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ASSESSMENT OF CHROMIUM CONTAMINATION IN SEDIMENTS OF SOUTHERN KAOHSIUNG HARBOR, TAIWAN

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ABSTRACT: Major objectives of this study are to evaluate the enrichment, accumulation, and potential ecological risk of chromium (Cr) in the surface sediments of southern Kaohsiung Harbor, Taiwan. Twelve sampling locations were installed of southern Kaohsiung Harbor to collect sediment samples for analyzing Cr. Results showed that the Cr concentrations varied from 13.4–265.7 mg/kg with an average of 53.2±71.2 mg/kg. The spatial distribution of Cr reveals that the Cr concentration is relatively high in the river mouth region, especially in Jen-Gen River, and gradually diminishes toward the harbor entrance region. This indicates that upstream industrial and municipal wastewater discharges along the river bank are major sources of Cr pollution. Results from the enrichment factor and geo-accumulation index analyses imply that the sediments collected from the river mouth can be characterized between severe and very severe degree enrichment and between moderately strong and strong to very strong accumulation of Cr, respectively. However, results of potential ecological risk index indicate that the sediment has low ecological potential risk.

Keywords: Accumulation, Chromium, Ecological Risk, Enrichment, Sediment

1. INTRODUCTION

Chromium (Cr) is moderately toxic to aquatic organisms; its presence threatens the water ecological environment. [1]. Therefore, much research effort has been directed toward the distribution of Cr in water environment. Anthropogenic activities including tanning, mining, smelting, domestic and industrial wastewaters, steam electrical production, and sewage sludge are the major source of Cr pollution [1,2]. In receiving water body, Cr is presented essentially as hydroxy-complexes of low solubility associated with the water-borne suspended particles [3,4]. After a series of natural processes, the water-borne Cr finally accumulates in the sediment, and the quantity of Cr contained in the sediment reflects the degree of pollution for the water body [5].

Kaohsiung Harbor is located on the southwestern shore, and it is the largest international harbor in Taiwan. the harbor receiving effluents from four contaminated rivers, including Love River, Canon River, Jen-Gen River, and Salt River. Results of previous research indicate that the Kaohsiung Harbor is heavily polluted with Cr, and the Jen-Gen River and Salt River are both major pollution sources [6]. The two rivers flow through the downtown area of Kaohsiung City and finally discharged into Kaohsiung Harbor (Fig. 1). The major pollution source includes domestic wastewater discharges, industrial wastewater discharges (e.g. tanning, metal processing, chemical production, electronic and foundry), municipal surface runoff, and transportation pollution [6]. All the pollutants will eventually be transported to the river mouth and/or harbor to deposit and accumulate in the bottom sediment.

The objective of this study is to investigate the Cr distribution in the surface sediment of the water body between river mouths (i.e., Jen-Gen River and Salt River) and harbor entrance of Kaohsiung Harbor so that the degree of Cr enrichment, accumulation, and potential ecological risk can be evaluated.

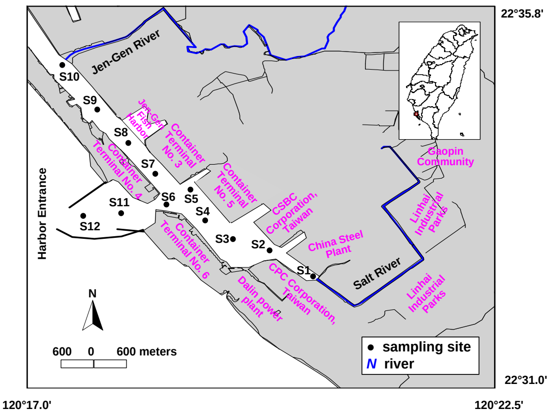

Fig. 1 Map of the study area and sampling locations.

2. MATERIALS AND METHODS

Twelve sampling stations were distributed in southern Kaohsiung Harbor, Taiwan (Fig. 1). Surface sediment samples were collected at 12 stations selected in this study in February, 2011 with Ekman Dredge Grab aboard a fishing boat. The collection, pre-processing and analysis program of sediment sample have been detailed previously [7,8]. The collected samples were characterized for aluminum (Al), chromium (Cr), grain size, water content, and organic matter (OM). The Al and Pb contents were determined using a flame atomic absorption spectrophotometry (Hitachi Z-6100, Japan) after digestion procedures [7,8]. The sediment grain size was measured using a Coulter LS Particle Size Analyzer; water contents were determined by oven-drying at 105°C; OM was determined using the LOI (loss-on-ignition) method at 550°C. The characteristics of sediment (e.g. grain size, water content, and OM) have been reported in detail previously [8].

3. RESULTS AND DISCUSSION

3.1 Distribution of Chromium in Sediments

All surface sediment samples collected at 12 monitoring stations studied contain 13.4–265.7 mg/kg with an average of 53.2±71.2 mg/kg. Spatial distributions of Cr concentration in the surface sediment shown in Fig. 2 reveal that the sediment Cr content is relatively higher near the mouths of Jen-Gen River (site 10), and Salt River (site 1), and gradually decreases in the direction toward the mouth of harbor (sites 11 and 12). These observations clearly indicate that the upstream pollutants brought over by rivers are the major source of harbor Cr pollution. The both rivers receive a great amount of industrial and domestic Cr from Kaohsiung city because about 40% domestic wastewater is discharged directly without adequate treatment [6]. Moreover, several industrial plants (e.g. metal processing, paint and dye, chemical manufacturing, electronic, motor vehicle plating and finishing, and foundries) discharge industrial wastewater effluents into the tributaries in or adjacent to Kaohsiung city, and the pollutants are transported by river flow and finally accumulate near the river mouth. Some pollutants may drift with sea current to be dispersed into open sea [6].
The Pearson correlation between the sediment characteristics and Cr content was carried out. The surface sediment Cr content is not obviously correlated to OM content ($p>0.05$) and particle size ($p>0.05$). However, based on the 11 sites, except site 10, the significant correlation ($r=0.920$, $p<0.01$) between Cr and organic matter content was found (Fig. 3). The results suggest that the sediment organic matter played an important role in controlling the Cr distribution in sediments, whereas pollution source can influence the partition of Cr in sediment organic matter.

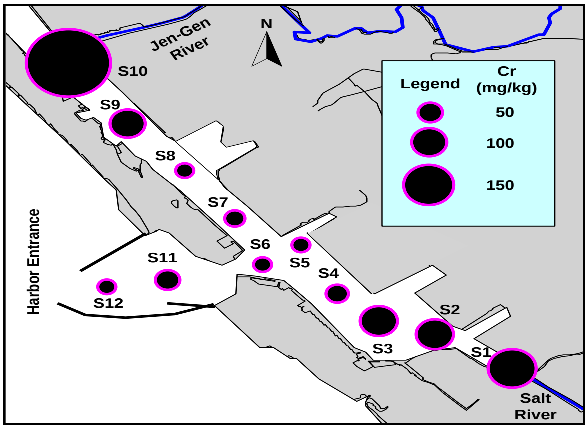

Fig. 2 Spatial distribution of chromium (Cr) contents in the surface sediment of southern Kaohsiung Harbor.

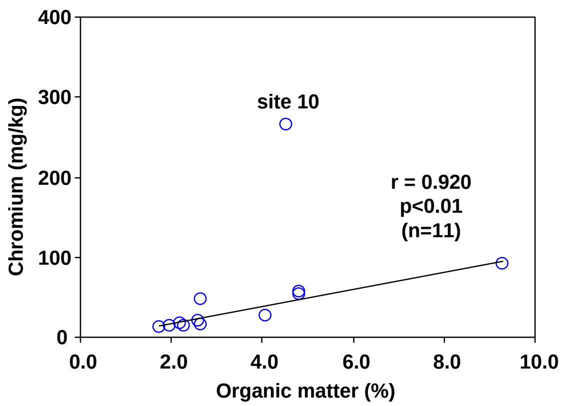

Fig. 3 Correlation between the organic matter and Cr content in the surface sediment of southern Kaohsiung Harbor (except site 10).

3.2 Comparison with Sediment Quality Guidelines

Several numerical sediment quality guidelines have been developed for assessing the contamination levels and the biological significance of chemical pollutants recently [9,10]. One of the widely used sediment toxicity screening guideline of the US National Oceanic and Atmospheric Administration provides two target values to estimate potential biological effects: effects range low (ERL) and effect range median (ERM) [10]. The guideline was developed by comparing various sediment toxicity responses of marine organisms or communities with observed metals concentrations in sediments. These two values delineate three concentration ranges for each particular chemical. When the concentration is below the ERL, it indicates that the biological effect is rare. If concentration equals to or greater than the ERL but below the ERM, it indicates that a biological effect would occur occasionally. Concentrations at or above the ERM indicate that a negative biological effect would frequently occur. Fig. 4 shows the measured concentrations of Cr in comparison with the ERM and ERL values. Among the 12 sediment samples collected, the Cr is between ERL (81 mg/kg) and ERM (370 mg/kg) in 2 samples. This indicates that the sediment concentrations of Cr found in sites 1 and 10 may cause adverse impact on aquatic lives. All other samples are below ERL for Cr indicates that biological effects would rarely occur.

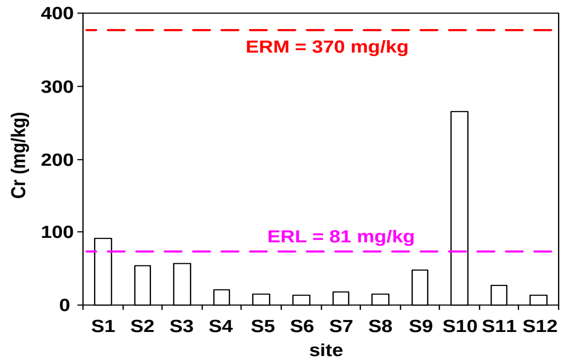

Fig. 4 Distribution of chromium (Cr) contents in the surface sediment of southern Kaohsiung Harbor.

3.3 Enrichment Factor

The enrichment factor (EF) is a good tool for differentiating the man-made and natural sources of metal contamination [6,11]. This evaluating technique is carried out by normalizing the metal concentration based on geological characteristics of sediment. Aluminum is a major metallic element found in the earth 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 [6,11]. EF is defined as: $EF = (X/Al)_{sediment}/(X/Al)_{crust}$, where (X/Al) is the ratio of Cr to Al. The average Cr and Al content in the earth crust were 100 mg/kg and 8.23%, respectively, which excerpted from the data published by Taylor (1964) [12]. When the EF of a metal is greater than 1, the metal in the sediment originates from man-made activities, and vice versa. The EF value can be classified into 7 categories [13]: 1, no enrichment for EF < 1; 2, minor for 1 < EF < 3; 3, moderate for 3 ≤ EF < 5; 4, moderately severe for 5 ≤ EF < 10; 5, severe for 10 ≤ EF < 25; 6, very severe for 25 ≤ EF < 50; and 7, extremely severe for EF ≥50.

Table 1 show EF values of the sediment Cr for 12 monitoring stations studied; the Cr concentration is consistent with the Cr EF value for all sampling stations, and EF values in the river mouths of Jen-Gen River (site 10) and Salt River (sites 1-3) are greater than 1. This indicates that the sediment Cr has enrichment phenomenon with respect to the earth crust and that the Cr originates from man-made sources. Sites 1–3 are classified as minor enrichment, site 10 is classified as moderate enrichment, and the other sites are classified as no enrichment, respectively. These results point out that the sediment near the mouth of rivers experiences minor to moderate enrichment of Cr that originates from the upstream sources of pollution. Additionally, the average EF value of 4.5 obtained in site 10 (Jen-Gen River mouth) is lower than the average EF value of 8.4 reported earlier [11] indicating that the upstream pollution has been reduced so that the accumulation of pollutants in sediments is not as serious as during earlier years. This observation may show the effectiveness of intercepting the river flow and dredging the river mouth.

Table 1 Enrichment factor of Cr for each station studied at southern Kaohsiung Harbor

Site	EF value	EF class	EF level
S1	1.4	2	minor
S2	1.1	2	minor
S3	1.1	2	minor
S4	0.4	1	no enrichment
S5	0.3	1	no enrichment
S6	0.3	1	no enrichment
S7	0.3	1	no enrichment
S8	0.3	1	no enrichment
S9	0.9	1	no enrichment
S10	4.5	3	moderate
S11	0.5	1	no enrichment
S12	0.3	1	no enrichment

[a] 1: EF <1 (no enrichment), 2: 1 < EF ≤ 3 (minor), 3: 3 < EF ≤ 5 (moderate), 4: 5 < EF ≤ 10 (moderately severe), 5: 10 < EF ≤ 25 (severe), 6: 25 < EF ≤ 50 (very severe), and 7: EF ≥50 (extremely severe) [13].

3.4 Geo-accumulation Index

Similar to metal enrichment factor, geo-accumulation (I_{geo}) index can be used as a reference to estimate the extent of metal accumulation. The I_{geo} values for the metals studied were calculated using the Muller's (1979) [14] expression: $I_{geo} = log_2 (C_n/1.5B_n)$, where C_n is the measured content of element Cr, and B_n is the background content of Cr 100 mg/kg, in the average shale [6]. Factor 1.5 is the background matrix correction factor due to lithogenic effects. The I_{geo} value can be classified into 7 classes: 0, none for I_{geo} <0; 1, none to medium for I_{geo} = 0–1; 2, moderate for I_{geo} = 1–2; 3, moderately strong for I_{geo} = 2–3; 4, strong for I_{geo} = 3–4; 5, strong to very strong for I_{geo} = 4–5; and 6, very strong for I_{geo} >5. Based on the I_{geo} data and Muller's (1979) [14] geo-accumulation indexes, the accumulation levels with respect to Cr at each site are ranked in Table 2. Site 10 is classified as none to medium accumulation, and all other sites are classified as none accumulation.

Table 2 Geo-accumulation (I_{geo}) index of Cr for each station studied at southern Kaohsiung Harbor

Site	I_{geo} value	I_{geo} class	I_{geo} level
S1	-0.7	0	none
S2	-1.5	0	none
S3	-1.4	0	none
S4	-2.9	0	none
S5	-3.4	0	none
S6	-3.5	0	none
S7	-3.1	0	none
S8	-3.3	0	none
S9	-1.7	0	none
S10	0.8	1	none to medium
S11	-2.5	0	none
S12	-3.4	0	none

[b] 0: I_{geo} <0 (none), 1: I_{geo} = 0–1 (none to medium), 2: I_{geo} = 1–2 (moderate), 3: I_{geo} = 2–3 (moderate to strong), 4: I_{geo} = 3–4 (strong), 5: I_{geo} = 4–5 (strong to very strong), and 6: I_{geo} >5 (very strong) [14].

3.5 Potential Ecological Risk

The potential ecological risk index (PERI) is applied to evaluate the potential risk associated with the accumulation of Cr in surface sediments. PERI that was proposed by Hakanson (1980) [15] can be used to evaluate the potential risk of one metal or combination of multiple metals. The PERI is defined as [15]: $PERI = PI \times T_i$, where *PI (pollution index)* = (C_i/C_f); C_i is the measure concentration of Cr in sediment; C_f is the background concentration of Cr; T_i is its corresponding coefficient, i.e. 2 for Cr [15]. In this study, the average Cr concentration in earth crust of 100 mg/kg Taylor (1964) [11] was taken as the Cr background concentration. The calculated PERI values can be categorized into 5 classes of potential ecological risks [15]: low risk (PERI < 40), moderate risk (40 ≤ PERI < 80), higher risk (80 ≤ PERI < 160), high risk (160 ≤ PERI < 320), and serious risk (PERI ≥ 320). Table 3 lists the PI value, PERI value, and risk classification for the Cr contained in the surface sediment samples collected in this study. All stations are classified as low risk with respect to Cr pollution. The above evaluation results indicate that the Cr contained in surface sediments at the study area has low potential ecological risks. However, the PERI value near the river mouth of sites (sites 1–3 and 10) are higher than other sites (Table 3).

Table 3 Potential ecological risk index of Cr for each station studied at southern Kaohsiung Harbor

Site	PI	PERI	Risk level
S1	0.9	1.8	low
S2	0.5	1.1	low
S3	0.6	1.1	low
S4	0.2	0.4	low
S5	0.1	0.3	low
S6	0.1	0.3	low
S7	0.2	0.4	low
S8	0.2	0.3	low
S9	0.5	0.9	low
S10	2.7	5.3	low
S11	0.3	0.5	low
S12	0.1	0.3	low

[c] PERI < 40 indicates low risk, 40 ≤ PERI < 80 is moderate risk, 80 ≤ PERI < 160 is higher risk, 160 ≤ PERI < 320 is high risk, and PERI ≥ 320 is serious risk [15].

4. CONCLUSIONS

The surface sediment samples collected from the southern Kaohsiung Harbor contain 3.4–265.7 mg/kg with an average of 53.2±71.2 mg/kg. The distribution of Cr in surface sediments reveals that the Cr 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 sediments collected from the river mouth can be characterized between minor and moderate degree enrichment and between none to medium accumulation of Cr, respectively. Compared to the EF values reported earlier [4], the degree of Cr enrichment at the Jen-Gen river mouth has been obviously reduced. Base on the comparison with SQGs, the concentrations of Cr in the mouths of

Jen-Gen River and Salt River sediments may cause acute biological damage. Results of PERI evaluation show that the Cr contained in surface sediment at southern Kaohsiung Harbor has low potential ecological risks. The results can provide regulatory valuable information to be referenced for developing future strategies to renovate and manage river mouth and harbor.

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