations in sediments varied from 1.16 to 1.83 mg/g and 1.13 to 1.39 mg/g during the monsoon and premonsoon seasons respectively. Alkali soluble fractions of phosphorus in sediments varied from 0.40 to 0.70 mg/g and 0.22 to 0.67 mg/g during the monsoon and premonsoon seasons. Iron bound organic phosphorus and calcium bound organic phosphorus were slightly higher in the seaward region than freshwater region. Irregular variations of alkali soluble and acid soluble fractions of phosphorus noted in sediments at Stations 1 to 5 are due to varying load of phosphates from non-point pollution sources (agricultural effluents), in the Cochin estuary [1,2].

Total phosphorus and phosphorus fractions in sediments (mg/g)	Monsoon					Pre-monsoon				
Stations	1	2	3	4	5	1	2	3	4	5
Total phosphorus	5.78	5.73	5.48	5.56	5.42	4.53	4.35	4.45	5.22	5.12
Inorganic Fe-P	0.74	0.73	0.72	0.78	0.71	0.51	0.52	0.48	0.7	0.71
Organic Fe-P	1.2	1.15	1.1	1.04	1.12	1.18	1.22	1.25	1.3	1.23
Inorganic Ca-P	1.44	1.46	1.48	1.56	1.54	0.78	0.85	1.1	1.24	1.31
Organic Ca-P	1.83	1.64	1.45	1.47	1.16	1.13	1.39	1.28	1.14	1.15
Alkali soluble P	0.4	0.55	0.7	0.51	0.6	0.22	0.28	0.23	0.67	0.59
Acid soluble P	0.17	0.19	0.21	0.19	0.16	0.07	0.09	0.1	0.17	0.11

Table 3: Total phosphorus (mg/g) and phosphorus fractionations (mg/g) in sediments of the Cochin estuary.

Discussion

The influence of hydrography on the phosphorus biogeochemical cycling

The hydrography of the Cochin estuary is controlled by the monsoonal cycle with heavy fresh water runoff from the rivers and saline water intrusion from the Arabian Sea, thereby inducing stratification [4,33]. Saline waters were pulled into the estuary through the bottom layers with heavy freshwater outflow at the surface. During this process, vertical mixing take place as a result of entrainment between the surface and bottom layers with tidal cycles. Heavy river runoff during the summer monsoon lowers the surface salinity to ~0 during the low tide and concurrent with this fresh water discharges an intrusion of high salinity (~20) waters of the Arabian Sea was also observed in the bottom layers of the Cochin estuary during the high tide (Figure 3a-3b). During the summer monsoon, low tidal energy of the neap tide diminishes vertical mixing, which increases stratification, but during the pre-monsoon the high tidal energy at spring tide favours vertical mixing which lowers stratification [31].

River runoff brings in a high concentration of nutrients to the Cochin estuary as evidenced with an inverse relationship between salinity and dissolved inorganic phosphate during the summer monsoon period [34]. This is supported by the contrasting behaviour of DIP with salinity in the estuary during the monsoon and pre-monsoon seasons (Figure 7a-7d). During the monsoon, the higher DIP values (>3 μM) that encountered in the upper estuary corresponds with low saline waters, suggesting its origin from freshwater discharges through the river Periyar, but during the pre-monsoon, higher DIP values (>2 μM) that concentrated in the lower estuary corresponds with high saline waters suggesting its origin through internal re-cycling via. sediment re-suspension [1,35].

TP content in sediments showed a noteworthy regional increase in concentration during the monsoon and a decrease towards the ocean during the pre-monsoon. In contrast, water column DIP concentrations decreased towards the ocean during the monsoon and increased during the pre-monsoon. During the monsoon, the low pH and low salinity enhance adsorption of phosphorus to the sediment particles which decreases the DIP concentrations towards the ocean, whereas during the pre-monsoon, the high pH and high saline waters enhances desorption of phosphorus from sediments increasing DIP concentrations towards the seawater head [36,37].

During both seasons, strong tidal currents (>50 cm/s) observed in the seaward region at the high tide and in the riverine end of the low tide (Figure 2a-2d), mixes the water column eventually transporting suspended particles rich in phosphate towards the downstream and upstream regions to create a phosphorus enrichment in the water column of the north estuary [38]. During the peak high tide and a spring tide, the increased residence time of water bodies in the lower estuary, favours sediment re-suspension through strong underwater currents and under the prevailing environmental conditions of pH, redox potential and salinity, the interstitial and adsorbed phosphates leaches out in the overlying water column [18,37]. Thus, the predominant tidal circulation during the monsoon and pre-monsoon seasons, transports high concentrations of dissolved inorganic phosphate from the freshwater head to the seawater end of the lower estuary and its neighbouring shelf waters which can enhance coastal eutrophication [39].

The Cochin estuarine sediments act as a P source as well as a sink, which is very important in regulating the trophic status of the overlying water column [1,40]. The ability of sediments to adsorb phosphorus is higher during the monsoon than the pre-monsoon season. This gives an indication that as the rate of sorption of phosphate from the water column decreases the phosphorus content in sediments increases since the ability of sediments to adsorb and store phosphorus decreases as the estuary tends to become more eutrophic. During the pre-monsoon, the internal re-cycling of phosphorus in sediments can supply sufficient phosphorus into the water column to maintain eutrophic conditions in the Cochin backwaters. Since excess phosphate loadings can stimulate algal growth, the prevalent dredging activities for maintaining navigation channels in the estuary can accelerate the release of phosphate from the bottom sediments into the water column, which can further exacerbate eutrophication problems [1]. The increase in phosphorus availability in this eutrophic system intensifies nitrogen limitation and encourages the growth of algae and other heterotrophic organisms with high phosphorus requirements [4].

Phosphorus speciation in sediments

Phosphorus is present in sediments of the Cochin backwaters in inorganic and organic forms. The various forms of phosphorus detected in sediments were iron bound inorganic (Fe-IP) and organic fractions (Fe-OP), calcium bound inorganic (Ca-lP) and organic fractions (Ca-OP), acid soluble organic fraction (Acid-OP) and alkali soluble organic fraction (Alkali-OP). During monsoon the sequence of various fractions of phosphorus in sediments at Stations 1 and 2 were as follows: Organic Ca-P>Inorganic Ca-P >Organic Fe-P>Inorganic Fe-P>Alkali soluble P>Acid soluble P. However, during monsoon the sequence of different fractions of phosphorus in sediments at Stations 3, 4 and 5 it follows another order: Inorganic Ca-P>Organic Ca-P>Organic Fe-P>Inorganic Fe-P>Alkali soluble P>Acid soluble P. Similarly, during pre-monsoon the sequence of different fractions of phosphorus in sediments at Stations 2, 3 and 4 were as follows: Organic Ca-P>Organic Fe-P>Inorganic Ca-P>Inorganic Fe-P>Alkali soluble P>Acid soluble P. However, during pre-monsoon the sequence of different fractions of phosphorus in sediments at Station 1 follows another order: Organic Fe-P>Organic Ca-P>Inorganic Ca-P>Inorganic Fe-P>Alkali soluble P>Acid soluble P. During pre-monsoon the sequence of different fractions of phosphorus in sediments at Station 5 follows another order: Inorganic Ca-P>Organic Fe-P>Organic Ca-P>Inorganic Fe-P>Alkali soluble P>Acid soluble P.

The chemical forms of phosphorus in sediment have an important effect on its release. During the monsoon and pre-monsoon seasons, calcium bound inorganic and organic fractions (~25 to 28%) followed by iron bound inorganic and organic fractions (~12 to 25%) was found to be the main phosphorus pool in sediments of a majority of stations. The changes in various fractions of phosphorus noted in the sediments during the monsoon and pre-monsoon seasons are associated with the salinity changes [20]. For instance, during the pre-monsoon, the low values of inorganic Fe and Ca bound phosphorus in the sediments towards the ocean suggest that a release of phosphorus to water column which is favoured by high salinity conditions (~25-30). Contrary the high values of inorganic Fe and Ca bound P in sediments at the low salinity areas suggest an adsorption of phosphorus from the overlying water column which is favoured by moderate salinity conditions (~15-20).

The fractionation of phosphorus in sediments during the monsoon and pre-monsoon seasons reveals that Ca and Fe bound inorganic fractions are lower in concentrations than the organic fractions implying that these are the major forms that are precipitating/flocculating from the water column [21]. Since DIP transported from rivers to estuaries is strongly particle active it readily undergoes scavenging by Ca and Fe which gets adsorbed onto sediments [9,41,42]. Organic Ca bound phosphorus forms present in sediments showed an increase in concentration towards the seaward end, whereas inorganic Fe bound phosphorus present in sediments showed an increase in concentration towards the freshwater end. The increase of organic Ca bound phosphorus towards the ocean during the monsoon is due to interactions of dissolved inorganic phosphate with biogenic calcium carbonate minerals with increasing salinity [21,43]. Hence, the precipitation/flocculation of DIP within the salinity gradients (~15-30) of the water column followed by its adsorption/desorption with Fe and Ca minerals that settling towards bottom sediments governs the phosphorus biogeochemistry of the Cochin estuary [44-49].

Conclusion

The sequential extraction procedure used in this study gave a better understanding of the biogeochemical cycling of phosphorus revealing its bioavailability and mobility in the Cochin estuary. The main form of phosphorus in Cochin estuary sediments is precipitating/flocculating calcium- and iron-bound phosphorus compound adsorbed onto calcium carbonate. Cochin estuary sediments can act as a source and a sink of phosphorus that can alter eutrophication events. Since high phosphorus availability in sediments can regulate the eutrophic conditions in the estuary, this factor should be managed by controlling phosphorus inputs. Effective management techniques and protocols are required to control direct and indirect phosphorus pollution to reduce the adverse impact of eutrophication and to conserve the Cochin backwaters.

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