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Metal pollution and ecological risk assessment in the surface sediments of Anping Harbor, Taiwan

Cheng-Di Dong, Chih-Feng Chen, Yun-Ru Ju, Chiu-Wen Chen*

Department of Marine Environmental Engineering, National Kaohsiung Marine University, Kaohsiung 81157, Taiwan, Tel. +886 7 3617141 3762; Fax: +886 7 365 0548; emails: cddong@mail.nkmu.edu.tw (C.-D. Dong), dong3762@mail.nkmu.edu.tw (C.-F. Chen), Tel. +886 7 3617141 3765; Fax: +886 7 365 0548; email: yrju@webmail.nkmu.edu.tw (Y.-R. Ju), Tel. +886 7 3617141 3761; Fax: +886 7 365 0548; email: cwchen@mail.nkmu.edu.tw (C.-W. Chen)

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ABSTRACT

Surface sediments from 10 stations were sampled in Anping Harbor for heavy metals (Hg, Pb, Cd, Cr, Cu, Zn, and Al), water content, organic matter, total grease as well as grain size. Geo-accumulation index (I_{geo}), enrichment factor (EF), effect range median quotient, and potential ecological risk index were applied to estimate the degree of metal contamination and the potential ecological risk in sediments. The mean metals concentration with standard deviations (mg/kg) in the surface sediments was 0.28 ± 0.17 of Hg, 0.40 ± 0.27 of Cd, 202 ± 260 of Cr, 99 ± 102 of Cu, 36 ± 16 of Pb, and 257 ± 194 of Zn. For spatial distribution of heavy metals, a relatively high metal content was observed in the Bamboo River mouth region and it progressively decreased towards the harbor region. The estimates of I_{geo} and EF revealed that sediments of Bamboo River mouth were severely metal contamination. Results showed that upstream industrial and municipal wastewater discharges along the river bank may be the major sources of pollution. For the potential ecological risk assessment, the river mouth of Anping Harbor showed considerable ecological risk, while the other areas posed low and moderate ecological risk. This study can provide valuable information for developing future strategies for the management of river mouth and harbor.

Keywords: Ecological risk; Enrichment factor; Geo-accumulation index; Heavy metals; Sediment

1. Introduction

Aquatic sediments can absorb chemicals to levels many times higher than the water column concentration, so it is considered a sink and reservoir of contaminants, such as metals [1]. Metals can be classified into two parts, essential and nonessential elements for organisms. Excessively essential metals and nonessential metals are toxic to aquatic organisms and further they could threaten the aquatic ecology system [2]. Therefore, many studies effort has been directed toward the distribution of metals in aquatic

*Corresponding author.

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environment. Anthropogenic activities, such as mining, smelting, domestic and industrial wastewaters, tanning, steam electrical production, and sewage sludge are the major sources of metal pollution [2,3]. Metals have a characteristic low solubility; they are easily adsorbed on waterborne suspended particles [4,5]. After a series of natural processes, the waterborne metals would deposit in the sediment finally. Hence, the quantity of metals contained in the sediment reflects the degree of pollution for the water body [6].

Anping Harbor is the most important auxiliary port of Kaohsiung Harbor, Taiwan. It is located on Taiwan's southwestern shore nearby 40 km north of Kaohsiung Harbor. It receives effluents from two contaminated rivers, including Tainan Canal and Bamboo River (Fig. 1). These rivers flow through the downtown area of Tainan City and discharge into Anping Harbor. The lack of sanitary sewer system (sanitation coverage of 35.0%) [7] results in the discharge of untreated raw wastewater directly into adjacent water bodies, which leads to serious deterioration of water quality. The major source of pollution includes domestic wastewater discharges, industrial wastewater discharges (e.g. metal processing, electronic, and foundry), municipal surface run-off, and transportation pollution. All pollutants will eventually be transported to the river mouth and/or harbor and become deposited and accumulated in the bottom sediments [8]. The objective of this study is to investigate the heavy metal contents (Hg, Cd, Cr, Cu, Pb, and Zn) in the surface sediment of Anping Harbor so that the degree of metals accumulation and potential ecological risk can be evaluated.

2. Materials and methods

2.1. Sample collection and laboratory analysis

Surface sediment samples were collected from 10 sampling sites at Anping Harbor (Fig. 1). In this study, on-site sampling of all 40 surface sediments was done on a fishing boat in February, May, August, and October, 2011 at 10 sites selected in Anping Harbor (Fig. 1). The precise location of each sampling site was pinpointed using global positioning system (GPS). Ekman Dredge grab sampler (Jae Sung International Co., Taiwan) was used to collect the surface sediments, the surface sediment (0–15 cm) samples were placed in double-layer zipped sample bags and temporarily stored in a cooler filled with crushed ice before being transported to laboratory for analyses.

In the laboratory, a small portion of the sample was subject to analysis of water content (dried to constant weight at 105˚C), and the remaining portion sediments were air-dried in a dark and cool place to be analyzed later. Prior to being analyzed, each sample was lightly crushed with a wooden board, and then screened through 1-mm nylon net to remove particles with diameters larger than 1 mm. One portion of the screened portion was subject to particle size analyses using a Coulter LS Particle Size Analyzer [9,10]; the particles were classified into three groups, i.e. clay (<2 μm), silt (2–63 μm), and sand (>63 μm) [11]. Another portion was washed with ultra-pure water to remove sea salts; the salt-free particles were dried naturally in a dark place, grounded into fine powder with mortar and pestle made of agate, and then analyzed for organic matter (OM), total grease (TG), aluminum (Al), mercury (Hg), lead (Pb), cadmium (Cd),

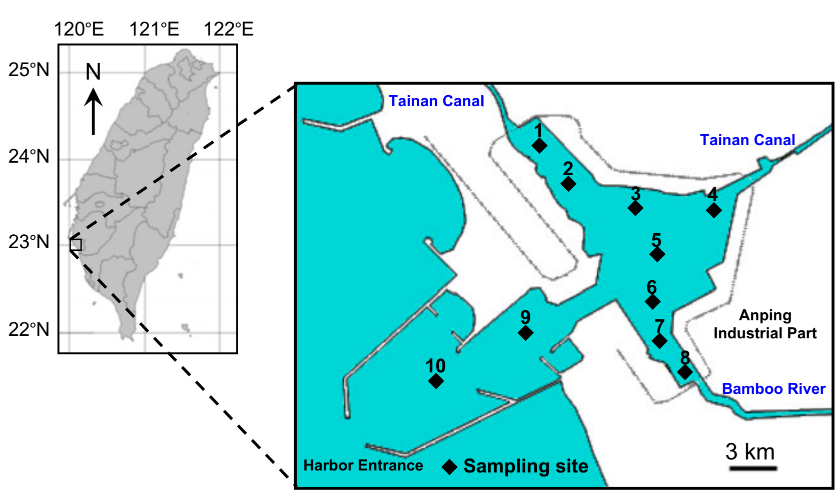

Fig. 1. Map of the study area and sampling locations.

chromium (Cr), copper (Cu), and zinc (Zn). OM was analyzed using the loss-on-ignition (LOI) method at 550℃; TG was determined according to procedures 5520E published in Standard Method [12]. The analysis of Al and the six metals contained in the sediments is described below.

About 0.50 g dry weight of the sediment sample was mixed with a mixture of ultra-pure acids (HNO_3:HCl:HF = 5:2:5, V/V/V), and then was heated to digestion. The digested sample was filtered through 0.45-μm filter paper; the filtrate was diluted with ultra-pure water to a pre-selected final volume. The Al and metals content were determined using a flame atomic absorption spectrophotometry (Hitachi Z-6100, Japan). The MHS-10 technique was used for Hg analysis (USEPA Method 7471A) [13]. Each batch of analyses was accompanied with a certified reference material PACS-2 (marine sediment) from the National Research Council of Canada. Differences between certified and measured results were less than 10% for all metals reported in this study. For every 10 samples analyzed, the examination of standard solutions was carried out to assure the stability of the instrument used. The detection limits (mg/kg dry weight) for these metals were: 5, 0.01, 0.01, 0.1, 0.5, 0.1, and 0.8 for Al, Hg, Cd, Cr, Cu, Pb, and Zn, respectively.

2.2. Data analysis

Data analyses (e.g. mean, standard deviation, maximum and minimum concentrations), using statistical methods, were performed in this study. The correlation between sediment characteristics (i.e. particle size, water content, OM, and TG) and metals contents, Person correlation analysis was done with SPSS software (SPSS, version 12.0). The geo-accumulation index (I_{geo}), enrichment factor (EF), and modified pollution index (MPI) were applied to estimate the degree of metals contamination. The I_{geo} values for the metals studied were calculated using the Müller's expression [14]:

$$I_{\text{geo}} = \log_2\left(\frac{C_\text{m}}{1.5B_\text{m}}\right) \tag{1}$$

where B_m is the background content of metals in the earth's crust [8,15–18]. The mean contents of Hg, Pb, Cr, Cd, Cu, Zn, and Al in the earth crust are 0.08, 12.5, 100, 0.2, 55, 70 mg/kg and 8.23%, respectively, which were adopted from the data published by Taylor [19]. Factor value of 1.5 is the background matrix correction factor for adjusting the lithogenic effects.

The EF is carried out by normalizing the metal concentration based on geological characteristics of the sediment. It is defined as follows,

$$\text{EF} = \frac{(C_\text{m}/C_\text{Al})_\text{sediment}}{(C_\text{m}/C_\text{Al})_\text{crust}} \tag{2}$$

where C_m and C_{Al} are the metals and Al content in sediments or in earth crust, respectively. Aluminum is a major metallic element found in the earth's crust; its concentration is somewhat high in sediments and is not affected by man-made factors. Thus, Al has been widely used for normalizing the metal concentration in sediments [8,15–18].

The MPI is calculated using the formula developed by Brady et al. [20]:

$$\text{MPI} = \sqrt{\frac{(\text{EF}_\text{average})^2 + (\text{EF}_\text{max})^2}{2}} \tag{3}$$

where $EF_{average}$ and EF_{max} are average and max value, respectively, in all the EF of metals studied. The MPI is a combination of the Nemerow Pollution Index [21], and EF. The MPI can provide a qualitative assessment of site pollution with multiple metals.

The mean effect range median quotient (m-ERM-q) and potential ecological risk index (RI) were employed to assess the biological effects and potential ecological risk in sediments. The RI can be calculated from the equation [22]:

$$\text{RI} = \sum \text{Er}_\text{m} \tag{4}$$

$$\text{Er}_\text{m} = \text{CF} \times T_\text{m} \tag{5}$$

where Er_m is the potential ecological risk factor for metal, CF is the contamination factor, CF = C_m/B_m, C_m is the measure concentration of metals in sediment, B_m is the background concentration of metals, and T_m is the biological toxicity factor, i.e. 40, 30, 2, 5, 5, and 1 for Hg, Cd, Cr, Cu, Pb, and Zn, respectively. In this study, the mean metal concentration in the earth crust was taken as the background concentration [23,24].

The m-ERM-q is calculated using the formula suggested by Long et al. [25],

$$\text{m-ERM-q} = \frac{\sum\left(\frac{C_\text{m}}{\text{ERM}_\text{m}}\right)}{n} \tag{6}$$

where C_m is the sediment concentration of metals, ERM_m is the corresponding ERM value, i.e. 0.71, 9.6, 370, 270, 218, and 410 for Hg, Cd, Cr, Cu, Pb, and Zn [26] and n is the number of metals.

3. Results and discussion

3.1. General sediment characteristics

Sediment characteristics at each sites are summarized in Table 1, the mean water content ranged from 40.8 to 115.9%, while the OM and TG contents varied from 2.2 to 4.2% and 570 to 3,942 mg/kg, respectively. The water content, OM, and TG in the sediments from the study area have a similar spatial evolution characterized by the highest levels at Sites 4 and 8, which are located at the vicinity of Tainan Canal and Bamboo River mouths. OM and TG were relatively high in the vicinity of the river mouths compared with those at the harbor entrance areas (Sites 9 and 10). The results show that the anthropogenic contribution from the harbor tributaries is the major source of OM and TG [8,27]. The results of sediment particle diameter analyses showed that the major particles of surface sediments are silt with diameter between 2 and 63 μm. The ranges of percentage compositions are 30.8–82.6, 4.1–18.0, and 0.0–65.0% for silt (2–63 μm), clay (<2 μm), and sand (>63 μm), respectively. Chen et al. [28] and Dong et al. [27] found that fine particles (<63 μm) can easily adsorb and accumulate pollutants and it is the major part among the particles found in the harbor sediments. Additionally, the surface sediment samples collected at 10 monitoring stations studied contain 3.76–5.18% of Al with a mean of 4.29 ± 0.54%. Aluminum is used as a normalized element although it has some limitations, including the increasing Al mobility by human activities, or the low Al content in the natural sediment (e.g. sands) [20]. However, Al is one of the refractory elements which is extremely immobile in the marine environment [29], and the high content of Al is observed in the present study area. Therefore, those limitations of mobile Al and sediment characteristics could be ignored.

3.2. Distribution of heavy metals in sediments

Metal concentrations in the surface sediments from 10 sampling sites are presented in Fig. 2. Mean concentrations with standard deviations in the surface sediments from 10 sites were 0.28 ± 0.17 mg/kg for Hg, 0.40 ± 0.27 for Cd, 202 ± 260 for Cr, 99 ± 102 for Cu, 36 ± 16 for Pb, and 257 ± 194 for Zn. The mean Hg, Cd, Cu, Pb, and Zn contents were highest in Sites 8 (0.64 ± 0.19, 0.79 ± 0.29, 359 ± 103, 67 ± 18, and 641 ± 285 mg/kg) and 4 (0.42 ± 0.15, 0.75 ± 0.38, 143 ± 11, 53 ± 13, and 414 ± 168 mg/kg), while the highest mean concentration of Cr was found in Site 8 (774 ± 369 mg/kg). Extremely high Cr concentration was observed in Site 8 and was 2–30 folds than other sampling sites. This phenomenon might be contributed by the upstream of Bamboo River mouth, which is through the Anping Industrial Park and has more than 522 registered industrial factories that discharge their treated and untreated wastewaters into the Bamboo River, and is discharged into southern Anping Harbor (Fig. 1).

Concentration distributions of these metals in the Anping Harbor sediment are shown in Fig. 2. Results revealed that the sediment metal content is relatively higher near the river mouths, especially in Tainan Canal and Bamboo River mouth (Sites 4 and 8), and gradually decreases in the direction toward the harbor entrance. These observations clearly indicate that the upstream pollutants brought over by rivers are the major sources of harbor metals pollution. Because these rivers are subject to upstream discharges of untreated domestic and industrial wastewaters, the pollutants are transported by river flow and finally accumulate near the river mouth. Table 2 presents the metals concentrations in sediments at different locations around the Asian area. Compared with those reported in different regions of the Asian area, the sediments collected from Anping Harbor have higher metals level than those reported in most other regions, especially Cr, Cu, and Zn.

The coefficient of the Pearson correlation between the sediment characteristics and six metals contents are shown in Table 3. The contents of most metals are obviously correlated with the OM and TG contents (Table 3), but not to particle size ($p > 0.05$), indicating that particle size may not be a major factor to be concerned for controlling the metals distribution. Although most studies presented significant negative correlation between sediment particle sizes and metals concentrations [15,16,29,45,46], the results of this study indicate the opposite that the OM and TG contents are more important than particle size in controlling the distribution of metals in the sediments. The results suggest that the sorption mechanism of metals in the study areas sediments is mainly influenced by chemical adsorption rather than physical adsorption or deposition of metals with organic compounds on surface sediments. The metals distribution in sediments is noted to exhibit significant positive correlation with TG contents (Table 3), which were usually derived from the upstream rivers either through industrial effluents or municipal sewage discharges [47].

Table 1
Location, water depth, and basic characteristics of surface sediments of Anping Harbor (mean ± SD)

Site	Location (latitude, longitude)	Water depth (m)	Water content (%)	Organic matter (%)	Total grease (mg/kg)	Clay (<2 μm) (%)	Silt (2–63 μm) (%)	Sand (>63 μm) (%)	Aluminum (%)
1	22°58′49.8′′, 120°09′41.3′′	7.5	45.4 ± 20.9	2.9 ± 1.4	899 ± 752	4.1 ± 4.1	30.8 ± 32.1	65.0 ± 36.2	4.48 ± 0.53
2	22°58′41.5′′, 120°09′48.3′′	9.0	64.2 ± 14.4	3.2 ± 1.0	1,536 ± 1,411	12.1 ± 3.6	72.6 ± 22.3	15.3 ± 25.6	4.01 ± 0.33
3	22°58′36.1′′, 120°09′58.1′′	9.3	40.8 ± 7.3	2.2 ± 0.4	613 ± 197	8.1 ± 6.8	36.9 ± 25.3	55.1 ± 32.1	3.90 ± 0.20
4	22°58′40.2′′, 120°10′29.1′′	7.6	82.2 ± 30.8	4.1 ± 0.9	2,597 ± 1,146	9.0 ± 2.6	71.9 ± 21.4	19.1 ± 23.9	4.39 ± 0.38
5	22°58′24.1′′, 120°10′20.3′′	10.3	115.9 ± 25.2	3.8 ± 0.6	1,752 ± 577	16.2 ± 2.4	82.6 ± 2.8	1.2 ± 0.7	4.28 ± 0.24
6	22°58′18.0′′, 120°10′08.0′′	10.6	88.1 ± 12.9	3.1 ± 0.3	2,314 ± 760	17.5 ± 1.7	82.4 ± 1.7	0.0 ± 0.0	5.18 ± 0.67
7	22°58′07.2′′, 120°10′13.6′′	10.6	60.2 ± 22.6	2.2 ± 0.2	1,427 ± 237	11.2 ± 4.2	66.2 ± 22.8	22.6 ± 26.9	4.30 ± 0.24
8	22°57′57.8′′, 120°10′19.8′′	9.3	83.9 ± 21.2	4.2 ± 1.4	3,942 ± 663	4.3 ± 2.0	55.3 ± 11.9	40.4 ± 13.9	4.54 ± 0.35
9	22°57′57.9′′, 120°09′30.4′′	11.4	80.6 ± 11.9	3.0 ± 0.7	939 ± 313	18.0 ± 2.6	81.8 ± 2.7	0.2 ± 0.2	4.05 ± 0.25
10	22°57′43.3′′, 120°09′09.7′′	11.4	62.4 ± 12.8	2.6 ± 0.7	570 ± 315	17.0 ± 1.9	82.3 ± 2.1	0.7 ± 1.0	3.76 ± 0.18

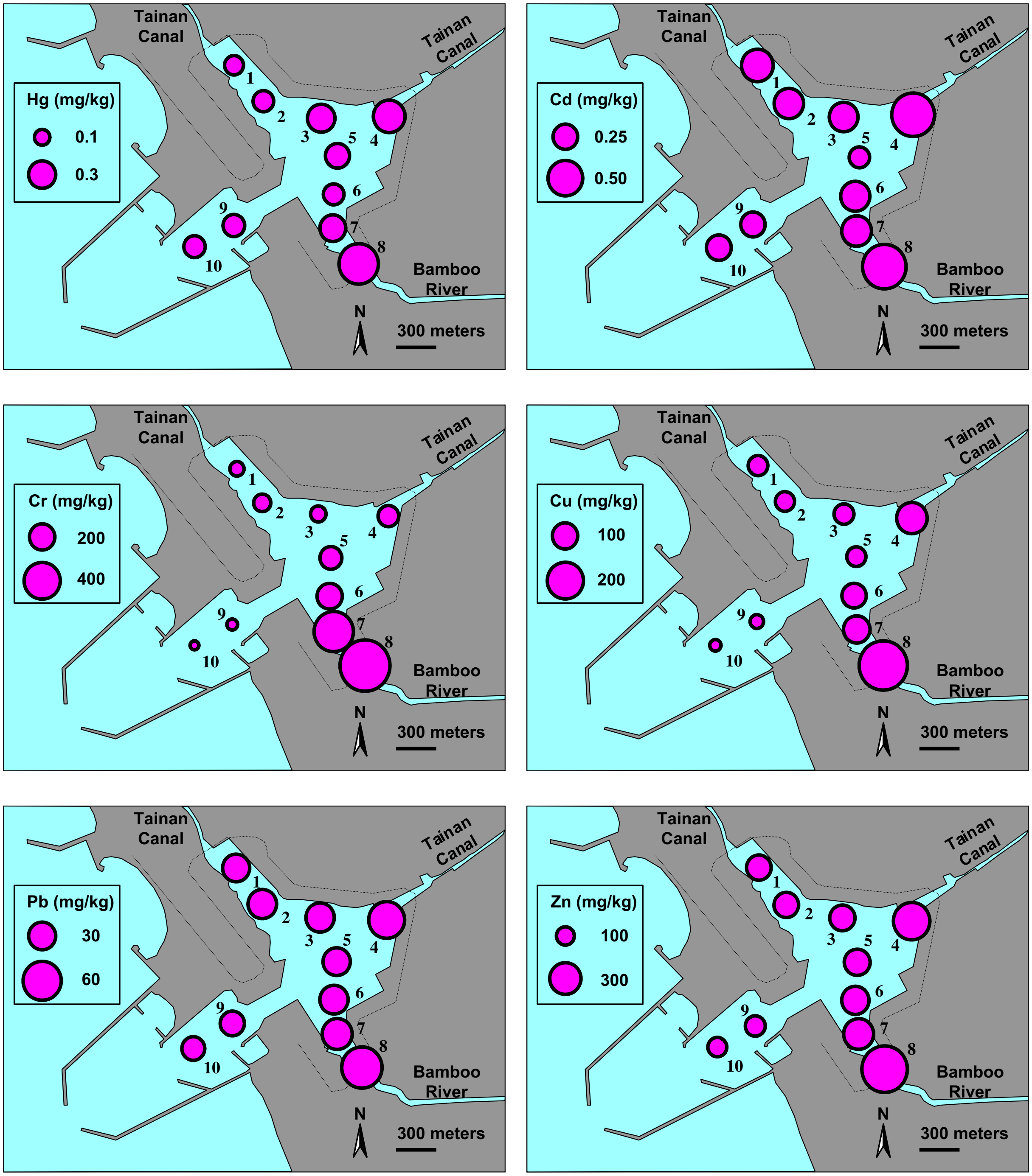

Fig. 2. Spatial distribution of metal contents in the surface sediment of Anping Harbor.

3.3. Contamination of heavy metals in sediments

The I_{geo} index can be used as a reference to estimate the extent of metal accumulation. Based on the I_{geo} data and Müller's geo-accumulation indexes [14], the accumulation levels with respect to the metals at each site are ranked in Table 4. The results showed that in the vicinity of Tainan Canal and Bamboo River mouths, the sediment is in the moderated to strong polluted class for most metals as compared with the other harbor areas, which usually had none to medium class of metal pollutant. Among the six metals studied, I_{geo} classes of Hg were ranked as the

Table 2
Comparison of metal concentrations in sediments of Anping Harbor with other regions (mg/kg dw)

Location	Hg	Pb	Cd	Cr	Cu	Zn	Refs.
Anping Harbor, Taiwan	0.10–0.92	15.1–89.1	0.04–1.39	14.4–1,311	11.0–439	62–911	Present study
Kaohsiung Coast, Taiwan	–	2.5–23.8	0.05–0.42	12.5–95.0	1.3–23.8	45.0–128	[30]
Kaohsiung Harbor, Taiwan	0.15–1.12	16–109	0.15–1.11	23–523	10–562	70–1,602	[8]
Xiamen Bay, China	–	44.9–59.8	0.11–1.01	36.7–134	18.5–97.2	65–223	[31]
Quanzhou Bay, China	0.17–0.74	34.3–101	0.28–0.89	51.1–122	24.8–120	106–242	[32]
Tianjin Bohai Bay, China	0.02–0.85	17.5–34.9	0.14–1.82	18–191	11.4–27.3	68.7–393	[33]
East China Sea, China	–	10.0–44.8	–	–	4.29–41.5	18.2–114	[34]
North Yellow Sea, China	–	17–44	0.02–0.31	11–113	3–56	15–125	[35]
Eastern Coast of the Gulf of Thailand	0.005–0.121	1.69–66.3	<0.006–0.19	–	14.4–103	7.48–131	[36]
Masan Bay, Korea	–	13.0–82.2	0.1–7.5	30.5–99.8	13.5–90.7	80.0–379	[37]
Youngil Bay, Korea	–	22.0–53.2	0.3–4.0	15.0–39.2	10.9–134	86.6–377	[38]
Korea Coast, Korea	ND–0.63	1.9–107	ND–1.97	0.8–223	0.4–125	6–452	[39]
Ise-Tokai region, Japan	–	6.26–82.7	0.06–1.48	43.0–168	13.5–81.6	66.7–210	[40]
Hokkaido, Japan	0.01–0.50	0.8–80	0.01–0.71	6–336	3–206	12–200	[41]
Manila Bay, Philippines	–	7.3–19.0	–	–	22.9–38.6	50–96	[42]
Port Klang, Malaysia	–	31.3–105	0.16–2.10	22.0–83.2	8.6–57.0	17.0–193	[43]
Coastal of Dumai, Indonesia	–	14.6–84.9	0.46–1.89	–	1.6–13.8	31.5–87.1	[44]

Table 3
Pearson correlation coefficients among sediment characteristics and metals concentrations (n = 40)

Item	Clay + Silt	Sand	Water content	Organic matter	Total grease	Hg	Cd	Cr	Cu	Pb	Zn
Sand	−1.00[a]										
Water content	0.57[a]	−0.57[a]									
Organic matter	0.30	−0.30	0.53[a]								
Total grease	0.15	−0.15	0.47[a]	0.49[a]							
Hg	−0.17	0.17	0.11	0.16	0.65[a]						
Cd	−0.28	0.28	−0.05	0.29	0.35[b]	0.44[a]					
Cr	−0.16	0.16	0.15	0.04	0.61[a]	0.72[a]	0.22				
Cu	−0.23	0.23	0.21	0.34[b]	0.71[a]	0.76[a]	0.52[a]	0.86[a]			
Pb	−0.21	0.21	0.21	0.32[b]	0.55[a]	0.68[a]	0.65[a]	0.62[a]	0.79[a]		
Zn	−0.16	0.16	0.32[b]	0.34[b]	0.68[a]	0.67[a]	0.30	0.78[a]	0.89[a]	0.79[a]	
Al	0.14	−0.14	0.25	0.15	0.43[a]	0.15	0.30	0.23	0.27	0.19	0.08

[a]Correlation is significant at the 0.01 level (2-tailed).
[b]Correlation is significant at the 0.05 level (2-tailed).

moderate to strong class (Class = 2–3) for sediments from the output areas of rivers and as the none to medium class (Class = 1) for sediments from the other sites. This might indicate that the Anping Harbor has moderately accumulated with Hg metal originating from the upstream of rivers. Similar to mercury, Cd, Cr, Cu, Pb, and Zn in the output areas of rivers compared to other areas have higher pollution class.

The EF values of analyzed six metals were calculated to differentiate the man-made and natural sources of metal contamination in the surface sediments of Anping Harbor. When the EF of a metal is greater than 1, the metal in the sediment originates from man-made activities, and vice versa [9,15,47,48]. Furthermore, the EF value can be classified into 7 categories [49]: Class 0: no enrichment for EF < 1; Class 1: minor for 1 ≤ EF < 3; Class 2: moderate for 3 ≤ EF < 5; Class 3: moderately severe for 5 ≤ EF < 10; Class 4: severe for 10 ≤ EF < 25; Class 5: very severe for 25 ≤ EF < 50; and Class 7: extremely severe for EF ≥ 50. Table 5 presents the EF values and classes for the metals obtained in this study with respect to

Table 4
Geo-accumulation index of metals and classification of sediment in Anping Harbor

	Geo-accumulation index (I_{geo})					
Site	Hg	Cd	Cr	Cu	Pb	Zn
1	0.3	0.5	−1.2	−0.5	0.7	0.8
2	0.6	0.3	−0.7	−0.5	0.8	0.8
3	1.4	0.2	−1.0	−0.4	0.8	0.9
4	1.8	1.3	−0.2	0.8	1.5	2.0
5	1.0	−0.8	0.0	−0.5	0.7	1.0
6	0.5	0.2	0.4	0.1	0.8	1.1
7	1.2	0.3	1.7	0.4	1.0	1.4
8	2.4	1.4	2.4	2.1	1.8	2.6
9	0.7	−0.3	−2.1	−1.5	0.4	0.2
10	0.6	−0.2	−2.6	−2.1	0.2	0.1
All sites	1.2	0.4	0.4	0.3	1.0	1.3
Pollution class	2	1	1	1	2	2
Pollution level	Moderate	None to medium	None to medium	None to medium	Moderate	Moderate

the crustal average. The EF values of Hg and Zn were highest with the means of 6.6 and 7.0, respectively. This indicates that the sediment Hg and Zn has a high enrichment phenomenon with respect to the earth crust and that all Hg and Zn originates from man-made sources. The mean EF values of Cd, Cr, Cu, and Pb were 3.9, 3.9, 3.4, and 5.5, respectively, indicating that they also originated from anthropogenic sources in most samples. Spatially, high EF values (e.g. 14.6 for Hg, 7.1 for Cd, 14.0 for Cr, 11.8 for Cu, 9.5 for Pb, and 16.6 for Zn) were noted in sediments at Site 8, located in the vicinity of the Bamboo River mouth, which receives much quantity of metallic pollutants from industrial plants. The mean EF classes of the 6 metals ranged from 3 to 4, which represent minor to moderate enrichment levels. Site 8 had the highest EF classes among the 10 monitoring sites studied; its EF classes were severe as 4–5.

Comparison of the results of pollution level derived by I_{geo} and EF (Tables 4 and 5) reveals that the pollution level is lower for the I_{geo} than EF. Using a value of 1.5 as the background adjustment factor

Table 5
Enrichment of metals and classification of sediment in Anping Harbor

	Enrichment factors (EF)								
Site	Hg	Cd	Cr	Cu	Pb	Zn	$EF_{aver.}$	EF_{max}	MPI
1	3.4	3.8	1.2	2	4.5	5	3.3	7.3	5.6
2	4.4	3.7	1.9	2.1	5.5	5.6	3.9	8	6.3
3	8.1	3.6	1.6	2.4	5.5	6	4.5	11.3	8.6
4	9.9	6.9	2.5	4.9	7.9	11.5	7.3	18.2	13.9
5	5.8	1.7	2.9	2	4.6	5.6	3.8	8.6	6.6
6	3.4	2.8	3.1	2.6	4.2	5.6	3.6	9.7	7.3
7	6.8	3.4	9.1	3.9	5.6	7.6	6.1	10.8	8.8
8	14.7	7.1	14.3	12	9.4	16.9	12.4	22.9	18.4
9	4.9	2.4	0.7	1.1	3.8	3.6	2.8	5.9	4.6
10	5.1	2.9	0.5	0.8	3.7	3.5	2.8	6.6	5.0
All sites	6.7	3.8	3.8	3.4	5.5	7.1	5.1	22.9	16.6
Pollution class	3	2	2	2	3	3	–	–	5
Pollution level	Moderately severe	Moderate	Moderate	Moderate	Moderately severe	Moderately severe	–	–	Severe

could be the possible reason for underestimating the pollution level, because it did not consider the complicated interaction and sedimentation occurred in the river mouth and marine environment [20].

The MPI is a comprehensive index that can be employed to conduct an overall assessment and comparison of the heavy metal contamination of different areas. The derivation of MPI is calculated from EFs, moreover the classification of MPI is also based on the EF thresholds as a basis to conduct the pollution level assessment [20,50]. The 6 MPI classes were: Class 0: unpolluted for MPI < 1; Class 1: slight for 1 ≤ MPI < 2; Class 2: moderate for 2 ≤ MPI < 3; Class 3: moderate to heavy for 3 ≤ MPI < 5; Class 4: heavy for 5 ≤ MPI < 10; Class 5: severe for MPI ≥ 10 [20]. In this study, the pollution level were presented that the river mouths (severe) > harbor (heavy) > entrance (moderate to heavy), and all sediment samples collected from Anping Harbor were belong to severe polluted level (Table 5).

3.4. Potential ecological risk of heavy metals in sediments

The potential ecological risk associated with the six metals in the surface sediments of the study area was assessed by Er_m and RI index. The Er_m and RI are applied to evaluate the potential ecological risk associated with the accumulation of metals in surface sediments. Er_m and RI that were proposed by Hakanson [22] can be used to evaluate the potential risk of one metal and combination of multiple metals, respectively. The calculated Er_m values can be categorized into five classes of potential ecological risks: low risk ($Er_m < 40$), moderate risk ($40 \le Er_m < 80$), higher risk ($80 \le Er_m < 160$), high risk ($160 \le Er_m < 320$), and serious risk ($Er_m \ge 320$). The calculated RI values can be categorized into four classes of potential ecological risks: low risk (RI < 150), moderate risk (150 ≤ RI < 300), considerable risk (300 ≤ RI < 600), and very high risk (RI ≥ 600) [22].

Table 6 and Fig. 3 list the Er_m value, RI value, and risk classification for the studied metals contained in the surface sediment samples collected in this study. The sequence of Er_m was Hg > Cd > Pb > Cu > Cr > Zn, and the Hg and Cd were classified as higher and moderate risks, while the Pb, Cu, Cr, and Zn were classified as low risk. The high Er_m values (e.g. 321.5 for Hg, 118.1 for Cd, 15.5 for Cr, 32.7 for Cu, 26.8 for Pb, and 9.2 for Zn) were observed in sediments at Site 8, indicating high metal contamination of the surface sediments in the Bamboo River mouth of study area. These findings were consistent with the results obtained from EF and I_{geo}. The mean RI values of the surface sediments were from 144 to 524 with a mean of 231 (Fig. 3). Sites 9 and 10 are classified as low risk, Site 4 and 8 are classified as considerable risk, and the other sites are classified as moderate risk, respectively, with respect to combination of the study metals pollution (Fig. 3).

Besides using sediment quality guidelines, the m-ERM-q, which calculates the mean quotients for studied metals, can be used as approach to assess possible biological effects for pollutants by comparing their concentrations with the limit concentrations. According to Long et al. [25], the m-ERM-q, which is related to toxicity, can be divided to four categories, less than 0.1, 0.11–0.5, 0.51–1.5, and greater than 1.5. The m-ERM-q of less than 0.1 indicates a 12% probability of toxicity; 0.11–0.5 represents 30% probability of toxicity; 0.51–1.5 indicates 46% probability of toxicity; and greater than 1.5 has a 74% of toxicity. Furthermore,

Table 6
Potential ecological risk factor of the surface sediment for each site for Anping Harbor

	Potential ecological risk factor (Er_m)					
Site	Hg	Cd	Cr	Cu	Pb	Zn
1	73.7	62.4	1.3	5.3	12.1	2.7
2	88.2	54.1	1.9	5.2	13.5	2.7
3	155.6	51.0	1.5	5.6	13.4	2.8
4	208.9	112.7	2.7	13.0	21.2	5.9
5	119.8	25.9	3.0	5.2	12.2	2.9
6	87.3	53.4	3.9	8.3	13.1	3.3
7	139.8	54.8	9.5	10.0	15.0	3.9
8	321.5	118.1	15.5	32.7	26.8	9.2
9	96.8	36.5	0.7	2.6	9.7	1.7
10	93.4	38.4	0.5	1.8	8.7	1.6
Mean	138.5	60.7	4.0	9.0	14.6	3.7

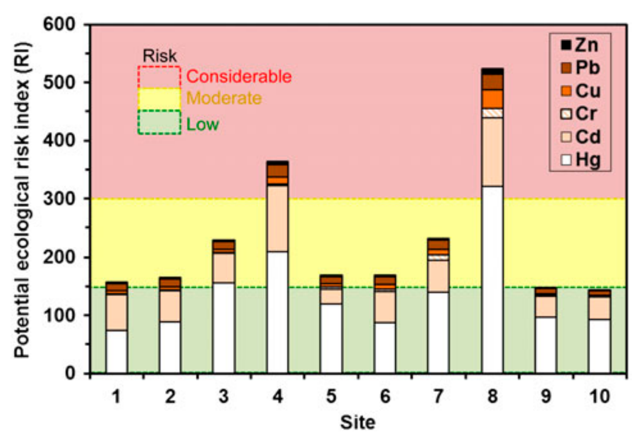

Fig. 3. Distribution of potential ecological risk indices for six metals in the surface sediment of Anping Harbor.

Table 7
Classification of sediment samples for Anping Harbor into four categories of mean ERM quotient values

Site category	Mean ERM quotient range	Percentage of samples in each category	Probability of toxicity[a]
Highest priority sites	>1.5	2.5	74
Medium–high priority sites	0.51–1.5	12.5	46
Medium–low priority sites	0.11–0.5	85.0	30
Lowest priority sites	<0.1	0	12

[a]Probability of acute toxicity in amphipod survival laboratory bioassays, from Long et al. [25].

the percentage of samples in these four categories can also be used to classify the site as low, medium-low, medium-high, and high-priority sites, respectively. The distribution of all samples ($n = 40$) shows that 85.0% of samples belonged to medium-low priority sites and 12.5% of samples were of medium-high priority sites. Only 2.5% of the samples were of high-priority sites and 0% of samples were of low-priority sites (Table 7). According to this classification, most samples (97.5%) have medium-low and medium-high (30–46%) probability of toxicity. Except Site 8 (Bamboo River mouth), that is classified as high-priority site, all sites can be classified as medium-low and medium-high priority sites. The above evaluation results indicated that the metals contained in surface sediment at mouth of river has high potential ecological risks. Therefore, effective management and control of upstream pollution should be immediately implemented to improve the river mouth sediment quality and lower the associated ecological risk.

4. Conclusions

It is concluded from the present study that the vicinity of the Tainan Canal and Bamboo River mouths in Anping Harbor has been significantly enriched and accumulated metals and had the higher ecological risks. The distribution of the metals in surface sediments reveals that the metals originates from the river upstream discharges of industrial and domestic wastewaters; it is transported along the river and finally deposited and accumulated near the river mouth. Results from the EF and I_{geo} analyses imply that the Hg, Pb, and Zn of sediments have relatively high enrichment and accumulation. However, results of potential ecological risk evaluation showed that the Hg and Cd contained in surface sediment of Anping Harbor have relatively high potential ecological risks. The results can provide regulatory valuable information for references with the aim of extending future strategies to renovate and manage river mouth and harbor.

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