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Spatial Distribution of Bioavailable Metal Concentrations and Total Metal Concentration-depth Relationship along the Sediment Profile within Phuket Bay

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Abstract

Heavy metals in coastal sediments can adversely affect human health and the environment. The distribution and metal bioavailability of Pb and Zn in 21 sediment samples collected from Phuket Bay, Phuket, Thailand using the first-two steps of sequential extraction proposed by the Standards, Measurements and Testing programme (known as BCR) was determined. The results showed that Pb formed weak complexes contributing up to 11.2% to 33% of its total concentration (1.7 to 7.5 mg kg^{-1}) in the first fraction (BCR1), while Zn in the BCR1 fraction ranged from 4.9% to 9.9%. The results suggest that Pb could easily enter the food chain and the main cause of heavy metal contamination is related to local anthropogenic activities and effects of urbanization in the region, such as the ferry terminal, boatyards, and other maritime activities. Meanwhile, the enrichment factors of the metals showed minor to moderately severe enrichment. The metal concentration-depth relationship along the sediment profile showed metal concentration in each layer of the sediment core ranging from 45.4 to 88 mg Zn kg^{-1} and from 12.7 to 44.5 mg Pb kg^{-1}. Based on the changes in heavy metal accumulation in the sediment core, and the calculated the enrichment factor versus depth, these allowed us to understand the historical variability in pollutant linked to past activities in Phuket Bay.

Keywords: Bioavailability; Heavy metals; Phuket; Sediment

Introduction

In recent years pollution of the aquatic environment has become a more serious problem and is now a matter of worldwide concern due to the accumulation of contaminants from rapidly expanding economies, mining activities,

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industrial development, and wastewater discharge from municipal areas [1]. Heavy metals are pollutants of increasing concern that can adversely affect human health and the natural ecosystems because of their accumulation and persistence in the environment [2]. Significant amounts of heavy metals have been discarded into the environment, and sediments are the principal reservoir or sink for these heavy metals, especially in coastal environments [3]. The transfer of heavy metals to the food chain can cause problems to human health, including cell death, changes into the structure and function of cells, cancer, disorders related to the transcription of the genetic code, and damage to the chromosomes, genes, and DNA [4]. When heavy metals are discharged into coastal ecosystems, their transport depends largely on the metal species, and how readily they can be dissolved and suspended in water and adsorbed or accumulated in sediments [5]. The mobility of heavy metals in sediments are very important for understanding the migration of these contaminants. The information on the distribution of heavy metals can be used to deduce the sources of contaminants [6]. Naturally occurring metals are mainly found as silicates and primary minerals, while the high mobility of metals introduced by anthropogenic activities are often associated with their solubility and mobile-reactive form, including soluble, ion-exchangeable Fe/Mn oxides, carbonates, and hydroxides which can be potentially available for biological uptake by an aquatic organism [2, 7]. For these reasons, coastal sediments are an essential determinant of the contamination level and toxicity in a coastal environment. Sediment gradually accumulates elements from environmental water; the older elements are in deeper layers and buried with older sediments, while recent sediments are found in the upper layers [8]. The changes observed in the marine environment preserved in the sediments can act as a record of human impact in the area [9]. A combination of sediment dating with the vertical distribution of heavy metals in sediments can be used in environmental status assessments to allow the identification of potential pollution sources and the pollution history based on dating of the sediment core [9–10].

Phuket is the largest island in Thailand, located in the Andaman Sea in southern Thailand and is Thailand's most popular tourist island [11]. Phuket Bay is located at the southeast of the Phuket Island and considered to be a primary area for maritime activities [12]. However, Phuket Bay is becoming increasingly polluted from anthropogenic sources, and there is an increased risk to public health from heavy metal contamination due to rapid urbanization, discontinued tin (Sn)-mining done with ponds, discharge of wastewater from local communities, and the development of human activities including maritime activities in the coastal zone [13]. The importance of sediments to coastal ecosystems and the environment has been discussed in relation to various parts of Thailand, but the pollution levels and toxicity caused by heavy metal contamination in Phuket Bay has attracted little prior research attention [14–15]. Determinations of metal contamination in this area have been conducted in the past and a high Pb concentration was observed in the sediments at Phuket Bay, in the range from 17 to 113 mg kg^{-1}, due to effluents from various community sources [16]. Excessive metals in the environment can have a detrimental effect on humans because of their tendency to bioaccumulate in the food chain, and studies should be conducted, along with continuous monitoring, to determine whether this risk is increasing. In this study, surface and core sediment samples from Phuket Bay were analyzed with the following objectives: (1) to determine the distribution of lead (Pb) and zinc (Zn) in sediments in Phuket Bay; (2) to assess the status of marine environment regarding its pollution with heavy metals (Pb and Zn) by using bioavailable metal concentrations, risk

assessment code (RAC), and enrichment factor (EF). The information relating to the heavy metals selected for this study in the sediments can be used to obtain site-specific information about the environmental and contamination characteristics of Phuket Bay, which are necessary for good management and environmental risk assessment in the Andaman region in relation to human activities.

Materials and methods

1) Sample collection

Twenty-one sediment samples (R1 to R21) were collected in September 2017 at 21 stations identified as potentially significant pollution sources within the area, having maritime activities such as commercial piers, fishing piers, and boatyards at R1 to R14, and sources of wastewater from the communities, maritime activities and other anthropogenic sources at R15 to R21 (Figure 1). The sediment sampling was carried out based on a design in the form of grid lines in order to cover the area of Phuket Bay. The sediments from each sampling station were collected from the surface layer of sediment at depths varying between -0.6 and -15.5 m. The coordinates of each sampling site were recorded based on the Global Positioning System (GPS) and the depths of the sediments collected were also recorded (Table 1). The sediment core from station R15 was sampled using a Russian corer (100 cm in length and 12 cm in diameter) and cut into 5 cm-sections, producing a total of 20 sediment samples from 20 layers. Then, the sediment samples were stored in clean plastic bags and kept frozen in an icebox prior to processing and analysis. In the laboratory, the sediment samples were then transferred to an oven and dried at 60 ºC until constant weight was obtained, and the fraction smaller than 63 µm (sieve No. 230) was used for sediment analysis due to the strong association of metals with fine-grained sediments [17].

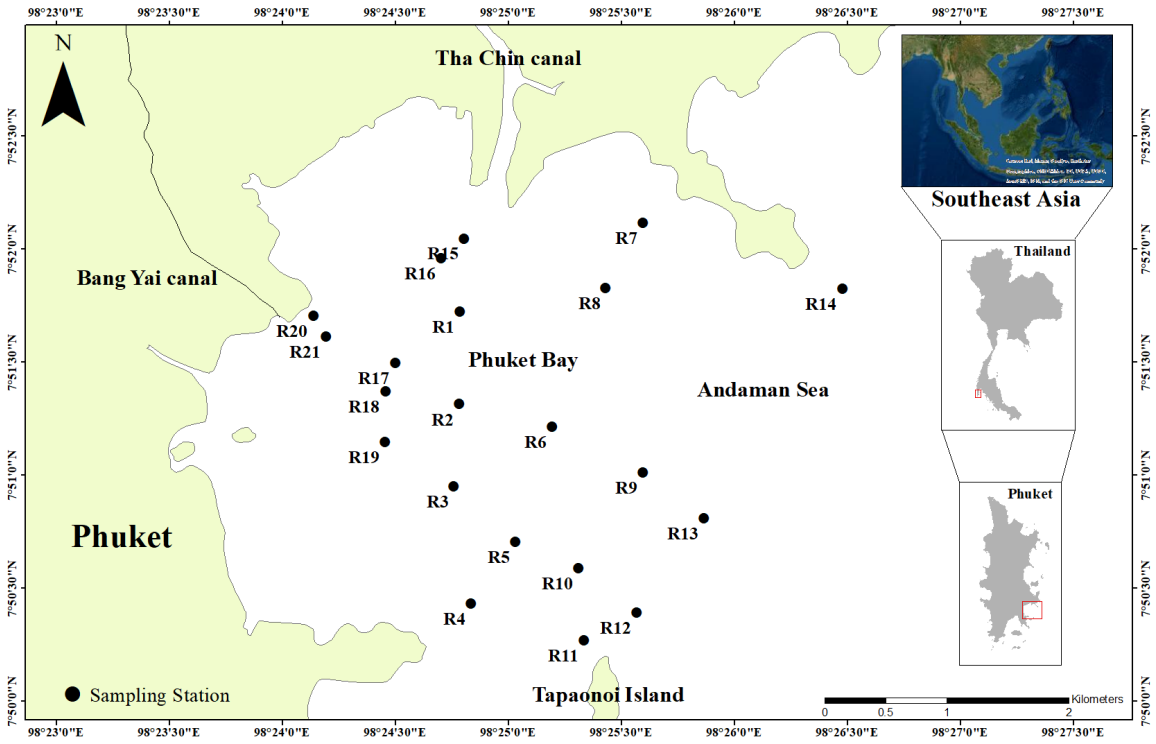

Figure 1 Study area at Phuket Bay, Thailand.

Table 1 Physico-chemical characteristic of sediments samples in Phuket Bay

Sediment location (UTM)		Depth from the surface layer of sediment (m)	pH	%TOC
R1	7°51'43.3"N 98°24'47.1"E	1.6	8.32±0.06	1.44
R2	7°51'18.8"N 98°24'47.0"E	4.4	8.34±0.01	0.61
R3	7°50'57.0"N 98°24'45.6"E	3.5	8.23±0.00	3.55
R4	7°50'25.9"N 98°24'50.1"E	6.1	8.11±0.01	0.99
R5	7°50'42.4"N 98°25'01.9"E	7.1	8.36±0.01	0.38
R6	7°51'12.9"N 98°25'11.7"E	3.2	8.71±0.08	0.03
R7	7°52'06.9"N 98°25'35.8"E	2.3	9.23±0.07	0.68
R8	7°51'49.6"N 98°25'25.9"E	3.9	8.57±0.03	1.64
R9	7°51'00.7"N 98°25'35.7"E	4.2	8.68±0.03	0.94
R10	7°50'35.3"N 98°25'18.7"E	4.0	8.58±0.00	0.24
R11	7°50'16.2"N 98°25'20.0"E	4.0	8.50±0.01	0.45
R12	7°50'23.6"N 98°25'34.2"E	4.8	8.84±0.01	0.22
R13	7°50'48.5"N 98°25'52.0"E	5.7	9.25±0.02	2.7
R14	7°51'49.5"N 98°26'28.6"E	15.5	8.82±0.07	0.16
R15	7°52'02.7"N 98°24'48.3"E	0.7	8.87±0.09	0.38
R16	7°51'57.5"N 98°24'42.3"E	0.6	9.25±0.05	1.13
R17	7°51'29.8"N 98°24'30.1"E	0.9	8.75±0.03	0.12
R18	7°51'22.2"N 98°24'27.5"E	0.9	8.80±0.01	0.22
R19	7°51'08.9"N 98°24'27.4"E	1.2	8.85±0.00	1.82
R20	7°51'42.2"N 98°24'08.3"E	3.75	7.1±0.62	0.19
R21	7°51'36.7"N 98°24'11.7"E	3.0	7.14±0.15	0.29
Min**imum**		0.6	8.11	0.03
Max**imum**		15.5	9.25	3.55

2) Sample analysis

Triplicate sediment samples from 21 stations were used for metal determinations (n = 63 samples). Other soil characteristics were determined to clarify their effects on the bioavailability of heavy metals in this study, using field-moist samples in the field. These included pH (of 1:5 soil/water suspensions) by pH meter and electrical conductivity (EC). The total organic carbon (%TOC) was analyzed in a laboratory using a CHNS/O element analyzer (2400 Series II; Perkin Elmer) after removing the carbonate with 10% HCl. The total Pb, Zn, Al, and Sn concentrations were determined by the Standard US-EPA Method 3052 (1996) [18] using aqua regia digestion with analysis by graphite furnace atomic absorption spectrometry (GFAAS) (AASZEEnit700 Analytik). All the laboratory glassware was cleaned in an HNO_3 (3%, v/v) bath overnight, followed by repeated rinsing with doubly distilled water and drying in an electric oven prior to use [18–19]. Metal fractionation according to the Standards, Measurements and Testing Programme (SM&T, known as BCR) was performed and the details of each extraction step are described in [20–21]. In this study, only the first two steps of BCR sequential extraction were analyzed under defined conditions to determine the more bioavailable forms of the metals [22–23]. The

exchangeable fraction (BCR1) extracted with acetic acid (CH_3COOH) is the metal sorbed to the surfaces of sediment particles [24]; and the reducible fraction (BCR2) extracted with hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) has the metals bound to hydrous oxides of Fe and Mn [22]. These two fractions (BCR1 and BCR2) are considered to be weakly bound and may equilibrate with the aqueous phase, thus becoming readily bioavailable [25]. Alternatively, the oxidizable fraction (BCR3) was metal bounded to organic substance and some precipitated sulfide-metal compounds; while the residual fraction (BCR4) refers was the remainder forms of metals. It is generally comprised of some primary (sulfide form) and secondary minerals.

3) Metal risk assessment

In this study, the enrichment factor (EF) was used to assess the enrichment degree or the intensity of metal deposition on the surface sediment (R1 to R21) and a sediment core from station R15 to differentiate between anthropogenic and natural sources of the metals [26–27]. The enrichment factor was calculated using aluminum (Al) as the normalizing element for crust-derived elements. Aluminum is the most abundant metal in the Earth's crust with few or no chemical reactions and not subjected to environmental influences such as oxidation or reduction in the marine sediment [28]. The EF is defined as Eq. 1.

$$EF = \frac{\left[\frac{M_x}{Al_x}\right]_{sample}}{\left[\frac{M_c}{Al_c}\right]_{crust}} \qquad \text{(Eq. 1)}$$

Here (Mx/Al_x) sample is the ratio of metal and Al concentrations in the sediment samples, and (Mc/Al_c) crust is the ratio of metal and Al concentrations of the background. The background average concentrations of Al, Pb and Zn in the Earth's crust of Phuket Province used in this study were: 115,360 mg kg^{-1}, 20 mg kg^{-1} and 80 mg kg^{-1}, respectively [29]. The EF can be interpreted as follows: EF <1 shows no enrichment; 1 to 3 minor enrichment; 3 to 5 moderate enrichment; 5 to 10 moderately severe enrichment; 10 to 25 severe enrichment; 25 to 50 very severe enrichment; and >50 extremely severe enrichment [30].

The risk assessment code (RAC) is an index used to determine the bioaccessibility of heavy metals based on chemical fractions. The percent contribution of exchangeable metal concentrations (%BCR1) with the total metal concentration obtained by aqua regia digestion was calculated to assess the risk associated with the release of heavy metals from the sediments. An RAC < 1% indicates no risk; 1% to 10%, low risk; 11 to 30%, medium risk; 31% to 50%, high risk; and >50%, very high risk [31]. Further, the accuracy of the analytical procedures of the total digestion was validated using marine sediment certified reference material (MESS-4) [32] and the results show that the recovery for elements were acceptable (96.42% and 83.3% for Cd and Pb, respectively).

4) Statistical analysis

Statistical analysis was conducted using the Statistical Product and Service Solutions (SPSS) version 20.0. Principal component analysis (PCA), a multivariate statistical technique used for linear dimension reduction while minimizing the loss of information [33], was used to determine and classify the relationships among the variables including total metal concentrations, exchangeable metal concentrations (BCR1) and the soil characteristics (pH, EC, and TOC). PCA allows the visualization of information derived from the data set into principal components (PCs), while retaining the maximum possible variability within that set [34].

Results and discussion

1) Physico-chemical characteristics of sediments

The sediment characteristics are the main factors controlling the concentrations of heavy metals and the metal transportation. Sediment samples were assessed for physicochemical characteristics and the results show a narrow pH range (8.11 to 9.21) among the various sampling locations (Table 1). It is known that a high pH promotes adsorption and precipitation and consequently decreases the mobility of heavy metals, while a low pH is associated with the release of heavy metals [35]. According to a previous study, the pH of the sediments from Phuket Bay ranged from 6.8 to 8.2 [14] which differs from the present study. However, the pH ranges from 6.5 to 9.0 is reported to be normal for freshwater aquatic life, required for sustaining it [35]. The comparatively elevated pH observed at some stations (R7 and R16) may be due to urban discharges in this region from Tha Chin canal. The results of this study are consistent with Sankaran et al. [36] that showed sediment samples collected from Thondi coastal regions in southeast coast of India, were alkaline with a pH range from 7.5 to 8.9.

The %TOC of the sediment samples was determined in order to study the effects of the organic carbon content on metal distribution and transportation. The interaction between TOC and metal concentration levels in sediments has been widely studied, demonstrating positive correlations [37–39] with a high TOC content tending to increase the adsorption capacity of metals. It has been reported that the %TOC of global seabed sediments ranges from 0.01% to 20%, and the average %TOC is between 0.5% in the deep ocean and 2% along the margins [40]. In the present study, the %TOC ranged between 0.03% and 3.55% by dry weight (Table 1) and the highest %TOC was observed at station R3. The water movement from the mouth of canal near R3 might play a role in causing the sediment to drift away and affect the high amount of particulate organic matter transported from land to sea [41]. Organic materials are regarded as a principal sorbent for heavy metals, which may influence their distribution and transport, but in this study no such relationship was found between TOC and heavy metal concentrations. This is probably due to the low organic carbon concentrations, so other physical and chemical factors may dominate in determining metal loadings in this current study. The contribution of low organic carbon to the sediment may be limited by relatively low nutrient concentrations or by high turbidity in the water column caused by ships frequently passing by the sampling stations in the central of the Phuket Bay [42].

2) Distribution of metals

A classed post map prepared by Arc Map 10.5 is a map where symbols at specific XY point locations showed a group of heavy metal concentrations in Phuket Bay to identify pollution sources and vulnerable sites that may be affected by intense anthropogenic activities. Maps of the total metal concentrations (Pb and Zn) in the sediments show a dissimilarity in metal distribution by sampling location (Figure 2). The total Pb and Zn concentrations in the study area of Phuket Bay ranged from 8.21 to 18.1 mg kg^{-1} and 35.1 to 46.4 mg kg^{-1}, respectively (Table 2). Based on mean value, sediments were ranked in the following order: Zn > Pb. The concentration of Zn was observed to be highest at R20 to R21 due to municipal wastewater discharge from the Bang Yai canal, and at R4 and R11 probably as a result of metal transported from the former tin mining area at Tapaonoi Island. In contrast, the highest Pb concentrations in the current study were found at the sampling locations near piers and boatyards at R7 to R12 and at R1 to R2, respectively, which may be caused by pollution sources at the ferry terminal, boatyards and other maritime activities, including paint stripping, and painting by the Tha Chin canal. The total concentrations of these metals (Pb and Zn)

were compared to national standards [43] and the world averages [44]. We found that metals in this study was also higher than in other regions of Thailand, for example, Surat Thani and Chumphon provinces in southern Thailand have shown Pb and Zn ranged from 8.12 to 25.99 mg kg^{-1}, 0.24 to 12.36 mg kg^{-1}, 7.50 to 46.43 mg Zn kg^{-1}, and 0.53 to 40.85 mg kg^{-1}, respectively [45, 46].

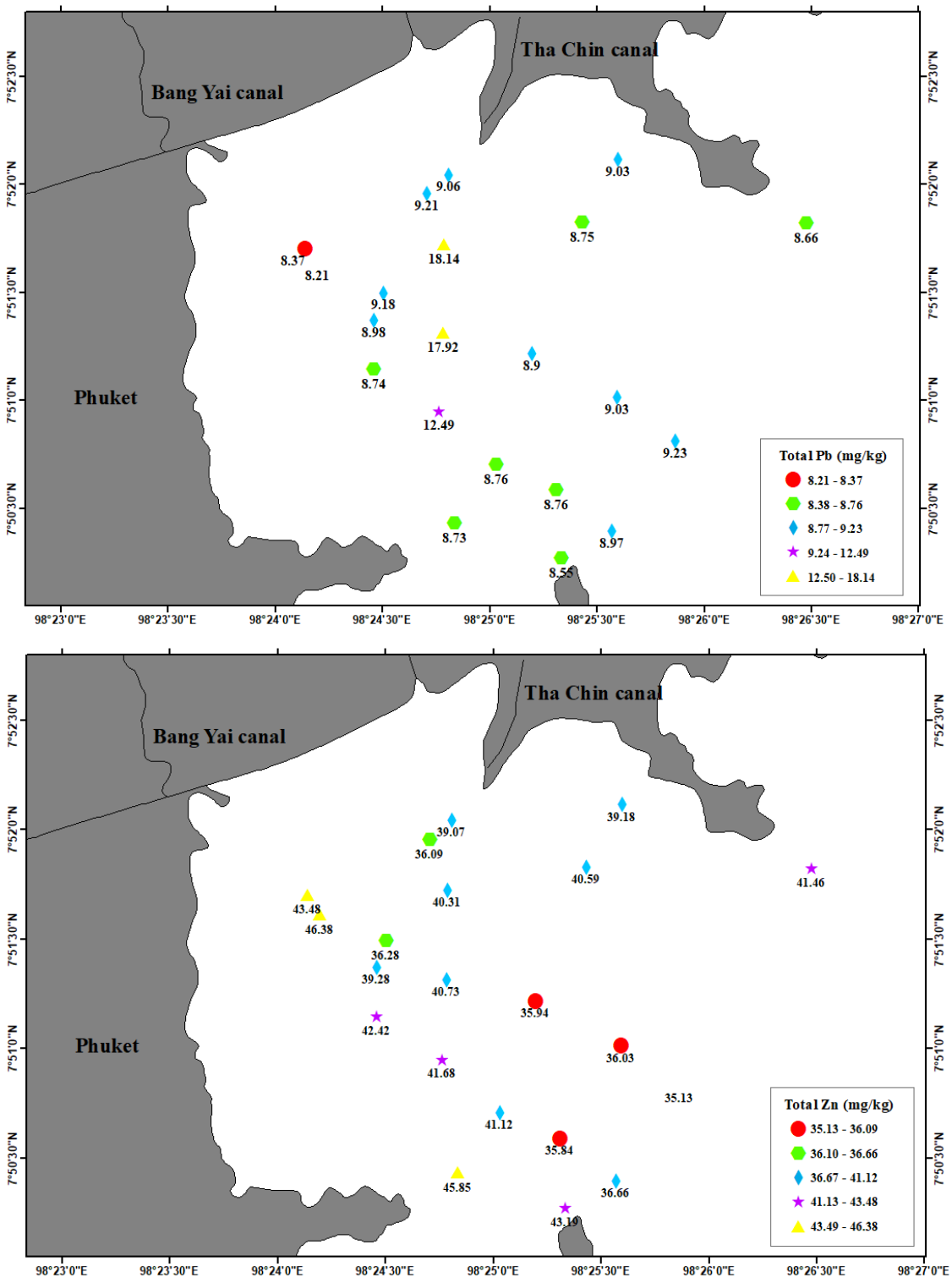

Figure 2 Total Pb and Zn concentrations (mg kg^{-1}) in sediment at Phuket Bay.

Table 2 Heavy metal concentrations (mg kg^{-1}) observed along with national and international standard limits

Heavy metal	Metal concentration (mg kg^{-1})				
	Range in this study	World average[a]	Pollution Control Department[b]	Proposed sediment quality guidelines for Thailand	
				Effects range low (ERL)[c]	Effects range median (ERM)[d]
Pb	8.21–18.1	20	Not exceed 53	46.7	218
Zn	35.1–46.4	95	Not exceed 102	150	410

Remark: [a] Turekian and Wedepohl (1961)
[b] Coastal Sediment Quality Guidelines [46]
[c] ERL = Effects range low [48]
[d] ERM = Effects range median [48]

3) The metal bioavailability with their fractionation

The bioavailable distributions of Pb and Zn extracted by sequential extraction in this study showed differences among the sampling locations (Figure 3). In this study, Pb and Zn exhibited the high percentages in these mobile form of exchangeable and reducible fractions (1.7 to 7.5 mg Pb kg^{-1} and 2.60 to 12.30 mg Pb kg^{-1} for BCR1 and BCR2; and 2.80 to 6.33 mg Zn kg^{-1}, and 1.71 to 4.67 mg Zn kg^{-1}, for BCR1 and BCR2, respectively). The risks associated with the presence of metals in the aquatic ecosystem depend on the forms of the metals [31]. It is known that metals released from the exchangeable (BCR1) are weakly absorbed, easily solubilized into bioavailable forms and can transfer easily in the food chain [24]. In the exchangeable fraction (BCR1), Pb and Zn were dominant at sampling stations R6, R9 and R10 (Figure 3), showing the highest exchangeable Pb (7.4 mg kg^{-1}, 7.5 mg kg^{-1}, 7.49 mg kg^{-1} at R6, R9 and R10) and the high Zn concentrations (5.57 mg kg^{-1}, 4.64 mg kg^{-1}, 4.85 mg kg^{-1} at R6, R9 and R10) in sediments at these sampling stations (Figure 3). In the reducible fractions (BCR2), the Pb ranged from 14.4% to 49.1%, while Zn ranges from 3.4% to 8.9%. The metals in this fraction could be released and/or mobilized by reducing anoxic conditions since precipitation and co-precipitation act as important metal sinks of Fe/Mn oxides and hydroxides [47]. Fractionation of Pb and Zn in the first two fractions (%BCR1+%BCR2) relative to the total metal content in sediment samples as digested by aqua regia can be ranked as: Pb > Zn (Figure 4). The results showed the fractionation of these three metals had similar rank order in the BCR1 and BCR2 fractions. More than one-third of the total metals was contained in the two extracts (%BCR1+%BCR2), especially Pb.

The high Pb extractability in the exchangeable (BCR1) fraction is potentially bioavailable through the food chain, and this may be harmful to the ecosystem [6] and could cause acute and chronic toxicities in humans [48]. Therefore, the assessment of associated risk on heavy metal accumulation was determined. Based on the RAC, there was a medium risk for Pb (6.9% to 28.2%) while there was low risks for Zn (3.8% to 9.2%). The two proposed marine and coastal sediment quality guidelines including effects range low (ERL) and effects range median (ERM) [49] were also used in this study to assess the risk caused by the metals (Table 2). According to these criteria, our present study showed that the concentrations of metals in the sediment samples were lower than the proposed sediment quality guidelines for Thailand (ERL and ERM), indicating no adverse harmful effects on sediment dwelling organisms are expected.

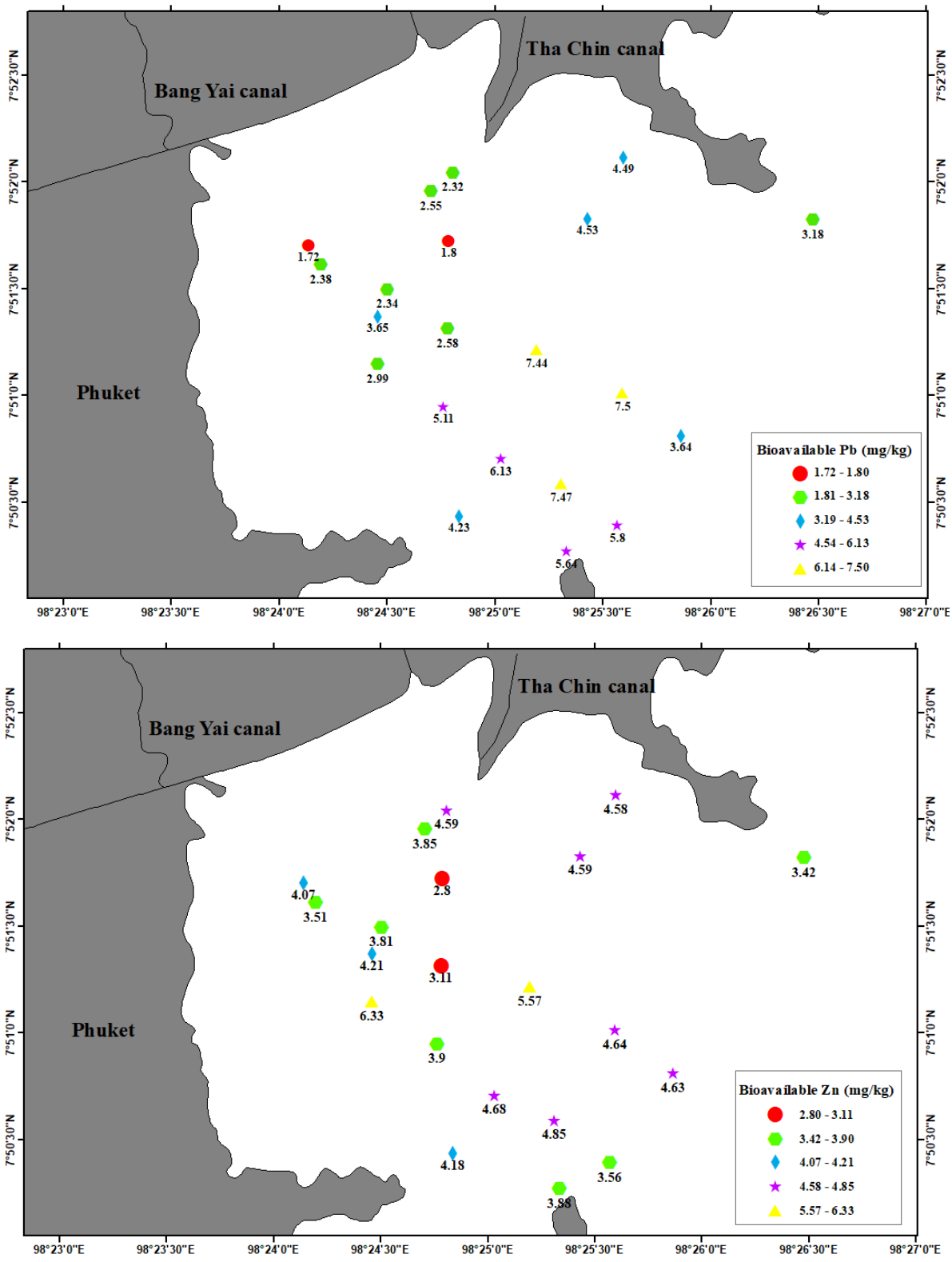

Figure 3 Bioavailable Pb and Zn distributions (mg kg^{-1}) in sediment at Phuket Bay.

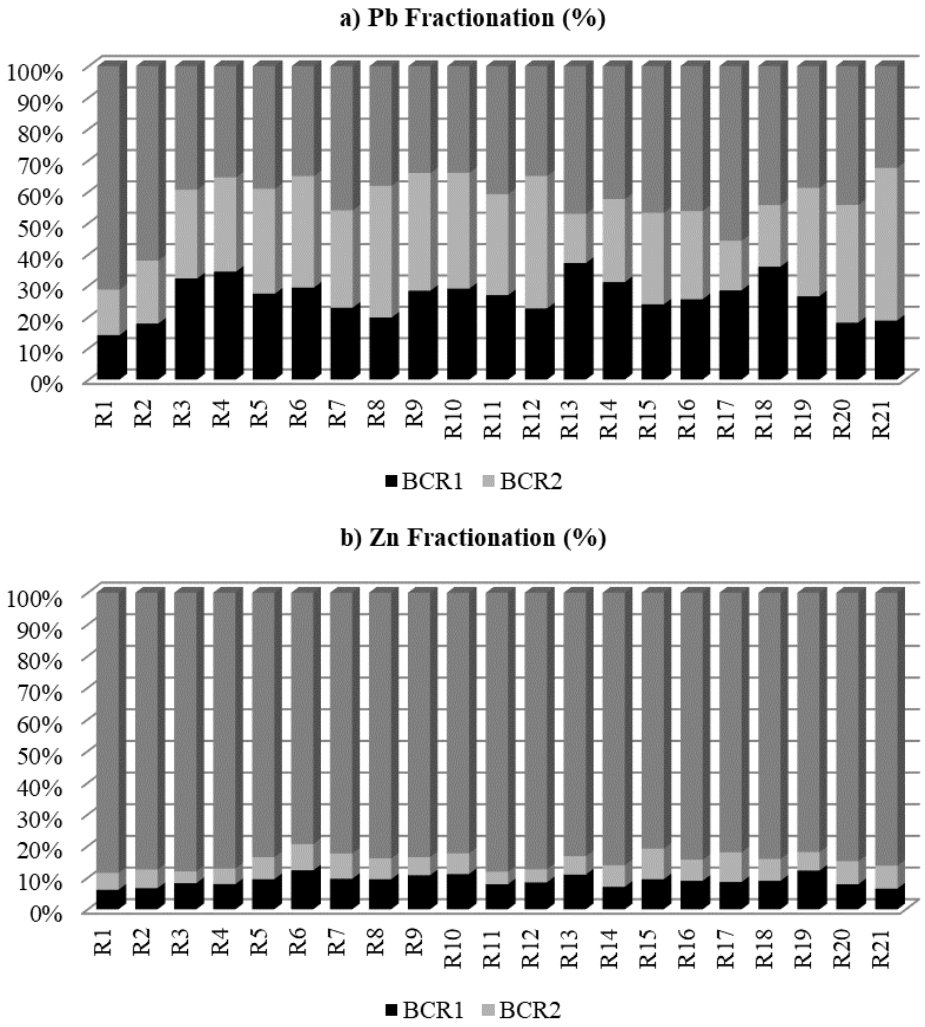

Figure 4 The relative percentage of Pb and Zn (%) from the total concentration.

4) The correlation between heavy metals and sediment characteristics

In this study, the total and bioavailable (BCR1) metal concentrations (mg kg^{-1}) and sediment characteristics (pH and %TOC) were subjected to PCA to assess the interrelationships among the data collected (Table 3). Four principal components (PC1, PC2, PC3, and PC4) were extracted from PCA with Varimax rotation explaining 85.8% of the total variance. The identified principal components (PCs) account for most of the variability in the data, and the factor loadings in the components suggest underlying correlations or relationships between the variables. In this study, the first component (PC1) accounts for the most important associations (29.1% of the total variance), and is loaded heavily on total Zn and pH, suggesting that the pH significantly influenced what concentration of Zn was released to the environment. On the other hand, the second component (PC2) explained 23.6% of the total variance comprised total Pb and bioavailable Zn (BCR1), which might be because of the unusually high Pb concentrations in the sediment samples. The third component (PC3) could only explain 19.8% of the total variance and loaded on bioavailable Pb (BCR1) and reducible Pb (BCR2). The presence of different forms of Pb in the component reveals the correlation between different phases of transformation between dissolved and other fractions [6]. Based on the PCA results, the TOC showed no significant effect on the abundance and distribution of heavy metals in this study and was in

the fourth component (PC4) explaining 13.3% of the total variance. This agrees with the high proportion of metals released in the first two fractions (BCR1 and BCR2) and is also consistent with the study of [6], which found no significant correlation between TOC and metal concentrations, and that of [50], which showed that TOC and grain size are important factors controlling metal composition but not metal distribution.

5) Assessment of anthropogenic impacts on heavy metal accumulation

To assess the possible extent of anthropogenic contamination by Pb and Zn in the sediments, the EF profile of the sediment core R15 for all the sediment layers and in the surface sediments at all sampling locations (R1 to R21) were determined. The EF by using a mean surface concentration from each station (R1 to R21) ranged from 2.5 to 5.5 and from 2.7 to 3.5 for Pb and Zn, respectively; and the EF profile in the core ranged from 3.9 to 9.8 for Pb, and from 2.0 to 7.0 for Zn (Figure 5), indicating minimal to significant enrichment of heavy metals from human activities in the area studied. The average levels of Zn and Pb in sediments were generally higher than in the prevailing background, as indicated by their corresponding enrichment factors [51] and this suggests anthropogenic sources of Zn and Pb.

Table 3 Varimax rotated principal components

	Component			
	1	**2**	**3**	**4**
BCR1 Pb	-0.299	0.245	**0.863**	-0.089
BCR2 Pb	0.465	0.246	**0.763**	-0.081
Total Pb	-0.034	**-0.809**	-0.160	0.207
BCR1 Zn	-0.226	**0.873**	0.149	0.178
BCR2 Zn	0.137	0.496	-0.590	-0.519
Total Zn	**0.883**	-0.046	-0.110	0.091
pH	**-0.926**	0.106	-0.042	0.007
%TOC	0.099	0.000	-0.091	**0.966**

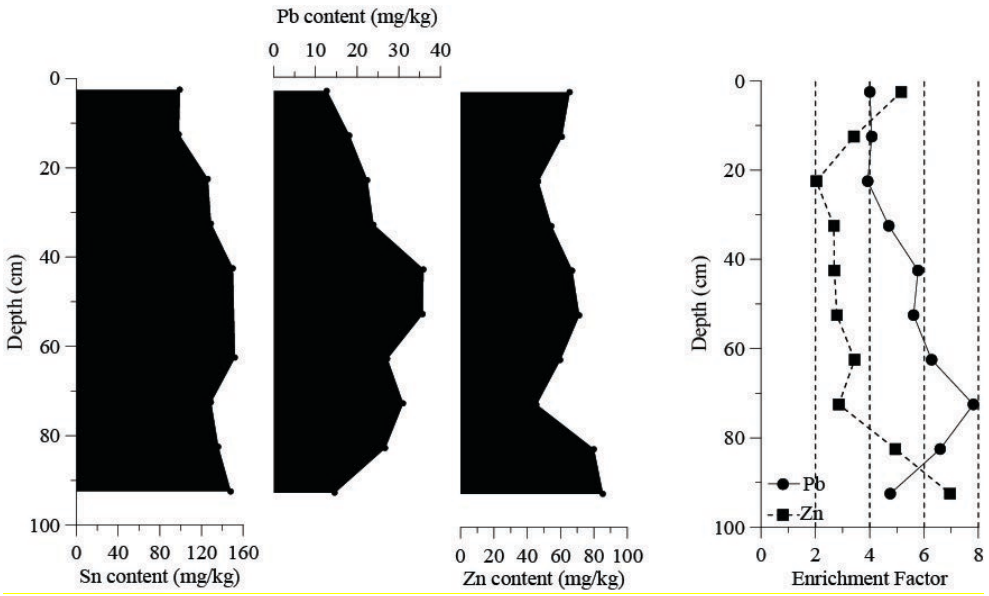

Figure 5 The metal concentration-depth relationship and the calculated EFs of Pb and Zn.

The metal concentration-depth relationship along the sediment profile and the calculated EFs of Pb and Zn are given in Figure 5, with metal concentration in each layer of the sediment core ranging from 45.4 to 88 mg Zn kg^{-1} and from 12.7 to 44.5 mg Pb kg^{-1}. The profile of Sn concentration along the sediment core (from 49.9 to 167 mg Sn kg^{-1}) was assessed due to having had a major tin-producing center in Phuket in the past. The concentrations of Sn and Pb showed similar trends through the profile between 10 and 40 cm depth (Figure 5). Based on the changes in heavy metal accumulation in the sediment core, and the calculated EFs versus depth, these allowed us to understand the historical variability in pollutant linked to past activities in Phuket Bay as follows:

- **The mixing of seafloor sediments by bioturbation of the 2004 tsunami event**

The EF values for metals in this study indicated moderately enriched heavy metal concentrations in the sediments. The 2004 tsunami event caused large volumes of debris to fall into the water in Phuket Bay. Flows of water retreating from inland had a flushing effect which resulted in elevated metal loads in the water column, especially in the west coast of Phuket Island, to almost all the major beaches. The 2004 tsunami upflow produced a vast area of erosion on the coastline and, in turn, the deposition of tsunami carried sediments caused much debris from the sea floor resembling muddy sludge [52]. The mixing of seafloor sediments by bioturbation or by the 2004 tsunami event are important to the marine environment, because these influenced bioturbation structures that had been produced in the past. The disturbance caused by the tsunami wave led to the deposition of sandy layers along Phuket Bay. Tsunami sediments showed higher contents of Pb and Zn and other heavy metals in the bioavailable fraction than the reference samples, and this may be used as supplementary proxy to identify paleotsunami deposits [53].

- **The era of Phuket's tin-mining industry**

Phuket is one of the provinces in the Southern Thailand with strong tin mining industry in the past, contributing to its economic development. The existence of Sn deposits in Phuket has been known since the 17th century, but after World War II there was increased demand for Sn as a coating metal. The discovery of Sn as the most crucial elements for development in Phuket began in 1909 with Sn mining in the Kathu District, continued until 1992 when the last mine was closed [15]. During 1961 to 1990, more than 400,000 tons of Sn concentrate was produced on-shore and off-shore, and much of the tin was recovered from alluvium by dredging and gravel pump methods [54]. In 1975, Sn-dredging operations commenced in the sea off of Phuket [55]. Significant amounts of Sn were also mined from primary deposits of ilmenite, monazite, columbite-tantalite, zircon and wolframite, which are the chief by-product minerals of Sn mining operations [54]. As a result, high concentrations of Sn and other heavy metals were released to the environment. According to a previous study, sediment cores collected from Phuket Bay showed Sn level range from 49.9 to 167 mg kg^{-1} and from 77.5 to 153 mg kg^{-1} [56] and the metal concentrations in the sediments were generally consistent which the socio-economic developments during this period. The EF values of Pb and Zn showed significant to moderate enrichment, consistent with the time sequence of events. Later, Sn-mining died out because the market price declined and the tin mining industry in Phuket ended in 1992. However, urban development can be considered a factors causing enrichment of metals found in this study, which corresponds to a period when tourism began on the island in the 1970s.

Conclusions

Heavy metals in the sediments of Phuket Bay showed wide ranges of concentrations due to spatial variations in the metal distributions. This study showed that the total concentrations of Pb and Zn in the sediment samples in Phuket Bay were lower than their world averages, and the bioavailable Pb concentration by the first two steps of the BCR sequential extraction procedure represented weakly absorbed metal fractions. The presence of these metals needs to be monitored because they are readily transferred and biomagnified through food chains, resulting health risks to humans. Further, it was corroborated by PCA that Pb may originate from shared sources related to anthropogenic activities, such as urban discharges, boatyards, and other maritime activities. Therefore, there is a need for the authorities to take appropriate actions and adopt measures to prevent pollution.

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