Contamination of Zinc in Sediments at River Mouths and Channel in Northern Kaohsiung Harbor, Taiwan

Cheng-Di Dong, Chih-Feng Chen, and Chiu-Wen Chen

Abstract—The distribution, enrichment, accumulation, and potential ecological risk of zinc (Zn) in sediments at river mouths and channel of northern Kaohsiung Harbor, Taiwan were investigated. Sediment samples from 12 locations of northern Kaohsiung Harbor were collected and characterized for Zn, aluminum, water content, organic matter, total nitrogen, total phosphorous, total grease and grain size. Results showed that the Zn concentrations varied from 75–2,537 mg/kg with an average of 590 ± 677 mg/kg. The spatial distribution of Zn reveals that the Zn concentration is relatively high in the river mouth region, 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 Zn pollution. Results from the enrichment factor analyses imply that the sediments collected from the river mouth can be characterized between severe and very severe degree enrichment of Zn. However, results of potential ecological risk index indicate that the sediment has low ecological potential risk.

Index Terms—Accumulation, ecological risk, enrichment, sediment, zinc.

I. INTRODUCTION

Zinc (Zn) is a very common environmental contaminant; its presence may be threatens the water ecological environment. Therefore, much research effort has been directed toward the distribution of Zn in water environment. Anthropogenic activities including municipal wastewater discharges, coal-burning power plants; manufacturing processes involving metals; and atmospheric fallout are the major source of Zn pollution [1]. Zn has low solubility in aqueous solution; it is easily adsorbed on water-borne suspended particles. After a series of natural processes, the water-borne Zn finally accumulates in the sediment, and the quantity of Zn contained in the sediment reflect the degree of pollution for the water body [2].

Kaohsiung Harbor is located on the southwestern shore, and it is the largest international harbor in Taiwan. However, it receiving effluents from four contaminated rivers, including Love River, Canon River, Jen-Gen River, and Salt River. Results of recent research indicate that the Kaohsiung Harbor is heavily polluted with Zn, and the Love River and Canon River are both major pollution sources [2]. The two rivers flow through the downtown area of Kaohsiung City and finally discharged into Kaohsiung Harbor (Fig. 1). Love

River and Canon River are located in Kaohsiung City's northern, basin area of about 45% of the entire Kaohsiung City, and regions along river have dense population with prosperous business and industrial establishments. The major pollution source includes domestic wastewater discharges, industrial wastewater discharges (e.g. paint and dye, chemical production, metal processing, electronic and foundry), municipal surface runoff, and transportation pollution [2]. 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 Zn distribution in the surface sediment at river mouths and channel of northern Kaohsiung Harbor, Taiwan so that the degree of Zn enrichment, accumulation, and potential ecological risk can be evaluated.

II. MATERIALS AND METHODS

Twelve sampling stations were distributed in northern Kaohsiung Harbor, Taiwan (Fig. 1). Sediment samples were collected at 12 stations selected in this study in February, 2011 with Ekman Dredge Grab aboard a fishing boat. After transported back to the laboratory, a small portion of the sample was subject to direct water content analysis (105°C), and the remaining portion was preserved in -20°C freezer 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

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

subject to particle size analyses using a Coulter LS Particle Size Analyzer [2, 3]. Another portion was washed with ultra-pure water to remove sea salt; the salt-free particles were dried naturally in a dark place, grounded into fine powder with mortar and pestle made of agate, and then

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analyzed for organic matter (OM), total nitrogen (TN), total phosphorus (TP), total grease (TG), zinc (Zn), and aluminum (Al). For Al and Zn analyses, 0.5 g dry weight of the sediment sample was mixed with a mixture of ultra-pure acids ($\text{HNO}_3\text{:HCl:HF} = 5:2:5$), and was then heated to digest. 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 Zn content were determined using a flame atomic absorption spectrophotometry (Hitachi Z-6100, Japan).

III. RESULTS AND DISCUSSION

A. Sediment Characteristics

It has been reported that the distribution of particle size, OM, TN, TP, and TG content were correlated to metal distribution in sediments [2]. Table I present the distribution of the major sediment characteristics in surface sediments at 12 monitoring stations studied. Results of sediment particle diameter analyses show that except Station S12, the major particles in sediment samples are silt (2–63 μm) with a range

Clay contents were in the range of 0.8–19.9%. Fine particles (dia. <63 μm) that can easily adsorb and accumulate pollutants are the major component of particles found in the studied sediment. The water content, OM, TN, TP, and TG in the sediments from the study area have a similar spatial evolution characterized by the highest levels at Stations 1–4, which are located at the vicinity of the mouths of Love River, and Canon River. TN, TP, and TG were relatively high in the vicinity of the mouths of river compared with those at the harbor entrance areas (Station 12). The results show that the anthropogenic contribution from the harbor tributaries is the major source of TN, TP, and TG.

B. Distribution of Zn in Sediments

The contents of Al in the study sediments are between 4.18 and 5.29% with an average of $4.65 \pm 0.43\%$ (Table I). All surface sediment samples collected at 12 monitoring stations studied contain 75–2,537 mg/kg of Zn with an average of 590 ± 677 mg/kg. Spatial distributions of Zn concentration in the surface sediment shown in Fig. 2 reveal that the sediment Zn content is relatively higher near the mouths of Love River,

TABLE I: SEDIMENT CHARACTERISTICS AND ZN CONTENTS IN THE SEDIMENTS OF NORTHERN KAOHSIUNG HARBOR

Station	Clay (%)	Silt (%)	Sand (%)	Water content (%)	OM (%)	TN (mg/kg)	TP (mg/kg)	TG (mg/kg)	Al (%)	Zn (mg/kg)
S1	16.5	83.5	0.0	57.9	7.3	2665	655	1990	5.27	690
S2	17.8	82.2	0.0	113.2	6.0	2120	376	2284	5.29	808
S3	15.7	84.4	0.0	81.1	8.1	2762	736	1203	5.27	2537
S4	13.6	86.2	0.2	93.0	6.6	2000	514	960	4.50	1030
S5	14.5	84.9	0.6	86.7	3.7	1370	308	620	4.73	382
S6	18.0	82.0	0.0	91.2	4.9	1380	273	2440	4.40	386
S7	16.7	83.3	0.0	57.7	2.2	1089	213	410	4.40	216
S8	16.9	83.1	0.0	91.7	3.7	1103	261	1949	4.33	341
S9	14.3	85.2	0.5	86.1	4.0	1198	224	630	4.18	268
S10	13.9	84.9	1.1	42.1	2.8	1074	192	335	4.20	192
S11	19.9	80.1	0.0	58.9	3.9	1020	215	470	4.36	154
S12	0.8	6.3	92.9	28.6	3.4	875	294	305	4.84	75
Mean	14.9	77.2	7.9	74.0	4.7	1555	355	1133	4.65	590
SD	4.8	22.4	26.7	24.7	1.9	661	182	813	0.43	677

Fig. 2. Spatial distribution of Zn contents in surface sediment of northern Kaohsiung Harbor.

from 80.1% to 86.6%. Station S12, located at the harbor entrance, had the highest sand contents (92.9%) and the lowest silt contents (6.3%); whereas Stations 1 and 11 had the highest silt contents and the lowest sand contents (0.0–1.1%).

Fig. 3. Distribution of Zn contents in surface sediment of northern Kaohsiung Harbor.

and Canon River (Stations 1–4), and gradually decreases in the direction toward the mouth of harbor (Station 12). These observations clearly indicate that the upstream pollutants brought over by rivers are the major source of harbor Zn

pollution. The two rivers receive a great amount of industrial and domestic Zn from Kaohsiung city because about 44% domestic wastewater is discharged directly without adequate treatment. 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 [2],[4].

Coefficient of the Pearson correlation between the sediment characteristics and Zn content is shown in Table II. The surface sediment Zn content is obviously correlated to OM content ($p < 0.01$) but not to particle size ($p > 0.05$)

indicating that particle size are not major factors to control the Zn distribution. Although most studies presented significant negative correlation between sediment particle sizes and Zn concentrations [2],[5], results of this study indicated that OM contents were more important than grain size in controlling the distribution of Zn in the sediments. The results might suggest that the sorption mechanism of Zn at the study areas sediments is mainly controlled by chemical adsorption, rather than physical or deposition of Zn with OM on surface sediments [2]. It is noted that the Zn distribution in sediments were also significant positive correlation to TN, and TP contents (Table II) which were usually derived from the upstream rivers with either industrial effluents or municipal sewage discharges.

TABLE II: PEARSON CORRELATION COEFFICIENTS AMONG SEDIMENT CHARACTERISTICS AND ZN CONTENTS (N = 12)

	clay	Silt	Sand	Water content	OM	TN	TP	TG	Al
Silt	0.889 ^a								
Sand	-0.924a	-0.997a							
Water content	0.545	0.581b	-0.583b						
OM	0.196	0.231	-0.228	0.407					
TN	0.154	0.210	-0.202	0.185	0.922a				
TP	0.048	0.203	-0.177	0.081	0.845a	0.882a			
TG	0.396	0.363	-0.374	0.720a	0.548	0.401	0.236		
Al	-0.078	-0.147	0.138	0.141	0.718a	0.802a	0.520	0.375	
Zn	0.160	0.258	-0.243	0.345	0.816a	0.800a	0.738a	0.250	0.604b

^aCorrelation is significant at the 0.01 level (2-tailed). ^bCorrelation is significant at the 0.05 level (2-tailed).

A. 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 [10, 11]. 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) [11]. 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. 3 shows the measured concentrations of Zn in comparison with the ERM and ERL values. Among the 12 sediment samples collected, the Zn is between ERL (150 mg/kg) and ERM (410 mg/kg) in 7 samples (58.3%), and exceeds ERM in 4 samples (33.3%). Only one sample collected from Station S12 is below ERL for Zn. This indicates that the concentration of Zn found in the study area sediments may cause adverse impact on aquatic lives. The study area is adjacent to the output of an industrial park that accommodates several chemical industrial plants using Zn

compounds as raw materials. These plants are expected to release chemical pollutants which will accumulate in the bottom sediment of river mouth and harbor.

B. Enrichment Factor

The enrichment factor (EF) is a useful tool for differentiating the man-made and natural sources of metal contamination [5]. 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 [2,5]. EF is defined as: $EF = (X/Al)_{\text{sediment}} / (X/Al)_{\text{crust}}$, where (X/Al) is the ratio of Zn to Al. The average Zn and Al content in the earth crust were 70 mg/kg and 8.23%, respectively, which excerpted from the data published by Taylor (1964)[6]. 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: 1, no enrichment for $EF < 1$; 2, minor for $1 < EF < 3$; 3, moderate for $3 \leq EF < 5$; 4, moderately severe for $5 \leq EF < 10$; 5, severe for $10 \leq EF < 25$; 6, very severe for $25 \leq EF < 50$; and 7, extremely severe for $EF \geq 50$. Table III(a) show EF values of the sediment Zn for 12 monitoring stations studied; the Zn concentration is consistent with the Zn EF value for all sampling stations, and all EF values are greater than 1. This indicates that the sediment Zn has enrichment phenomenon with respect to the earth crust and that all Zn originates from man-made sources.

Stations S1–S4 are classified between severe and extremely severe enrichment, Stations S5–S10 are classified as either moderately severe or severe enrichment, and Stations S11 and S12 are classified as moderate and minor enrichment, respectively. These results point out that the sediment near the mouth of rivers experiences severe enrichment of Zn that originates from the upstream sources of pollution.

Additionally, the EF value of 45.1 obtained in Station S3 (Canon River mouth) is higher than the EF value of 13.8 reported earlier [2] indicating that the upstream pollution has been continued to increase so that the accumulation of pollutants in sediments is more serious than that during earlier years.

TABLE III: EF, I_{geo} , AND PERI OF ZN FOR EACH STATION STUDIED AT NORTHERN KAOHSIUNG HARBOR

Station	(a) Enrichment factor			(b) Geo-accumulation index			(c) Potential ecological risk		
	EF value	EF class	EF level	I_{geo} value	I_{geo} class	I_{geo} level	PI	PERI	Risk level
S1	15.4	5	severe	2.7	3	moderate to strong	9.9	10	low
S2	18.0	5	severe	2.9	3	moderate to strong	11.5	12	low
S3	56.6	7	extremely severe	4.6	5	strong to very strong	36.2	36	low
S4	26.9	6	very severe	3.3	4	strong	14.7	15	low
S5	9.5	4	moderately severe	1.9	2	moderate	5.5	5	low
S6	10.3	5	severe	1.9	2	moderate	5.5	6	low
S7	5.8	4	moderately severe	1.0	2	moderate	3.1	3	low
S8	9.3	4	moderately severe	1.7	2	moderate	4.9	5	low
S9	7.5	4	moderately severe	1.4	2	moderate	3.8	4	low
S10	5.4	4	moderately severe	0.9	1	none to medium	2.7	3	low
S11	4.1	3	moderate	0.5	1	none to medium	2.2	2	low
S12	1.8	2	minor	-0.5	0	none	1.1	1	low
Mean	14.2	5	severe	1.9	2	moderate	8.4	8	low

^a 1: $EF < 1$ (no enrichment), 2: $1 < EF \leq 3$ (minor), 3: $3 < EF \leq 5$ (moderate), 4: $5 < EF \leq 10$ (moderately severe), 5: $10 < EF \leq 25$ (severe), 6: $25 < EF \leq 50$ (very severe), and 7: $EF \geq 50$ (extremely severe) [2].

^b 0: $I_{\text{geo}} < 0$ (none), 1: $I_{\text{geo}} = 0-1$ (none to medium), 2: $I_{\text{geo}} = 1-2$ (moderate), 3: $I_{\text{geo}} = 2-3$ (moderate to strong), 4: $I_{\text{geo}} = 3-4$ (strong), 5: $I_{\text{geo}} = 4-5$ (strong to very strong), and 6: $I_{\text{geo}} > 5$ (very strong) [7].

^c $PERI < 40$ indicates low risk, $40 \leq PERI < 80$ is moderate risk, $80 \leq PERI < 160$ is higher risk, $160 \leq PERI < 320$ is high risk, and $PERI \geq 320$ is serious risk [10].

A. 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) [7] expression: $I_{\text{geo}} = \log_2 (C_n / 1.5B_n)$, where C_n is the measured content of element Zn, and B_n is the background content of Zn 70 mg/kg, in the average shale. 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 $I_{\text{geo}} < 0$; 1, none to medium for $I_{\text{geo}} = 0-1$; 2, moderate for $I_{\text{geo}} = 1-2$; 3, moderately strong for $I_{\text{geo}} = 2-3$; 4, strong for $I_{\text{geo}} = 3-4$; 5, strong to very strong for $I_{\text{geo}} = 4-5$; and 6, very strong for $I_{\text{geo}} > 5$. Based on the I_{geo} data and geo-accumulation indexes, the accumulation levels with respect to Zn at each station are ranked in Table III(b). Stations S1–S4 are classified between moderately strong and strong to very strong accumulation, Stations S5–S9 are classified as moderate accumulation, and Stations S10–S12 are classified as either none to medium or none accumulation.

B. Potential Ecological Risk

The potential ecological risk index (PERI) is applied to evaluate the potential risk associated with the accumulation of Zn in surface sediments. PERI that was proposed by Hakanson (1980) [10] can be used to evaluate the potential risk of one metal or combination of multiple metals. The

PERI is defined as [10]: $PERI = PI \times T_i$, where PI (pollution index) $= (C_i / C_f)$; C_i is the measure concentration of Zn in sediment; C_f is the background concentration of Zn; T_i is its corresponding coefficient, i.e. 1 for Zn [11]. In this study, the average Zn concentration in earth crust of 70 mg/kg [6] was taken as the Zn background concentration. The calculated PERI values can be categorized into 5 classes of potential ecological risks [10,11]: low risk ($PERI < 40$), moderate risk ($40 \leq PERI < 80$), higher risk ($80 \leq PERI < 160$), high risk ($160 \leq PERI < 320$), and serious risk ($PERI \geq 320$). Table III(c) lists the PI value, PERI value, and risk classification for the Zn contained in the surface sediment samples collected in this study. All stations are classified as low risk with respect to Zn pollution. The above evaluation results indicate that the Zn contained in surface sediments at the study area has low potential ecological risks. However, the PERI value near the river mouth of Stations S1–4 is higher than other sites (Table III(c)).

IV. CONCLUSIONS

The surface sediment samples collected from the northern Kaohsiung Harbor contain 75–2,537 mg/kg of Zn with an average of 590 ± 677 mg/kg. The distribution of Zn in surface sediments reveals that the Zn 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. Base on the comparison

with SQGs, the concentrations of Zn in the mouths of Love River and Canon River sediments may cause acute biological damage. OM content is a more important factor than grain size in controlling the Zn distribution in the sediments. Results from the EF and I_{geo} analyses imply that the sediments collected from the river mouth can be characterized between severe and extremely severe degree enrichment and between moderately strong and strong to very strong accumulation of Zn, respectively. Compared to the EF values reported earlier [2], the degree of Zn enrichment at the river mouths has been obviously increased. Results of potential ecological risk evaluation show that the Zn contained in surface sediment at northern 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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