

Assessment of Cd and Pb bioavailability in sediments in Phuket Bay, Thailand.

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Abstract

Heavy metals are significant environmental pollutants and their toxicity is a problem of increasing concern due to their accumulation and their persistence in the environment that can potentially pose a risk to the ecosystems and human health. The behavior of metals in sediments reflects the historical deposition, sources of contaminants, and information on the impact of human activities on the coastal ecosystem. The transportation of metals is depending mainly on the metal speciation. Therefore, bioavailable fraction is of the interest in this study. The objectives of this study are: i) to determine the pollution levels and the distribution of the selected metals (Cd and Pb) in sediments at the Phuket Bay, Phuket province; ii) to examine the relative bioavailability of heavy metals (Cd and Pb) in the sediments. The spatial distribution of selected heavy metals (Cd and Pb) in the sediments was evaluated for heavy metal contamination. The sediment samples was analyzed using *aqua regia* digestion according to the Standard US EPA Method 3052 (1996) and the first step of BCR sequential extraction proposed by the Standards, Measurements and Testing programme of the European Union (SM&T) to determine the total and bioavailability of Cd and Pb in sediments. The results showed Cd formed a weak complex and easily removed at the initial stages of the extraction accounted for up to 27.8% of the total metal concentration ($10.6\text{-}53.5\text{ mg kg}^{-1}$) and up to 11.7% for Pb ($8.55\text{-}18.1\text{ mg kg}^{-1}$), respectively. However, the estimate metal levels in the sediments of this study were found relatively lower than other reported studies at other location in Phuket Province and below the Sediment Quality Guidelines of Threshold Effects Concentration (TEC) and Thai soil quality standard for other purposes.

Keywords: Bioavailability, Cadmium, Lead, Phuket, Sediment

1. Introduction

Heavy metals are significant environmental pollutants and their toxicity is a problem of increasing concern due to their accumulation and their persistence in the environment [Hasan *et al.* (2013); Saleem *et al.* (2015)]. Heavy metal contaminations can potentially pose a risk to the ecosystems and human health. The multiple sources of heavy metals have led to the distribution in the environment (Tchounwou *et al.*, 2014). The main sources of the heavy metals in the coastal environment cannot be clearly identified. High level of heavy metals can often be attributed to anthropogenic influences such as agricultural runoff, mining activities, industrial effluents, rather than natural enrichment by geological weathering (Saher and Siddiqu, 2016). When heavy metal is discharged into aquatic ecosystems, it can be absorbed by suspended solids, accumulated in sediments and biomagnified in aquatic food chains (Tchoroun *et al.*, 2015). Metals introduced by human activities often show higher mobility and are associated with carbonates, oxides, hydroxides and sulfides; while, metals which are naturally occurring are mainly associated with silicates and primary minerals [Saleem *et al.* (2015); Kabata-Pendias and Pendias (2001)]. Sediments are the principal reservoir for heavy metals and as indicator of the heavy metal burden in a coastal environment. The behavior of metals in sediments reflects the historical deposition, sources of contaminants, and information on the impact of human activities on the coastal ecosystem (Saher and Siddiqu, 2016). For that reason, the study of coastal sediment is very crucial in the determination of the intensity of contamination and toxicity in a coastal environment that could provide a record of the spatial and temporal history of pollution in a particular area. Metal distribution and transportation in sediment is considered to be significant that can cause the adverse effects to human health and environment. The importance of sediments on aquatic ecosystems and the environment has been discussed by many researchers in different part of Thailand, however, there have been a few research in the literature that investigate the heavy metal

Table 1. Detail of sediment samples collected from Phuket Bay, Phuket Province

Sediment samples	Location (UTM)	Activities	Depth (cm)	pH	Cd (mg kg ⁻¹)	Pb (mg kg ⁻¹)
R1	7°51'43.3"N 98°24'47.1"E	maritime activities, oil spill	1.6	8.32±0.06	29.3±0.05	18.1±0.24
R2	7°51'18.8"N 98°24'47.0"E	maritime activities, oil spill	4.4	8.34±0.01	28.8±0.10	17.9±0.36
R3	7°50'57.0"N 98°24'45.6"E	maritime activities, oil spill	3.5	8.23±0.00	30.3±0.63	12.5±0.56
R4	7°50'25.9"N 98°24'50.1"E	maritime activities, oil spill	6.1	8.11±0.01	29.8±0.05	8.73±0.23
R5	7°50'42.4"N 98°25'01.9"E	maritime activities, oil spill	7.1	8.36±0.01	29.1±0.02	8.76±0.14
R6	7°51'12.9"N 98°25'11.7"E	maritime activities, oil spill	3.2	8.71±0.08	28.6±0.12	8.90±0.20
R7	7°52'06.9"N 98°25'35.8"E	maritime activities, oil spill	2.3	9.23±0.07	52.6±0.03	9.03±0.40
R8	7°51'49.6"N 98°25'25.9"E	maritime activities, oil spill	3.9	8.57±0.03	51.9±0.08	8.75±0.15
R9	7°51'00.7"N 98°25'35.7"E	maritime activities, oil spill	4.2	8.68±0.03	51.0±0.10	9.03±0.87
R10	7°50'35.3"N 98°25'18.7"E	maritime activities, oil spill	4.0	8.58±0.00	53.5±0.04	8.76±0.58
R11	7°50'16.2"N 98°25'20.0"E	maritime activities, oil spill	4.0	8.50±0.01	53.0±0.10	8.55±0.52
R12	7°50'23.6"N 98°25'34.2"E	maritime activities, oil spill	4.8	8.84±0.01	52.5±0.03	8.97±0.09
R13	7°50'48.5"N 98°25'52.0"E	maritime activities, oil spill	5.7	9.25±0.02	10.8±0.08	9.23±0.05
R14	7°51'49.5"N 98°26'28.6"E	maritime activities, oil spill	15.5	8.82±0.07	10.7±0.05	8.66±0.06
RG	7°52'02.7"N 98°24'48.3"E	Discharge of wastewater from the communities, maritime activities	0.7	8.87±0.09	10.8±0.04	9.06±0.02
RH	7°51'57.5"N 98°24'42.3"E	Discharge of wastewater from the communities, maritime activities	0.6	9.25±0.05	10.8±0.05	9.21±0.06
RJ	7°51'29.8"N 98°24'30.1"E	Discharge of wastewater from the communities, maritime activities	0.9	8.75±0.03	10.8±0.04	9.18±0.08
RK	7°51'22.2"N 98°24'27.5"E	Discharge of wastewater from the communities, maritime activities	0.9	8.80±0.01	10.8±0.02	8.98±0.08
RL	7°51'08.9"N 98°24'27.4"E	Discharge of wastewater from the communities, maritime activities	1.2	8.85±0.00	10.6±0.03	8.74±0.09
Min.				8.11±0.01	10.6±0.03	8.55±0.52
Max.				9.25±0.05	53.5±0.04	18.1±0.24

contamination in Phuket Bay, Phuket Province as affected from human activities and/or tin mining in the past. Regarding this aspect, heavy metal contamination in the sediments along the bay is of a significant concern in order to evaluate the pollution levels and the potential toxicity by heavy metals. The transportation of metals is depending mainly on the metal speciation. Therefore, association of the metals with different geochemical phase, especially bioavailable fraction is of the interest in this study.

Knowing the distribution and transformation of metals is therefore very important for understanding the migration and movement of the contaminants and therefore the bioavailability of metals (Akkajit, P., 2015). Therefore, the objectives of this study are: i) to determine the pollution levels and the distribution of the selected metals (Cd and Pb) in sediments at the Phuket Bay, Phuket province; ii) to examine the relative bioavailability of heavy metals (Cd and Pb) in the sediments. The spatial distribution of

selected heavy metals (Cd and Pb) in the sediments was evaluated for heavy metal contamination. The results of this study can be used to determine the pollution levels and spatial distributions of Cd and Pb in sediments in this particular area of Phuket Bay, Phuket province as affected from human activities and/or tin mining in the past. The investigation of sediment in this site helps to get the information about environmental and contamination characteristics in order to have the information on how sources of contamination change over the years that can influence the contaminant fate in the environment. Therefore, pollution control measures and/or guidelines could be developed and implemented for site management

2. Methodology

2.1. Study area

The study area is located at Phuket Bay, the western of Phuket province, Thailand. Phuket Bay can be considered as one of primary waterway used for maritime activities, flows from the upstream from Phuket town into the sea coast at Phuket Bay. Therefore, it is potentially significant sources of heavy metal pollution, especially with the rapid industrial and economic development in the area. Nineteen sediment samples were collected in September 2015 at nineteen different stations. A Global Positioning System (GPS) was used to determine the actual coordinates of the sampling sites and the depth of sediments were also recorded. The detail of sediment samples and sampling locations are given in Table 1.

2.2 Sample Collection

The sediments were collected using a Van Veen Grab for sediment sampling. There are 19 sediment samples with triplicates ($n = 57$ samples) for metal determination. All sediment samples from each sampling sites were immediately stored in polypropylene bags and kept in the icebox (at 4 °C) before taken to the laboratory at Prince of Songkla University, Phuket campus for further processing and analysis.

2.3 Sample Preparation and Analysis

Sediment samples were dried at 60 °C until constant weight is achieved and ground manually in a porcelain mortar. Sub-samples of sediment were then analyzed for pH at the ratio of 1:5 (sediment: water suspensions) by pH meter. For determination of total Cd and Pb concentrations, *aqua regia* digestion according to the Standard US-EPA Method 3052 (1996) was performed. Extracts were analyzed by flame atomic absorption spectrometry (FAAS) (AASZEEnit700 Analytik). All laboratory glassware was cleaned using a HNO₃ (3%, v/v) bath overnight, followed by repeated rinsing with doubly distilled water and dried in an electric oven prior to use. For method validation, the accuracy of the analytical procedures was checked using Marine sediment certified reference material (MESS-4) from the National Research Council of Canada (National Research Council Canada, 2016). The results of the certified reference materials (MESS-4), in the form of the mean values and their standard deviations, by the total digestion (US EPA

Method 3052) showed good agreement (Cd 0.27 ± 0.06) with the certified values (0.28 ± 0.04 mg kg⁻¹), except for Pb (measured Pb value 17.91 ± 0.47 mg kg⁻¹ and certified value 21.5 ± 1.2 mg kg⁻¹).

2.4 Statistical Analysis

Statistical analysis was based on two-way analysis of variance (ANOVA) for comparison of statistical significance among different treatments using Statistical Product and Service Solutions (SPSS) version 17.0 and Duncan's test at $*p < 0.05$ was used for mean separation.

3. Results and Discussion

3.1 Physicochemical Characteristics of Sediments

Analysis of the sediment samples demonstrate a wide range of pH ranging from pH 8.11 (± 0.01) to 9.25 (± 0.05) (Table 1). Sediment compositions are the main factors controlling the concentrations of heavy metals, while the hydrodynamic conditions, in particular the seasonal eddies, were an important factor controlling their distribution (Liu *et al.*, 2016). In this research, the pH of the studied sediments were slightly alkaline with a rather narrow range in soil pH (pH 8.11-9.21).

3.2 Total Metal Concentrations

The Cd and Pb concentrations in sediments are shown in Figure 1 and Figure 2, respectively. In this study, the ranges of Cd and Pb concentrations in the studied area at Phuket Bay are 10.6-53.5 mg kg⁻¹ and 8.55-18.1 mg kg⁻¹, respectively. Spatial distribution maps of heavy metals would aid in the identification of pollution sources and vulnerable sites (Sany *et al.* 2013). Overall, the estimate metal levels in the sediments of this study were found relatively lower than other reported studies at other location in Phuket Province. Suteerasak and Bhongsuwan (2008) found high concentrations of Pb in the sediments from Bang-Yai canal in the range of 17-113 mg kg⁻¹. The measure concentrations of these metals were compared with the national and international standards. The observed Pb concentration was below the Sediment Quality Guidelines of Threshold Effects Concentration (TEC) (36 mg kg⁻¹ Pb) (Helen *et al.*, 2016), except that of Cd that showed higher value than soil quality standards for habitat and agriculture (not exceed 37 mg kg⁻¹) but lower than soil quality standard for other purposes (not exceed 810 mg kg⁻¹) (Pollution Control Department, 2004). According to other study, Cd and Pb are found to be the dominant pollutants that are heavily polluted in the upstream with their concentrations reaching moderate to serious pollution levels (Nguyen *et al.*, 2016). In this study, high Cd and Pb concentrations were observed in the middle of Phuket Bay; at R7-R12 where maritime activities, and pollution from ports including oil spills are dominated; and at R1-R2 where the discharge of wastewater from the communities are the main sources, respectively.

3.3 Bioavailability of metals

For determination of bioavailable Cd and Pb concentrations in sediments, the first step of BCR sequential extraction (BCR1) proposed by the Standards,

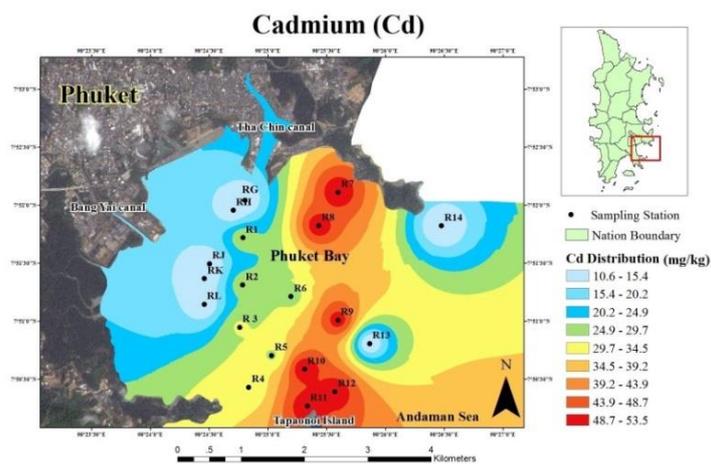


Figure 1. Cd concentrations (mg kg^{-1}) in sediment samples at Phuket Bay, Phuket Province

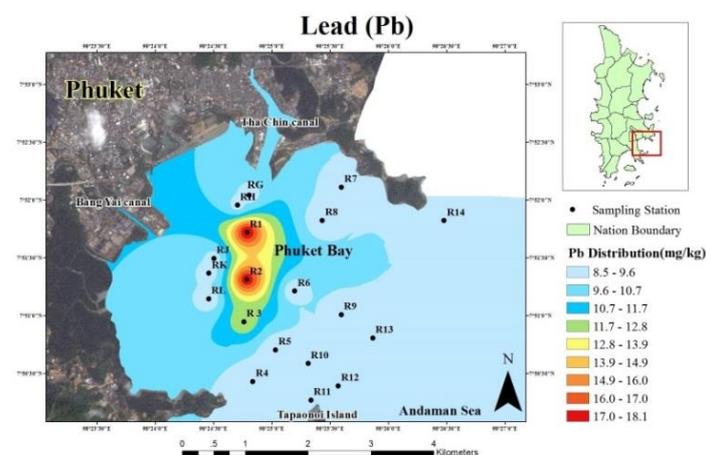


Figure 2. Pb concentrations (mg kg^{-1}) in sediment samples at Phuket Bay, Phuket Province

Measurements and Testing Programme of the European Union (SM&T) (Quevauviller 2002) was performed. Metal fractionation according to the first step of BCR procedure is classified into specific forms/fractions that are exchangeable or easily released form (BCR1). The details of each extraction step are described in Gadepalle *et al.* (2009) and Quevauviller (2002). Results showed that concentrations in bioavailable fraction vary site by site. Cd ranges from 0.73 to 14.9 mg kg^{-1} and Pb from not detectable to 2.13 mg kg^{-1} . Higher Cd extractability in the exchangeable (BCR1) fraction suggested that Cd can be easily mobilized and potentially bioavailable. Portions of metals in exchangeable fractions are weakly adsorbed to the colloidal and particulate material of the sediment, and susceptible to pH changes (Akkajit *et al.*, 2013). The proportions of metals of interest in the first fraction as compared to the total metal contents are 6.8% to 27.8% (Cd) in BCR1 and up to 11.7% for Pb, respectively.

4. Conclusion

The determination of bioavailable Cd and Pb concentrations through partitioning by the first step of BCR sequential extraction procedure (BCR1) allowed identifying a weakly absorbed fraction which is readily bioavailable to biota. This should be a major concern since

it can expose to the ecosystem and hence to the food chain. According to the results, it indicated that Cd formed a weak complex and was easily removed at the initial stages of the extraction accounted for up to 27.8% of the total metal concentration ($10.6\text{-}53.5 \text{ mg kg}^{-1}$) and up to 11.7% for Pb (total Pb $8.55\text{-}18.1 \text{ mg kg}^{-1}$), respectively. However, the estimated metal levels in the sediments of this study were found relatively lower than other reported studies at other location in Phuket Province.

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