ACCUMULATION OF HEAVY METALS IN MANGROVE SEDIMENTS OF CHUMPHON PROVINCE, THAILAND

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Received: February 14, 2012 Accepted: June 26, 2012

Abstract

The objective of this study was two-fold: to examine the heavy metal (Cd, Cu, Cr, Ni, Mn, Pb and Zn) levels that have accumulated in mangrove forest sediments in Chumphon Province, Thailand, and to determine the relationship between heavy metals and the physiochemical properties of sediment. The sediment was digested with HNO3 and HCl using a milestone microwave digestion system (model MLS-1200 MEGA), followed by the addition of 50 ml distilled water. The concentrations of Cu, Cr, Ni, Mn, and Zn in the filtered and digested samples were determined by air-acetylene flame atomic absorption spectrophotometry (FAAS, model Varian SpectrAA 220FS). Cd and Pb were analyzed by a graphite furnace atomic absorption spectrophotometer (GASS, model Varian SpectrAA220). The accumulation of heavy metals originated largely upstream and decreased towards the canal mouths. The highest levels of heavy metals were found at E-let canal (Thung Kha Bay). The heavy metals present in our study area, listed from the most to least prevalent, were Mn, Cu, Zn, Cr, Ni, Pb, and Cd. A striking relationship was found between heavy metal type and sediment physiochemical properties (pH, OM, EC, and CEC).

Key Words: heavy metal, mangrove sediment, Chumphon Province, Thailand
Introduction

The mangrove tree grows only in tropical and subtropical zones. With the expansion of urbanization, shrimp farms, and agricultural enclosures have resulted in the death of mangrove areas\(^{(1)}\). Global warming problems have affected sea level rise, loss of biodiversity, and salt-water intrusion of all coastal areas\(^{(2)}\). These problems also directly impact mangrove forest areas. Chumphon province’s coastal area remains one of the world’s most vulnerable areas, with a history of natural catastrophes\(^{(3)}\) and human destruction. Humans have changed this land from mangrove and wetland to shrimp farming, palm oil harvesting, and rubber tree plantations\(^{(4)}\). In the past, mangrove forests at Thung Kha bay and Sawi bay in the Chumphon province were the second largest in Thailand and exhibited much biodiversity. When mangrove logging was banned in 1983, only small trees remained. The local inhabitants have since realized the benefits a mangrove ecosystem could provide, and have thus attempted to propagate and extend the mangrove forest area.

Materials and Methods

Accumulation of heavy metals in mangrove sediments of coastal Chumphon province

The Bang Son bay mangrove forest is located between 10°40' and 10°41' N latitude and 99°19' and 99°20' E longitude at the mouth of Bang Son canal (B) in the
Pathio district of Chumphon province. This area is near the Chumphon airport, possibly receiving wastewater discharge from paddy fields, oil palm/coconut fields, para rubber fields, shrimp farms, and household wastewater\(^6\).

Thung Kha bay and Sawi bay originate from the coastal uplift. The area is located between 10°13’ and 10°24’ N latitude and 99°5’ and 99°15’ E longitude. The deposition of river sediment and soil is sandy, muddy, and covered by mangroves. With a length of more than 20 km, the mangrove forest is approximately 20.8 km\(^2\) (32,880.71 rai), and the dominant tree species in the area are Rhizophora sp. and Ceriops tagal. The mud flat is approximately 17.6 km\(^2\) (27,822.14 rai), and the main canals that flow into Thung Kha bay are Chumphon (or Bang Yai), Visai, Sawi, and Sawi Thao canals. The E-let canal (T) and Sawi canal (S) flow through these mangrove forests in the Mueang district and the Sawi district of Chumphon province. These areas receive discharge from shrimp farms, oil palm/coconut fields, and household wastewater.

Three mangrove forest sediment transects (B, T and S) were collected along canals (Bang Son, E-let and Sawi). Each transect was sampled at six points, with each point 300 m away from the mouth of the canal towards the land. At each sampling site, sediment sample was taken at a level 0-30 cm from the surface. Samples were kept in tightly closed plastic bags and collected in April of 2009 (Figure1).
Figure 1 Illustration of the three sampling sites for mangrove sediment collection
Sediment samples were air-dried at room temperature and passed through a 2 mm sieve to remove larger particles. Soil texture analyses were performed using the hydrometer method. The soil reaction (pH) was measured (soil: water 1:1) using a pH meter and glass electrode. The electrical conductivity (EC) was measured using a conductivity meter in an extracted solution of a 1:5 ratio of sediment to distilled water. The organic matter (OM) content was determined by the Walkley and Black Rapid Tritration Method. The cation exchange capacity (CEC) in me/100 g was determined using a NaOAC 1N, pH 8.2, and processed with a mechanical vacuum extractor. All samples were analyzed in triplicate.

For heavy metal analysis, approximately 0.5 g of dried, homogenized sediment samples was transferred into digestion vessels. Sediments were digested with HNO₃ and HCl using a milestone microwave digestion system (model MLS-1200 MEGA). The digestates were left to cool at room temperature and then filtered through Whatman filter paper No. 42. Filtered digestates were diluted with distilled deionised water to 50 ml in a volumetric flask, stored in acid-washed 60 ml polyethylene bottles, and kept in the refrigerator until analysis.

Samples were analyzed for Cu, Cr, Ni, Mn and Zn contents using an air-acetylene flame atomic absorption spectrophotometer (FASS, Model Varian SpectrAA 220FS). Cd and Pb were analysed with a graphite furnace atomic absorption spectrophotometer (GASS, Model Varian SpectrAA 220). Data is presented as mg kg⁻¹ dry weight (dw).

Results and Discussion

Physiochemical parameters of the mangrove sediment

Sediment sample were taken at three transect lines: the first at Bang Son canal (B1-B6), and the second and third lines at E-let canal (T1-T6) (Thung Kha Bay) and Sawi canal (S1-S6) (Sawi bay). These results are shown in Table 1.

At Bang Son canal (B1-B6), sandy loam was the most common sediment texture found. The pH of sediments ranged from 2.39 to 5.02, with B2 and B4 having the lowest pH (2.39 and 2.65). The % OM fluctuated from the riverbank toward land. The highest % OM was found at B3. The EC fluctuated from the riverbank toward land (3.86 to 4.20 mS/cm), with B3 having the highest EC (9.46 mS/cm). The CEC is related to the % OM; when the % OM increased, CEC also increased. The highest CEC was found at B3 (8.48 Cmol/kg).
Sandy loam was found to be the most common sediment texture at E-let canal (Thung Kha bay), with the exceptions of T4 and T6, which had sediment textures of loam and clay loam, respectively. This texture difference most likely exists due to the interaction between freshwater inflow and sea waves. Sediment pH ranged from 2.67 to 5.49. The % OM of the sediment ranged from 1.70 to 5.76. T3 had the highest % OM. The EC value ranged from 4.93 to 11.44 mS/cm, with T3 having the highest (11.44 mS/cm). CEC values fluctuated from 2.57 to 10.75 Cmol/kg.

At Sawi canal (Sawi bay) (S1-S6), sandy loam was the most common sediment texture, except for S5 and S6, which exhibited a sediment texture of clay loam and sandy clay loam, respectively. Sediment pH ranged from 2.67 to 5.49 (pH at Sawi canal equals E-let canal). The % OM ranged from 2.12 to 5.27, EC values from 4.25 to 9.08 mS/cm, and CEC from 2.50 to 8.20 Cmol/kg.

Water levels of Thung Kha and Sawi bays are low, with weak current and principle diurnal tidal. Beinkman et al\(^{(3)}\) found that at the Sawi bay, currents were primarily controlled by prevailing circulation of the adjoining Gulf of Thailand and river runoff, and most of sediment was fine silt and clay. The pH of the sediments ranged from 2.39 to 5.49. The sediment samples located close to the estuary were more due to intrusion of salt water during high tide. OM content in the mangrove sediments ranged from 1.70 to 5.76%. In each of the three canals, the OM level was lowest at the mouth of the canal and highest in middle of the transect line. The major source of soil OM was the autochthonous algal production, which increased the OM relative to the surface soil eroded by water and wind.
We compared OM levels in our study with those of mangrove sediments from the Huay Sai Royal Development Study in Phechaburi province\textsuperscript{(11)}. This area is also located in the Gulf of Thailand, and has soil texture similar to sandy loam. Sediment at Huay Sai, however, contained a lower amount of OM (0.34-0.73\%) than our study sites. A low to medium level of OM (1.0 – 1.5\%) was found at our study sites at the mouth of the canal. Most upstream stations exhibited OM > 4.5\%, which is considered very high\textsuperscript{(12)}. EC and CEC of sediment were affected by tidal changes, soil texture, rain distribution, and percentage of clay and OM. Sediments in this study area differed from those reported by Buajan and Pumijumnong\textsuperscript{(13)}, who found mainly silt-clay sediments. We attribute this to the Buajan and Pumijumnong study site.

\begin{table}
\centering
\caption{Physiochemical characteristics in mangrove sediments at depth 0-30 cm}
\begin{tabular}{llllllllll}
\hline
Canal & Site & Soil Texture & pH & OM & EC & CEC \\
& & Sand & Silt & Clay & Texture & & (mS/cm) & (Cmol/kg) \\
\hline
Bang Son & B1 & 72.52 & 22.85 & 4.63 & Sandy loam & 5.02 & 2.14 & 3.86 & 3.50 \\
& B2 & 64.52 & 26.82 & 8.66 & Sandy loam & 2.39 & 5.44 & 9.21 & 7.60 \\
& B3 & 49.52 & 30.84 & 19.64 & Sandy loam & 4.42 & 5.09 & 9.46 & 8.48 \\
& B4 & 68.52 & 27.84 & 3.64 & Sandy loam & 2.65 & 4.30 & 6.47 & 4.68 \\
& B5 & 52.52 & 27.84 & 19.64 & Sandy loam & 4.83 & 3.40 & 6.31 & 5.58 \\
& B6 & 65.52 & 23.84 & 10.64 & Sandy loam & 4.79 & 1.38 & 4.20 & 2.14 \\
E-let & T1 & 70.80 & 21.50 & 7.70 & Sandy loam & 5.49 & 1.70 & 4.93 & 2.57 \\
& T2 & 68.24 & 21.48 & 10.28 & Sandy loam & 2.67 & 4.71 & 10.70 & 6.80 \\
& T3 & 60.24 & 27.48 & 12.28 & Sandy loam & 3.31 & 5.76 & 11.44 & 10.75 \\
& T4 & 47.24 & 31.84 & 20.92 & loam & 3.71 & 2.93 & 8.96 & 6.55 \\
& T5 & 57.52 & 25.20 & 17.28 & Sandy loam & 3.80 & 4.63 & 11.21 & 7.53 \\
& T6 & 43.52 & 27.26 & 29.22 & Clay loam & 3.89 & 4.60 & 10.35 & 9.63 \\
Sawi & S1 & 5.50 & 22.20 & 18.30 & Sandy loam & 5.49 & 1.25 & 5.15 & 2.50 \\
& S2 & 66.50 & 23.20 & 10.30 & Sandy loam & 2.67 & 4.35 & 7.59 & 3.80 \\
& S3 & 57.36 & 27.20 & 15.44 & Sandy loam & 3.31 & 4.46 & 9.08 & 6.80 \\
& S4 & 43.52 & 27.20 & 29.28 & Sandy loam & 3.71 & 2.12 & 4.25 & 3.10 \\
& S5 & 60.50 & 28.20 & 11.30 & Clay loam & 3.80 & 4.20 & 7.30 & 6.55 \\
& S6 & 46.52 & 25.20 & 28.28 & Sandy clay loam & 3.89 & 5.27 & 7.88 & 8.20 \\
\hline
\end{tabular}
\end{table}

Note: nr.1 is at the mouth of canal and nr. 2-6 is toward the land.
location in the Samut Sakorn province (upper Gulf of Thailand). Samut Sakorn province is affected more by upstream water runoff, and the sediment texture differs due to sediment deposition source and upstream discharge. Sediments in this study were similar to the results of Dunpradit (14) in Surat Thani province that also reported mostly sandy loam. Most chemical parameters discerned by Dunpradit showed values higher than those found in our study (% OM, CEC).

Concentrations of heavy metals

Concentrations of heavy metals varied from the mouth of Bang Son canal (B1-B6), Thung Kha canal (T1-T6) and Sawi canal (S1-S6), and from upstream areas. The averages of these values are shown in Table 2.

### Table 2: Concentrations of heavy metals in mangrove sediments (mg/kg dry weight) from the mouth of canals and upstream of Bang Son (B), Thung Kha (T) and Sawi (S)

<table>
<thead>
<tr>
<th>Canal</th>
<th>Site</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bang Son</td>
<td>B1</td>
<td>0.002±0.001</td>
<td>2.73±0.15</td>
<td>14.36±1.14</td>
<td>3.47±0.21</td>
<td>0.47±0.06</td>
<td>0.24±3.08</td>
<td>0.53±0.15</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>0.032±0.002</td>
<td>19.52±2.11</td>
<td>12.57±1.17</td>
<td>74.68±1.46</td>
<td>9.64±0.86</td>
<td>5.08±5.23</td>
<td>7.36±0.72</td>
</tr>
<tr>
<td></td>
<td>B3</td>
<td>0.037±0.001</td>
<td>20.86±1.97</td>
<td>20.16±1.12</td>
<td>267.90±2.54</td>
<td>10.45±0.85</td>
<td>6.45±4.15</td>
<td>9.59±0.31</td>
</tr>
<tr>
<td></td>
<td>B4</td>
<td>0.012±0.001</td>
<td>9.21±0.27</td>
<td>12.57±1.17</td>
<td>74.68±1.46</td>
<td>9.64±0.86</td>
<td>5.08±5.23</td>
<td>7.36±0.72</td>
</tr>
<tr>
<td></td>
<td>B5</td>
<td>0.016±0.000</td>
<td>12.84±1.04</td>
<td>8.72±0.45</td>
<td>183.28±1.90</td>
<td>5.30±0.63</td>
<td>4.03±0.34</td>
<td>4.91±0.71</td>
</tr>
<tr>
<td></td>
<td>B6</td>
<td>0.007±0.001</td>
<td>5.27±1.19</td>
<td>3.57±0.51</td>
<td>12.00±1.62</td>
<td>1.45±0.48</td>
<td>2.02±1.17</td>
<td>3.26±0.15</td>
</tr>
<tr>
<td>E-let</td>
<td>T1</td>
<td>0.012±0.000</td>
<td>8.36±0.43</td>
<td>2.26±0.01</td>
<td>233.15±2.17</td>
<td>5.18±2.14</td>
<td>3.59±12.03</td>
<td>15.39±0.33</td>
</tr>
<tr>
<td></td>
<td>T2</td>
<td>0.028±0.000</td>
<td>16.32±0.50</td>
<td>23.13±1.08</td>
<td>173.40±2.12</td>
<td>6.26±1.45</td>
<td>7.61±33.98</td>
<td>10.38±0.16</td>
</tr>
<tr>
<td></td>
<td>T3</td>
<td>0.031±0.001</td>
<td>13.34±0.14</td>
<td>44.62±0.40</td>
<td>192.85±0.93</td>
<td>12.03±0.30</td>
<td>12.50±16.56</td>
<td>39.76±0.55</td>
</tr>
<tr>
<td></td>
<td>T4</td>
<td>0.017±0.000</td>
<td>26.78±0.20</td>
<td>33.65±0.23</td>
<td>165.65±0.78</td>
<td>11.36±0.22</td>
<td>10.03±8.56</td>
<td>37.24±0.82</td>
</tr>
<tr>
<td></td>
<td>T5</td>
<td>0.022±0.000</td>
<td>22.36±0.32</td>
<td>37.67±0.22</td>
<td>183.06±0.82</td>
<td>11.43±0.34</td>
<td>10.84±17.00</td>
<td>40.85±0.51</td>
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<td>T6</td>
<td>0.023±0.001</td>
<td>30.25±1.24</td>
<td>51.19±0.46</td>
<td>159.20±1.14</td>
<td>14.00±0.96</td>
<td>12.36±21.26</td>
<td>32.86±0.92</td>
</tr>
<tr>
<td>Sawi</td>
<td>S1</td>
<td>0.006±0.000</td>
<td>11.45±2.40</td>
<td>17.56±2.48</td>
<td>189.99±8.00</td>
<td>6.49±0.86</td>
<td>3.94±2.96</td>
<td>14.58±0.59</td>
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<tr>
<td></td>
<td>S2</td>
<td>0.028±0.000</td>
<td>8.17±1.02</td>
<td>4.80±0.20</td>
<td>14.59±1.44</td>
<td>2.35±0.69</td>
<td>2.06±2.66</td>
<td>13.78±0.35</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>0.020±0.001</td>
<td>26.73±0.97</td>
<td>31.41±0.46</td>
<td>150.14±3.65</td>
<td>10.78±1.59</td>
<td>7.39±1.97</td>
<td>26.50±0.94</td>
</tr>
<tr>
<td></td>
<td>S4</td>
<td>0.009±0.000</td>
<td>11.01±2.04</td>
<td>9.76±1.01</td>
<td>50.75±6.08</td>
<td>4.40±0.14</td>
<td>4.28±1.17</td>
<td>15.35±1.30</td>
</tr>
<tr>
<td></td>
<td>S5</td>
<td>0.021±0.001</td>
<td>20.08±3.41</td>
<td>33.87±1.48</td>
<td>170.64±2.23</td>
<td>8.94±0.08</td>
<td>8.58±4.25</td>
<td>29.98±1.43</td>
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<tr>
<td></td>
<td>S6</td>
<td>0.028±0.000</td>
<td>28.54±2.10</td>
<td>39.83±1.17</td>
<td>197.07±4.36</td>
<td>9.74±0.78</td>
<td>10.53±7.09</td>
<td>35.92±0.41</td>
</tr>
</tbody>
</table>

Sediment quality for freshwater ecosystem (15)

|               | 0.99 | 43.4 | 31.6 | -   | 22.7 | 35.8 | 121 |

World Average (24)

|               | 72   | 33   | 770  | -   | 95   | 28  |
Cadmium (Cd)

At the Bang Son canal, Cd was shown to have the highest accumulation (0.037±0.001 mg/kg, dw) in the middle transects of B3 and the lowest of heavy metal concentration (0.002±0.001 mg/kg, dw) at the mouth of B1. At the E-let canal, Cd concentration the lowest at the mouth (0.012±0.00 mg/kg, dw) and highest (0.031±0.001 mg/kg, dw) at the middle transect line (T3). At the Sawi canal, Cd concentration was shown to be highest upstream (0.028±0.00 mg/kg, dw) and lowest at the mount (S1, 0.006±0.00 mg/kg, dw).

Chromium (Cr)

At the E-let canal in the Thung Kha mangrove forest, the concentration of Cr was highest (30.25±1.24 mg/kg, dw) in the upstream transects of T6 exhibited lowest heavy metal concentration (2.73±0.15 mg/kg, dw) at the mouth of B1 (2.73±0.15 mg/kg, dw). The accumulation of Cr was strongly affected by the sediment characteristics in the middle and upstream transects (T6, S6, T4, S3, and B3, respectively).

Copper (Cu)

At the E-let canal, the concentration of Cu was shown to have the highest accumulation (30.25±1.24 mg/kg, dw) in the upstream transects of T6 and the lowest heavy metal concentration (2.73±0.15 mg/kg, dw) at the mouth of B1. The accumulation of Cu was affected strongly by the sediment characteristics in the middle and last transects (T3 and T6). Most wastewater from upstream human activity was discharged into adjoining middle transects.

Manganese (Mn)

At the Bang Son canal, the concentration of Mn was shown to have the highest accumulation (267.90±2.54 mg/kg, dw) in the middle transects of B3 and the lowest heavy metal concentration (3.47±0.21 mg/kg, dw) at the mouth of B1.

Nickel (Ni)

At the E-let canal, the concentration of Ni was shown to have the highest accumulation (0.037±1.44 mg/kg, dw) at the last point of the T6 transects and the lowest heavy metal concentration (0.47±0.06 mg/kg, dw) at the mouth of B1. Average heavy metal concentrations fluctuated between the mouth of the canal and upstream areas.

Lead (Pb)

At the E-let canal, Pb concentration was shown to have the highest accumulation (12.50±16.56 mg/kg, dw) in the middle transects of T3 and the lowest Pb concentration (0.24±3.08 mg/kg, dw) at the mouth of B1. Average heavy metal
concentrations fluctuated between the mouth of the canal and upstream areas.

Zinc (Zn)

At the E-let canal, the concentration of Zn was shown to have the highest accumulation (40.85±0.51 mg/kg, dw) at the fifth point of the transect (T5) and the lowest heavy metal concentration (0.53±0.15 mg/kg, dw) at the mouth of B1.

Figure 2 Variations of heavy metal concentration in the sediments at three mangrove areas from canal mouths to upstream areas
Comparison of heavy metal accumulation levels with physiochemical parameters in mangrove sediments

The correlation of seven heavy metal (Cd, Cr, Cu, Mn, Ni, Pb, and Zn) concentrations and physiochemical properties was tested by the Pearson Correlation.

Bang Son Canal

The relationship between heavy metal accumulation and physiochemical properties was demonstrated by significant positive correlations between pH, OM, EC, and CEC for all heavy metals except Cu and Mn, as shown in Table 3. Mn positively correlated with silt and clay, but showed a negative correlation with sand. Based on the correlation matrix obtained for sediments (Table 3), pH, OM, EC, and CEC were the dominant factors controlling Cd, Cr, Ni, Pb, and Zn accumulation, as these metals were distributed in the Bang Son mangrove sediment. A significant positive correlation also exists between heavy metals and some soil properties (e.g. clay).

E-let Canal, Thung Kha mangrove sediment

The relationship between heavy metals and physiochemical properties was highlighted by strong positive correlations for Cd, OM, EC, and CEC only. Clay content showed a significant positive correlation with Cr and Ni in the upper layer (Table 4).

Sawi Canal, mangrove sediment

In Sawi, we found no significant correlation between physiochemical parameters for all of the heavy metals. The exception was for CEC, which showed a positive correlation with Cd, Cr, Cu, Pb and Zn accumulation (Table 5).
Table 3 Correlation coefficient matrix showing inter-element and physiochemical relationships in the Bang Son mangrove sediment

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>OM</th>
<th>EC</th>
<th>CEC</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
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<td>.94**</td>
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</tr>
<tr>
<td>CEC</td>
<td>1.00**</td>
<td>.92**</td>
<td>.96**</td>
<td>1</td>
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</tr>
<tr>
<td>Sand</td>
<td>-0.66</td>
<td>-0.43</td>
<td>-0.62</td>
<td>-0.66</td>
<td>1</td>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td>Silt</td>
<td>0.54</td>
<td>0.44</td>
<td>0.63</td>
<td>0.54</td>
<td>-0.75</td>
<td>1</td>
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</tr>
<tr>
<td>Clay</td>
<td>0.61</td>
<td>0.35</td>
<td>0.51</td>
<td>0.61</td>
<td>-0.96**</td>
<td>0.51</td>
<td>1</td>
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</tr>
<tr>
<td>Cd</td>
<td>.91**</td>
<td>.85*</td>
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<td>.91**</td>
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<tr>
<td>Cr</td>
<td>.96**</td>
<td>.88**</td>
<td>.98**</td>
<td>.96**</td>
<td>-0.73</td>
<td>0.68</td>
<td>0.63</td>
<td>.93**</td>
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<tr>
<td>Cu</td>
<td>0.70</td>
<td>0.46</td>
<td>0.54</td>
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<tr>
<td>Mn</td>
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<td>0.48</td>
<td>0.66</td>
<td>0.71</td>
<td>-0.98**</td>
<td>.76*</td>
<td>.93**</td>
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<td>0.74</td>
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</tr>
<tr>
<td>Ni</td>
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<td>.86*</td>
<td>.98**</td>
<td>.96**</td>
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<td>0.70</td>
<td>0.60</td>
<td>.91**</td>
<td>.99**</td>
<td>0.60</td>
<td>0.73</td>
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<tr>
<td>Pb</td>
<td>.90**</td>
<td>.77*</td>
<td>.93**</td>
<td>.90**</td>
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<td>.97**</td>
<td>0.53</td>
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<tr>
<td>Zn</td>
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<td>.76*</td>
<td>.93**</td>
<td>.89**</td>
<td>-0.79*</td>
<td>0.72</td>
<td>0.70</td>
<td>.95**</td>
<td>.96**</td>
<td>0.56</td>
<td>.82*</td>
<td>.95**</td>
<td>.99**</td>
<td>1</td>
</tr>
</tbody>
</table>

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed). n = 18

Table 4 Correlation coefficient matrix showing inter-element and physiochemical relationships in the Thung Kha mangrove sediment

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>OM</th>
<th>EC</th>
<th>CEC</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
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</thead>
<tbody>
<tr>
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<tr>
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<td>-0.86*</td>
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</tr>
<tr>
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<td>.88*</td>
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<td></td>
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</tr>
<tr>
<td>Sand</td>
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<td>-0.37</td>
<td>-0.54</td>
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<td></td>
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<tr>
<td>Silt</td>
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</tr>
<tr>
<td>Clay</td>
<td>-0.14</td>
<td>0.20</td>
<td>0.35</td>
<td>0.50</td>
<td>-0.97**</td>
<td>0.66</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
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<td>.96**</td>
<td>.87*</td>
<td>.82*</td>
<td>-0.02</td>
<td>0.04</td>
<td>0.01</td>
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</tr>
<tr>
<td>Cr</td>
<td>-0.31</td>
<td>0.21</td>
<td>0.44</td>
<td>0.45</td>
<td>-0.93**</td>
<td>0.66</td>
<td>.95**</td>
<td>0.04</td>
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<tr>
<td>Cu</td>
<td>-0.55</td>
<td>0.76</td>
<td>.82*</td>
<td>.94**</td>
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<td>0.65</td>
<td>0.75</td>
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<td>0.71</td>
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<tr>
<td>Mn</td>
<td>0.72</td>
<td>-0.51</td>
<td>-0.71</td>
<td>-0.63</td>
<td>0.75</td>
<td>0.56</td>
<td>-0.76</td>
<td>-0.44</td>
<td>-0.87*</td>
<td>-0.76</td>
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<tr>
<td>Ni</td>
<td>-0.29</td>
<td>0.54</td>
<td>0.62</td>
<td>0.81</td>
<td>-0.88*</td>
<td>0.78</td>
<td>.83*</td>
<td>0.34</td>
<td>0.75</td>
<td>.95**</td>
<td>-0.65</td>
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<tr>
<td>Pb</td>
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<td>0.78</td>
<td>.84*</td>
<td>.95**</td>
<td>-0.73</td>
<td>0.68</td>
<td>0.67</td>
<td>0.63</td>
<td>0.65</td>
<td>.99**</td>
<td>-0.72</td>
<td>.94**</td>
<td>1</td>
<td></td>
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<tr>
<td>Zn</td>
<td>-0.12</td>
<td>0.39</td>
<td>0.49</td>
<td>0.62</td>
<td>-0.68</td>
<td>0.80</td>
<td>0.55</td>
<td>0.18</td>
<td>0.51</td>
<td>0.75</td>
<td>-0.36</td>
<td>.87*</td>
<td>0.80</td>
<td>1</td>
</tr>
</tbody>
</table>

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed). n = 18
Almost all heavy metal concentrations in the surface layer (0-30 cm) were still below the standard level except Cu\textsuperscript{(15)} (Table 2). At Thung Ka, the mean concentrations of Cr, Cu, Mn, Ni, Pb, and Zn were higher than at the rest of the sampling sites (Bang Son Bay and Sawi Bay mangrove sediments). At these sites, these heavy metals came from human activity (i.e., shrimp farms, oil palm/coconut farms, and domestic waste from communities). More shrimp culture happens in the Thung Kha mangrove forest than other locations and large amounts of pollutants were released from pond effluents\textsuperscript{(16)}. A large amount organic matter remaining in ponds and coastal waters also contributed to the deterioration of several major shrimp farming areas.

The relationship between the sediment properties and heavy metal concentrations was tested using the Pearson simple correlation, and results indicated that the organic content greatly influenced the heavy metal accumulation in the sediments. The pH did not exhibit a clear effect on heavy metal accumulation (in either the Thung Kha or Sawi mangrove forests). Mn, Cr, and Cu in sediment is associated with fine-grain. Vaithiyanathan et al.\textsuperscript{(17)} reported that

\begin{table}
\centering
\caption{Correlation coefficient matrix showing inter-element and physiochemical relationships in the Sawi mangrove sediment}
\begin{tabular}{cccccccccccc}
\hline
 & pH & OM & EC & CEC & Sand & Silt & Clay & Cd & Cr & Cu & Mn & Ni & Pb & Zn \\
\hline
pH & 1 &   &   &   &   &   &   &   &   &   &   &   &   &   \\
OM & -0.68 & 1 &   &   &   &   &   &   &   &   &   &   &   &   \\
EC & -0.53 & 0.87* & 1 &   &   &   &   &   &   &   &   &   &   &   \\
CEC & -0.30 & 0.66* & 0.77 & 1 &   &   &   &   &   &   &   &   &   &   \\
Sand & -0.15 & 0.09 & 0.37 & -0.18 & 1 &   &   &   &   &   &   &   &   &   \\
Silt & -0.35 & 0.32 & 0.19 & 0.50 & -0.37 & 1 &   &   &   &   &   &   &   &   \\
Clay & 0.27 & -0.19 & -0.45 & 0.04 & -0.96** & 0.10 & 1 &   &   &   &   &   &   &   \\
Cd & -0.19 & 0.78 & 0.66 & .99** & -0.30 & 0.52 & 0.17 & 1 &   &   &   &   &   &   \\
Cr & -0.07 & 0.66 & 0.68 & .93** & -0.31 & 0.47 & 0.19 & .94** & 1 &   &   &   &   &   \\
Cu & 0.15 & 0.55 & 0.55 & .89* & -0.23 & 0.44 & 0.12 & .92** & .94** & 1 &   &   &   &   \\
Mn & 0.65 & 0.07 & 0.22 & 0.51 & -0.13 & 0.06 & 0.12 & 0.57 & 0.67 & .83* & 1 &   &   &   \\
Ni & 0.20 & 0.41 & 0.55 & 0.79 & -0.21 & 0.47 & 0.08 & 0.81 & .93** & .95** & .83* & 1 &   &   \\
Pb & 0.06 & 0.59 & 0.48 & .91* & -0.40 & 0.54 & 0.27 & .96** & .93** & .97** & 0.73 & .88* & 1 &   \\
Zn & -0.08 & 0.72 & 0.61 & .97** & -0.28 & 0.5 & 0.16 & .99** & .93** & .96** & 0.66 & .84* & .98** & 1 \\
\hline
\end{tabular}
\textsuperscript{**} Correlation is significant at the 0.01 level (2-tailed). \textsuperscript{*} Correlation is significant at the 0.05 level (2-tailed). \textit{n} = 18
\end{table}
metal absorption rates varied with different sediment grain sizes. Hart\textsuperscript{18} also reported that organic content correlated strongly with the heavy metal concentrations in sediment.

Research on the impact of solid shrimp pond waste materials on mangrove growth and mortality has found that excess sediment discharged from the vicinity of shrimp ponds is the major cause of mangrove decline. Additionally, research has found that Bruguiera cylindrica is the weakest species to survive and that Excoecaria agallocha, Lumnitzera racemosa and Avicennia marina are better able to withstand the effects of sediment changes\textsuperscript{5}. Our study focused mainly on the accumulation of heavy metals and on physical and chemical soil parameters. We did not examine the relationship between tree growth and heavy metal accumulation on soil properties, but recommend this study in future research. We believe that the mangrove forest is tolerant to polluted discharge.

Results from Bang Son bay, Thung Kha bay, and Sawi bay of Chumphon province sediments found that Mn accumulated most (259.75 mg kg\textsuperscript{-1}) followed by Cu (32.09 mg kg\textsuperscript{-1}), Zn (29.42 mg kg\textsuperscript{-1}), Cr (20.04 mg kg\textsuperscript{-1}), Ni (10.72 mg kg\textsuperscript{-1}), Pb (9.49 mg kg\textsuperscript{-1}), and Cd (0.028 mg kg\textsuperscript{-1}). We found that the Cd, Pb and Zn concentrations in this study were lower than those reported in the Samut Sakhon mangrove forest in Thailand\textsuperscript{19}. The results of this study revealed that Cd, Cr, Cu, Ni, Mn, Pb and Zn concentrations in sediments were much lower than those present in sediments from the Quilon mangrove forest in India\textsuperscript{20}, Punta Mala bay in Panama\textsuperscript{21} and Hong Kong mangrove swamps\textsuperscript{22}. The Cu and Zn concentrations in this study were higher than those in the Terengganu mangrove forest in Malaysia\textsuperscript{23}. Human activity causes a variable amount of heavy metal accumulation in the surrounding environment. The results of this study were compared to the worldwide average sedimentary heavy metal concentrations\textsuperscript{24}, and all of the concentrations of heavy metals from this study were lower than those of the worldwide average (Table 6).

In the last decade, the Thung Kha bay and Sawi mangrove forests have had the largest coastal heavy metal deposits. In the last decade, these areas experienced coastal changes not only from natural processes, but also from human activity along the coast (land reclamation, port development, and shrimp farming). As a result, levels of heavy metals have increased along the coast through fluvial processes, direct effluent discharge, atmospheric effects, and the sewage discharge of effluents. Many mangrove areas in peninsular Thailand (e.g., the Thung Kha
and Sawi mangrove forests) have been converted to agricultural areas, shrimp ponds, roads, industrial sites, and urban areas, all with heavy metals as main pollutants that accumulate in mangrove ecosystems. The mangrove forests have been used as convenient waste disposal sites with sinks or reservoirs of various man-made pollutants. Mangrove forest mud has an extraordinary capacity to accumulate all discharge to the near shore marine environment, where it’s used as an important food source. Mangrove forests act as a filter of polluted substances, even though higher toxic heavy metal accumulation in sediment and plants will affect plant growth. The mangrove forest is the last zone to prevent pollutant distribution to the food chain and food web to the sea and ocean.

**Table 6** Concentration of heavy metals in sediments (mg kg⁻¹) measured in this study compared with values from the literature

<table>
<thead>
<tr>
<th>Location</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
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</thead>
<tbody>
<tr>
<td>Chumphon mangrove sediment (this study)</td>
<td>0.002-0.037</td>
<td>2.73-30.25</td>
<td>2.26-51.19</td>
<td>3.47-267.90</td>
<td>0.47-14.00</td>
<td>0.24-12.50</td>
<td>0.53-40.85</td>
</tr>
<tr>
<td>Samut Sakhon mangrove forest sediment, Thailand (13)</td>
<td>0.04-0.07</td>
<td>-</td>
<td>2.26-51.19</td>
<td>-</td>
<td>-</td>
<td>0.24-12.36</td>
<td>0.53-40.85</td>
</tr>
<tr>
<td>Surat Thani mangrove forest sediment, Thailand (14)</td>
<td>&lt;0.04</td>
<td>-</td>
<td>2.90-13.75</td>
<td>-</td>
<td>-</td>
<td>8.15-25.99</td>
<td>7.50-46.43</td>
</tr>
<tr>
<td>Terengganu mangrove forest sediment, Malaysia (23)</td>
<td>-</td>
<td>-</td>
<td>31.1-8.15</td>
<td>-</td>
<td>-</td>
<td>10.5-25.99</td>
<td>20.8</td>
</tr>
<tr>
<td>Quilon mangrove forest sediment, India (20)</td>
<td>-</td>
<td>-</td>
<td>758-7.50</td>
<td>881-244</td>
<td>-</td>
<td>1888-47</td>
<td>1880-98-259</td>
</tr>
<tr>
<td>Punta Mala Bay mangrove forest sediment, Panama (21)</td>
<td>&lt;10</td>
<td>23.3-258</td>
<td>56.3-74.8</td>
<td>295-324</td>
<td>27.3-31.8</td>
<td>78.2-76.4</td>
<td>105-247</td>
</tr>
<tr>
<td>Hong Kong mangrove swamps (22)</td>
<td>2.9</td>
<td>39.2-72</td>
<td>74.8-33</td>
<td>324-770</td>
<td>31.8-95</td>
<td>76.4-95</td>
<td>247-95</td>
</tr>
<tr>
<td>Victoria Harbour mangrove forest sediment, Hong Kong (28)</td>
<td>2.6</td>
<td>58-72</td>
<td>45-33</td>
<td>244-770</td>
<td>47-95</td>
<td>47-95</td>
<td>244-98-259</td>
</tr>
<tr>
<td>Sinnamary mangrove forest sediment, French Guiana (29)</td>
<td>-</td>
<td>59.8</td>
<td>17.79-17.79</td>
<td>539.51-539.51</td>
<td>31.69-31.69</td>
<td>26.91-26.91</td>
<td>164.08</td>
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<tr>
<td>World average sediment (24)</td>
<td>72</td>
<td>33</td>
<td>770</td>
<td>95</td>
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</tbody>
</table>
Conclusion

Heavy metals accumulated in mangrove sediments in Thailand, but this overall amount was less than the average levels of accumulated heavy metals in sediments in other parts of the world. The average heavy metal concentrations in all mangrove sediments were Mn > Cu > Zn > Cr > Ni > Pb > Cd. Our results showed that heavy metal concentrations in Thung Kha bay were higher than those at other sampling sites in Thailand. Overall, there was a positive correlation between the heavy metals in the sediments and physiochemical properties (pH, OM, EC and CEC) in each area surveyed. At Thung Kha bay, Cd showed a significant positive correlation with OM content. Generally, mangrove sediments are anaerobic, abundant in sulfide and organic matter, supporting the retention of water-born heavy metals. This study revealed that the accumulation of heavy metals upstream was higher than that river mouths. Mangrove forests have the potential to accumulate heavy metals. Further research should determine how mangrove vegetation tolerates these accumulated heavy metals, and address the need for strict law enforcement to regulate the discharge of heavy metals to public areas. Heavy metal content in various mangrove species should also be discerned to better understand heavy metal translocation.

Acknowledgments

This research is supported by a grant from the Center for Toxicology, Environmental Health and Management of Toxic Chemicals, under Science & Technology Postgraduate Education and Research Development Office (PERDO) of the Ministry of Education, Thailand.

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