Residue in the Mangrove Surface Sediment with the Feasibility of Phytoremediation Application

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Abstract. The present study investigated heavy metal contaminations in the mangrove surface sediment of Rayong coast, Thailand. Sediment samples were collected from 5 locations with each 3 sampling sites and analyzed for heavy metal (Cu, Pb, Cr, Zn and Mn) contents using microwave digestion and MP-AES. The results revealed that concentrations of the heavy metals ranged from 10.54-66.53 mg/kg for Cu, 21.71-116.40 mg/kg for Pb, 21.21-66.66 mg/kg for Cr, 17.67-397.01 mg/kg for Zn and 46.55-1609.53 mg/kg for Mn. Although, the concentrations of Cu, Pb and Zn in surface sediments exceed the effects range low (ERL), did not exceed the effects range median (ERM) of the guidelines. Meanwhile, the feasibility of treating a heavy metal-contaminated soil via mangrove phytoremediation showed the removal efficiency of heavy metals contaminated in sediment occurred in descending order of Mn>Pb>Cr>Cu>Zn (93.11, 80.42, 70.03, 67.09 and 52.50 %, respectively). After spiked more concentration of heavy metals, decreasing removal efficiency was occurred in all treatments that might be caused of the higher heavy metal intake. Beside of these contaminated conditions, the mangrove plants can still survived after 30 days. Which indicated the tolerated to the high level of heavy metals.

1. Introduction

Environmental contamination by heavy metals has become a world-wide problem during recent years due to the fact that heavy metals are not biodegradable [1]. The most common trace elements found in the environment are cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), arsenic (As), lead (Pb), zinc (Zn), and mercury (Hg) [2]. The coast of Rayong province which is located along the Upper Gulf of Thailand has been faced the problems from heavy metals which are caused by rapid economic, social, agricultural, and industrial development and urbanization. Industrial development projects have been suspected to contribute to trace element contamination in the Upper Gulf [3]. Specially, Map Ta Phut Industrial Estate established in Rayong Province along the east coast has developed as a national heavy metal center, including a gas separation plant, oil refineries and petrochemical and chemical plants. [4]. Since sediment serves as a source as well as an ultimate sink of many pollutants in the aquatic environment. In particular, the mangrove sediments have high metal binding capacity because sediments have anaerobic nature with richness of sulfide content, which can easily adsorb the metals [5]. Therefore, it is considered to be a good indicator for assessment of metal pollution in mangrove area. The level of trace elements including Cd, Cu, Fe, Hg, Mn, Ni, Pb, and Zn in sediments along the eastern coast of the Gulf of Thailand, which is an area with heavy industrial development were investigated, did not exceed the standard values of NOAA with the exception of Pb, Cu, and Ni. Pb
Contamination was high at some locations, including the Map Ta Phut Industrial Estate in Rayong Province [6]. However, metals entering the coastal area can be accumulated in the environment such as mangrove plants and sediment.

Recently, remediation of contaminated soil has been concerned while the remediation techniques are available for metal-contaminated soil, phytoremediation is relatively low-cost, environmentally friendly technology and practical approach. Moreover, it has proven successful in treating a range of soil contaminants [7]. According to the previous study, *Rhizophora mucronata* was considered one of the most effective excluder mangrove trees due to the ability to stabilize Cu, Cd, Cr, Fe, Mg, Ni, Pb and Zn in root. [8-9]. Various mangrove plant species in Pattani Bay, have high potential for phytoremediation even if tissue metal levels are relatively modest; a high biomass producer still has potential for significant metal removal from soil [10].

The eastern coast has further developed with a rapid expansion of industrialization and urbanization, these activities will increase the degree of heavy metal pollution in the coastal area and its bordering ecosystem of mangroves. Continued monitoring of heavy metals in sediment must be carried out to investigate tolerant species suitable for phytoremediation. Therefore, this study aimed 1) to provide information about content of Cu, Pb, Cr, Zn and Mn heavy metals in mangrove sediments of Rayong coast and 2) to study the feasibility of treating a heavy metal contaminated soil via *Rhizophora apiculata*.

### 2. Materials and methods

#### 2.1 Study Area and Sediment sampling

Surface mangrove sediment were collected in five different sites: Khlong Chak Mak (A), Pak Nam (B), Phe (C), Khlong La Won (D) and Pak Nam Prasae (E) along the coast of Rayong province, Thailand. The location and geographic coordinates is shown in Table 1 and the map of the study area is shown in Figure 1. At each location, composite sediments of 3 subsampling sites (15 sediment sample sites) were collected. Sampling procedures were performed in two phases: firstly, May 2018 and secondly, September 2018. Sediments were placed in a clean polyethylene zip-lock bag. Afterward, the collected soil samples were oven dried at 105°C and were then sieved through a 500 µm mesh size nylon sieve. Triplet of subsamples of each composite sediment were subjected to microwave digestion and heavy metals were analysed by MP-AES.

**Table 1. Sampling sites and geographic coordinates**

| Area code | Location         | Location of Station |
|-----------|------------------|---------------------|
| A         | Khlong Chak Mak  | 12°42'40.2"N 101°08'02.5"E |
| B         | Pak Nam          | 12°39'57.4"N 101°14'59.6"E |
| C         | Phe              | 12°36'37.3"N 101°25'29.9"E |
| D         | Khlong La Won    | 12°40'56.6"N 101°35'47.0"E |
| E         | Pak Nam Prasae   | 12°42'19.2"N 101°42'59.5"E |
2.2 Heavy metal analysis

Sediment sample of 1.00 g were accurately weighed and placed in a dry and clean Teflon microwave digestion vessel, with 9 ml of nitric acid (HNO₃ 65%) and 3 ml of hydrochloric (37%) added to the vessel. The mixture was initially digested at 180°C for 10 minutes using microwave digestion equipment (Speedwave four, Berghof). Afterward, the mixture was allowed to cool down. The digested samples were determined for the concentrations of heavy metals (Cu, Pb, Cr, Zn and Mn) using Microwave Plasma-Atomic Emission Spectroscopy (MP-AES 4100, Agilent Technologies). Five series of working standard solutions were constructed and final concentrations of the metals in the soil samples were calculated using the following formula (1).

\[
\text{Heavy metal concentration (mg/kg)} = \frac{\text{Concentration (mg/L) } \times V}{W}
\]

Where \( V \) = Final volume, and \( W \) = Sample weight

The quality control of the analytical results, laboratory quality assurance and quality control methods were implemented such as pre-cleaning of laboratory materials with 10% HNO₃, use of standard operating procedures, analysis of blanks, calibration with the standard, and recovery of known additions. The percent recoveries of the known additions were 91.16% (Cu), 103.31% (Pb), 105.94% (Cr), 96.06% (Zn), and 107.63% (Mn).

2.3 Phytoremediation of heavy metals

One year of mangrove plants were cultivated in 3 kg contaminated soil and spiking heavy metal contaminated soil. The higher dose of heavy metals were spiked to increase the contents of Cu, Pb, Cr, Zn and Mn. About 3 kg of soil were contaminated with 3 litres of distilled water containing dissolved Cu(NO₃)₂·3H₂O, Pb(NO₃)₂, Cr(NO₃)₃, Zn(NO₃)₂·6H₂O and Mn(NO₃)₂. After 30 days, the sediments were processed in microwave digestion for analysis of heavy metals, which was performed through MP-AES. The removal efficiency was determined and calculated using the following equation (2). Direct observation was used to evaluate the phytotoxicity in mangrove plants. The score of each symptom was exhibited in Table 2.

\[
\text{Heavy metal removal efficiency} = \frac{C_i-C_t}{C_i} \times 100
\]

Where \( C_i \) was the initial heavy metal concentration (mg/kg) and \( C_t \) was heavy metal concentration after 30 days (mg/kg)
Table 2. Guidelines for evaluating the phytotoxicity of plant based on direct observation

| Score | Appearance and symptoms                                |
|-------|--------------------------------------------------------|
| 0     | Normal, green leaf                                     |
| 1     | Slight toxicity, small area of pale yellow on leaf     |
| 2     | Slight moderate toxicity, large area of pale yellow on leaf |
| 3     | Moderate toxicity, small area of blight leaf was observed |
| 4     | High toxicity, large area of blight leaf was observed  |
| 5     | Critical toxicity, whole area of blight leaf was observed |

2.4 Statistic analysis
All concentrations were repeated three times and the results expressed are expressed as the mean ± standard deviation and were analyzed. Significant differences between heavy metal concentrations in samples different seasons were analysed using two sample T-test of SPSS 22. Differences were considered significant when p < 0.05.

3. Results and discussions

3.1 Heavy metal concentration
Concentration of heavy metals in surface sediments of coast in Rayong province, Thailand were shown in Figure 2. The almost trend of heavy metal concentrations in sediments was Mn > Zn > Pb > Cr > Cu except for site D where Pb concentration was higher than Cr.
In sediments at all sampling sites, concentration of Cu ranged from 10.54 to 66.53 mg/kg. The highest concentration of copper (66.53 mg/kg) was detected in site B2 in September. Which come from the widely use of Cu in electrical wiring and components of electronic equipment, roofing, production of alloys, and cooking utensils [11].

The concentration of Pb are varied from 21.71 to 116.40 mg/kg. The highest concentration of Pb (116.40 mg/kg) was detected in site B3 in September. Pb used in batteries, metal products, ammunition, paint, and ceramic products [2].

The concentration of Cr ranged from 21.21 to 66.66 mg/kg. Chromium (Cr) was the least abundant element in the soil samples studied. The highest concentration of Cr (66.66 mg/kg) was detected in site B2 in May. The metal can be primarily used in manufacturing steel and other alloys, chrome plating, and pigment production [12].

The level of Zn in the sediment ranged from 17.67-397.01 mg/kg. The highest concentration of Zn (397.01 kg/kg) was detected in site A2 in September. Zn has been used in various industries such as coating steel for construction, coating metal products, metal plating, wood preservative, dry batteries, textile machines, printers, paints, and pesticides [2]. The increased concentration of Zn in the sediments could be attributed to industrial and commercial discharges, and vehicular emissions [13]. Total content of Mn in the sediments ranged from 46.55 to 1609.53 mg/kg. The highest concentration of Mn (1609.53 mg/kg) was detected in site A3 in September. Mn is naturally present in rocks or soils. It has been used for steel production, aluminum alloy, dried cell battery paints, and fertilizer [2]. The distributions of Iron and Manganese in Upper Gulf sediments are apparently dominated by natural inputs. Enrichment of Mn due to precipitation of MnO₂ in oxic surface sediments is associated with the relict
sediment [14]. There was significant difference (p<0.05) in Cr and Mn levels between different seasons.

A wide range of values for heavy metal concentrations was observed for the sediments. The comparison between the sampling stations showed that the amount of metals varied from site to site. The highest average concentrations of Cu, Pb and Cr in sediments were observed in site B (Pak Nam area). This was possibly due to industrial and domestic wastes discharged from Rayong estuary. Whereas, the highest average concentrations of Mn and Zn were observed in site A (Khlong Chak Mak). The site A is the nearest station to Map Ta Phut Industrial Estate. According to the previous study, average heavy metal concentration in sediments ranged from the highest in Iron followed by Manganese, Zinc, Copper, Lead and Cadmium, respectively. Chak Mak Canal also appeared to be the place with high level of heavy metals. [15]

The previous study [6] reported that the content of Cu, Pb, Zn and Mn in sediments of eastern coast of the Gulf of Thailand were 14.4-103, 1.69-66.3, 7.48-131 and 30-1710 mg/kg, respectively. Comparing the contents of sediment heavy metals in this study with the previous report, the Mn, Zn and Pb concentration in sediments have increased, which are caused by rapid economic, social, agricultural, and industrial development and urbanization. Whereas, Cu concentrations have either been stable or have decreased in the study area. The contents of heavy metals in this study were compared with the proposed marine and coastal sediment quality guidelines of Thailand (Pollution Control Department, 2006). The guidelines suggested that the effect range low (ERL) of Cu, Pb, Cr and Zn were 34, 46.7, 81 and 150 mg/kg dry wt., respectively. There are no guideline value for Mn. The concentrations of Cu, Pb and Zn in surface sediments exceed the effects range low (ERL), but did not exceed the effects range median (ERM) of the guidelines.

3.2 Phytoremediation of mangrove plants

To access the heavy metal phytoremediation potential of *Rhizophora apiculata*, sediments contaminated with Cu, Pb, Cr, Zn and Mn concentration of 6, 10, 18, 18 and 54 mg/kg were used. The potential of mangroves for the removal of metals in contaminated and spiking heavy metal contaminated soils within 30 days were shown in the Figure 3.

![Figure 3](image-url)

**Figure 3.** The heavy metal removal efficiencies of mangrove onto contaminated and spiked sediments

The removal efficiencies of heavy metals of Cu, Pb, Cr, Zn and Mn were 67.09, 80.42, 70.03, 52.50 and 93.11 %, respectively. The value occurs in descending order of Mn>Pb>Cr>Cu>Zn. This result is consistent with report on Mn behaviour that the plant organs accumulated in high quantities [10].

In a treatment with more spiked level of heavy metal, the Cu, Pb, Cr, Zn and Mn concentrations in mangrove sediment were 25, 52, 42, 102 and 529 mg/kg, respectively. It was found that the removal efficiencies of heavy metals of Cu, Pb, Cr, Zn and Mn were 47.11, 13.50, 12.23, 27.74 and 68.36 %, respectively. The maximum removal was still observed for Mn (68.36%), and minimum removal was observed for Cr (12.23%). After spiked more concentration of heavy metal, decreasing removal efficiency was occurred in all treatment that might be caused of the higher heavy metal intake.
Therefore, the mangroves need the acclimatization period for adaptation to tolerate and remediate the heavy metals in sediments.

![Image](image-url)

**Figure. 4** Pots containing mangrove grown in contaminated sediments spiked with different heavy metals at day 0 and 30.

At day 30, the score of phytotoxicity of plant under high Cu, Pb, Cr, Zn and Mn were 0, 3, 0, 0 and 4, respectively (Figure 4). Green leaves and shoots were observed in the Cu, Cr and Zn experiments. Small area of blight leaf and leaf burn were observed in the Pb experiment. Meanwhile, large area of blight leaf were observed in the Mn experiment. However, the mangrove plants were high tolerated to high level of Cu, Pb, Cr, Zn and Mn in sediments.

4. Conclusions
The examined heavy metals in mangrove sediments of the Rayong Coast in the Upper Gulf of Thailand showed wide ranges of concentrations, 10.54 to 66.53 mg/kg for Cu, 21.71 to 116.40 mg/kg for Pb, 21.21 to 66.66 mg/kg for Cr, 17.67 to 397.01 mg/kg for Zn and 46.55 to 1609.53 mg/kg for Mn, due to heavy metal distribution. Comparing with Thailand’s sediment quality guidelines, the concentrations of Cu, Pb and Zn in surface sediments exceed the ERL, but did not exceed the ERM of the guidelines. According to remediation of contaminated soil, mangrove phytoremediation revealed the high removal efficiency (67.09 % for Cu, 80.42% for Pb, 70.03% for Cr, 52.50 % for Zn and 93.11% for Mn) and tolerance for all heavy metal treatments in this study. Therefore, the mangrove trees can be useful to reduce heavy metal in contaminated sediment due to their high heavy metal accumulation ability.

5. References
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