Chapter 3

Geochemistry

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References
3.1 Introduction

Mangrove ecosystems play an important role in the biogeochemistry of nutrients, organic matter and heavy metals in the coastal environment. The potential role of the mangrove ecosystems as sinks for anthropogenic contaminants in the tropical and subtropical areas has been widely recognised (Silva et al., 1990; Badarudeen et al., 1996; Machado et al., 2002; Alongi et al., 2004). Mangrove systems have a high adaptation capacity to the extreme environmental conditions and are characterised by the high rates of organic carbon accumulations (Marchand et al., 2004). Mangrove ecosystems play an important role in nutrient cycling and energy flow in most of the tropical coasts (Odum and Heald, 1974; Lacerda et al., 1993; Silva and Mozeto, 1997). However, the knowledge of biogeochemical processes in the sediments of the tropical mangrove forests are still limited (Kristensen et al., 1995; Robertson and Phillips, 1995).

3.1.1 Heavy Metals in Mangrove Sediments

Tidal activities, land runoff and rainfall are the major sources of heavy metals into the mangrove systems. Besides this, the mangroves are at risk from heavy metals that are associated with a diverse range of anthropogenic activities including shipping, dredging, and urban wastewater discharges. Many mangrove ecosystems are close to the urban development areas and are impacted by urban and industrial run-off, which contains trace and heavy metals in the dissolved or particulate form (Tam and Wong, 2000; MacFarlane, 2002; Preda and Cox, 2002). Therefore concentrations of metals in the mangrove sediments could reflect the degree and sources of anthropogenic pollution (Tam and Wong, 1995). Mangrove
sediments, being anaerobic, reduced and rich in organic matter and sulphide, favour the retention and accumulation of heavy metals (Lacerda et al., 1991; Tam and Wong, 1995; Badarudeen et al., 1996). Several studies indicate that these anoxic, fine-grained, and organic-rich mangrove sediments can reduce the potentially deleterious effects of metal contamination because of the low availability of metals accumulated within the sediments for remobilization and biotic uptake (Lacerda et al., 1991; Sadiq and Zaidi, 1994; Tam and Wong, 1995). However, the degradation of mangrove forests tends to increase worldwide (Farnsworth and Ellison, 1997), which can promote the remobilization of sediment-trapped metals and facilitate its transport to adjacent areas (Lacerda, 1998).

The adsorption and desorption of heavy metals in the mangrove sediments depend on one or a combination of sediment properties including pH, redox potential, cationic exchange capacity, organic matter, clay content, salinity, iron and manganese oxides and the presence of other metals (Lacerda et al., 1993; Tam and Wong, 1995). The cycling of organic matter through litter production, decomposition and tidal transport, may eventually export a fraction of the accumulated heavy metals, and therefore convey it to detritus food chains in the adjacent coastal waters (Murray, 1985; Silva, 1988).

3.1.2 Phosphorus Geochemistry

Phosphorus is an essential element that limits marine primary productivity, by which it is intimately involved in the marine biogeochemical cycles (Howarth et al., 1995; Tyrell, 1999). Phosphorus cycle in tropical mangroves is multifarious because of the periodic flooding
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of sediment with both fresh and saline waters (Salcedo and Medeiros, 1995). Phosphorus retention and release in mangrove sediments depends on several factors including pH, redox potential, tidal inundation, the nature of phosphorus compounds supplied to the sediment-water interface, sedimentation rate, bioturbation, diagenetic processes etc. (Ingall and Van Cappellen, 1990; Ruttenberg and Berner, 1993; Silva and Sampaio, 1998; Schenau and de Lange, 2001). Sediment phosphorus is particularly important in shallow systems as various forms of bioavailable phosphorus in the upper sediments can be a major source of phosphorus to the water column biota via numerous physically, chemically and biologically mediated processes (Reddy and D’Angelo, 1994; Kufel et al., 1997). Analysis of total phosphorus loading alone does not provide information regarding the phosphorus availability to the biota or the potential for recycling through sediment-water interactions as it is transported to downstream locations (James et al., 2001). An exact stoichiometric and structural identification and quantification of inorganic phosphorus species are very complicated (Luderitz and Gerlach, 2002). A common route to estimate the stock of potentially accessible forms is to fractionate phosphorus based on the extractability by leaching reagents of increasing aggressiveness (Golterman, 1996; Ting and Appan, 1996; Perkins and Underwood, 2001; Tiyapongpattana et al., 2004).

Sequential leaching extractions were proposed to understand the association of phosphorus with various sedimentary components and to estimate its mobility, solubility, or biological availability (Reynolds and Davies, 2001). Phosphorus fractionation in the sediments can provide valuable information on the origin of phosphorus in sediments, diagenetic
transformations of organic phosphorus in sediments, the degree of pollution from anthropogenic activities, the bioavailability of phosphorus in sediments and the biogeochemical processes (Andrieux and Aminot, 1997; Jensen et al., 1998; Schenau and De Lange, 2001; Filippelli et al., 2003). Although many different extraction schemes may exist, the underlying extraction mechanisms are the same (Table 3.1).

It must be kept in mind that sequential fractionation schemes are rather crude methods; with many extractants causing the dissolution of more than one type of phosphorus solid phase as various extractants are unlikely to be either exhaustive or unique with respect to the target compounds (Turner et al., 2005). Sequential extraction techniques are rather laborious, tedious, time consuming and it is subjected to several potential errors including the risks of contamination due to sample manipulation and underestimation of given fractions due to re-adsorption phenomena (Buanuam et al., 2006).

In spite of these shortcomings these fractionation schemes are used widely since these schemes use only small quantity of soil samples (≤0.5 g), relatively simple to perform, and require only basic laboratory equipments. To avoid disadvantages like the uncertainty in the bioavailable and the non-specific nature of the extraction solutions, an extraction scheme using chelating agents was developed by Golterman, (1996). This “EDTA method” is useful for the extraction of inorganic phosphorus pools with lesser modifications of the organic pool (Golterman, 1996).
<table>
<thead>
<tr>
<th>Scheme</th>
<th>Extractants</th>
<th>Phosphorus Fraction</th>
</tr>
</thead>
</table>
| **1. Chang and Jackson (1957)** modified by Hartikainen (1979) | a) 1 M Ammonium Chloride  
b) 0.05 M Ammonium Fluoride  
c) 0.1 N Sodium Hydroxide  
d) KCl-C$_6$H$_5$O$_7$-EDTA | Loose bind P  
Aluminium bound P  
Iron bound P  
Occluded P |
| **2. Hieltjes and Lijkema (1980) and Nurnberg (1998)** | a) 1 M Ammonium Chloride  
b) 0.11 M Sodium bicarbonate and Dithionate  
c) 0.1 N Sodium Hydroxide  
d) 0.5 N Hydrochloric acid  
e) Persulphate digestion of NaOH extraction  
f) Persulphate digestion of remaining sediment | Loose bind P  
Iron bound P  
Aluminium bound P  
Calcium bound P  
Labile organic/Polyphosphate P  
Refractory Organic P |
b) Buffered dithionite  
c) NaOH  
d) HC  
e) Digestion | Labile, loosely bind or adsorbed P  
Reducant soluble P, bound to Fe oxides and hydroxides  
P adsorbed to metal oxides and bound to humic substances  
P bound to carbonates, apatite-P and released by the dissolution of oxides  
Organic and refractory P |
b) 1 M sodium acetate buffered to pH 4  
c) 1 N hydrochloric acid  
d) 50% magnesium nitrate to sediments, drying in oven at 80°C, and ashing at 550°C, 1 N HCl | Labile and oxide-associated P  
Authigenic CFA  
Detrital Apatite P  
Organic P |
| **5. De Groot and Golterman (1993)** | a) Buffered CaEDTA/dithionite  
b) Na$_2$EDTA  
c) H$_2$SO$_4$  
d) 2M NaOH  
pH 1 with H$_2$SO$_4$  
e) Digestion | Iron bound P  
Calcium bound P  
Acid soluble P  
Alkali soluble P  
Humic & Fulvic P  
Residual Organic P |
| **6. Jensen and Thamdrup (1993)** | a) MgCl$_2$  
b) Buffered dithionite extraction  
c) NaOH  
d) HCl  
e) Digestion | Loosely sorbed P  
Iron bound P  
Al/clay mineral and humic bound  
Calcium bound P  
Refractory organic P |
Sediments conserve important environmental information (VonGunten et al., 1997), and are increasingly recognised as both a carrier and a possible source of contaminants in aquatic systems (Forstner and Salomons, 1991; Tessier et al., 1994). The distribution of heavy metals in the mangrove sediments were assessed to find the geochemical characteristics and also the degree of anthropogenic influence on these systems. The phosphorus fractions in the mangrove systems were analysed to quantify the different forms of phosphorus in these systems and to find the processes leading to the fractional distribution of phosphorus.

3.2 Results

The spatial and seasonal variations of different geochemical parameters in the surficial sediments of the study region, including texture, mineralogy, major and trace elemental composition are explained in this chapter. Different fractions of phosphorus and their seasonal variations are also detailed.

3.2.1 General Sedimentary Characteristics

General sedimentary characteristics of the surficial sediments of the mangrove systems are given in Table 3.2. Texture analysis revealed that silt was the major fraction during all seasons in these mangrove sediments. By applying Folk (1974) classification (Fig.3.1), station 1 is silty during pre-monsoon and changes to sandy mud during monsoon. It was muddy during post-monsoon season. Station 2 did not show any seasonal variations in texture and was muddy in nature. Station 3 was sandy mud in nature during pre-monsoon and changed to silty in post-monsoon. The sediment pH1
ranged from 5.85 to 7.1 in the mangrove stations. Eh values showed that the sediments were generally anoxic and station 3 was found to be highly reducing.

Table 3.2 General sedimentary characteristics of the study region (± SD)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Station 1</th>
<th></th>
<th>Station 2</th>
<th></th>
<th>Station 3</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pre</td>
<td>Mon</td>
<td>Post</td>
<td>Pre</td>
<td>Mon</td>
<td>Post</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>6.73 ± 1.9</td>
<td>36.60 ± 4.8</td>
<td>8.87 ± 2.86</td>
<td>4.34 ± 1.1</td>
<td>2.32 ± 0.91</td>
<td>0.94 ± 0.09</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>71.79 ± 6.8</td>
<td>28.51 ± 3.0</td>
<td>58.92 ± 4.17</td>
<td>59.97 ± 2.1</td>
<td>63.78 ± 6.7</td>
<td>59.38 ± 6.9</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>21.45 ± 2.21</td>
<td>34.89 ± 2.69</td>
<td>32.20 ± 2.32</td>
<td>35.69 ± 2.71</td>
<td>33.90 ± 2.78</td>
<td>39.68 ± 2.79</td>
</tr>
<tr>
<td>pH</td>
<td>6.2 ± 1.2</td>
<td>5.85 ± 1.0</td>
<td>7.0 ± 1.0</td>
<td>6.46 ± 0.7</td>
<td>6.48 ± 0.7</td>
<td>7.1 ± 0.7</td>
</tr>
<tr>
<td>Eh</td>
<td>-98 ± 2.7</td>
<td>-16 ± 1.0</td>
<td>-10 ± 1.0</td>
<td>12.0 ± 1.0</td>
<td>-41 ± 1.2</td>
<td>-53 ± 1.2</td>
</tr>
</tbody>
</table>

Figure 3.1 Ternary diagram showing the grain size distribution. Sediment nomenclature after (Folk, 1974)

3.2.2 Mineralogy

X-ray diffraction (XRD) is an important tool in the mineralogy for identifying, quantifying and characterising minerals in complex mineral
assemblages (Moore and Reynolds, 1997). Powder X-ray diffraction analyses of the representative sediments of the study region showed that perovskite and sodalite were the dominant minerals at station 1 and 2 respectively. Presence of monetite, a rare calcium phosphate mineral, was observed at station 3 along with silica. (Fig. 3.2).

3.2.3 Major Elements

Since the major elements are conservative in nature and unlikely to be affected by diagenesis, only the post-monsoon samples were analysed to access their background levels (Table 3.3). XRF analysis showed that Silicon was the major element in all the three stations, followed by Aluminium and Iron. XRF analysis revealed very high calcium and phosphorus at station 3, when compared to the other two stations. The SEM-EDS analysis of station 3 sediment (Fig. 3.3) also showed high mass percentages of calcium (9.79) and phosphorous (5.33). Sulphur content was also significantly higher at station 3. But Silicon, Aluminium and Iron were comparatively lower at station 3, compared to the other stations. TGA analysis showed a moisture content of 7 % and the weight loss after 900°C was about 25%.

CHN-S analysis of the mangrove sediments (Table 3.4 and Fig. 3.4) showed that they were rich in total carbon. It ranged from 2.91 to 7.64 % and was higher at station 3. Generally, post-monsoon season was found to have higher carbon content, except for station 1. Organic carbon constituted 75 to 93% of total carbon and was also higher at station 3. It also followed the seasonal trend of total carbon. Total nitrogen content ranged from 0.27 to 0.66 % and was higher during the post-monsoon season, except at station
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1. It was also higher at station 3 during all the seasons. Total sulphur varied from 0.22 to 1.96 % and was very high at station 3. It was found to be higher during the post-monsoon season at station 1 and 2, but station 3 showed high concentration during pre-monsoon.

Analysis of variance (ANOVA, Two-Factor without replication) showed that sediment texture did not have any significant seasonal variations in these ecosystems. Carbon and nitrogen showed no significant variations in mangroves, while sulphur was significantly higher at station 3.

Table 3. 3 Major elemental composition and TGA results (weight %) of the mangrove sediments

<table>
<thead>
<tr>
<th>Compound</th>
<th>Station 1</th>
<th>Station 2</th>
<th>Station 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>40.030</td>
<td>39.570</td>
<td>35.060</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.748</td>
<td>0.820</td>
<td>0.552</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16.63</td>
<td>17.94</td>
<td>13.14</td>
</tr>
<tr>
<td>MnO</td>
<td>0.033</td>
<td>0.04</td>
<td>0.034</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>7.99</td>
<td>8.96</td>
<td>4.86</td>
</tr>
<tr>
<td>CaO</td>
<td>1.434</td>
<td>0.807</td>
<td>7.278</td>
</tr>
<tr>
<td>MgO</td>
<td>2.901</td>
<td>2.799</td>
<td>1.947</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.250</td>
<td>2.325</td>
<td>2.302</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.547</td>
<td>1.316</td>
<td>0.885</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.630</td>
<td>0.622</td>
<td>6.760</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.096</td>
<td>0.158</td>
<td>1.25</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.034</td>
<td>0.033</td>
<td>0.02</td>
</tr>
<tr>
<td>CuO</td>
<td>0.009</td>
<td>0.007</td>
<td>0.01</td>
</tr>
<tr>
<td>NiO</td>
<td>0.010</td>
<td>0.010</td>
<td>0.000</td>
</tr>
<tr>
<td>Rb₂O</td>
<td>0.006</td>
<td>0.006</td>
<td>0.003</td>
</tr>
<tr>
<td>SrO</td>
<td>0.029</td>
<td>0.016</td>
<td>0.054</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.000</td>
<td>0.012</td>
<td>0.044</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.013</td>
<td>0.010</td>
<td>0.012</td>
</tr>
<tr>
<td>Loss of Ignition at 110°C</td>
<td>7.40</td>
<td>7.67</td>
<td>7.34</td>
</tr>
<tr>
<td>Loss of Ignition at 900°C</td>
<td>24.61</td>
<td>24.63</td>
<td>26.66</td>
</tr>
</tbody>
</table>
Figure 3.2 XRD spectra of the sediments in the study region
Chapter 3

Figure 3.3 SEM-EDS spectrum of station 3 sediment

Table 3.4 Seasonal variations of Carbon, Nitrogen and Sulphur in the study region.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Station 1</th>
<th></th>
<th>Station 2</th>
<th></th>
<th>Station 3</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>Pre</td>
<td>Mon</td>
<td>Post</td>
<td>Pre</td>
<td>Mon</td>
<td>Post</td>
</tr>
<tr>
<td>Total Carbon (%)</td>
<td>3.73</td>
<td>6.75</td>
<td>4.72</td>
<td>2.91</td>
<td>3.31</td>
<td>6.25</td>
</tr>
<tr>
<td>Organic Carbon (%)</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
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<tr>
<td></td>
<td>0.11</td>
<td>0.07</td>
<td>0.04</td>
<td>0.06</td>
<td>0.05</td>
<td>0.11</td>
</tr>
<tr>
<td>Total Nitrogen (%)</td>
<td>2.8</td>
<td>6.3</td>
<td>3.9</td>
<td>2.2</td>
<td>2.5</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
</tr>
<tr>
<td>Total Sulphur (%)</td>
<td>0.01</td>
<td>0.13</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
<td>0.34</td>
<td>0.50</td>
<td>0.32</td>
<td>0.27</td>
<td>0.29</td>
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<tr>
<td></td>
<td>0.07</td>
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<tr>
<td></td>
<td>0.32</td>
<td>0.25</td>
<td>0.62</td>
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<td></td>
<td>0.006</td>
<td>0.005</td>
<td>0.1</td>
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<td>0.005</td>
<td>0.012</td>
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<td>0.02</td>
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</tr>
<tr>
<td></td>
<td>0.013</td>
<td>0.02</td>
<td>0.013</td>
<td>0.005</td>
<td>0.013</td>
<td>0.023</td>
</tr>
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</table>
3.2.4 Heavy Metals

The heavy metals analysed during the study were Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn. The total concentrations of the various heavy metals estimated in the surface sediments of the three mangrove ecosystems are furnished in Table 3.5 and Fig.3.5. Cadmium ranged between 0.06 and 0.22 µg/g and was higher at station 3. Seasonal variations were not prominent in the case of Cd. Cobalt ranged between 12.83 and 23.08 µg/g and did not show any seasonal variations. Co was found to be lower at
station 3, compared to the other stations. Chromium was low at station 3 and the range was from 53.30 to 90.23 µg/g. Cr also did not show any seasonal trend. Copper varied from 23.98 to 39.13 µg/g and showed no significant spatial and temporal variations. Iron varied from 42554 to 58304 µg/g and did not show any variations between seasons and stations. Magnesium was found to be comparatively lower at station 3 and the overall range was 12386-17817 µg/g. Mn did not show any seasonal and spatial trend and the range obtained was 210.5-315.35 µg/g. Nickel varied from 30.60 to 69.35 µg/g and was higher at station 2 and lower at station 3. Lead also showed the similar distributional trend and the range was from 19.5 to 39.50 µg/g. Zinc ranged between 101.3 and 455.68 µg/g and showed very high concentration at station 3 when compared to other stations.

Table 3.5 Average Concentrations of heavy metals estimated in the surface sediments of the mangrove systems (µg/g)

<table>
<thead>
<tr>
<th>Metal</th>
<th>station 1</th>
<th></th>
<th>station 2</th>
<th></th>
<th>station 3</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>pre</td>
<td>mon</td>
<td>post</td>
<td></td>
<td>pre</td>
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</tr>
<tr>
<td>Cd</td>
<td>0.07</td>
<td>0.064</td>
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<td></td>
<td>0.10</td>
<td>0.06</td>
</tr>
<tr>
<td>Co</td>
<td>22.3</td>
<td>17.73</td>
<td>21.43</td>
<td></td>
<td>22.2</td>
<td>22.8</td>
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<td>Cr</td>
<td>90.23</td>
<td>73.18</td>
<td>76.08</td>
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<td>85.28</td>
<td>89.78</td>
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<td>Cu</td>
<td>30.75</td>
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</tr>
<tr>
<td>Fe</td>
<td>58304</td>
<td>42554</td>
<td>45617</td>
<td></td>
<td>57554</td>
<td>57429</td>
</tr>
<tr>
<td>Mg</td>
<td>17817</td>
<td>12386</td>
<td>15299</td>
<td></td>
<td>17242</td>
<td>16886</td>
</tr>
<tr>
<td>Mn</td>
<td>315.33</td>
<td>227.83</td>
<td>257.83</td>
<td></td>
<td>227.2</td>
<td>210.5</td>
</tr>
<tr>
<td>Ni</td>
<td>55.5</td>
<td>55.43</td>
<td>54.75</td>
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<td>101.3</td>
<td>111.3</td>
<td></td>
<td>116.3</td>
<td>112.55</td>
</tr>
</tbody>
</table>

3.2.5 Phosphorus Fractionation

Fractionation of phosphorus in mangrove sediments (Table 3.6, Fig. 3.6) revealed significant spatial variations for different phosphorous
fractions among the three systems under study. Fe-IP varied from 825 to 2080 μg/g among the mangrove systems. Fe-IP was the major fraction in the first two stations accounting for 38.2 % and 37.57 % of the total phosphorus. Ca-IP ranged from 505 to 24764 μg/g. Station3 was exclusively dominated by Ca-IP contributing to about 87% of total phosphorous. ASOP varied from 201 to 1555 μg/g and was almost uniformly distributed in all the three systems with a percentage range of 5.2-13. Alk-OP ranged from 428 to 738 μg/g. This fraction was very low at station 3 (2.2 %), while it showed similar distribution pattern in other two stations. R-OP ranged from 48 to 92 μg/g. R-OP was the smallest fraction (0.2-3.8% of total phosphorous).
Chapter 3

Cadmium Cobalt

0.25
0.2
0.15
0.1
0.05
0.05
0

µg/g

0
1
2
3

pre
mon
post

Cobalt

25
20
15
10
5
0

µg/g

0
1
2
3

pre
mon
post

Chromium

100
90
80
70
60
50
40
30
20
10
0

µg/g

0
1
2
3

pre
mon
post

Copper

50
40
30
20
10
0

µg/g

0
1
2
3

pre
mon
post

Iron Magnesium

7.5
6.5
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0

Percentage

0
1
2
3
4
5
6
7

0
1
2
3

pre
mon
post

pre
mon
post

pre
mon
post

pre
mon
post

pre
mon
post

pre
mon
post
Figure 3.5 Seasonal variations of Heavy metals in the study region

Total phosphorous, calculated as the sum of all fractions, varied between 2226 to 28665 μg/g. Comparing to other two stations, station 3 showed about 10 fold increases in total phosphorous content. First two stations did not show any noticeable difference in phosphorous fractions and inorganic fractions constituted to about 65% of total phosphorus. But at station 3, inorganic fractions were about 92%. Bioavailable fractions of phosphorus at stations 1 and 2 were about 75% whereas at station 3, these were about 98%. Analysis of variance (ANOVA) showed that there are no
significant seasonal variations for any of the phosphorus fractions in the study region. But considerable spatial variations were observed for Ca-IP and ASOP (p<<0.001), which were significantly higher at station 3. Fe-IP did not show any significant variation between stations, while ROP was significantly (p= 0.01) lower at station 3.

Table 3.6 Different fractions of phosphorus in the study region (µg/g ± SD)

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<tr>
<th>Parameters</th>
<th>Station 1</th>
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<th>Station 2</th>
<th></th>
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<td></td>
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<td>Mon</td>
<td>Post</td>
<td>Pre</td>
<td>Mon</td>
<td>Post</td>
<td>Pre</td>
<td>Mon</td>
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<tr>
<td>Fe-IP</td>
<td>856 ± 22</td>
<td>825 ± 19</td>
<td>909 ± 24</td>
<td>1142 ± 34</td>
<td>979 ± 26</td>
<td>982 ± 32</td>
<td>1129 ± 36</td>
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<tr>
<td>Ca-IP</td>
<td>727 ± 21</td>
<td>541 ± 13</td>
<td>532 ± 17</td>
<td>1019 ± 26</td>
<td>505 ± 28</td>
<td>803 ± 17</td>
<td>24764 ± 171</td>
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<td>ASOP</td>
<td>201 ± 3</td>
<td>289 ± 7</td>
<td>236 ± 5</td>
<td>322 ± 8</td>
<td>274 ± 10</td>
<td>318 ± 6</td>
<td>1555 ± 6</td>
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<tr>
<td>Alkali-OP</td>
<td>452 ± 13</td>
<td>501 ± 21</td>
<td>506 ± 12</td>
<td>428 ± 11</td>
<td>539 ± 17</td>
<td>738 ± 21</td>
<td>504 ± 10</td>
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<td>R-OP</td>
<td>72 ± 1.5</td>
<td>70 ± 2.1</td>
<td>66 ± 1.9</td>
<td>76 ± 1.2</td>
<td>90 ± 2.1</td>
<td>92 ± 2.7</td>
<td>48 ± 1.4</td>
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<tr>
<td>Total-P</td>
<td>2308 ± 58</td>
<td>2226 ± 54</td>
<td>2249 ± 56</td>
<td>2987 ± 73</td>
<td>2387 ± 59</td>
<td>2933 ± 71</td>
<td>28000 ± 192</td>
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</tr>
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</table>
Figure 3.6 Seasonal variations of different phosphorus fractions. Pre, Mon and Post denote pre-monsoon, monsoon and post-monsoon seasons respectively.
3.3 Discussion

General sedimentary analysis showed the predominance of fine substratum and silt was the major fraction in all the seasons in these mangrove sediments. The texture of the sediments has a significant role on the physico-chemical processes as well as on the species diversity of the depositional environment (Badarudeen et al., 1996). It is well documented that fine particles often concentrate metals due to their greater surface area and amounts of organic carbon, clay, iron, or aluminium (Santschi et al., 2001) and also proportionally higher concentrations of associated trace elements (Myers and Thorbjørnsen, 2004). The sediments were slightly acidic also. High redox potential indicates that the sediments were generally anoxic in nature and station 3 was found to be highly reducing.

Mineralogical fingerprints might be employed as tools to explore the dynamics and transport of particle and sediments associated with local environments. XRD analysis showed that perovskite and sodalite were the dominant minerals at station 1 and 2 respectively. Perovskite is a calcium titanium oxide mineral (CaTiO$_3$) and Sodalite is a Sodium aluminium silicate chloride mineral (Na$_4$Al$_3$(SiO$_4$)$_3$Cl). Monetite, an anhydrous calcium phosphate mineral (CaHPO$_4$) was detected at station 3.

Station 3 is a congregation of communally breeding birds. The bird excreta and their remains are not effectively flushed away by tides as this mangrove system is linked to the adjacent micro-tidal estuary by a narrow canal, the only source for tidal propagation. This results in the accumulation of bird guano and death and decay of the birds, rich source of phosphorous. Monetite formation is interpreted as being the result of
reaction between guano and clay mineral or carbonate rocks (Onac and Veres, 2003). Eh analysis revealed that this unique system is highly reducing during tidal influx. There are also reported evidences for high anoxic condition of this unique ecosystem. Authigenic filaments pyrites have been reported at Mangalavanam (Rosily, 2002), the presence of which can be taken for the highly anoxic conditions (Jeng and Huh, 2001). 5α-cholestan-3β-ol, which is reported in anaerobic sediments (Volkman et al., 1998) is also found in Mangalavanam (Narayanan, 2006). During low tide, the sediments get exposed to the atmosphere for considerably longer periods. These periodic fluctuations in redox potential create a metastable condition, which might favour the formation of monetite. Drier and acidic conditions of the sediment favour the formation of monetite (Onac and Veres, 2003). The presence of monetite indicates the complexity of the system as it is a thermodynamically metastable calcium phosphate mineral (Effler, 1987).

Major elemental analysis using XRF and SEM-EDS revealed high mass percentages of calcium and phosphorous at station 3, which was about 10 times higher than the other two stations. This could be taken as a confirmation for the existence of the rare mineral monetite.

Nutrient elements in the study region did not show any seasonal trend. No correlation was observed between CNS composition and texture indicating the absence of any granulometric dependence. The positive correlation of sediment carbon with total nitrogen indicates a common source of organic matter to these elements. These elements also showed significant negative correlations with the redox potential suggesting their
preservation in the anoxic condition. It is reported that organic matter is better preserved under anoxic conditions (Lehmann et al., 2002).

Stoichiometric ratios of nutrients are utilised to determine the origin and transformation of organic matter (Yamamuro, 2000). By mass, Redfield (1958) predicts a C:P ratio of 40 and N:P ratio of 7 for algal material, while Hecky et al., (1993) indicated that a wider range of C: P and N:P ratios in aquatic sediments can still be considered to follow Redfield (C:P = 28 to 56 and N:P = 4 to 9). The C: P ratio varied widely in the study region (1.8 to 28.3) and was very low at station 3. N:P ratio also showed considerable variations among stations and ranged between 0.17 and 2.25. It was also very low at station 3, indicating high enrichment of phosphorus at station 3. Both these ratios did not show any seasonal variations and were far below than Redfield ratio. Hence there is phosphorus enrichment in all the systems. The lower N:P ratios also indicate that benthic nitrogen recycling is in excess of phosphorous and denitrification and the benthic release of nitrogen might play a role in sustaining the productivity of the system. The very high silt + clay content in these systems might favour the higher retention of phosphorus. Clay mineral, such as kaolinite which is abundant in tropical sediments is very efficient in phosphate adsorption (Alongi et al., 1992).

The overall order of heavy metal concentration in sediments was Fe > Mg > Mn > Zn > Cr > Ni > Pb > Cu > Co > Cd. The heavy metal composition in the study region was comparable to the other reported works (Table 3.7), but showed higher values for zinc. ANOVA showed that cadmium was significantly higher at station 3 (p=0.0040) and no significant
Table 3.7 Previous reported works on the heavy metal distribution of different aquatic sediments

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<tr>
<th>Location</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
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<th>Fe(%)</th>
<th>Mg(%)</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
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<td>14.259</td>
<td>116-1385</td>
<td>Paul and Pillai, 1983</td>
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<td>Mangroves of Panama</td>
<td>0.6-10</td>
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<td>4-56.3</td>
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<td>143-295</td>
<td>27.3-91.8</td>
<td>32.5-78.2</td>
<td>10.9-105</td>
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<td>Cuverny Estuary</td>
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<td>Cuong et al., 2005</td>
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<td>Brisbane and Logan Estuaries</td>
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<td>2.54-35</td>
<td>2.34-6.78</td>
<td>Ramanathan et al., 1993</td>
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<td>Mangroves of Kerala</td>
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<td>0.13-1.94</td>
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<td>Balachandran et al., 2006</td>
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<td>19.5-50.50</td>
<td>161.3-455.68</td>
<td>Present Study</td>
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seasonal variations were observed. Cobalt also did not show any seasonal
trend, but was significantly lower ($p= 0.0055$) at station 3. Cr also followed
the trend of Co and was also significantly lower ($p= 0.0156$) at station 3.
Copper, iron, magnesium and manganese did not show any significant
spatial and seasonal variations. But nickel was significantly lower ($p=
0.0008$) at station 3. Lead showed no significant seasonal and spatial
variations. Zinc was significantly higher ($p=0.0023$) at station 3.

Correlation analysis of the chemical parameters of the mangrove
sediments (Table 3.8) revealed that there was no granulometric dependence
on heavy metal distribution. Mg and Pb showed highly significant negative
correlation with organic carbon and Zn showed significant positive
correlation with total nitrogen. No correlation with pH was observed for all
the metals. Co, Cr and Ni had significant positive correlations with redox
potential and negative correlation with sulphur. Cd and Zinc showed
significant inverse correlation with Eh and positive correlation with sulphur.
The interrelations between the heavy metals are tabulated in Table 3.9.

Mangrove systems play an important role in the biogeochemistry of
heavy metals in tropical coastal areas, and are considered to have the
capacity to act as a sink or buffer and to remove or immobilize heavy
metals before they reach nearby aquatic ecosystems (Tam and Wong,
1995). The major processes of metal retention in aquatic sediments include
cation exchange, complexing with organic molecules, precipitation as
oxides, oxyhydroxides and carbonates, and precipitation as sulphides
(Dunbabin and Bowmer, 1992).
Table 3.8 Correlations of heavy metals with other sedimentary parameters

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<th>Silt</th>
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<th>Total N</th>
<th>Total P</th>
<th>Total S</th>
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</tr>
<tr>
<td>Co</td>
<td>-0.49</td>
<td>0.42</td>
<td>0.62</td>
<td>0.16</td>
<td>0.83</td>
<td>-0.6</td>
<td>-0.68</td>
<td>-0.89</td>
<td>-0.82</td>
<td>-0.86</td>
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</tr>
<tr>
<td>Cr</td>
<td>-0.82</td>
<td>0.59</td>
<td>0.56</td>
<td>-0.01</td>
<td>0.77</td>
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<td>-0.64</td>
<td>-0.86</td>
<td>-0.87</td>
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<tr>
<td>Cu</td>
<td>-0.36</td>
<td>0.6</td>
<td>-0.5</td>
<td>0.14</td>
<td>-0.69</td>
<td>0.33</td>
<td>0.37</td>
<td>0.58</td>
<td>0.28</td>
<td>0.94</td>
<td>-0.12</td>
<td>1</td>
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<td></td>
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</tr>
<tr>
<td>Fe</td>
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<td>0.71</td>
<td>-0.5</td>
<td>0.24</td>
<td>-0.36</td>
<td>-0.5</td>
<td>-0.37</td>
<td>-0.06</td>
<td>0.29</td>
<td>0.21</td>
<td>0.26</td>
<td>0.32</td>
<td>0.2</td>
<td>0.69</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Mg</td>
<td>-0.66</td>
<td>0.59</td>
<td>0.37</td>
<td>0.19</td>
<td>0.64</td>
<td>-0.76</td>
<td>-0.85</td>
<td>-0.75</td>
<td>-0.69</td>
<td>-0.61</td>
<td>0.92</td>
<td>0.91</td>
<td>0.66</td>
<td>0.45</td>
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<tr>
<td>Mn</td>
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<td>-0.14</td>
<td>0.26</td>
<td>0.03</td>
<td>-0.02</td>
<td>-0.1</td>
<td>-0.07</td>
<td>-0.16</td>
<td>0.07</td>
<td>-0.18</td>
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<td>0.25</td>
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<td>0.37</td>
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<tr>
<td>Ni</td>
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<td>0.79</td>
<td>0</td>
<td>0.86</td>
<td>-0.55</td>
<td>-0.61</td>
<td>-0.65</td>
<td>-0.87</td>
<td>-0.87</td>
<td>0.92</td>
<td>0.92</td>
<td>0.24</td>
<td>0.04</td>
<td>0.78</td>
<td>-0.07</td>
<td>1</td>
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<tr>
<td>Pb</td>
<td>-0.67</td>
<td>0.41</td>
<td>-0.22</td>
<td>0.53</td>
<td>0.67</td>
<td>-0.85</td>
<td>-0.89</td>
<td>-0.91</td>
<td>-0.66</td>
<td>-0.45</td>
<td>0.56</td>
<td>0.79</td>
<td>0.69</td>
<td>0.41</td>
<td>0.2</td>
<td>0.87</td>
<td>0.28</td>
<td>0.65</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.12</td>
<td>0.24</td>
<td>-0.74</td>
<td>0.15</td>
<td>-0.97</td>
<td>0.59</td>
<td>0.59</td>
<td>0.78</td>
<td>0.96</td>
<td>0.76</td>
<td>-0.74</td>
<td>0.74</td>
<td>0.35</td>
<td>-0.61</td>
<td>-0.16</td>
<td>-0.78</td>
<td>-0.67</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3.9 Significant inter relations between the heavy metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>Positive</th>
<th>Negative</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>Zn</td>
<td>Co, Cr, Ni</td>
</tr>
<tr>
<td>Co</td>
<td>Cr, Mg, Ni</td>
<td>Cd, Zn</td>
</tr>
<tr>
<td>Cr</td>
<td>Co, Mg, Ni</td>
<td>Cd, Zn</td>
</tr>
<tr>
<td>Cu</td>
<td>Zn</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mg</td>
<td>Co, Cr, Ni, Pb</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>Co, Cr, Mg</td>
<td>Cd, Zn</td>
</tr>
<tr>
<td>Pb</td>
<td>Co, Mg</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>Cd, Cu</td>
<td>Co, Cr, Ni</td>
</tr>
</tbody>
</table>

Transformations during early diagenesis and changing redox state characterize the chemical forms of metals in aquatic sediments. The major changes that occur in redox conditions between oxic waters and anoxic sediments had profound influences on the speciation and bioavailability of many heavy metals. Sulfate is the major electron acceptor driving organic matter oxidation in anaerobic marine sediments, after oxygen utilization in the top few millimeters (Gaillard et al., 1989). Under oxic conditions, Pb, Ni and Co can be easily adsorbed on oxide fractions (Lienemann et al., 1997; Zwolsman and van Eck, 1999; Dong et al., 2000). On the contrary, in anaerobic conditions, active sulphide co-precipitation rapidly removes Co, Cu, Ni, Pb and Zn from the dissolved phase (Balistrieri et al., 1994; Clark et al., 1998; Schlieker et al., 2001). These specific behaviour of the heavy metals under varying redox conditions can be used as tracers of geochemical characteristics. The mangrove sediments can be considered as a massive, suboxic bed reactor (Aller, 1988), the repetitive redox cycling may induce dissolution of some forms of heavy metals.
Pyrite is an important sink for heavy metals since many of them are incorporated during its formation (Boulegue et al., 1982). As soon as sulphate-reduction began, dissolved Fe concentrations will decrease, reflecting the co-precipitation of Fe and S in the form of framboidal pyrite (Marchand et al., 2003). Active sulphide co-precipitation during anaerobic conditions results in preferential rapid removal of metals from the dissolved phase (Clark et al. 1998; Schlieker et al. 2001). This seems to be the plausible mechanism for higher concentrations of heavy metals in the study region. The presence of rich organic matter and the reducing environment in this substratum creates a selective affinity for heavy metals.

Cd showed highly significant negative correlation with Eh and positive correlation with sulphur. Adsorption and desorption of Cd is highly variable depending on the type of colloid and local pH-Eh conditions. Cd can be adsorbed in larger quantities by organic matter or Fe oxyhydroxides, but the presence of other metals, especially Zn, can inhibit the adsorption of Cd (Alloway, 1990). Zinc is a very mobile element under oxidizing and acid conditions; however in reducing environments, Zn substantially decreases in mobility due to its affinity for sulphur and the tendency to form sulphide phases (Thornton, 1983; Alloway, 1990). Its significant negative correlation with Eh and positive correlation with sulphur support the retention under anoxic conditions.

Under oxic conditions, Pb, Ni and Co can be easily adsorbed on Mn oxides (Lienemann et al., 1997; Zwolsman and van Eck, 1999; Dong et al., 2000). Chromium is of low geochemical mobility in any conditions of pH-Eh, although at low pH the presence of Mn oxides can promote Cr
oxidation to more mobile phases (McGrath and Smith, 1990). This particular heavy metal which does not form sulphide minerals is immobilized in refractory organic compounds in mangrove sediments (Lacerda et al., 1991). In the present study, the poor association of Mn with other metals suggests that Mn-oxide may be only a minor host phase for these elements in this reducing mangrove environment. Lead is the only chalcophile element that is immobile under any pH-Eh conditions, although acidic conditions can trigger Pb desorption to a greater degree than alkaline environments.

**Enrichment Factor (EF)**

Normalisation is a powerful tool for the regional comparison of heavy metals content in sediments and can also be applied to determine enrichment factors for the studied metals with respect to crusted average (Nolting et al., 1999). However, the most readily interpretable information on anthropogenic contamination is often provided by examining the concentrations of single elements, after adjustment for grain size effects. Differentiating the metals originating from human activity and those from natural weathering is an essential part of geochemical studies. One such technique largely applied is ‘normalisation’ where metal concentrations were normalised to a textural or compositional characteristic of sediments. Iron (Fe) was chosen as geochemical normaliser because of its conservative nature during diagenesis (Berner, 1980).

The enrichment factor was calculated for each metal using iron as normalising element by the following equation,

$$EF = \frac{\text{metal/Fe}}{\text{metal/Fe crust}}$$
EF values were interpreted as suggested by Birth (2003) for metals studied with respect to natural background concentration. EF < 1 indicates no enrichment, EF < 3 is minor enrichment, EF = 3–5 is moderate enrichment, EF = 5–10 is moderately severe enrichment, EF = 10–25 is severe enrichment, EF = 25–50 is very severe enrichment and EF >50 is extremely severe enrichment.

An EF value less than 1.5 suggests that the metals may be entirely from crustal materials or natural weathering processes (Zhang and Liu, 2002; Feng et al., 2004). However, an EF value greater than 1.5 suggests that a significant portion of the heavy metal is delivered from non-crustal materials or non-natural weathering processes and that the heavy metals are provided by other sources (Feng et al., 2004).

The analysis of the estimated enrichment factors of the various heavy metals in the study area (Table 3.10) indicated a minor enrichment for Pb and Zn and no enrichment for other metals.

Table 3.10 Enrichment of heavy metals in the mangrove sediments.

<table>
<thead>
<tr>
<th>metal</th>
<th>station 1</th>
<th>station 2</th>
<th>station 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pre</td>
<td>mon</td>
<td>post</td>
</tr>
<tr>
<td>Cd</td>
<td>0.18</td>
<td>0.23</td>
<td>0.3</td>
</tr>
<tr>
<td>Co</td>
<td>0.26</td>
<td>0.28</td>
<td>0.32</td>
</tr>
<tr>
<td>Cu</td>
<td>0.54</td>
<td>0.6</td>
<td>0.53</td>
</tr>
<tr>
<td>Cr</td>
<td>0.79</td>
<td>0.87</td>
<td>0.85</td>
</tr>
<tr>
<td>Mg</td>
<td>0.87</td>
<td>0.83</td>
<td>0.96</td>
</tr>
<tr>
<td>Mn</td>
<td>0.29</td>
<td>0.29</td>
<td>0.3</td>
</tr>
<tr>
<td>Ni</td>
<td>0.64</td>
<td>0.88</td>
<td>0.81</td>
</tr>
<tr>
<td>Pb</td>
<td>1.38</td>
<td>1.14</td>
<td>1.88</td>
</tr>
<tr>
<td>Zn</td>
<td>1.06</td>
<td>1.15</td>
<td>1.17</td>
</tr>
</tbody>
</table>
Chapter 3

Geoaccumulation Index (Igeo)

The Geoaccumulation Index (Igeo) introduced by Muller (1979) was used to assess metal pollution in sediments. Igeo is expressed as $I_{geo} = \log_2 \left( \frac{C_n}{1.5B_n} \right)$, where $C_n$ = measured concentration of heavy metal in the mangrove sediment, $B_n$ = geochemical background value in average shale (Turekian and Wedepohl, 1961) of element $n$, $1.5$ is the background matrix correction factor due to lithogenic effects. The Average Shale value is a quick and practical means of assessing metal enrichments in fine grained sediments (Forstner and Wittmann, 1981).

According to $I_{geo}$ classification, pollution degrees can be delimited as: very strongly polluted ($I_{geo} > 5$), strongly to very strongly polluted ($I_{geo} = 4–5$), strongly polluted ($I_{geo} = 3–4$), moderately to strongly polluted ($I_{geo} = 2–3$), moderately polluted ($I_{geo} = 1–2$), unpolluted to moderately polluted ($I_{geo} = 0–1$) and unpolluted ($I_{geo} < 0$).

The geo accumulation index estimated for the heavy metals from the sediments of the study area (Table 3.11) exhibited very low values ($<0$) in the case of almost all metals except Zn ($>1.0$ in station 3), indicating the sediments of the mangrove ecosystem are unpolluted to moderately polluted.
Table 3.11 Geoaccumulation index for heavy metals in the mangrove sediments.

<table>
<thead>
<tr>
<th>metal</th>
<th>station 1</th>
<th>station 2</th>
<th>station 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pre</td>
<td>mon</td>
<td>post</td>
</tr>
<tr>
<td>Cd</td>
<td>-6.16</td>
<td>-6.29</td>
<td>-5.81</td>
</tr>
<tr>
<td>Co</td>
<td>-2.19</td>
<td>-2.52</td>
<td>-2.25</td>
</tr>
<tr>
<td>Cr</td>
<td>-0.58</td>
<td>-0.88</td>
<td>-0.83</td>
</tr>
<tr>
<td>Cu</td>
<td>-1.13</td>
<td>-1.43</td>
<td>-1.49</td>
</tr>
<tr>
<td>Fe</td>
<td>-0.23</td>
<td>-0.69</td>
<td>-0.59</td>
</tr>
<tr>
<td>Mg</td>
<td>-0.43</td>
<td>-0.95</td>
<td>-0.65</td>
</tr>
<tr>
<td>Mn</td>
<td>-2.02</td>
<td>-2.48</td>
<td>-2.31</td>
</tr>
<tr>
<td>Ni</td>
<td>-0.88</td>
<td>-0.88</td>
<td>-0.90</td>
</tr>
<tr>
<td>Pb</td>
<td>0.23</td>
<td>-0.50</td>
<td>0.32</td>
</tr>
<tr>
<td>Zn</td>
<td>-0.15</td>
<td>-0.49</td>
<td>-0.36</td>
</tr>
</tbody>
</table>

Enrichment Factor and geo accumulation index confirm the absence of heavy metal pollution in these systems. Under reducing environments, mobility of Zn substantially decreases due to its affinity for sulphur (Thornton, 1983; Alloway, 1990). The Zn rich contaminant discharging from Zn smelting industries located at the northern part of the study area can enhance the content of Zn in these sulphur rich sediments. The lack of a clear enrichment in mangrove sediments of other metals may be caused by their strong soluble complexes with reduced sulphur (Emerson et al., 1983), which will increase the migration of these elements from sediments to the water column (Huerta-Díaz and Morse, 1992).

The biogeochemical processes operating in the system will lead to chemical transformations of the element and an in situ identification and monitoring of individual processes and their contribution to the total dynamicty is an unapproachable task. The speciation study thus can be considered as an indexing of various biogeochemical processes to get a
Chapter 3

thorough understanding of the processes. If we consider the chemical transformations as redox reactions, a better index can be developed by potential elements, which exhibit a definite redox character and sufficient concentration to monitor the transformations. The advantage with phosphorus is that it is available in various oxidation states (Morton and Edwards, 2005) and the monitoring of phosphorus in various forms can be easily done. Hence phosphorus is taken as the element to identify the geochemistry of the system. The study is organised in such a way to identify all the geochemical forms with an intention to assess the interrelations for the identification of the geochemical processes. The speciation scheme is selected in such a way that the maximum variability and species diversity can be estimated.

Some of the earlier works on the fractionation of phosphorus in the sediments of different aquatic systems and some reported works in India, especially near the Cochin area are tabulated in Table 3.12.

Table 3.12 Important works on the fractionation of phosphorus in the sediments of different aquatic systems

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Aquatic system and reference</th>
<th>Extraction scheme</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Southwest coast of India (Nair et al., 1993)</td>
<td>8 different schemes</td>
<td>The major forms of P namely exchangeable P, Carbonate bound P, labile and resistant organic P, Fe-, Al- and Ca bound P etc.</td>
</tr>
<tr>
<td>2.</td>
<td>Cochin estuary (Balchand and Nair, 1994)</td>
<td>8 different schemes</td>
<td>The major forms of P namely exchangeable P, Carbonate bound P, labile and resistant organic P, Fe-, Al- and Ca bound P etc.</td>
</tr>
<tr>
<td>3.</td>
<td>Tidal floodplain forest in the Amazon estuary (Silva and Sampaio, 1998)</td>
<td>Kurumies (1972), Salomons and Gerritse (1981) and Leeg and</td>
<td>The P combined with iron and aluminum was the main fraction of P in the soil (0.05±0.02 mg/g to 0.20±0.05 mg/g).</td>
</tr>
<tr>
<td>No.</td>
<td>Location/Study</td>
<td>Authors/References</td>
<td>Summary</td>
</tr>
<tr>
<td>-----</td>
<td>----------------</td>
<td>--------------------</td>
<td>---------</td>
</tr>
<tr>
<td>4.</td>
<td>Cauvery Estuary and Pichavaram mangroves (Ramanathan, 1999)</td>
<td>Black's (1955)</td>
<td>In the estuary P was mainly associated with Al-P followed by Ca-P and Fe-P.</td>
</tr>
<tr>
<td>5.</td>
<td>Mangrove sediments of French Guiana (Fabre et al., 1999)</td>
<td>Golterman and Booman, (1988) modified by Golterman (1996).</td>
<td>Four stages of mangrove sediments were studied: pioneer, mature, mixed and dead mangrove sediments. The sum of the fractions varied between 638 to 804 μg/g in pioneer and mixed mangroves respectively. In all the stages investigated, the sum of the inorganic fractions (Fe(OH)₃-P + CaCO₃-P) represented more than 50% of the sum of the fractions.</td>
</tr>
<tr>
<td>6.</td>
<td>Mediterranean French coastal lagoons (Thau and Méjean) (Paing et al., 1999)</td>
<td>De Groot and Golterman (1993)</td>
<td>Fe-P constituted about 25% of P, Ca-bound (30%) was the most important inorganic fraction. Organic-P represented a substantial proportion of the Total-P (38% of Total-P in Thau and 28% in Méjean).</td>
</tr>
<tr>
<td>7.</td>
<td>Kuttanad region, Vembanad Lake (Lizen, 2000)</td>
<td>Hilijtjes and Lijkema (1980) and van Eck (1982)</td>
<td>Residual P (40.06-91.65%) dominated in the region with very low contribution of exchangeable P (0.06-0.6%). Fe- and Al-bound P (2.76-37.25%) and Ca bound P (1.49-33.50%) were the other dominant forms.</td>
</tr>
<tr>
<td>8.</td>
<td>Mangrove ecosystems around Cochin (Shaly, 2003)</td>
<td>Golterman (1996) modification by Pardo et al., (1998)</td>
<td>Total P in surficial sediments was in the range from 480.72 to 1967.60 μg/g. Fe-IP was the dominant fraction (21.82-28.31%), followed by Ca-IP (15.55-20.47%) and Alk-OP (14.22-21.35%).</td>
</tr>
<tr>
<td>9.</td>
<td>Mattaponi River, Virginia, USA (Morse et al., 2004)</td>
<td>Paludan and Jensen (1995)</td>
<td>Al-Po and Fe-Pi comprising 64% and 53% of total P at the upstream and downstream sites, respectively. Organic P represented a larger percentage of total P - 88% versus 59% for the upstream marsh and 70% versus 50% for the downstream marsh.</td>
</tr>
</tbody>
</table>
Fractionation analysis of phosphorus in the mangrove sediments showed that station 3 is abnormally enriched with Ca-IP. Presence of monetite at station 3 supports the enrichment of Ca-IP in this station. The diagenesis of sediments containing bird or bat guano can also lead to the crystallization of apatite and other phosphorus minerals (Tiessen et al.,

<table>
<thead>
<tr>
<th></th>
<th>10</th>
<th>Different oceanic regimes (Faul et al., 2005)</th>
<th>SEDEX procedure Ruttenberg, (1992) Modified by Anderson and Delaney (2000)</th>
<th>Org. P was the largest contributor to total P, especially in the Ross Sea (average 53% of total P) and detrital P is a more significant contributor to total P on the California Coast.</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Japan Sea (Chah et al., 2005)</td>
<td>Ruttenberg (1990) modified by Rao (1994)</td>
<td>The total P ranged 13.0–35.5 µmol/g. The concentrations of Det-P were very low (0.7–2.6 µmol/g) accounting less than 10% (by weight) of total P. The Fe-P concentration was 0.9–23 µmol/g, accounting for 7–63% of the total P. The CFA-P concentration was 3.1–6.1 µmol/g (9–44% of the total P), while Org-P was the major form (3.6–10 µmol/g), accounting for more than 40% of the total P.</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Eastern Arabian Sea (Babu and Nath, 2005)</td>
<td>SEDEX procedure Ruttenberg, (1992) Modified by Anderson and Delaney (2000)</td>
<td>Total phosphorus ranged between 920 and 2496 ppm, while it was 1070–1632 ppm in off Cochin region. Porg was low in shelf (6%), and relatively high in deep-sea sediments (12–17%). In sediments overlain by OMZ, Porg proportion is relatively high in the SF Arabian Sea (10–26%) when compared to the NE Arabian Sea (8–13%), which have less Porg than the deep-sea sediments.</td>
<td></td>
</tr>
</tbody>
</table>
The high mass percentages of calcium and phosphorous by XRF and SEM-EDS analysis confirm the phosphorous enrichment at station 3.

Correlation analysis (Table 3.13) showed that Eh had highly significant negative correlation with Ca-IP and ASOP. pH did not show correlations with any of the parameters. Total sulphur showed highly significant positive correlations with Ca-IP and ASOP. Fe-IP had no correlation with Fe, while it showed highly significant positive correlations with other two bioavailable fractions. Ca-IP showed highly significant positive correlation with ASOP and significant negative correlation with clay.

Calcium bound phosphorus dominate in mangrove sediment (Silva and Mozeto, 1997), due to its stability under the redox (Eh) variations observed in the mangroves (Nriagu, 1976; Silva et al., 1998). Highly significant negative correlation of Ca-IP with Eh and its highly significant positive correlation with sulphur, the redox indicator also suggested that there is a preferential accumulation of Ca-IP when the system is highly reducing. The slight acidic pH of the sediments at the station 3 provides high stability to Ca-IP (Silva and Sampaio, 1998).

The increase in Ca-IP during pre-monsoon at all the stations might be due to the increase in salinity. Similar trend is reported in marine sediments presumably by the accumulation of calcium under high salinity, which favours apatite formation (Ryden et al., 1997). Silva and Mozeto (1997) also suggested that phosphorous combined with calcium under high salinity acts as a principal mechanism for its retention.
Table 3.13 Pearson correlation between the sedimentary parameters in the study region

<table>
<thead>
<tr>
<th></th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
<th>pH</th>
<th>Eh</th>
<th>Total Carbon</th>
<th>Organic Carbon</th>
<th>Total Nitrogen</th>
<th>Total Sulphur</th>
<th>Fe</th>
<th>Fe-IP</th>
<th>Ca-IP</th>
<th>Acid-OP</th>
<th>Alkali-OP</th>
<th>R-OP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>-0.97</td>
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Fe-IP was the major fraction at stations 1 and 2. Generally release of this phosphate fraction from the sediment is controlled by sulphate reduction (Caraco et al., 1989) and is considered more bioavailable under the redox (Eh) variations observed in the mangrove sediments (Caraco et al., 1989; Silva and Mozeto, 1997). Sulphide produced from sulphate respiration may reduce the iron-oxides and thus promote a release of iron-bound phosphorus (Howarth et al., 1995; Jensen et al., 1995). However, sulphate reduction is generally of less importance in intertidal zones because of periodic aeration in the environment (Kristensen et al., 1992; Alongi, 1998; Holmer et al., 1999) causing the formation of Fe(OH)$_3$ (Crosby et al., 1984). Furthermore, the mangrove trees are able to excrete oxygen through their root system, producing an oxygenated microenvironment (Silva et al., 1991) capable of trapping phosphorus as FePO$_4$ through the formation of Fe(OH)$_3$.

The involvement of iron in the dynamic equilibrium between the sediment and water as explained above has led to the suggestion that an iron dependent threshold exists for the sediment’s ability to bind phosphorus. Jensen et al., (1992) showed that the retention capacity was high as long as the Fe: P ratio exceeds 15 (by weight) while Caraco et al., (1993) suggested that this ratio should be above 10 to regulate phosphorus release. Fe:P ratios of the sediments were higher than 15 in the study region, except at station 3. This justifies higher concentration of Fe-IP at stations 1 and 2. The Fe:P ratio was very low at station 3, resulting in lower percentage of iron bound phosphorous in the system. Periodic fluctuations
in the redox potential of this system might also result in lower Fe-IP content at station 3.

ASOP includes apatite bound phosphate and biochemical components such as nucleic acids, lipids and sugars that bound to phosphate (De Groot, 1990). ASOP had highly significant negative correlation with Eh and highly significant positive correlation with total sulphur. This indicates that highly reducing environment is favourable for ASOP similar to Ca-IP. Alk-OP generally constitutes humic phosphate and phytate phosphate (Golterman et al., 1998). Phytate or phytic acid (inositol hexa phosphate) is an organic phosphate that is widely spread in plants (Hess, 1975), soils (Stevenson, 1982) and aquatic sediments (De Groot and Golterman, 1993). Phytate is relatively stable as it can be strongly adsorbed onto iron hydroxide and multivalent cations (De Groot and Golterman, 1993). Irrespective of the higher content of total organic matter, the labile fraction was very low in these mangrove sediments, signalling to the refractory organic matter accumulation (Chapter 4). This might results in the higher concentration of Alk-OP, which is non-bioavailable. As a result of the diagenetic reorganization of phosphorus within sediments, organic phosphorus concentrations usually decrease with time as it is ultimately transformed to authigenic phosphorus during diagenesis (Ruttenberg and Berner, 1993; Anderson et al., 2001).

Organic phosphorous in the study region ranged from 8 (station 3) to 38.6 % (station 1) of total phosphorous. Generally organic bound phosphorus accounted for 6 -19% of total in coastal sediments (Hirata, 1985). The high percentage organic bound phosphorous at stations 1 and 2
indicated that the mineralisation of phosphorus is less, where as at station 3, active mineralization is taking place. C:P ratio at station 3 was very low and it is reported that mineralisation of organic phosphorous and C:P ratio are inversely related (Reddy and Delaune, 2008). Also, organic phosphorous mineralization is high under anaerobic condition than under aerobic conditions (Bridgham et al., 1998). Very high reduction potential at this station results in higher mineralisation and subsequently lower concentration of organic phosphorus.

The variations in the phosphorus content in the three systems could also be favoured by the difference in local vegetation (Alongi, 1989). Organic matter associated with Avicennia sediments, because of the presence of more degradable organic matter, can sustain a higher rate of microbial activity than Rhizophora and, as a consequence, better recycling of nutrient elements (Lacerda et al., 1995). In Rhizophora sediments either microbial conversion is negligible or the organic components are more refractory (Alongi, 1989). Station 3 is dominated by Avicennia and the high amount of inorganic phosphorus in this system could be deduced to be a signal of higher levels of diagenetic activity.

3.4 Conclusions

General sedimentary analysis showed the predominance of fine substratum and silt was the major fraction in all the seasons in these mangrove sediments. XRD analysis of the sediments showed the presence of monetite, an anhydrous calcium phosphate mineral (CaHPO₄) at station 3. The high mass percentages of calcium and phosphorous by XRF and SEM-EDS analysis confirm the existence of calcium phosphate mineral at
station 3. Stoichiometric ratios of nutrients revealed phosphorus enrichment in all the systems. The overall order of heavy metal concentration in sediments was: Fe > Mg > Mn > Zn > Cr > Pb > Ni > Pb > Cu > Co > Cd. The enrichment factor calculated, using iron as normalizing element, indicated a minor enrichment for Pb and Zn and no enrichment for all other metals. The geo accumulation index estimated for the present study exhibited very low values (<0) in the case of almost all metals, except Zn (>1.0 in station 3), indicating sediments of the mangrove ecosystem are unpolluted to moderately polluted. Phosphorus fractionation analysis showed that these mangrove systems act as a sink of phosphorus, primarily as Ca-IP and Fe-IP fractions. Internal loading in these systems acts as a source of phosphorus to the adjacent coastal waters. The first two stations behave identically and Fe-IP was the major fraction in these stations. Station 3 is unique because of the accumulation of bird guano in this bird sanctuary and it resulted in about 10 fold increase in the total phosphorous content. This station is exclusively dominated by Ca-IP and a rare mineral, monetite was detected in the system.

References


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