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Research Article

The study of historical contamination of Tin (Sn) and Zinc (Zn) in sediments at the Bang-Yai River estuary, Phuket Province

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Abstract

Metal distribution and transportation in sediment is considered to be significant that can cause the adverse effects to human health and environment. Tin (Sn) and other metal contamination in the sediments at Bang-Yai River estuary, Phuket province, is a significant concern affected by the abandoned Tin mining in the past. Percolation from the tailing ponds and the ground water discharges could result in contaminated ground water of the ponds to a nearby stream and receiving water. Therefore, the objective of this study is to determine the pollution levels of Tin and Zinc in sediment cores using a 60-cm long of Russian corer. The sub-samples of sediment was separated and cut into an interval using a stainless steel blade, digested using *aqua regia* digestion according to the Standard US EPA Method 3052 (1996), and analyzed by ICP-OES. The results showed that Tin concentrations in all sediment samples are below detection limit (< 0.03 mg kg^{-1}). Zinc concentration in Core A and B was ranged from 32.83-68.49 mg $kg^{-1}$and 21.63-73.59 mg kg^{-1}, respectively. The geoaccumulation index (Igeo) and the enrichment factor (EF) values of Sn in the sediments cannot be found due to the very low Tin concentration, except Igeo ($Igeo_{Zn}$ < 0) and EF values of Zn (3.17-3.97 and 3.67-3.84 of Core A and B, respectively). This revealed that the study area was unpolluted and not enriched by Tin and Zinc. However, the high EF values of Zn in the superficial sediment as compared to the lower sediment layer was explained the cause of contamination from the human activities. Therefore, the determination of other metals should be considered further.

Keywords: heavy metal, Phuket, sediment, tin mining

Introduction

Phuket is located in the Southern part of Thailand and is well known as tourism hub of the region. Tin (Sn) mining in the past is very popular and is a major contributor in terms of income generation for the economies of the island. Mineral resources are the most crucial

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elements for development throughout the world. The discovery of Sn in Phuket began in 1909 in the Kathu district of Phuket until 1992 when the last mine on Phuket closed (KoPhuket, 2016). Cassiterite (SnO_2), a tin oxide mineral, was found in abundance in Phuket and the neighboring Andaman coast (United Nations Economic & Social Comission for Asia and the Pacific, 1988). However, mining activities generated a large amount of waste rock and tailings, which results in heavy metal contamination in water, soils, and sediments that could contribute to the accumulation of heavy metals in environment. The Sn mining has caused the environmental impact as open-cut Tin mines devastated the landscape of Phuket and significantly damaged air and water quality (KoPhuket, 2016). Tin and other metal contamination in the sediments at Bang-Yai River estuary, Phuket province, is a significant concern affected by the abandoned Tin mining in the past. Percolation from the tailing ponds and the ground water discharges could result in contaminated ground water of the ponds to a nearby stream and receiving water (Alshaeb et al., 2009). Tin is not very toxic to organism, however, the toxic form is the organic form. Organic Tin can resist and not literally biodegradable in the environment for periods of time where it can spread through the water systems when adsorbed on sediment and are known to disturb growth, reproduction, enzymatic systems and feeding patterns of aquatic organisms (Maria M. & Williams, 2011). Tributyltins are the most toxic Tin components to fish and fungi, whereas trifenyltin is much more toxic to phytoplankton. The exposure mainly takes place in the top layer of the water, as that is where organic Tin compounds accumulate. High concentration of metals in the bottom sediments from six abandoned Tin mines in Phuket Province (75.3-169 mg kg^{-1}, 98.6-547.5 mg kg^{-1}, and 120.4-323.3 mg kg^{-1}, of Arsenic (As), Lead (Pb), and Zinc (Zn), respectively) (Suteerasak & Bhongsuwan, 2006) and in the sediments from Bang-Yai canal (471-15,174 mg kg^{-1} and 17-113 mg kg^{-1} of Sn and Pb, respectively) had been found and that could be affected from the carried sediment from Sn mine activities (Suteerasak & Bhongsuwan, 2008). According to the previous studies as mentioned, the current situation of heavy metal contamination as affected from the abandoned Tin mining that has flow through Bang-Yai canel is still of greatest concern and the risks associated with heavy metals should be considered.

Metal distribution and transportation in sediment is considered to be significant that can cause the adverse effects to human health and environment. However, there have been a few researches in the literature that investigate the heavy metal contamination in Phuket Province as affected from abandoned Sn mining. Therefore, the objective of this study is to determine the pollution levels of Sn and Zn in sediment cores at Bang-Yai River estuary, Phuket province. 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.

Materials and methods

Study area

The study area is located at Saphan Hin (7°51'40.7"N 98°24'02.2"E), Muang District, Phuket province that has received water from Bang-Yai canal which runs through Phuket Town. A Global Positioning System (GPS) was used to determine the coordinates of the sampling sites

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that are shown in Figure 1. There are two sampling points and that resulted in two sediment cores in this study namely Core A and Core B, respectively.

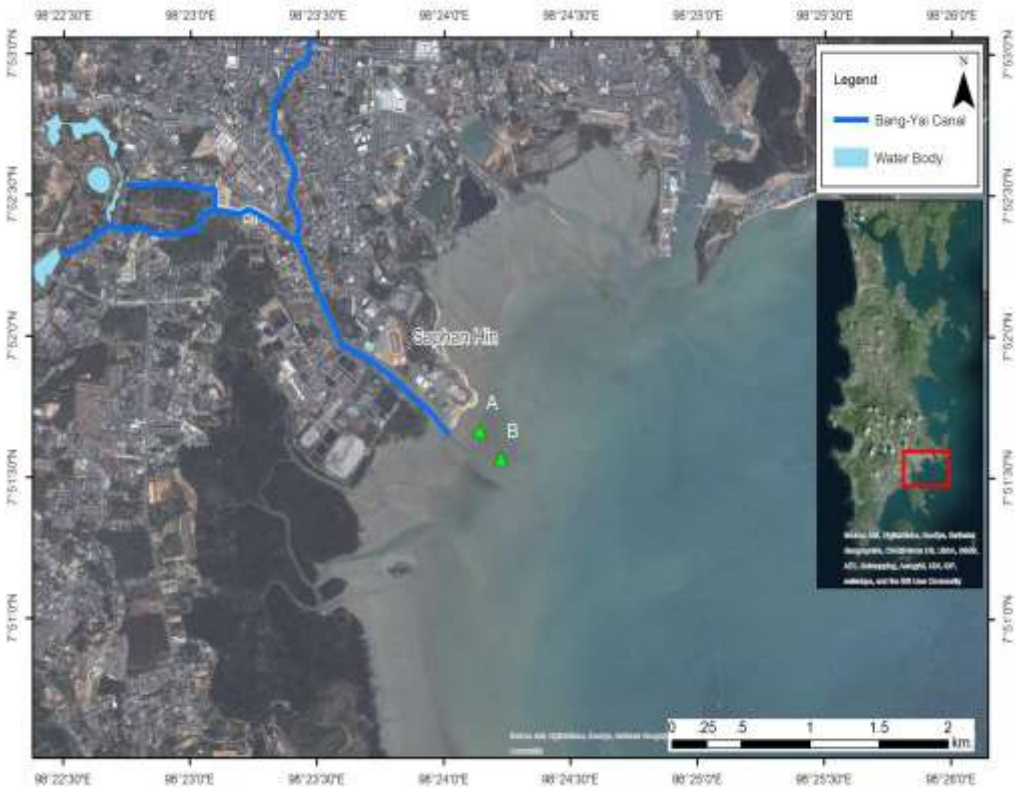

Figure 1. Two sampling sites (Core A and B) at Saphan Hin, Phuket Province

Sample collection

Two sediment cores were collected manually on May 2016 using a Russian corer, a 60 cm long stainless steel (7.5 cm x 60 cm), to achieve complete sediment profile collection (Figure 2) to a depth of 52 cm from two points within the sea coast at Saphan Hin area. After sampling, the sediment samples were carefully removed from the cores and were sub-sampled on site precisely by cut into a slice using a stainless steel blade based on the difference in sediment color and texture observed visually. There are 24 and 22 sediment sub-samples of Core A and B, respectively and then they are immediately stored in polypropylene bags and kept in the ice box at 4 °C before taken to the laboratory at Prince of Songkla University, Phuket campus for further processing and analysis.

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 from each core were then analyzed for the selected physico-chemical properties as followings; 1) pH at the ratio of 1:5 (sediment:

water suspensions) by pH meter and 2) oxidation reduction potential (ORP) by Oxidation-Reduction potential meter. For determination of total Sn and Zn concentrations, aqua regia digestion according to the Standard US-EPA Method 3052 (1996) was performed. Extracts were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Perkin Elmer Optima, 4300 DV/Perkin Elmer Optima 800). All laboratory glassware was cleaned using a HNO_3 (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). Marine Sediment Reference Material for Trace Metals and other Constituents (MESS-4) was analyzed. 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) (Pb 73.25±2.92 mg kg^{-1}) showed good agreement with the certified values (Pb 21.5 mg kg^{-1}).

Figure 2. Sediment profile of Core A and Core B

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Environmental risk assessment

In this study, the degree and the origin of metal pollution in sediments were assessed using the geoaccumulation index (I_{geo}) and the enrichment factor (EF), respectively. The I_{geo} allows the assessment of heavy metal contamination by comparing the measured metal concentration with the metals in earth crust and is calculated as;

$$I_{geo} = \log_2 (C_n/B_n \times 1.5)$$

where C_n is the total metal concentration in sediments, B_n is the concentration of background value for the metal in sediments, and 1.5 is a factor for normalization of background metal concentrations in sediments to minimize the effect of possible variations (Nowrouzi & Pourkhabbaz, 2014); Saleem et al., 2015). In addition, the enrichment factor (EF) is a tool for assessing the enrichment degree of the metals in order to differentiate the sources of heavy metals between human sources and naturally occurring element (Potipat et al., 2015). In this study, the enrichment factor (EF) is calculated using aluminium (Al) as the normalizing element for crust-derived material. The EF is defined as;

$$EF = (M_x/Al_x)_{sample} / (M_c/Al_c)_{crust}$$

Where $(M_x/Al_x)_{sample}$ is the ratio of metal and Al concentrations in the sediment sample, and $(M_c/Al_c)_{crust}$ is the ratio of metal and Al concentrations of the background (Uduma & Jimoh, 2013). The background concentrations of Al, Pb, and Zn in the average earth crust of the Phuket Province were used in this study that are: 115,360 mg kg^{-1}, 20 mg kg^{-1}, and 80 mg kg^{-1}, respectively (Liu et al., 2016). The interpretation of the geoaccumulation index and EF value is given in Table 1. below.

Table 1. The interpretation of the geoaccumulation index (Igeo) and enrichment factor (EF) value used in this study

Geoaccumulation index (Igeo)		**Enrichment factor (EF)**	
Igeo value	Meaning	EF value	Meaning
Igeo < 0	unpolluted	EF < 1	no enrichment
0.01 - 0.99	Unpolluted to moderately polluted	1 - 3	minor enrichment
1.00 - 1.99	moderately polluted	3 - 5	moderate enrichment
2.00 - 2.99	moderately to strongly polluted	5 - 10	moderately severe enrichment
3.00 - 3.99	strongly polluted	10 - 25	severe enrichment
4.00 - 4.99	strongly to very strongly polluted	25 - 50	very severe enrichment
Igeo > 5.00	very strongly polluted	> 50	EF extremely severe enrichment

Source: Omotoso & Ojo (2015)

Results and discussion

Sediment characterization

The physico-chemical properties included pH and ORP and metal concentrations of the sediment samples of Core A and B are presented in Table 2. In this study, it was found that the pH values of sediment samples in Core A is slightly acidic to slightly alkaline (pH 6.8-8.3), and Core B exhibited the similar trend (pH 6.9-8.1). High pH values promote adsorption and precipitation and subsequently decrease the mobility of heavy metal (Li et al., 2013), while the low pH associated with the release of heavy metal. In this study, the pH was observed to exhibit minor fluctuation from surface to bottoms as consistent with Zhang et al. (2014).

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The oxidation reduction potential (ORP) of Core A and Core B were ranged from 158-236 mV and 172-245 mV, respectively. The ORP of sediment samples were measured as it is an important parameter controlling heavy metal stability and mobility and as indicator to understand relative status of the soil and sediment (Zhang et al., 2014). The results showed that the sediments in the two sampling sites were in oxidized form. The mobility of metals increases in low oxidation stage when Eh < 100 mV (Kabata Pendias & Pendias, 2001). Changes in the oxidation state of the metals associated with the oxides can greatly affect their solubility and mobility in soil and aqueous environments (Lee, 2006). The high ORP in sediment facilitate the oxidization rate of sulfides and the degradation of organic compounds, accelerating the liberation of the adsorbed/complexing heavy metal and thus transform to a more mobile form with ORP in sediment increase (Zhang et al., 2014). As soils become anaerobic, the redox potential decreases and transform to the more soluble reduced forms of metals.

Table 2. Physico-chemical properties and metal concentrations in different sediment layer depths (cm) of Core A and B

Core A					Core B				
Layer depth (cm)	pH	ORP (µS)	Zn (mg/kg)	Sn (mg/kg)	Layer depth (cm)	pH	ORP (µS)	Zn (mg/kg)	Sn (mg/kg)
1.25	7.05	212	50.65	< 0.03	1	6.91	219	56.27	< 0.03
3.75	7.11	212	49.77	< 0.03	3	7.14	203	48.13	< 0.03
6.5	6.78	222	44.19	< 0.03	5	7.20	206	53.94	< 0.03
9.5	7.23	200	54.31	< 0.03	7.5	7.03	230	69.38	< 0.03
12.5	7.00	219	68.49	< 0.03	10.5	6.89	245	73.59	< 0.03
15	7.19	217	45.83	< 0.03	13.5	7.10	215	64.68	< 0.03
17	6.81	226	59.62	< 0.03	16	7.00	206	52.07	< 0.03
19	7.43	208	55.15	< 0.03	18	7.11	207	60.91	< 0.03
21	7.16	207	59.80	< 0.03	20	7.08	201	43.88	< 0.03
23	6.92	233	53.68	< 0.03	22	7.12	195	50.89	< 0.03
25	7.45	236	56.01	< 0.03	24	6.95	204	46.31	< 0.03
27	7.20	224	55.77	< 0.03	26	7.40	194	43.77	< 0.03
29	8.14	188	58.13	< 0.03	28	7.21	189	49.89	< 0.03
31	7.86	190	54.00	< 0.03	30.5	7.25	202	57.25	< 0.03
32.5	8.15	184	56.96	< 0.03	33.5	7.37	203	57.29	< 0.03
34.25	8.30	178	50.62	< 0.03	36.5	7.40	204	49.07	< 0.03
36.75	7.78	184	53.15	< 0.03	39.5	7.51	192	41.93	< 0.03
39	7.67	180	44.62	< 0.03	42	7.46	173	38.03	< 0.03
41	7.51	168	48.69	< 0.03	44	7.75	172	25.70	< 0.03
42.75	7.84	162	44.90	< 0.03	46	7.40	197	22.50	< 0.03
44.75	7.52	159	50.23	< 0.03	48	8.10	175	22.30	< 0.03
47.25	7.64	158	41.63	< 0.03	50.5	7.82	183	21.63	< 0.03
49.25	7.82	160	39.51	< 0.03					
51	8.07	158	32.83	< 0.03					
Max	8.3	236	68.49	-		8.1	245	73.59	-
Min	6.8	158	32.83	-		6.9	172	21.63	-

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The grain size distribution of the two cores in every layer depths was studied in this study to investigate the overall composition of the sediment. The sediment composition of the sediment profile can be used to correlate and link with historical changes of industrial activities and/or natural events occurred in the past together when the concentrations of heavy metal detected (Ciszewski et al., 2012; Sanei et al., 2001). In this study, it was found that the sediment samples in Core A are orange brown and mixed with shells, debris minerals, and/or mineral fragments at the depth of 27 cm (12th layer) but not in the above and underbeneath layers (11th and 13th layers, respectively) (Figure 2).

Metal concentration

The Sn and Zn concentrations of the two sediment cores (Core A and B) are shown in Table 2. In this study, Zn concentrations ranged from 32.83-68.49 mg kg^{-1} and 21.63-73.59 mg kg^{-1} in Core A and B, respectively, whereas Sn concentration is below detection limit (< 0.03 mg kg^{-1}) of the instrument used. It was observed that Zn concentrations measured in the core bottom layers are much lower than those found in the top and middle sections. This element has similar concentration profile for both cores. Core A and B have a decrease in metal concentration as a function of increasing depth with the highest Zn concentrations in the 12.5 cm and 10.5 cm layer depth, respectively. The decreasing trend of metal concentrations in the sediment core was observed by others (Ciazela & Siepak, 2016; Maslennikova et al., 2016).
Overall, the estimated metal levels in the sediments of this study were found relatively lower than other reported studies. Suteerasak & Bhongsuwan (2008) found high concentrations of Sn and Pb in the sediments that collected from Bang-Yai canal (471-15,174 mg kg^{-1} and 17-113 mg kg^{-1}, respectively). The measure concentrations of theses metals were compared with the national and international standards. The observed metal concentration was below the Sediment Quality Guidelines of Threshold Effects Concentration (TEC) (121 mg kg^{-1} Zn) (Helen et al., 2016)

Metal risk assessment

Tin concentrations in all sediment samples are below detection limit (< 0.03 mg kg^{-1}), therefore, the geoaccumulation index (Igeo) and the enrichment factor (EF) values of Sn in the sediments cannot be found in this study due to the very low Tin concentration, except Igeo and EF of Zn. The degree of metal pollution in sediments assessed using the geoaccumulation index (Igeo) is showed in Figure 3. The $Igeo_{Zn}$ in all sediment layer depths showed the values of less than 0 exhibited unpolluted of the sediments. It is suggested that almost all the analyzed sediment samples were not being contaminated with the studied metal. The low Igeo values of the metals were found in other studies (Krishnakumar et al., 2016; Pascual-Aguilar et al., 2016). Moreover, the EF value was used in this study for assessing the enrichment degree of the metals in sediments in order to differentiate the sources of heavy metals. Normalization of the total Zn concentrations in sediment and Al concentration was applied to assess the anthropogenic inputs of elements in sediment. The results showed that the EF value of Zn was observed in the superficial sediment than the bottom sediment layers with the highest values were found at a depth of 3.75 and 3.0 m for Core A and B (EF = 4.0 and 3.8, respectively). Toward the bottoms of the core A (31-41 cm and 49.25-51 cm), the EF values of Zn are below 2, exhibited deficiency to minimal enrichment. From the data, the high EF values of Zn in

the superficial sediment ($p<0.05$) as compared to the lower sediment layer was explained the cause of contamination from the human activities.These results are comparable to those reported for Red river in Vietnam, where EF_{Zn} value was ranged from 1.4 to 4.5 (Nguyen, et al., 2016).

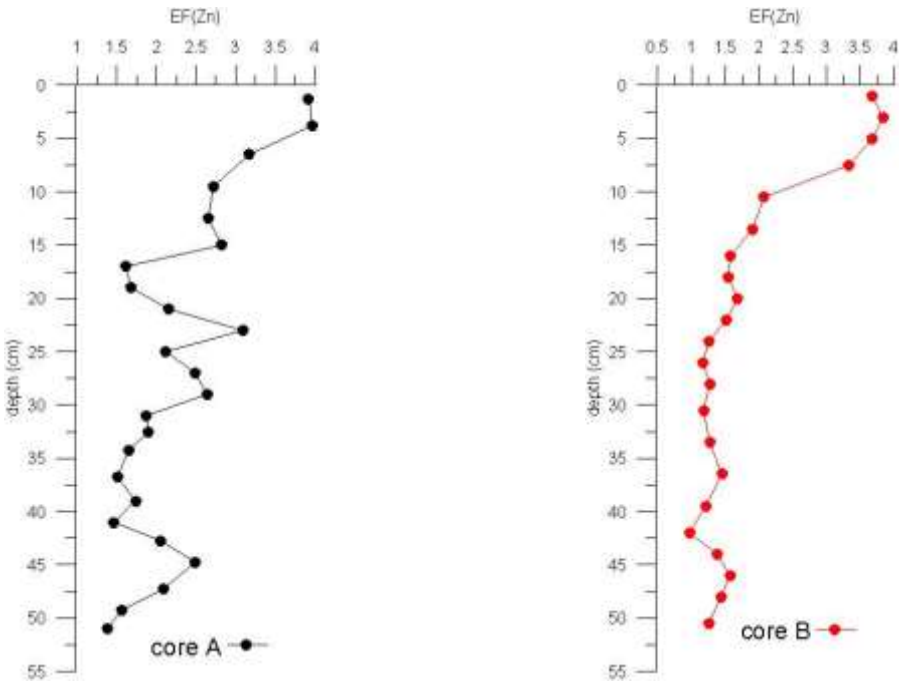

Figure 3. Geoaccumulation index (Igeo) and enrichment factor (EF) values of Zn of sediments (Core A and B)

Statistical analysis

The Zn concentration and sediment characteristics (pH and ORP) were used for statistical analysis to determine their interrelationships following PCA. The PCA allows the visualization of the information derived from the experimental data set into one principal component, retaining the maximum possible variability within that set (Worley & Powers, 2013) (Figure 4). The total variance shows the significant factors and the percent of variance explained by each of variables before undergoing rotation which accounted for 69.7% of the total variance. Loading values suggest a correlation between certain elements and soil characteristics of analyzed data. The PCA analysis results showed that the first component (PC1) has the highest factor loading (4.179) accounts for the most important associations, and is strongly correlated with Zn, pH and ORP in both cores as illustrated by the high factor loading in PC1. The results also implied that sediment characteristics (pH and ORP) have a strong influence on metal concentration; hence the strong correlations and interrelationships existed. Many previous studies have reported the effect of pH on metal bioavailability and have shown that a high pHcauses a reduction of metal bioavailability through an increase of metal sorption onto negativesites (Akkajit & Tongcumpou, 2016).

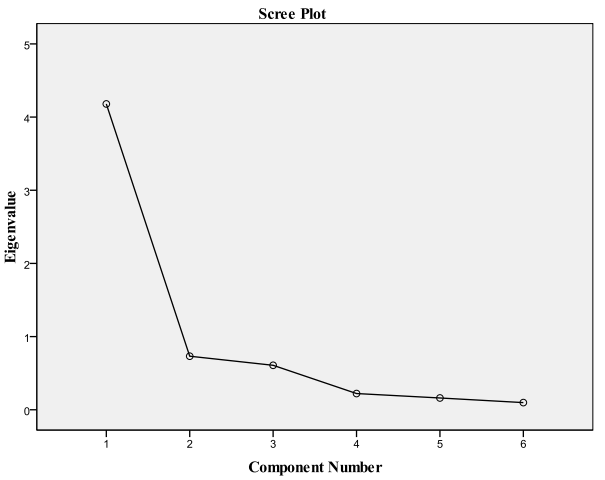

Figure 4. Scree plot of Principal Component Analysis (PCA)

Conclusion

It is suggested that all the analyzed sediment samples were not being contaminated with the studied metals ($Igeo_{Zn}$ < 0). The geoaccumulation index (Igeo) and the enrichment factor (EF) values of Sn in the sediments cannot be found due to the very low Tin concentration, except the EF values of Zn (3.17-3.97 and 3.67-3.84 of Core A and B, respectively). The EF_{Zn} value in the superficial sediment as compared to the lower sediment layer was explained the cause of contamination from the human activities. Zinc concentration in Core A and B was ranged from 32.83-68.49 mg kg^{-1} and 21.63-73.59 mg kg^{-1}, respectively and that are below the Sediment Quality Guidelines of Threshold Effects Concentration (TEC) of 121 mg kg^{-1}). This revealed that the study area was unpolluted and not enriched by Sn and Zn, however, the metal contamination in benthic organisms and animals in this coastal area should be investigated for the future work due to public awareness on pollution and risk assessment.

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