3.1 Geochemistry of the Cochin Estuary

Cochin estuary is a tropical micro-tidal monsoonal estuary having a highly complex geometry and bathymetry. The fluvial discharge of Cochin estuary is influenced by freshwater discharge from two rivers, Periyar and Muvattupuzha, as well as the tidal intrusion from the Arabian Sea. Seasonal salinity fluctuation is more or less governed by river discharge. The river discharge is maximum during monsoon (1346 m$^3$s$^{-1}$), moderate in post-monsoon (205 m$^3$s$^{-1}$) and minimum (142 m$^3$s$^{-1}$) in pre-monsoon period (Revichandarn et al., 2012). Salinity values remain close to zero over the surface layer of the estuary during the monsoon. The complete freshening of the estuary takes place during the peak monsoon period. During the monsoon season, the estuary is more dynamic and the pH is found to be less than 7. Post monsoon is a typical transition period. In post monsoon, river discharge gradually decreases and tidal influence gains momentum and the estuarine condition changes to partially mixed type. The productivity is high during this season. In pre monsoon, river discharge is
in minimum and the seawater influence is maximum, the estuary is well mixed and homogeneity exists in water. Estuary acquires more or less a stable condition during pre-monsoon season (Menon et al., 2000).

The spatial and seasonal variations in hydrographical properties of water including redox potential, salinity, pH, temperature, dissolved oxygen and particles in suspension influence the biogeochemical cycling of nutrients, trace metals and organic matter in the Cochin estuary. The low salinity and oxygenated water column conditions favours the formation of Fe and Mn hydroxides, whereas the geochemical formation of calcite is low. Trace metals and nutrients are either co-precipitated or adsorbed onto oxides or hydroxides of Fe/Mn (Deepulal et al., 2012). The high energy condition due to the enhanced flow may result in the accumulation of coarser particles in surface sediments. The coarse grained highly permeable sediment allows the dissolved oxygen penetration to the surface sediment keeping it oxic and metastable. Nutrients and trace metals released by anaerobic organic matter degradation diffuse to the oxic layer in the sediments, where it forms oxides or hydroxides and get precipitated. This mechanism effectively sorb nutrients and trace metals, restricting the mobilisation of these elements into the water column during the monsoon period in the entire portion of the estuary. Also these mechanisms operate throughout the year in the fresh water end of the estuary (Martin, 2009).

Increase in salinity during the post monsoon and pre monsoon seasons in Cochin estuary are accompanied by gradients in other variables including pH, dissolved oxygen, type and concentration of suspended particles and organic matter. Clay particles can be negatively charged by isomorphous substitution during the formation of clay minerals. The surface charge of the organic matter depends on the pH, as the negatively charged clay particles move from
freshwater to saline water, free cations neutralise the negatively charged surfaces, allowing molecular force of attraction to dominate when the particles are brought close enough. They flocculate leading to the increased deposition in high salinity region. The muddy impermeable sediment towards the high saline region allows only a minimum advective flow of oxygen which favours anaerobic redox processes. The major redox reactions in sediments are organic matter remineralisation and other reactions involving inorganic substances (Burdige, 2011). Microorganisms catalyze these redox reactions that combine most efficient electron donor with most efficient electron acceptor. The most common electron donor is organic matter, molecular oxygen act as the most preferred electron acceptor and if the supply of oxygen is terminated the microbial processes switch to facultative followed by anaerobic respiration which use nitrate, Mn^{4+}, Fe^{3+}, sulphate and finally carbon dioxide producing molecular nitrogen(N₂), ammonium (NH₄⁺), Fe^{2+}, Mn^{2+}, H₂S and CH₄. The reductive dissolution of the (oxyhydr)oxides of Fe/Mn releases Fe^{2+} and Mn^{2+} which in turn reacts with sulphide formed from sulphate reduction to form Fe/Mn sulphides (Du Laing, 2011). The adsorbed or co-precipitated trace metals and nutrients releases to the pore and water column which enhances the water column productivity. Carbonates are biogenically and geochemically formed in the high salinity region and directly precipitate metals and nutrients. When the pH decreases below a certain limit, calcification occurs, which results in the mobilisation of trace metals and nutrients.

Sulphates are ubiquitous in oxic estuarine environment and flow into estuary along with sea water or they can be released within sediments during organic matter remineralisation. Reduction of sulphates in anaerobic conditions leads to the formation of sulphides. Microbial communities initiate sulphate reduction of redox potential below -150mV (Mansfeldt, 2004) or -
220mV (Ross, 1989). When the medium turns saturated with sulphides, they serve as a sink for many discharged trace metals in sediments (Salomons et al., 1987), mean while the formation of sulphide of certain metals increase the concentration of such metals in solution. Although Cd, Cu and Zn can directly precipitate as sulphides; it is mainly Fe that generates sulphide precipitate in the estuarine environment. Fe sulphides are rapidly formed as Fe is often available in high concentrations. The dissolved sulphides produced by bacterial sulphate reduction in sediments have several possible fates; reaction with Fe oxides or Fe$^{2+}$ to form FeS, incorporation in sediment organic matter to form organic sulfur compounds, reaction with FeS to pyrite and oxidation leading to the formation of elemental sulphur (Du Laing, 2011).

### 3.2 Phosphorous as a Geochemical Index

Phosphorous in the estuarine environment usually exists in various forms, mainly; dissolved inorganic, dissolved organic, particulate organic, particulate inorganic, crystalline, occluded and adsorbed P (Gikuma-Njuru et al., 2010). In water column, P may exchange between particulate and dissolved phases through physical, chemical and biological processes (Suzumura et al., 2004). The particulate form can get settled from water column or can be dissolved into water column through microbial activity and through physical or chemical dissolution.

Among the soluble P forms, only ortho-phosphate can be directly utilised by phytoplankton (Gikuma-Njuru et al., 2010) and the amount of phosphate (PO$_4^{3-}$) present in a water body at any given time depends on external P loading and various influence mechanisms that regulate its release and retention in sediments (Garcia and Iorio, 2003). The mechanisms involved can be of chemical (adsorption/de-sorption and
precipitation/dissolution) or biological in nature (uptake or release by bacteria and algae, excretion by macrofauna), or a combination of both (e.g. anoxic conditions mediated by bacteria resulting in the release of sorbed P from iron oxides) (Slomp et al., 1996; Garcia and de Iorio, 2003).

Under aerobic conditions, $\text{PO}_4^{3-}$ interacts with many cations such as $\text{Fe}^{3+}$ and $\text{Ca}^{2+}$ to form relatively insoluble compounds that precipitate out of the water column to the sediments (Spivakov et al., 1999; Wetzel, 2001). The P bound to iron hydroxides can be released into overlying water when FeOOH get reduced in the anoxic layers of the sediment (Jordan et al. 2008). When this happens under aerobic fresh water, the resulting Fe (II) can diffuse upward into aerobic sediments, and get oxidised to FeOOH that can bind phosphate, thus preventing it from diffusing to the overlying water. In anoxic layers of salt water rich sediments, sulphides formed by sulphate reduction can bind with Fe (II) leading to pyrite formation thus preventing it from diffusing to aerobic layers where it might otherwise re-oxidise and bind to phosphate (Caraco et al., 1990; Gachter and Muller, 2003; Jordan et al., 2008; Gikuma-Njuru et al., 2010). It is well established that sulphides can promote FeOOH reduction in anoxic sediments (Jensen et al., 1995). $\text{PO}_4^{3-}$ can also co-precipitate with calcium carbonate in alkaline waters (Golterman, 1995). Furthermore, in saline water the reduction of FeOOH below the oxic layer of the sediment may release phosphate and fluoride into the water, leading to the formation of carbonate fluoroapatite, a P mineral that accumulates in marine sediments (Ruttenberg, 1992; Ruttenberg and Berner, 1993). P is not redox sensitive by itself, but is strongly coupled with redox dependant cycle of Fe and organic matter as well as precipitation and dissolution of calcium carbonate.
Therefore the fractionation of P can be used as an effective tool for unravelling the redox processes acting along the salinity gradients of the Cochin estuary. The schematic representation of aforementioned geochemical processes are furnished in Fig. 3.1

3.3 Results

3.3.1 General Water and Sediment Characteristics

Water column pH (Fig. 3.2) showed slightly alkaline character in pre monsoon season with an average of 7.91 and 7.98 in surface and bottom water respectively. It displayed slightly acidic character in monsoon season except in the bottom waters of barmouth to S7 which ranged from 6.08 to 6.89 (average ± standard deviation, 6.46±0.28) in surface water and 6.00 to 7.44 (6.66 ± 0.63) in bottom water. Salinity exhibited (Fig. 3.2) large fluctuations in the study region with a bimodal pattern, which ranged from 0.02 to 32.23. Fresh water condition was prevailing during monsoon when the river run off is very high and after that salinity started to increase. An increase in salinity was again noticed during pre monsoon period and it ranged from 17 to 31.5 during pre monsoon. PO$_4^{3-}$ showed (Fig. 3.2) a decreasing trend from bar mouth to Thanneermukkom bund in all seasons. PO$_4^{3-}$ ranged from 0.38 to 3.55 µM (1.74± 1.14) in surface water and 0.17 to 7.19 µM (2.41 ± 1.76) in bottom water during pre monsoon. In monsoon, it ranged from below detectable limit (n.d) to 2.22 µM (0.75 ± 0.80) in surface water and n.d to 5.88 µM (1.90 ± 2.11) in bottom water. In post monsoon the surface range was between 0.23 and 1.63 µM (0.69 ± 0.40) and at the bottom, the estimated range was between 0.09 and 1.96 µM (0. 78± 0.52).
Fig. 3.2 Spatial distributions of pH, salinity and dissolve inorganic phosphate in the Cochin estuary.
Surface sediments collected from Cochin estuary showed spatial variations in textural characteristics (Fig. 3.3). Sand and silt content dominated in the first three stations (barmouth region) as well as in the last four stations (southern end).

![Fig. 3.3 Distribution of sand, silt and clay in surface sediments (a-monsoon, b-post monsoon and c-pre monsoon)](image)

**Table 3.1 pH and Eh in surface sediments of the Cochin estuary**

<table>
<thead>
<tr>
<th>Stations</th>
<th>pH Mon</th>
<th>pH Post</th>
<th>pH Pre</th>
<th>Eh (mV) Mon</th>
<th>Eh (mV) Post</th>
<th>Eh (mV) Pre</th>
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<tbody>
<tr>
<td>1</td>
<td>7.18±0.06</td>
<td>7.16±0.04</td>
<td>7.8±0.04</td>
<td>-194±5</td>
<td>-182±9</td>
<td>-185±5</td>
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<td>2</td>
<td>7.24±0.07</td>
<td>6.93±0.03</td>
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<td>-151±7</td>
<td>-190±10</td>
<td>-242±7</td>
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<td>3</td>
<td>6.75±0.04</td>
<td>6.88±0.04</td>
<td>7.19±0.05</td>
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<td>-210±10</td>
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<td>4</td>
<td>6.43±0.05</td>
<td>7.03±0.07</td>
<td>7.78±0.04</td>
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<tr>
<td>5</td>
<td>7.14±0.0</td>
<td>6.95±0.05</td>
<td>8.64±0.07</td>
<td>-175±10</td>
<td>-187±8</td>
<td>-160±10</td>
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<td>6</td>
<td>7.13±0.08</td>
<td>7.41±0.06</td>
<td>8.34±0.07</td>
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<td>-164±5</td>
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<td>7</td>
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<td>8</td>
<td>6.63±0.07</td>
<td>6.98±0.04</td>
<td>7.65±0.04</td>
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<td>-160±8</td>
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<td>6.85±0.06</td>
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<td>10</td>
<td>6.59±0.05</td>
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<td>11</td>
<td>6.72±0.07</td>
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<td>12</td>
<td>6.7±0.07</td>
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<td>7.05±0.06</td>
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<tr>
<td>13</td>
<td>6.72±0.06</td>
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<tr>
<td>14</td>
<td>6.83±0.04</td>
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<td>8.11±0.06</td>
<td>-211±9</td>
<td>-215±7</td>
<td>-202±7</td>
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</table>
Other stations were characterised by high content of fine fractions. Sediment pH (Table 3.1) in the entire study area was slightly alkaline in pre monsoon and post monsoon while slightly acidic pH recorded in monsoon. The pH values ranged from 6.43 to 7.24 in monsoon, 6.88 to 7.41 in post monsoon and 7.05 to 8.64 in pre monsoon. The sediment is characterised by reducing conditions (the average Eh is below the redoxcline, i.e. 230 mV) and Eh values (Table 3.1) were in the range of -242 to -160 mV (pre monsoon), -211 to -52 mV (monsoon) and -220 to -160 mV (post monsoon).

3.3.2 Phosphorous Fractionation in Sediments

The variation of TP and different forms of P in the surface sediments are depicted in Fig.3.4. The concentration of TP in surface sediments ranged from 395 to 2383 µg g⁻¹ (1375 ± 763) in monsoon, 612 to 2190 µg g⁻¹ (1435 ± 616) in post monsoon and 313 to 2239 µg g⁻¹ (1173 ± 558) in pre monsoon. TP in surface sediments was dominated by TIP for stations S1-S7, while TOP dominated in the rest of the stations. Fe(OOH)₃P in surface sediment was highest in monsoon (147 to 963 µg g⁻¹, 510 ± 301) followed by post monsoon (103 to 503 µg g⁻¹, 257 ± 127) and pre monsoon (33 to 597 µg g⁻¹, 294 ± 191). Fe(OOH)₃P accounted for 4 to 61% of the total P pool in pre monsoon, 15 to 75% in monsoon and 6 to 60% in post monsoon.

CaCO₃P in the surface sediments varied from 25 to 809 µg g⁻¹ (292 ± 274), 44 to 945 µg g⁻¹ (381 ± 347) and 17 to 1355 µg g⁻¹ (387 ± 396) in monsoon, post monsoon and pre monsoon respectively. It constituted to about 6 to 61% of the total P pool in pre monsoon. In monsoon, its contribution was from 3 to 43% and in post monsoon 3 to 49%. Acid-OP ranged from 16 to 194 µg g⁻¹ (94 ± 70) in monsoon, 65 to 207 µg g⁻¹ (136 ± 56) in post monsoon and 32 to 194 µg g⁻¹ (106 ± 50) in pre monsoon.
Alkali-OP varied from 72 to 787µgg\(^{-1}\) (412 ± 212) and 176 to 1492µgg\(^{-1}\) (734 ± 440) and 198 to 568µgg\(^{-1}\) (362 ± 109) in pre monsoon, monsoon and post monsoon respectively. ROP was found to be comparatively smaller fraction and ranged from 2 to 142µgg\(^{-1}\) (66 ± 51) in monsoon, 8 to 47µgg\(^{-1}\) (26 ± 15) in post monsoon and 7 to 48µgg\(^{-1}\) (24 ± 12) in pre monsoon.

### 3.4 Discussion

#### 3.4.1 Ratios of Carbon, Nitrogen, Sulphur, Phosphorous and Iron as Redox Indicators

The OC: TP ratios (Fig. 3.5) showed large variations in the study region which ranged from 3 to 62 in pre monsoon, 9 to 47 in monsoon and 2 to 32 in post monsoon. The TN: TP ratios were very low and did not display much variation in the study region. Their values ranged from 0.4 to
6.6, 0.5 to 3.9 and 0.2 to 2.2 in pre monsoon, monsoon and post monsoon respectively. The OC: TP and TN: TP ratios were lower than the Redfield ratio (Hecky et al., 1993), indicating that the organic matter is enriched with P and tends to accumulate in surface sediments.

Chemistry of P in sediments is largely influenced by redox conditions, and the redox cycle of Fe greatly affects P geochemistry after burial (Cha et al., 2005). OC: TS ratio (Fig. 3.5) gives a qualitative indication of the redox status of the environment of deposition, when TS concentrations are high (Raiswell et al., 1987). OC: TS > 5 are considered as oxic sediment with oxygenated bottom water, OC: TS = 1.5–5 indicates deposition under periodic anoxia and OC: TS < 1.5 represents anoxic sediment with overlying anoxic water. The OC: TS values (Fig. 3.5) in the study region lie in the second category suggesting that these sediments undergo sulphate reduction below an oxygenated water column (Hedges and Keil, 1995; Renjith et al., 2011).

The involvement of Fe in the dynamic equilibrium between the sediment and water PO$_4^{3-}$ levels has led to suggestions that the Fe dependant threshold limit exists for the sediment ability to bind phosphate (Sondergaard et al., 2003). The Fe: TP ratios were considered as a measure of free sorption sites for PO$_4^{3-}$ ion on iron hydroxides (Jensen et al., 1992; Jensen and Thamdrup, 1993; Coelho et al., 2004). Caraco et al., (1990) suggested that the Fe: TP ratio should exceed 10 if it was to regulate P release. Fe: TP ratios lacked seasonal variations in the study region, but displayed significant spatial variation. The fresh water areas showed higher Fe: TP indicating the presence of enough Fe in surface sediments to bind with P, while lower ratios obtained towards the seaward sites suggest the
saturation of sorption sites or less capacity to bind with PO₄³⁻ may result in P efflux from the sediment to the overlying water column.

![Graphs showing elemental ratios in surface sediments](image)

**Fig. 3.5 Elemental ratios in surface sediments**

### 3.4.2 Forms of Phosphorous in the Estuary

Phosphorous fractions undergo series of chemical and biological transformations along the salinity gradients of estuaries. Previous studies demonstrated a shift from importance of Fe(OOH)≈P to CaCO₃≈P with increasing salinity (Coelho et al., 2004; Hartzell et al., 2010). Oxidative
decomposition of organic matter and reductive dissolution of Fe(OOH)\textasciitilde P releases the P to the sediment interstitial water and a portion of released P may return to the water column. A substantial portion of released P contributes to the formation of authigenic P minerals and thereby immobilised in the sediments (Ruttenburg and Berner, 1993; Schuffert et al., 1994; Kim et al., 1999; Cha et al., 2005). ANOVA and correlation analysis were carried out to measure the statistical significance of each processes along the salinity gradients of the estuary.

TP displayed spatial variation in the study area (p<0.01) but did not exhibit any significant seasonal variation. In general, the distribution of P fractions and other geochemical parameters in the surface sediments of Cochin estuary displayed relationship with sediment texture. Correlation analysis (Table 3.2) has revealed that silt and clay fractions have high positive correlations with most of the sedimentary parameters. Sand fraction showed similar negative correlations. These indicate that the main factor influencing the geochemistry of surface sediments in the study region could be sediment texture. These high correlations may have resulted from the greater surface area of fine particles resulting in more adsorption sites for phosphate ions (Andrieux-Loyer and Aminot, 2001; Liu et al., 2002; Zhou et al., 2005). It is 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; Renjith et al., 2011).
Table 3.2 Correlation between different phosphorus fractions and other geochemical parameters (n=42)

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<tr>
<th>pH</th>
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<th>Ca (OOH)</th>
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a Correlation is significant at the 0.01 level (2-tailed). b Correlation is significant at the 0.05 level (2-tailed)
One way ANOVA of Fe(OOH)≈P has revealed significant seasonal variation (p<0.01) but lacked significant spatial variations. During the monsoon season, the estuary is virtually converted into a freshwater basin even in areas around the barmouth where salt water penetration occurs at depths below 5 m depth only (Menon et al., 2000; Renjith et al., 2011). In post monsoon, river discharge gradually diminishes and tidal influence gains momentum as the estuarine conditions changes to a partially mixed type, weakening stratification. This is mainly a transitional period. In pre-monsoon, the river discharge is in minimum and seawater influence is maximum upstream; the estuary is well-mixed and homogeneity exists in the water column (Menon et al., 2000). Fe(OOH)≈P showed higher concentrations in the monsoon season followed by post-monsoon and pre-monsoon and the percentage contribution of Fe(OOH)≈P to TP displayed an increasing trend from barmouth to Thannermukkom bund. CaCO₃≈P exhibited significant spatial difference in the study region recording higher concentrations at the barmouth region and lower concentrations towards the bund (p<0.01) but did not display any seasonal variation. CaCO₃≈P showed strong positive correlation with salinity and its concentration increased towards the barmouth region. TS concentrations were higher towards the seaward sites and it exhibited strong positive correlation with Fe.

These trends may have resulted from several processes (Coelho et al., 2004; Hou et al., 2009). The increased pH and salinity in pre monsoon and post monsoon season may inhibit phosphate adsorption onto Fe oxides/hydroxides, by shifting speciation phosphate from H₂PO₄⁻ to HPO₄²⁻ and by changing surface charge on the Fe oxides and hydroxides (Lebo, 1991; Zwolsman, 1994). Also, the concentration of Fe oxides and hydroxides reduced in sulphide environments by the formation of solid Fe.
sulphides and the sulphate reduction rate may be the highest in more saline area (Paludan and Morris, 1999; Hou et al., 2009). The increased concentration of CaCO₃≈P may be caused by the interactions between PO₄³⁻ and CaCO₃ with increasing salinity (Gunnars et al., 2004; Anshumali and Ramanathan, 2007; Hou et al., 2009). Calcite is produced at high salinities through precipitation reactions, and biological activity in estuarine environment forming an adsorption substrate for dissolved phosphate (Coelho et al., 2004). CaCO₃≈P also showed strong positive correlations with Acid-OP which may have resulted from the mineralisation of organic P. During microbial decomposition, organic P may have transformed into authigenic fluroapatite (Anshumali and Ramanathan, 2007; Katsaounos et al., 2007; Hou et al., 2009). The southern part of the study region is well known for black clam fishery (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 sub fossil deposits (Renjith et al., 2011). The present results were in good agreement with this mechanism, since CaCO₃≈P is the most important fraction to the seaward side and Fe(OOH)≈P towards the fresh water end of the study region. Fe(OOH)≈P dominated in the entire estuary in monsoon season. The decrease of Fe(OOH)≈P with increasing salinity has been reported in many estuaries like Pamlico River-estuary (Upchurch et al., 1974), Dalware estuary (Strom and Biggs, 1982) Scheldt estuary (Hyacinthe and Van Cappellan, 2004), Mondego estuary (Coelho et al., 2004), Patuxent River-estuary (Jordan et al., 2008) and Chesapeake Bay estuaries (Hartzell and Jordan, 2010).

Acid-OP includes apatite-bound phosphate and biochemical components such as nucleic acids, lipids, and sugars that are bound to
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phosphate (De Groot, 1990). It showed lower concentrations in the study area which accounted for 5 to 13%, 3 to 20%, and 4 to 14% of the TP in pre monsoon, monsoon and post monsoon respectively. Acid-OP exhibited distinct seasonal (p<0.05) and spatial (p<0.01) difference with maximum concentrations in the post monsoon, and displayed an increasing trend towards the bar mouth region. The degradation of Acid-OP compounds release phosphate which is available to phytoplankton. 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 phosphate/metal/organic matter complex (Stevens and Stewart, 1982). This fraction also contains phytate, an organic phosphate that is common in plants and sediments (De Groot and Golterman, 1993; Dvorakova, 1998). Alkali-OP accounted for 10 to 73% in pre monsoon, 11 to 49% in monsoon and 9 to 86% in post monsoon. Alkali-OP displayed significant seasonal difference with maximum concentrations in the post monsoon and minimum in monsoon season. Higher Alkali-OP concentrations were observed in the southern part of the study region. This may be due to the flocculation and precipitation processes involving humic acids, Fe/Al oxides and dissolved reactive P complexes from advective mixing of salt water with fresh water (Coelho et al., 2004).

$PO_4^{3-}$ displayed significant spatial (p<0.05) and seasonal (p<0.01) variations in the study region. It was characterised with maximum concentrations in the pre monsoon and minimum in post monsoon season. Abrupt increase in $PO_4^{3-}$ concentration with increasing salinity was observed in the study region. $PO_4^{3-}$ also displayed highly significant positive correlations with TS, CaCO$_3$&P and TP. The percentage of
Fe(OOH)≈P showed a decreasing trend towards the seaward side and the Fe and TS showed strong positive correlation in all seasons. It is well established that P-Fe-S interactions promote the release of PO$_4^{3-}$ from sediments at higher salinities (Azzoni et al., 2005; Jordan et al., 2008). Boynton and Kemp (2008) found the lowest rate of PO$_4^{3-}$ efflux in tidal fresh water at a salinity range of 0-0.5 (4µM P m$^{-2}$ h$^{-1}$), higher at salinities 0.5-5 and highest at a salinity range of 5-10 (12µM P m$^{-2}$ h$^{-1}$ and 52µM P m$^{-2}$ h$^{-1}$ respectively) in estuarine sites outside the Chesapeake Bay. Boynton and Bailey (2008) also found a similar relationship between salinity and PO$_4^{3-}$ efflux. This PO$_4^{3-}$ efflux can alter the relative bioavailability of N and P (Hartzell and Jordan, 2010).

Bioavailable P (BAP) in the sediment can be defined as the sum of immediately available phosphorus and potential phosphorus that can be transformed into an available form by naturally occurring physical, chemical and biological processes (Wang et al., 2009). Fe(OOH)≈P, CaCO$_3$≈P and Acid–OP were considered as a source of BAP for phytoplankton (Diaz-Espejo et al., 1999). Knowledge of P fractions is of utmost importance in determining the upper limit of the potentially BAP in aquatic ecosystems (Hou et al., 2009). The bioavailability of Fe(OOH)≈P depends primarily on sediment redox intensity (Andrieux-Loyer and Aminot, 1997; Rozan et al., 2002; Álvarez-Rogel et al., 2007). In the areas characterised by frequent change of sediment redox potential, Fe(OOH)≈P can intermittently be reduced and released from sediments into the pelagic waters (Jensen and Thamdrup, 1993; Coelho et al., 2004). Organic P could become bioavailable by microbial remineralisation (Andrieux-Loyer and Aminot, 1997; Hou et al., 2009). The spatial and seasonal variation of BAP is depicted in Fig. 3.6. The BAP fractions
ranged from 25 to 79% (107 to 1770 µg g⁻¹) in pre monsoon, 48 to 78% (249 to 1716 µg g⁻¹) in monsoon and 13 to 71% (217 to 1465 µg g⁻¹) in post monsoon. One way ANOVA of the BAP in surface sediments displayed no significant seasonal variation (p > 0.05). However, the BAP concentrations varied significantly among the sampling stations (p < 0.05). BAP displayed a decreasing trend from barmouth to Thanner Mukkom bund. BAP was relatively higher in the Cochin estuary which also reveals that the sediment can act as an important internal source of P for the Cochin estuarine and coastal ecosystem.

![Fig. 3.6 Spatial and seasonal variations of bioavailable phosphorous (BAP) in surface sediments](image)

The high Fe: TP ratios in the freshwater side of the estuary ensure enough sorption sites for P and saline water region is characterised with lesser sorption sites for P. The processes of reductive dissolution of iron hydroxides and biogenic or geochemical formation of calcium carbonate minerals in the saline areas is indicated by the distributional dynamics of Fe(OOH)≈P and CaCO₃≈P in the estuary. The input of organic matter
enriched with P from rivers and from different industrial, agricultural and aquaculture activities lead to a large scale accumulation of refractory organic P in the surface sediments of the Cochin estuary.

3.5 Trace Metals Geochemistry

The sources of trace metals in estuaries include inputs from fresh water discharges, urban, domestic and industrial effluents and atmospheric deposition. Within the estuaries, trace metals are present in different physico-chemical forms or species such as dissolved, particulate and sedimentary metals. Sediments are final destination of trace metals, as a result of adsorption, desorption, precipitation, diffusion processes, chemical processes, biological activity and a combination of these phenomena. The thermodynamically stable form of metal ion in estuaries is controlled by the redox potential in the sediment water interface, which is essential in determining the fate and role of metals in biological systems. For example under oxic conditions Fe(II) get oxidised to Fe (III) which is insoluble in water and finally get deposited in sediments, lowering dissolved Fe concentrations (Du Laing et al., 2007; Du Laing, 2011). The sediment characteristics such as pH, cation exchange capacity, organic matter contents, redox conditions and salinity determine the metal sorption and precipitation processes, which is in turn related to metal mobility, bioavailability and potential toxicity (Du Laing et al., 2009).

Redox sensitive trace metal (Fe, Mn, Cu, Ni, Pb, Zn and Cd) concentrations are among the most widely used indicator of redox conditions. Fe and Mn oxides are excellent scavengers for metals and metals can exist as sulphides under anaerobic conditions and these processes affect sediment pH and Eh change (Gambrell et al., 1991;
Lery et al., 1992). Anoxic sediment conditions can exhibit significant changes in metal speciation and solubility across redox interface (Balistrieri et al., 1994). Redox sensitive elements are widely used as indicators of redox conditions. Many metals have multiple valence states and the reduced forms that exist under low oxygen conditions are more readily complexed with organic acids, taken into solid solutions by authigenic sulphides or precipitated as insoluble oxyhydroxides (Algeo and Maynard, 2004).

3.6 Distribution of Trace Metals

Fe, Mn, Mg, Co, Ni, Cu, Zn, Pb, Cr and Cd were analysed in surface sediments of the Cochin estuary and the spatial and seasonal variations of these trace metals is presented in Fig.3.7 (a, b & c). Fe showed highest concentrations in the study area which ranged from 4140 to 83000 µgg⁻¹ in monsoon, 1700 to 78437 µgg⁻¹ in post monsoon and 8687 to 83625 µgg⁻¹ in pre monsoon, while Mn displayed large spatial and seasonal fluctuations in the study region and it ranged from 67.50 to 657.50 µgg⁻¹, 65.00 to 428.13 µgg⁻¹ and 44.38 to 347.50 µgg⁻¹ in monsoon, post monsoon and pre monsoon respectively.

The variations of Mg ranged from 540 to 23937µgg⁻¹ in monsoon, 2856 to 23631µgg⁻¹ in post monsoon and 1456 to 23372µgg⁻¹ in pre monsoon, while for Co it was ranged from 5.44 to 24.09µgg⁻¹, 4.43 to 24.61µgg⁻¹ and 4.89 to 19.58µgg⁻¹ in monsoon, post monsoon and pre monsoon respectively. Ni ranged from 12.43 to 72.53µgg⁻¹ in monsoon, 10.50 to 62.56µgg⁻¹ in post monsoon and 5.91 to 60.74µgg⁻¹ in pre monsoon. For Cu, the spatial variation ranged from 4.44 to 46.88µgg⁻¹, 5.25 to 32.65µgg⁻¹ and 2.89 to 29.81µgg⁻¹ during the three seasons. The
spatial variation of Zn ranged from 16.25 to 390.63µgg⁻¹ in monsoon, 23.13 to 433.13µgg⁻¹ in post monsoon and 5.63 to 585µgg⁻¹ in pre monsoon, while that of Pb ranged from 1.88 to 28µgg⁻¹, 6.75 to 28.75µgg⁻¹ and 2.38 to 25.13µgg⁻¹ respectively during three seasons. Cr varied between 13.06 and 66.04µgg⁻¹ in monsoon, 11.24 and 79.16µgg⁻¹ in post monsoon and 4.81 and 76.83µgg⁻¹ in pre monsoon and Cd was in the range 0.31 to 5.13µgg⁻¹ in monsoon, 0.16 to 4.28µgg⁻¹ in post monsoon and 0.19 to 7.16µgg⁻¹ in pre monsoon.

From the result of one way ANOVA, it was found that the trace metals except Mn exhibited significant spatial variations, while Mn concentrations were characterised with significant seasonal variations. Both Cd and Zn displayed peak values at S2 and other trace metals showed a gradual decrease towards the Thanneermukkom bund. The Mn concentrations showed anomalous behaviour in the study region with higher enrichment in the low saline region.

![Fig. 3.7a Distributional variability of Fe and Mn in surface sediments](image)
Fig. 3.7b Distributional variability of Co, Ni, Pb and Mg in surface sediments

Fig. 3.7c Distributional variability of Cd, Zn, Cu and Cr in surface sediments
3.7 Discussion

There are scores of data sets available regarding the trace metal pollution and their ecological implications in surface sediments of the Cochin estuary (Balachandran et al., 2005; Nair et al., 2006; Mohan et al., 2012; Deepulal et al., 2012; Selvam et al., 2012; Ramasamy et al., 2012; Martin et al., 2012). The trace metal composition in sediments of the Cochin estuary is comparable with the aforesaid literatures. The main emphasis of the present work is to portray the redox conditions in surface sediments in the light of P fractions and trace metal composition. In the absence of a sequential extraction of metals in sediments, statistical procedures can be used for making inferences on the important pathways of elemental deposition (Isaac et al., 2005). Multivariate statistical tools like Principal Component Analysis can be effectively used to get signatures of major redox sensitive geochemical and biochemical processes acting along the salinity gradients of the estuary.

3.7.1 Principal Component Analysis

Principal Component Analysis (PCA) of geochemical parameters was done seasonally to discover and interpret various geochemical variables and thereby identifying the major geochemical processes acting in the estuary (Table 3.3). Varimax rotation was applied in order to identify the variables that are more significant to each factor based on the significance of their correlations that are expressed as factor loading (Buckley et al., 1995; Davis, 2002). The various geochemical and biochemical processes acting along the salinity gradients strongly depends on the hydrodynamic conditions prevailing in the water column. Therefore, the hydrodynamic conditions were taken into account while
interpreting the PCA result. Transformations during early diagenesis and changing redox states characterise the forms of metals in estuarine environment. The sedimentary distribution of certain elements like Fe, Mn, Cu and S provide information about the occurrence of oxidised forms of metals such as oxides and hydroxides of Fe and Mn and the conversion of these species to more reduced form such as sulphides (Canfield et al., 1993; Kuzyk et al., 2011). Therefore, these elements have potential to be used as qualitative indicators of various biogeochemical processes.

The PCA generated four components for the monsoon season with a total cumulative variance of 85%. The PC1 accounted for a total variance of 27% and exhibited positive correlations with OC, TN, TS, P fractions and water column variables (salinity and phosphate). The complete freshening of the estuary takes place during the peak monsoon period (Revichandran et al., 2012). This factor indicates that the major factor which strongly influences the geochemistry of surface sediment is the hydrodynamic forcing during the monsoon season. PC2 accounted for a total variance of 25% with high positive loading for clay particles, OC, TN, TS and some of the trace metals (Cd, Ni, Co, Zn and Cr). This factor attributes to different physical and chemical processes acting on the sediment surface. Close association of clay particles with organic matter and trace metals indicate the granulometric component and also the flocculation and sedimentation of organic matter. The physical adsorption of organic matter and trace metals and subsequent sinking to the surface sediments is a significant geochemical process during the monsoon season. This component also gives an indication about the diagenetic processes acting in the surface sediments. Diagenesis, a redox process, largely mediated by microorganisms and the suitable indicators of this
process is OC, TN and TS. Strong positive loading of Fe with silt particles and some of the trace metals (Pb, Ni, Mg and Cu) were observed in PC3 and accounted for a total variance of 24%. This component revealed the formation of stable Fe (oxy hydr) oxides and co-precipitation or adsorption of other trace metals (Pb, Ni and Cu) onto Fe (oxy hydr) oxides and subsequent sinking to the surface sediments.

For post monsoon season, PCA resolved three components accounting for a total cumulative variance of 89%. The close association of grain size, organic matter, trace metals (Cd, Pb, Ni, Zn, Mg, Cu, Cr), P fractions except Alk-OP and salinity in PC1 (46% of total variance) indicated the several process taking place in the salinity gradient. The adsorption of trace metals and P fractions onto clay minerals, organic matter complexation of trace metals and salinity induced flocculation of organic matter and trace metals are the major geochemical processes taking place during post monsoon season. Organic matter content and grain size are important controlling factors influencing the abundance of trace metals in estuarine sediments (Rubio et al., 2000). Adsorption of metal increases in the order: sand<silt<clay, due to an increase in their superficial area and mineral/organic matter contents (Haque and Subramanian, 1982). The presence of fine grained sediments leads to the accumulation of trace metals in contrast to the coarse grains. The larger surface area provided by finer sediments preferably adsorb metal scavenging phases such as Fe/Mn hydroxylates (Thuy et al., 2000; Bradl, 2004; Magesh et al., 2011). The grouping of OC, TN and TS pointed towards the diagenetic processes taking place in the surface sediments.

The PC2 exhibited a total variance of 31% and characterized the grouping of trace metals with organic matter and silt particles. This gave an
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indication about the heavy siltation process in the estuary and adsorption or 
co-precipitation of trace metals (Pb, Ni and Cu) onto Fe/Mn hydroxides and 
subsequent sinking with silt particles. Trace metal enrichment in sediments 
is linked to the scavenging mechanisms involving hydrous oxides. Fe and 
Mn being the abundant element in the study region exert a major control on 
the distribution of other metals in the sediments. The hydrous oxides of Fe 
and Mn constitute significant sinks to trace metals in estuarine environment 
through adsorption/co-precipitation of other trace metals and formation of 
complexes with various organic ligands. The grouping of salinity and 
phosphate and moderate negative loading of Fe(OOH)≈P in the PC3 (total 
variance of 11%) indicated the desorption of reductive dissolution of 
Fe(OOH) in the high saline area and release of Fe(OOH)≈P to the water 
column.

PCA resolved four components accounting for total cumulative 
variance of 87% during the pre monsoon season. The PC1, PC2, PC3 and PC4 
accounted for a total variance of 39%, 19%, 18% and 11% respectively. PC1 
was characterised by grouping of trace metals and phosphate, while 
significant correlations of clay particles with P fractions were observed in 
PC2. However, PC3 exhibited significant positive loading on silt particles, 
OC, TN and TS and this factor reflected the diagenetic processes operating 
in the sedimentary environment. The strong association of salinity, 
phosphate and Acid-OP is observed in PC4. The loading of trace metals in 
the first component indicate precipitation and settling as the major 
processes during pre monsoon season. Reducing condition prevails in the 
surface sediments during pre monsoon season and the P fractionation 
indicated lowest concentrations of Fe(OOH)≈P in surface sediments during 
this period. The high temperature induces greater bacterial activity in
sediments together with the high salinity initiate sulphate reduction, denitrification and iron redox reactions (iron cycling) in sediments. These processes results in the formation of sulphide minerals such as greigite (Fe$_3$S$_4$) and mackinawite (FeS) in sediments, minerals that grows as a precursor to pyrite during early diagenetic sedimentary sulphate reduction (Sobrinho et al., 2011). PC2 is characterised with high positive loading for the P fractions. Mean while, PC3 indicates the granulometric component as well as the diagenetic pathway operating in sediments. Significant positive loading of salinity and phosphate and significant negative loading of Fe(OOH)$\approx$P give indications about the reductive dissolution of iron oxides and subsequent release of P to the water column. Under anaerobic conditions, active sulphide formation and co-precipitation with other metal sulphides rapidly remove many trace metals from soluble form (water column and pore water) to insoluble forms (Balistrieri et al., 1994; Clark et al., 1998; Schlieker et al., 2001).

### 3.8 Conclusions

Sequential chemical extraction of P and distribution of trace metals were used for a better understanding of the sediment redox conditions of the Cochin estuary. The water column remains oxic throughout the year. Results of sedimentary P fractions show a shift in abundance of Fe(OOH)$\approx$P fraction to CaCO$_3$$\approx$P fraction with increasing salinity. An increase in TS was also observed with increase in salinity. An abrupt increase in the concentration of dissolved inorganic P with increase in salinity was observed in the study region. Fe(OOH)$\approx$P exhibited a distinct seasonal pattern with maximum values during the monsoon season, when estuary behaves as more or less a fresh water system.
### Table 3.3 Result of Principal Component Analysis

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Fractionation of P in sediments of the Cochin estuary gives a mixed or metastable diagenetic character with strong seasonal signatures. The surface sediments in the entire estuarine region remain oxic during the monsoon season and gradually become reducing during the post monsoon season which in turn shifts to strong reducing conditions during the pre monsoon season. The PCA results generated by considering various P fractions and trace metals supports the presence of dynamic interchange of oxidising and reducing character of the surface sediments. It also gives an indication about the formation of minerals such as greigite (Fe₃S₄) and mackinawite (FeS) in sediments which grow as a precursor to pyrite during the early diagenetic sedimentary sulphate reduction in the pre monsoon season.

References


