Chemical fractionation of trace elements in mangrove sediments from the Songkhla Lake, Thailand using BCR technique

Siriporn Pradit\textsuperscript{a,b,\ast}, Noor Azhar Mohamed Shazili\textsuperscript{c}, Manasawan S. Pattaratumrong\textsuperscript{a,b}, Ponlachart Chotikarn\textsuperscript{a,b}, Mathinee Yucharoen\textsuperscript{a,b}, Prawit Towatana\textsuperscript{a,b}

\textsuperscript{a} Marine and Coastal Resources Institute, Prince of Songkla University, Hat Yai, Songkhla 90110 Thailand
\textsuperscript{b} Coastal Oceanography and Climate Change Research Center, Prince of Songkla University, Hat Yai, Songkhla 90110 Thailand
\textsuperscript{c} Ocean Research Institute, Universiti Malaysia Terengganu, Kuala Terengganu 21030 Malaysia

\ast Corresponding author, e-mail: siriporn.pra@psu.ac.th

Received 19 Mar 2018
Accepted 30 Oct 2019

ABSTRACT: The aim of this work was to determine the concentration of trace elements (Zn, As, Cd, and Pb) in mangrove sediments using the European community bureau of reference (BCR) sequential extraction method. The sampling was conducted in August 2016 at 8 stations of Songkhla Lake in southern Thailand. Trace element concentrations were determined using the inductively coupled plasma mass spectrophotometer (ICPMS). Zn (37.20–64.42\%) and Cd (63.44–77.50\%) were found dominant in the acid-soluble fraction (F1). Pb (62.01–89.48\%) was detected dominantly in reducible fraction (F2). As (49.92–73.45\%) was found dominant in F2 (at stations 2, 4, 6, and 8) and in oxidizable fraction (F3) with the concentrations of 48.71–68.02\% (at stations 1, 3, 5, and 7). All trace elements (Zn, As, Cd, and Pb) were bound to the bioavailable fractions (first three fractions) and were low in residual fraction (F4). Calculation of ecological risk assessment of Cd revealed that the individual concentration factor (ICF) >6, the global concentration factor (GCF) >24 and the risk assessment code (RAC) >50\% in all stations were classified as high concentration and very high risk for aquatic organisms.

KEYWORDS: ICPMS, bioavailability, sequential extraction, risk assessment, trace elements

INTRODUCTION

Mangroves are potentially large depositories of sediment-associated trace metals due to their low redox potential and significant amount of $\text{H}_2\text{S}$ present\textsuperscript{1} making them important to assess the mobility of trace metals in such environments\textsuperscript{2}. Mangrove sediments are anaerobic and reduced, as well as being rich in sulphides and organic matter. Thus, they are useful in retaining heavy metals from anthropogenic and industrial pollutants. The total metal content of the sediments may not be able to provide a clear picture of the metal loadings and their behavior (such as mobility, toxicity, and bioavailability) with changing environmental conditions\textsuperscript{3}. Occasionally, in function of physical and chemical changing of environments, metals can be released into pore water and reach aquatic biota\textsuperscript{4}, where they may suffer bioaccumulation and biomagnification, as is the case of $\text{Hg}$\textsuperscript{3}. In sediments, heavy metals are present in different geochemical forms which determine their mobilization capacity and bioavailability\textsuperscript{5}. Assessment of heavy metal contamination of the coastal environment based on total metal concentration is not sufficient for an understanding of their environmental behavior since only a fraction of the total metal content is available for biological processes. Sequential extraction can provide better information about the identification of the main binding to the particulates and the phase associations of elements in sediment\textsuperscript{6}.

Thus, numerous sequential extraction methods have been developed according to the type of reagent being used as an extractant, the experimental conditions applied and the number of steps involved to achieve different chemically bound fractions\textsuperscript{7,8}. Dynamic metal speciation analysis in aquatic ecosystems is emerging as a powerful basis for development of predictions of bioavailability and reliable risk assessment strategies\textsuperscript{9}. Consequently, besides measuring their total concentrations, determining the geochemical fractionation of metals in...
The study area is the mangrove area in the Songkhla Lake. The Songkhla Lake is a coastal shallow lagoon, located in the southern part of Thailand with a surface of approximately 1042 km². The average depth of the inner, middle and outer sections of lake is about 2, 1.5, and 1.5 m, respectively. Salinity in the Songkhla Lake ranges from fresh water in the northern most to saline water in the outer section. The outer section is connected to the sea of the Gulf of Thailand through a deep and narrow outlet at Songkhla city. Several streams are flowing into the Lake. Two important canals are located in the outer section of the Lake. Firstly, U-Taphao canal which is the main source of freshwater draining into the outer part, with a length of 68 km, originating from the Sadao district, in the Songkhla province. The canal is flowing through a large city (Hat Yai) before entering the lake. Secondly, Phawong canal is a short canal with a length of around 5.5 km and both sides of canal are densely covered with the mangrove trees.

The total of 199 industrial plants (metals, metal products, machinery) are located in Songkhla province and only the Khlong U-Taphao basin serves a total of 110 factories. The population of Songkhla province in December 2015 is approximately 1410577 people, with a population of 719927 people belonging to the 4 districts adjacent to the study area. At present, the condition of Songkhla Lake is deteriorating due to many environmental problems such as waste water, mangrove deforestation and increases of shrimp farms around the lake. However, from the Lansat TM satellite data in 1991, the mangrove forest in Songkla Lake is approximately 5620 ha but it is presently found only a small patch and expected to not exceed 1600 ha attributed to the outbreak of shrimp diseases resulting in substantially abandoned shrimp farms. Mangrove forests in the Songkhla Lake basin found in Songkhla province are emerging mangrove forests. The mangrove forests are found at the mouths of the rivers and in the areas that are mostly muddy. The dominant mangrove species in the middle part of the lake is Sonneratia caseolaris whereas the dominant ones in the outer section of the lake are Rhizophora apiculate and Rhizophora mucronate.

Sample collection
The mangrove sediment samples were collected in August 2016 from eight stations at the Songkhla Lake. Stations 1 and 2 are in the middle section of the lake and the dominant mangrove plants is Sonneratia caseolaris while station 2 is Rhizophora apiculata. Stations 3 and 4 are located at Kuannieng district with the dominance of Rhizophora apiculata vegetation and Sonneratia caseolaris, respectively. Stations 5 and 6 are situated near to each other and in front of Phawong canal. Station 5 has dominant vegetation of Rhizophora apiculata whereas there is mostly Sonneratia caseolaris at station 6. Station 7 at Yoh island, the dominant plants is Rhizophora apiculata, while at station 8 located at the mouth of U-Taphao canal, Sonneratia caseolaris is the predominant plant species. Triplicates of sediment samples were collected at each site at a depth of 10 cm.
The samples were then measured by ICP-MS (Perkin Elmer Elan 9000). The sediment certified reference material (SRM 1646a) were displayed in Table 1, which demonstrated the accuracy of the analytical procedure. The actual and observed values with the percent recovery for the certified sediment material; SRM 1646/estuarine sediment was similarly analyzed to validate the accuracy of the analytical procedure. The actual and observed values with the percent recovery for the certified sediment material (SRM 1646a) were displayed in Table 1, which demonstrated the validity of the methods applied.

**Sequential extraction**

Sequential extraction was performed using the revised BCR protocol\(^\text{12}\), briefly described as follows.

**Step 1 (Fraction 1, exchangeable and acid soluble fractions):** 40 ml of 0.11 mol/l acetic acid was added to 1 g of the air-dried sediment sample in a 50 ml polyethylene centrifuge tube. The tube was shaken for 16 h at room temperature at a speed of 23 ± 1 rpm. The extract was separated from the solid residue by centrifugation (3000 rpm for 20 min), decanted into a polyethylene bottle and stored at 4°C. The residue was washed by shaking with 20 ml of distilled water for 15 min, centrifuging after which the supernatant was discarded. This step is for determining the dissolved and exchangeable metals.

**Step 2 (Fraction 2, reducible fraction):** 40 ml of 0.5 mol/l hydroxylamine hydrochloride (adjusted to pH 1.5 by addition of a fixed amount of HNO\(_3\)) was added to the residue from Step 1 and the extraction performed as in Step 1 above. This step is for analyzing the metals bound to organic matter.

**Step 3 (Fraction 3, oxidizable fraction):** 10 ml of 8.8 mol/l hydrogen peroxide was added in aliquots to the residue from Step 2. The vessel was covered loosely and the contents digested at room temperature for 1 h with occasional agitation. It was then placed in a water bath and digested at 85°C until the volume was reduced to less than 3 ml. Another 10 ml of the hydrogen peroxide was added, and further heated to near dryness. Thereafter, 50 ml of 1.0 mol/l ammonium acetate (adjusted to pH 2 with HNO\(_3\)) was added and the extraction performed as in the previous steps. This step is for determining the metals bound to carbonate and Fe-Mn oxides.

**Step 4 (Residual fraction):** The residue from Step 3 was transferred into a suitable vessel and the metal content determined by microwave-assisted digestion with *aqua regia*. This step is for analyzing the metals contained in their primary and secondary minerals.

The trace element (Zn, As, Cd, and Pb) content of each fraction was analyzed using ICP-MS model Perkin Elmer Elan 9000.

**Redox potential (Eh) and pH measurement**

The measurements of redox potential (Eh) and pH in the mangrove sediments were performed in the field with a combined pH/Eh meter (IQ 140 pH/mV/Temp/ORP). Redox was measured using a Pt redox electrode combined with a Ag/AgCl, [KCl] = 3 mol/l reference electrode (IQ/model ORP110-GS) and the pH measurements were performed using a combination glass electrode with a Ag/AgCl, [KCl] = 3 mol/l reference electrode (IQ 140/model pH30-GS). Before the measurement, the pH and Eh probes were calibrated with buffer solution of pH 4 and pH 7. 0.003 M Potassium ferrocyanide in 0.1 M KCl, and a saturated potassium chloride solution were used to store electrodes. The pH and Eh measurements were measured immediately in the field and before the measurement the electrode was marked at the desired depth of measurement. For this study the mark (desired depth) was 4–5 cm. Method for measuring: The

| No | Element | Certified (mg/kg) | Observed (mg/kg) | Recovery (%) |
|----|---------|------------------|------------------|-------------|
| 1  | Zn      | 48.90            | 44.60            | 91          |
| 2  | As      | 6.23             | 5.70             | 91          |
| 3  | Cd      | 0.15             | 0.13             | 87          |
| 4  | Pb      | 11.70            | 11.94            | 102         |
sediment sample was placed into a plastic container approximately at 10 cm depth. Measurement was conducted by carefully inserting each probe at a time to avoid disturbing the sediment as well as air contamination. Caution was taken not to have gaps between the electrode and the sediment. Start by inserting the Eh probe and wait until the reading values was quite stable which took longer time than that of the pH measurement and Eh values were recorded afterwards. Change to the pH probe for pH measurement and wait until the pH value was stable for recording.

Contamination and ecological risk assessment

Individual and global contamination factors

To study the retention of the studied elements in sediment samples, the individual contamination factors (ICF) were calculated from the results of the speciation study by dividing the sum of the first three extractions by the residual fraction for each site. The global contamination factor (GCF) for each site was calculated by summing the ICF obtained for the studied elements at each site. The equation is expressed as follows:

$$ICF_{metal} = \frac{C_{nonresistant}}{C_{resistant}}$$

$$GCF = \sum_{i=1}^{n} ICF_i$$

where $C_{nonresistant} = $ sum of first three extractions and $C_{resistant} = $ residual fraction.

In this study ICF and GCF classifications were explained as recommended by Zhao, et al as follows: ICF < 0 and GCF < 6 indicated low; 1 < ICF < 3 and GCF < 12 moderate; 3 < ICF < 6 and 12 < GCF < 24 considerable; and ICF > 6 and GCF > 24 high contamination.

Risk assessment code

Risk assessment code (RAC) is an assessment index of the risk of metal existence on the aquatic environment based on the chemical fraction of metal interaction with sediment particle which is potentially absorbed by the organisms. Risk assessment code was obtained by calculating the percentage of exchangeable and carbonate (acid soluble) fractions in the sediment. It is classified to be 5 classes as follows: < 1% there is no risk for aquatic system; 1–10% indicating low risk; 11–30% medium risk; 31–50% high risk; and > 50% very high risk.

Table 2  Sediment properties and trace elements in mangrove sediment samples obtained from Songkhla Lake.

| St. | pH water | Salinity | pH sed | Eh (mV) | As (µg/g dry weight) | Zn (µg/g dry weight) | Cd (µg/g dry weight) | Pb (µg/g dry weight) |
|-----|----------|----------|--------|--------|----------------------|---------------------|---------------------|---------------------|
| 1   | 9.49     | 4        | 9.00   | -179   | 33.7                 | 66.3                | 0.083               | 74.4                |
| 2   | 9.17     | 4        | 8.10   | -135   | 35.4                 | 77.0                | 0.075               | 79.7                |
| 3   | 7.45     | 25       | 6.95   | -106   | 30.0                 | 52.5                | 0.045               | 56.5                |
| 4   | 7.45     | 25       | 6.95   | -106   | 14.9                 | 34.5                | 0.036               | 38.9                |
| 5   | 7.93     | 26       | 7.27   | -200   | 58.1                 | 104.3               | 0.084               | 78.5                |
| 6   | 7.93     | 26       | 7.27   | -200   | 50.0                 | 100.5               | 0.074               | 78.4                |
| 7   | 7.70     | 30       | 7.21   | -206   | 34.6                 | 114.3               | 0.108               | 52.1                |
| 8   | 7.07     | 16       | 6.71   | -108   | 47.0                 | 116.7               | 0.071               | 43.4                |

St. = Station, sed = sediment.

Statistical analysis

Correlations between variables were carried out using a nonparametric test, the Spearman correlation test at the $p < 0.05$ significant level. All descriptive statistical tests were performed using Microsoft Excel.

RESULTS

Sediment characteristics

The level of pH in water ranged from 7.07–9.49 (Table 2) while in the sediment ranged from 6.71–9.00. Surprisingly the highest pH level of sediment and water was found at Kukhut (station 1) and Ko Khob (station 2) which were located in the middle of Songkhla Lake. The high pH values of both sediment and water were probably caused by the waste water from cleaning the animal farms (chicken, swine, fish) surrounding these areas was drained into rivers and eventually to the Songkhla Lake since lime was commonly used as disinfection agents for cleaning the animal farms to prevent and/or treat disease outbreaks. Hence, the lime present in cleaning water of animal farms was probably responsible for the high pH values of sediment and water in stations 1 and 2. Salinity ranged from 4–30 ppt. The salt water was in the outer section of the lake (stations 3–8) while low saline was found in the middle of the lake. Redox potential (Eh) value showed anoxic conditions in all stations with the maximum value at Koh Yoh (station 7).

Trace metal concentration in sediments

The range of heavy metal in µg/g dry weight ranged from 14.90–58.10 for As; 34.50–116.70 for Zn; 0.036–0.108 for Cd; 38.9–79.0 for Pb. The highest concentrations of As were found at the mouth of Phawong canal (stations 5 and 6) followed by Kokhob (station 2) and Ko Yoh (station 7). Zn was highest at the U-Taphao canal (station 8) followed
Fig. 1 (a-d) Fractionation of trace elements (Zn, As, Cd, Pb) in mangrove sediments in Songkhla Lake.

by Ko Yoh (station 7) and Phawong canal (stations 5 and 6). Cd showed a similar level trend in all stations but maximum at Ko Yoh. Pb concentrations were highest at Ko Khob (station 2) and Phawong canal (stations 5 and 6).

Element speciation

The speciation of Zn, As, Cd, and Pb in the mangrove sediment samples from the Songkhla Lake using the BCR protocol was presented in Fig. 1. The results of the sequential extraction for overall stations were as follows.

Exchangeable and acid soluble fraction (F1): Zn (37.20–64.42%) and Cd (63.44–77.50%) were found dominant in the acid-soluble fraction F1, associated with exchangeable cations and carbonates for all stations except station 7.

Reducible fraction (F2): Pb(62.01–89.48%) was found dominant in F2; As (49.92–73.45%) was found dominant in F2 at stations 2, 4, 6, and 8. This fraction is readily available with medium mobility and may be released into the environment under unstable anoxic conditions.

Oxidizable fraction (F3): As (48.71–68.02%) was found dominant in F3 at stations 1, 3, 5, and 7. Metals bound to organic matter are reasonably stable in nature, however, under strong oxidizing conditions such as currents, dredging, flooding and tides the organic matter can be degraded, hence leading to a release of heavy metals bound to this component.

Residual fraction (F4): The residual solid normally consists of mainly primary and secondary minerals that retained heavy metals within their crystal structure once the first three fractions have been removed, hence, they are regarded as immobile and unavailable. This study showed percentages of residual fraction as follows; Zn ranged from 1.43–6.34%, As ranged from 1.65–10.25%, Cd ranged from 2.17–13.18%, and Pb ranged from 2.88–12.30%. Overall, the relative contents of trace elements in all fractions at every station were summarized as follows.

Zn: acid soluble > reducible > oxidizable > residual;
As: oxidizable > reducible > residual > acid soluble (at stations 2,4,6,8);
As: reducible > oxidizable > residual > acid soluble (at stations 1,3,5,7);
Cd: acid soluble > reducible > residual > oxidizable;
Pb: reducible > oxidizable > residual > acid soluble.

Fractions of Cd and Zn in every station were found to be dominant in the acid-soluble fraction (F1), associated with exchangeable cations and carbonates. The second most dominant fraction for Zn was the Fe-Mn oxyhydroxide fraction (F2), which might be due to the high stability constants of Zn oxide and the ability of Fe oxides to adsorb considerable quantities of Zn. The As presence in samples was dominant and associated with oxidizable fraction (F3), bound to the sulphides and organic matter followed by reducible fraction (F2), associated with Fe-Mn oxyhydroxides and oxides fraction. Pb was dominant associated with reducible fraction (F2), associated with Fe-Mn oxyhydroxides and oxides fraction. Low abundance of Pb in the F1 and F4 fractions implied a low release and availability under subtoxic and natural conditions. Its abundance did not pose a threat to the sediment quality and biota. Cd was dominant with the exchangeable phase and the reducible form (F2).
Table 3  Sediment quality guidelines (SQGs) based on its
effects to benthic-dwelling species (µg/g dry weight).

| Element | US EPA toxicity | NOAA |
|---------|-----------------|------|
|         | None | Moderate | Heavy | ERL  | ERM  |
| Pb      | < 40 | 40–60    | >60   | 46.7 | 218  |
| As      | < 3  | 3–8      | >8    | 8.2  | 70   |
| Cd      |      |          | >6    | 1.2  | 9.6  |
| Zn      | < 90 | 90–200   | >200  | 150  | 410  |

EPA = United States Environmental Protection Agency; NOAA = National Oceanic and Atmospheric Administration.

Fig. 2  Mobility fraction of trace elements in mangrove sediment in Songkhla Lake.

DISCUSSION

In order to evaluate whether the level of contamination of the sediments is due to natural or anthropogenic sources. The metal concentrations are compared with regional background values. Regional background values assessed from core sediment samples were reported by Choi, et al\textsuperscript{25} and offshore sediments in the Gulf of Thailand by Shazili, et al\textsuperscript{26}. Background levels varied from 55–115 µg/g dry weight for Zn, from 5–9 µg/g dry weight for As, from 0.03–0.2 µg/g dry weight for Cd, and from 15–30 µg/g dry weight for Pb. In this study As and Pb concentrations were higher than those of the background values as reported by Choi, et al\textsuperscript{25}. Several sediment quality guidelines (SQGs) for the assessment of the sediment quality using chemical and biological effects databases have been established. These SQGs were summarized in Table 3. NOAA presents ERL (effects range low) and ERM (effects range mean) guidelines for estuarine and marine environments which represent the 10 and 50 percentiles of adverse biological effects\textsuperscript{27}. The US-EPA has also made classifications (non-polluted, moderately polluted, heavily polluted) based on toxicity tests\textsuperscript{28}. Based on US-EPA, As and Pb were classified to be moderately polluted except stations 1, 2, 5, and 6. According to NOAA, the maximum value of As was classified as effects of mean range whereas the observed Pb levels was classified as effects of low range. Regarding to the expansion and industrialization of the communities surrounded the Lake, it can make a lake system receiving runoff and wastewater from the surrounding areas. Therefore, sources of pollutants introduced to the mangrove system before entering the lake system include municipal wastes from the Hat Yai and Songkhla cities, industrial wastes mainly from the rubber industries, seafood processing industries, mining activities and pollution from boats in the Songkhla harbour\textsuperscript{29}.

The sequential extraction procedure employed in the study was used to assess the bioavailability of heavy metals in sediments. Bioavailability refers to the proportion of metals that can be released into the water (first three fractions). It is now widely recognized that the environmental impact by heavy metals does not simply depend on their concentrations but, critically, on their forms\textsuperscript{30}. Binding forms of heavy metals to sediment particles influence the metal bioavailability\textsuperscript{4} and the forms of metals in sediments that are important to determine their ecotoxicological risk to biota\textsuperscript{22}. Several authors\textsuperscript{22} have demonstrated that metals associated with the exchangeable and carbonate fractions (F1) have an anthropogenic origin, while the residual fraction (F4) corresponds to metals with a lithogenic origin\textsuperscript{5}. In this study the mobility fraction (F1+F2+F3) of trace elements are shown in Fig. 2. The association with the reducible fraction (F2) as the second most dominant fraction for Zn, As, and Cd suggested that these metals played an important role in the leaching of metals into the environment. Cd and Zn were released mostly in the acid exchangeable step as exchangeable cations which were concordant to the result from Li, et al\textsuperscript{31} resulting in their great bioavailability and potential risk to crops and animals. The behavior of As in natural waters depends on the pH and redox conditions. In oxidized sediments, arsenate (As\textsuperscript{5+}) is the dominant species, primarily bound to iron oxy-hydroxides. In reducing environments, arsenate may be reduced to the arsenite form (As\textsuperscript{3+}), which is more mobile and toxic than the arsenate form\textsuperscript{32}. The outer section of the lake is thus a vulnerable area regarding the mobility of As, combining both important riverine inputs and reduced sediment conditions that promote the mobilization of As.

The potential risks of the trace elements to
Table 4 The comparison of trace element concentrations (As, Cd, Pb, and Zn) in sediments (µg/g dry weight) from Songkhla Lake and other areas.

| Area                                      | As   | Cd   | Pb   | Zn   |
|-------------------------------------------|------|------|------|------|
| Songkhla Lake (Ref. 29)                   | 5.1–25.7 |      |      |      |
| Songkhla Lake (Ref. 34)                   | 20–22 | 0.21–0.28 | 31–35 |      |
| Songkhla Lake (Ref. 37)                   | 20.7 | 55 |      |      |
| Futian, China (Ref. 35)                   | 152.4 | 70.7 |      |      |
| Kelantan Delta (Ref. 37)                  | 18.3–34.9 | 31.3–75.8 |      |      |
| Punta Mala Bay, Panama (Ref. 36)          |      | 78.2 |      |      |
| Pearl River, China (Ref. 31)              | 2.79–4.66 | 24.8–112.1 |  |
| Hong Kong mangrove swamps (Ref. 38)       | 3 | 80 | 240 |      |
| Songkhla Lake (this study)                | 14.9–58.1 | 0.071–0.108 | 38.9–79.7 | 34.5–116.7 |

Table 5 Correlation coefficients (r) among the total amounts of different metals and other sediment properties.

| pHwater | Salinity | pHsed | Eh   | As   | Zn   | Cd   | Pb   |
|---------|----------|-------|------|------|------|------|------|
| pHwater |          |       |      |      |      |      |      |
| Salinity| −0.774*  |       |      |      |      |      |      |
| pHsed   | 0.943**  | −0.755* |      |      |      |      |      |
| Eh      | −0.322   | −0.207 | −0.315 |      |      |      |      |
| As      | −0.024   | 0.080 | −0.077 | −0.540 |      |      |      |
| Zn      | −0.175   | 0.173 | −0.197 | −0.550 | 0.800' |      |      |
| Cd      | 0.321    | −0.055 | 0.316 | −0.800' | 0.528 | 0.777' |      |
| Pb      | 0.714'   | −0.366 | 0.568 | −0.589 | 0.548 | 0.187 | 0.395 |

*, p < 0.05 (2-tailed); **, p < 0.01 (2-tailed).

Songkhla Lake, individual and global contamination factors were calculated. The GCF is important as it reflects the overall potential risks posed by the toxic elements to the environment and biota. Our study showed ICF > 6 and the GC > 24 for all elements (Zn, As, Cd, and Pb). For the risk assessment code, only Cd > 50% in all stations was classified as very high risk for aquatic organisms whereas As was classified as low risk. Pb was classified as low risk except at stations 2 and 4. Zn was classified as very high risk (stations 1, 3, and 8), medium risk (stations 2, 4, and 5), and low risk (station 7) for aquatic organisms. In previous study, the increased trace metal concentration was caused by anthropogenic activities in the surrounding areas. The result of the study of heavy metals in sediment-plant system in mangrove forest, South China Sea conducted by Li, et al. well agreed with our result. Furthermore, the geo-accumulation index, potential ecological risk index and risk assessment code demonstrated that heavy metals posed a considerable ecological risk, especially for cadmium (Cd).

Comparison of this study with the previous data from Songkhla Lake as well as other areas in the world is shown in Table 4. The result showed that especially the outer section of the lake, in particular the sediments at the mouths of the Phawong and U-Taphao canals and Yoh island were significantly enriched in trace elements due to municipal, agricultural and industrial discharges entering the lake through the canals. The U-Taphao and Phawong canals were important sources of As, Cd, and Pb. Considering the data obtained from the report since 2007, it could be observed that higher As and Pb concentrations in sediment were tend to increase especially in the outer section of Songkhla Lake due to urban expansion and industrialization. The maximum value of Pb of this study was similar to that of Punta Malala Bay, Panama, higher than that of Fuitan, China, but less than that of Kelantan Delta, Malaysia. Cd and Zn concentrations from this study was lower than those in Pearl River, China and Hong Kong mangrove swamp. According to the growth of the industries and the release of waste from factories and communities into the rivers, canals and mangrove forests suggested pollution from anthropogenic levels of trace metals in surface sediments. This indicated strong influence of anthropogenic processes, and diagenetic processes controlled the trace metal enrichment of core sediments of this estuary.
In conclusion, the trace element concentrations of As and Pb in mangrove sediments of the study area were classified to be moderately to heavily polluted according to USEPA except some stations. Furthermore, sequential extraction analysis using BCR technique of mangrove sediments revealed that they were predominantly found in bioavailability forms. This is a considerable environmental concern since they represent the most labile and potentially mobile forms and readily become bioavailable. Result from ecological risk assessment found that Cd was very high risk for aquatic organisms. It would be the main potential risk and the sediment quality was no longer meeting the demand of the current wetland utilization strategies. Therefore it urgently needs to regularly monitor especially for As, Pb, and Cd, since they might be harmful to the benthic organisms and finally threat to human health.

Acknowledgements: This work was financially supported by the Prince of Songkla University under contract No. CORS90528S.

REFERENCES

1. Jones B, Turkie A (1997) Distribution and speciation of heavy metals in surficial sediments from the Tees Estuary, northwest England. Mar Pollut Bull 34, 768–779.
2. Andrade RA, Sanders CJ, Boaventura G, Patchineelam SR (2012) Pyritization of trace metals in mangrove sediments. Environ Earth Sci 67, 1757–1762.
3. Kumar A, Ramanathan AL (2015) Speciation of selected trace metals (Fe, Mn, Cu and Zn) with depth in the sediments of Sundarban mangroves: India and Bangladesh. J Soil Sediment 15, 2476–2486.
4. Bacon JR, Davidson CM (2008) Is there a future for sequential chemical extraction? Analyst 133, 25–46.
5. Yu R, Hu G, Wang L (2001) Speciation and ecological risk of heavy metals in intertidal sediments of Quanzhou Bay, China. Environ Monit Assess 163, 241–252.
6. Luoma SN, Rainbow PS (2008) Metal Contamination in Aquatic Environments: Science and Lateral Management, Cambridge University Press, Cambridge.
7. Gibson MJ, Farmer JG (1986) Multi-step sequential chemical extraction of heavy metals from urban soils. Environ Pollut Ser B Chem Phys 11, 117–135.
8. Ure AM, Quevauviller P, Muntau H, Griepink B (1993) Speciation of heavy metal insoils and sediments an account of the improvement and harmonisation of extraction techniques undertaken under the auspices of the BCR of the commission of the European Communities. Int J Environ Anal Chem 51, 135–151.
9. Herman P, Leeuwen V, Town RM, Buffle J, Cleven RFMJ, Daison W, Puy J, Riemsdijk WHV, et al (2005) Dynamic speciation analysis and bioavailability of metals in aquatic systems. Environ Sci Technol 39, 8545–8556.
10. Das AK, Chakraborty R, Cervera ML, Guardia M (1995) Metal speciation in solid matrices. Talanta 42, 1007–1030.
11. Sahuquillo A, Rigol A, Rauret G (2003) Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments. TrAC Trends Anal Chem 22, 153–159.
12. Rauret G, López-Sarache JF, Sahuquillo A, Rubio R, Davidson C, Ure A, Quevauviller P (1999) Improvement of the BCR three-step sequential extraction procedure prior to the certification of new sediment and soil reference materials. J Environ Monit 1, 57–61.
13. Songkhla Development Plan 2018–2021 (2019) Available at www.songkhla.go.th/news_develop_plan. [Assessed on 24 Oct 2019]
14. Aunjjangwang N (2013) Contamination of arsenic and lead in sediment of U-Taphao canal. MSc thesis, Prince of Songkla Univ, Thailand.
15. Bamrungrat N (2010) Techniques for Restoring Songkhla Lake Mangrove Forests, Prince of Songkla Univ, Thailand.
16. Meksumpun J (2003) Sediments, Department of Fishery Biology, Faculty of Fisheries, Kasetsart Univ, Thailand.
17. Noriki SK, Nakanishi T, Fukawa M, Uematsu T, Uchida S, Tsunogai (1980) Use of a Teflon vessel for the decomposition followed by the determination of chemical constituents of various marine samples. Bull Fac Fish Hokkaido Univ 31, 354–362.
18. Soliman NF, El Zokim GM, Okbah MA (2018) Risk assessment and chemical fractionation of selected elements in surface sediments from Lake Qarun, Egypt using modified BCR technique. Chemosphere 191, 262–271.
19. Ikem A, Egiebor NO, Nyavor K (2003) Trace elements in water, fish and sediment from Tuskegee Lake, Southeastern USA. Water Air Soil Pollut 149, 51–75.
20. Zhao S, Feng C, Yang Y, Niu J, Shen Z (2012) Risk assessment of sedimentary metals in the Yangtze Estuary: new evidence of the relationships between two typical index methods. J Hazard Mater 241–242, 164–172.
21. Najamuddin Prartono T, Sanusi HS, Nurjaya IW (2016) Seasonal distribution and geochemical fractionation of heavy metals from surface sediment in a...
tropical estuary of Jeneberang River, Indonesia. *Mar Poll Bull* **111**, 456–462.

22. Sundaray SK, Nayak BB, Lina S, Bhatta D (2011) Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments: a case study: Mahanadi basin, India. *J Hazard Mater* **186**, 1837–1846.

23. Passos EA, Alves JPH (2011) Metal fractionation in the sediments for sergipe river, northeast, Brazil. *J Braz Chem Soc* **22**, 828–835.

24. MacFarlane GR, Burchett MD (2000) Cellular distribution of copper, lead and zinc in the grey mangrove, *Avicennia marina* (Forsk.) Vierh. *Aquat Bot* **68**, 45–59.

25. Choi KY, Kim SH, Chon HT (2008) Distributions and accumulations of heavy metals in the sediments of harbors and coastal areas in Korea. In: *Proceedings of the International Symposia on Geoscience Resources and Environments of Asian Terranes*, Bangkok, Thailand, pp 474–476.

26. Shazili NAM, Rashid MKA, Husain ML, Nordin A, Ali S (1999) Trace metals in the surface sediments of the South China Sea, Area I: Gulf of Thailand and East Coast of Peninsular Malaysia. In: *Proceedings of the First Technical Seminar on Marine Fishery Resources Survey in the South China Sea Area I: Gulf of Thailand and East Coast of Peninsular Malaysia*, Bangkok, Thailand, pp 73–85.

27. NOAA (1999) Sediment quality guidelines developed for the national status and trends program. Available at response.restoration.noaa.gov/book_shelf/121_sedi_qual_guide.pdf.

28. Filgueiras AV, Lavilla I, Bendicho C (2004) Evaluation of distribution, mobility and binding behaviour of heavy metals in superficial sediments of Louro River (Galicia, Spain) using chemometric analysis: A case study. *Sci Total Environ* **330**, 115–129.

29. Sompongchatayakul P, Sirinawin W (2007) Arsenic, chromium and mercury in surface sediment of Songkhla Lake system, Thailand. *Asian J Water Environ Pollut* **4**, 17–24.

30. Tokaloglu S, Kartal S, Elçi L (2000) Determination of heavy metals and their speciation in lake sediments by flame atomic absorption spectrometry after a four-stage sequential extraction procedure. *Anal Chim Acta* **413**, 33–40.

31. Li Q, Wu Z, Chu B, Zhang N, Cai S, Fang J (2007) Heavy metals in coastal wetland sediments of the Pearl River Estuary, China. *Environ Pollut* **149**, 158–164.

32. Ryu JI, Gao S, Dahlgren RA, Zierenberg RA (2002) Arsenic distribution, speciation and solubility in shallow groundwater of Owens Dry Lake, California. *Geochim Cosmochim Acta* **66**, 2981–2994.

33. Yao ZG, Bao ZY, Gao P, Zhang JL, Guo YP, Hu ZJ, Li BL (2006) Speciation of trace elements in sediments from Dongting Lake, central China. In: Brebbia CA, Antunes do Carmo JA (eds) *Water Pollution VIII: Modelling, Monitoring and Management*, WIT Press, Southampton, pp 119–128.

34. Pradit S, Gao Y, Failoon A, Baeyens W, Leermakers M (2013) Application of DET (diffusive equilibrium in thin films) and DGT (diffusive gradients in thin films) techniques in the study of the mobility of sediment-bound metals in the outer section of Songkhla Lake, Southern Thailand. *Environ Monitor Assess* **185**, 4207–4220.

35. Li R, Chai M, Qiu Y (2016) Distribution fraction and ecological assessment of heavy metals in sediment-plant system in mangrove forest, South China Sea. *Plos One* **11**, ID e0147308.

36. Defew LH, Mair JM, Guzman HM (2005) An assessment of metal contamination in mangrove sediments and leaves and from Punta Mala Bay, Pacific Panama. *Mar Pollut Bull* **50**, 547–552.

37. Baruddin NA, Shazili NAM, Pradit S (2017) Sequential extraction analysis of heavy metals in relation to bioaccumulation in mangrove, *Rhizophora mucronata* from Kelantan Delta, Malaysia. *AACL Bioflux* **10**, 172–181.

38. Tam NFY, Wong YS (2000) Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. *Environ Pollut* **110**, 195–205.

39. Miola B, Morais JO (2016) Trace metal concentrations in tropical mangrove sediments, NE Brazil. *Mar Pollut Bull* **102**, 206–209.