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Evaluation of Zinc Status in the Sediments of the Kaohsiung Ocean Disposal Site, Taiwan

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***Abstract*—**The distribution, enrichment, and accumulation of zinc (Zn) in the sediments of Kaohsiung Ocean Disposal Site (KODS), Taiwan were investigated. Sediment samples from two outer disposal site stations and nine disposed stations in the KODS were collected per quarterly in 2009 and characterized for Zn, aluminum, organic matter, and grain size. Results showed that the mean Zn concentrations varied from 48 mg/kg to 456 mg/kg. Results from the enrichment factor (EF) and geo-accumulation index (I_{geo}) analyses imply that the sediments collected from the KODS can be characterized between moderate and moderately severe degree enrichment and between none and none to medium accumulation of Zn, respectively. However, results of potential ecological risk index indicate that the sediment has low ecological potential risk. The EF, I_{geo}, and Zn concentrations at the disposed stations were slightly higher than those at outer disposal site. This indicated that the disposed area centers may be subjected to the disposal impaction of harbor dredged sediments.

***Keywords*—**ocean dispose; zinc; enrichment factor; potential ecological risk index.

I. Introduction

KAOHSIUNG Harbor is situated on the southwestern shore, and it is the largest international harbor in Taiwan. There are four major rivers, namely Love River, Canon River, Jen-Gen River, and Salt River flow into the harbor that bring in a large quantity of suspended solids and other pollutants [1]. As a result, a fast accumulation of sediment particles in the harbor occurs and periodical dredging of harbor sediments is necessary in order to maintain navigation in the harbor. Millions cubic meters of sediments are dredged annually. Currently, all dredged sediments from the Kaohsiung Harbor are dumped into the ocean at a specific area, Kaohsiung Ocean Disposal Site (KODS), designated by Taiwan Environmental Protection Agency (TEPA). Approximately 30 million cubic meter sediment were dredged and transported to the disposal area annually. The KODS was established since 2003. It is totally about 210 million cubic meter disposal already since the starting.

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Kaohsiung Harbor is located adjacent to Kaohsiung City, which is the largest industrial city in southern Taiwan with a population of over 1.5 million. Currently, the city sewage system serves about 42% of the metropolis [1]. Thus, about 58% domestic wastewater is discharged directly into receiving water bodies without adequate treatment. Moreover, several industrial plants (e.g. metal processing factories, paint and dye industries, chemical manufacturing plants, electronic industries, motor vehicle plating and finishing plants, paper and board mills, and foundries) located in or adjacent to Kaohsiung City [1-2] discharge industrial wastewater effluents into the receiving bodies. It makes the port showing the phenomenon of heavy metals accumulation in sediments. Previous studies pointed out that the port of sediment accumulated high concentrations of zinc (Zn) contents of 52–1,369 mg/kg, showed that the extent of Zn contamination was at the level of intermediate to strong [1]. However, when dumping harbor sediments into ocean, it simultaneously leads Zn releasing into the nearby water environment and ocean system, in which Zn is considered pollutant by its toxicity, cumulative and non-biodegradable characteristics in water environment [3]. Thus, quality assessments of sediments in ocean dumping area are needed for further understanding of Zn accumulation in sediments ecological system and its impaction upon the environment.

II. Materials and Methods

A. Study Area and Sampling

The study area, KODS off of southwestern Taiwan occupies 36 km^2 east of Kaohsiung Harbor at water depths of 500–700 m (Fig. 1), was established since 2003. It is totally about 210 million cubic meter disposal already since the starting. Eleven sampling stations selected in this study included two outer disposal site stations (S10 and S11 were reference stations) and nine disposed stations (S1, S2, S3, S4 were disposal site vertex angle, S5 was disposal site center and S6, S7, S8, S9 were disposed area centers, (Fig. 1). The Ocean Researcher III was hired to collect the sediment samples from various locations in the KODS during March, May, August, and October in 2009. About 3 kg of sediments were collected with an SIHPEK grab sampler. Immediately after collection, the samples were transferred into polyethylene bags and kept in an ice box and then transported to the laboratory for analysis. In the laboratory, the samples were kept at to -20º C until further processing and analysis.

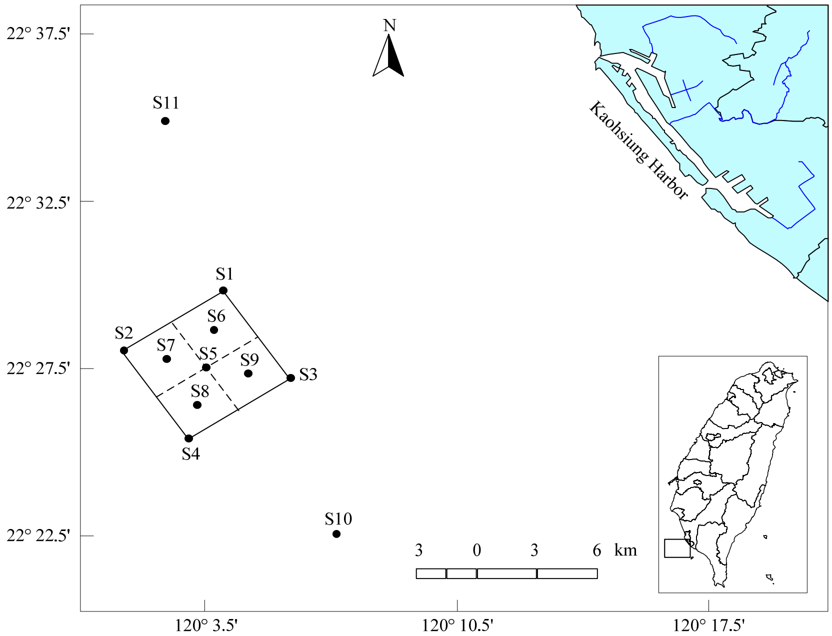

Fig. 1 Map of the study area and sampling locations.

B. Sample Processing and Analysis

Sediment samples were first screened through a 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 [1,2]; the particles were classified into three groups, i.e. clay (dia <2 µm), silt (2 µm < dia < 63 µm), and sand (dia >63 µm). 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 analyzed for organic matter (OM), Zn, and aluminum (Al). OM was determined using the LOI (loss-on-ignition) method at 550º C; For Al and Zn analyses, 1.0 g dry weight of the sediment sample was mixed with a mixture of ultra-pure acids (HNO_3: HCl = 1:3), and was then

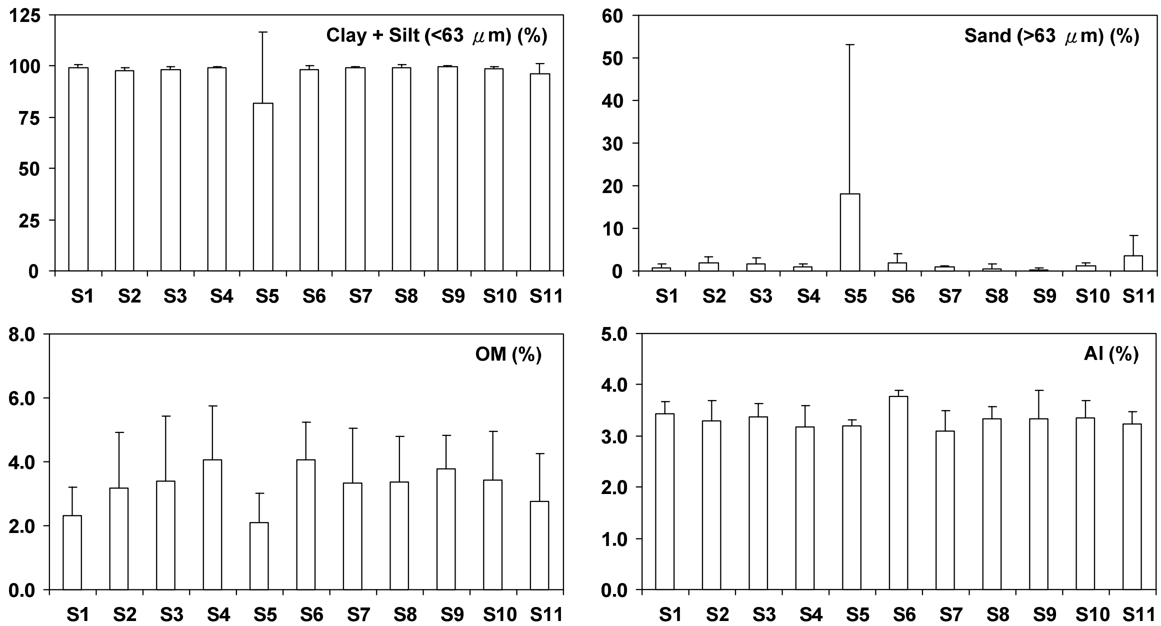

Fig. 1 Distribution of grain sizes (clay, silt, and sand), organic matter (OM), and aluminum (Al) contents in surface sediment of Kaohsiung Ocean Disposal Site. (S1–S4: disposal site vertex angle, S5: disposal site center, S6–S9: disposed area centers, and S10–S11: outer disposal site.)

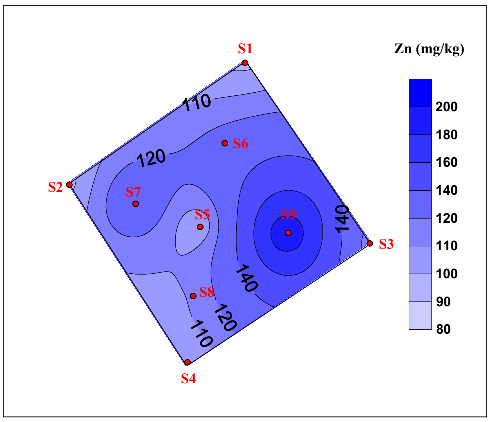

Fig. 2. Contour map of surface sediment Zn contents in Kaohsiung Ocean Disposal Site.

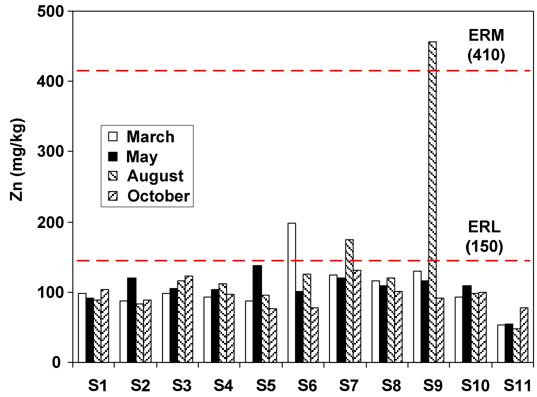

Fig. 3. Distribution of Zn contents in surface sediment of Kaohsiung Ocean Disposal Site. (S1–S4: disposal site vertex angle, S5: disposal site center, S6–S9: disposed area centers, and S10–S11: outer disposal site.)

TABLE I
PEARSON CORRELATION COEFFICIENTS AMONG SEDIMENT CHARACTERISTICS AND ZINC CONCENTRATIONS (N = 44)

	Clay	Silt	Sand	OM	Al
Silt	0.735[a]				
Sand	-0.827[a]	-0.989[a]			
OM	0.286	0.321[b]	-0.327[b]		
Al	0.193	0.017	-0.057	0.467[a]	
Zn	0.029	0.157	-0.137	0.120	0.196

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

heated to digest. The digested sample was filter through 0.45 µm filter paper; the filtrate was diluted with ultra-pure water to a pre-selected final volume. The Al and Zn contents were determined using a flame atomic absorption spectrophotometry (Hitachi Z-6100). Each batch of analyses was accompanied with a standard reference (marine sediment (PACS-2)) and a blank. For every 5 samples analyzed, the examination of standard solutions was carried out to assure the stability of the instrument used. The standard reference of marine sediment (PACS-2) was found to contain 373±12 mg/kg in our lab that is close to the certified values of 364±23 mg/kg (n = 3).

III. RESULTS AND DISCUSSION

A. Sediment Characteristics and Zn Concentrations

Fig. 1 showed the distribution of grain sizes, OM, and Al contents in surface sediment of KODS at 2009. The major particles in all sediment samples are silt with diameter between 2 µm to 63 µm. The percentage compositions are 67.0–81.7% for silt, 13.8–18.9% for Clay (<2 µm), and 0.2–18.2% for sand. The grain sizes distribution showed that the sediments in the KODS were composed by fine grained dominated. However, the standard deviations of grain sizes for every single disposed station varied slightly from time to time. This could be seen especially in Station S5. On the other hand, the observation values of OM contents in all sediment samples from the KODS at 2009 ranged from 2.1 to 4.1%.

All sediment samples collected from the KODS mean contain 48–456 mg/kg of Zn. The highest concentration of Zn was of disposal area: stations S6, S7, S8, and S9 (Fig. 2). The variances of Zn in disposed area centers (Area III) were higher than those of the disposal site vertex angle (Area I), disposal site center (Area II), and outer disposal site (Area R) while the variances of stations were among the lowest. Concentration distributions of Zn in KODS sediment shown in Fig. 2 reveal that the sediment Zn content is relatively higher near the disposed area centers. The sediment Zn content is not obviously correlated to sediment characteristics (Table I). All observed data showed that all stations in the KODS at 2009 may be subjected to the disposal impaction of harbor dredged sediments as we can tell.

B. 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 [4-5]. 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) [4]. 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 44 sediment samples collected, the Zn is between ERL (150 mg/kg) and ERM (410 mg/kg) in 2 samples (4.5%) and one sample collected from Station S9 is exceed ERM for Zn. This indicates that the concentration of Zn found in the sediments may cause adverse impact on aquatic

TABLE III
EF, I_{GEO}, AND PERI OF ZN FOR EACH STATION STUDIED AT KAOHSIUNG OCEAN DISPOSAL SITE

Area[a]	Station	(a) Enrichment factor[b]			(b) Geo-accumulation index[c]			(c) Potential ecological risk[d]		
		EF value	EF class	EF level	I_{geo} value	I_{geo} class	I_{geo} level	PI	PERI	Risk level
I	S1	3.28	3	moderate	-0.14	0	none	1.4	1.4	low
	S2	3.47	3	moderate	-0.16	0	none	1.4	1.4	low
	S3	3.86	3	moderate	0.07	1	none to medium	1.6	1.6	low
	S4	3.81	3	moderate	-0.06	0	none	1.4	1.4	low
II	S5	3.71	3	moderate	-0.11	0	none	1.4	1.4	low
III	S6	3.97	3	moderate	0.17	1	none to medium	1.8	1.8	low
	S7	5.27	4	moderately severe	0.38	1	none to medium	2.0	2.0	low
	S8	3.95	3	moderate	0.08	1	none to medium	1.6	1.6	low
	S9	6.70	4	moderately severe	0.59	1	none to medium	2.8	2.8	low
R1	S10	3.54	3	moderate	-0.07	0	none	1.4	1.4	low
R2	S11	2.12	2	minor	-0.87	0	none	0.8	0.8	low

[a]. I: disposal site vertex angle, II: disposal site center, III: disposed area centers, and R: outer disposal site.

[b.] 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) [10].

[c.] 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) [11].

[d.] 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 [12].

lives. All other sediment samples are blower ERL, indicates that the biological effect is rare.

C. Enrichment Factor

The enrichment factor (EF) is a useful tool for differentiating the man-made and natural sources of metal contamination [6-8]. 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 [6-8]. EF is defined as: $EF = (X/Al)_{sediment}/(X/Al)_{crust}$, 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) [9]. 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 [10]: 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 III(a) show EF values of the sediment Zn for the KODS; the Zn concentration is consistent with the Zn EF value for all sampling stations. In the 12 Stations, all EF values are greater than 1, indicates that the sediment Zn has enrichment phenomenon with respect to the earth crust and that Zn originates from man-made sources. Stations S7 and S9 are classified as moderately sever enrichment, Station S11 is classified as minor enrichment, and all other Stations are classified as moderate enrichment, respectively. These results point out that the sediment near the disposed area centers experiences moderately sever enrichment of Zn. This observation may be subjected to the disposal impaction of harbor dredged sediments.

D. 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) [11] expression: $I_{geo} = log_2 (C_n/1.5B_n)$, 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 [9]. 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 geo-accumulation indexes, the accumulation levels with respect to Zn at each station are ranked in Table III(b). Stations S3 and S6–S9 (Area III disposed area centers) are classified as none to medium accumulation, and all other stations are classified as none accumulation.

E. Assessment of potential ecological risk

The potential ecological risk index (PERI) is applied to evaluate the potential risk associated with the accumulation of Cu in surface sediments. PERI that was proposed by Hakanson (1980) [12] can be used to evaluate the potential risk of one metal or combination of multiple metals. The PERI is defined as [12]: $PERI = PI \times T_i$, 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 [12]. In this study, the average Zn concentration in earth crust of 70 mg/kg [9] was taken as the Zn background concentration. The calculated PERI values can be categorized into 5 classes of potential ecological risks [12-13]: 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 III(c) lists the PI value, PERI value, and risk classification of the Zn contained in the sediment samples collected in the KODS. All the areas are classified as low risk with respect to Zn pollution. The above evaluation results indicate that the Zn contained in sediments at the KODS has low potential ecological risks. However, the mean PERI value in disposed area centers (Area III) is higher than other sites (Table III(c)).

IV. Conlusions

The sediment samples collected at all sampling stations at the KODS contain 48–456 mg/kg of Zn. The highest concentration of Zn was of disposed area centers. Results of EF and I_{geo} analyses indicate that the KODS sediments were minor contaminated with Zn. Results of potential ecological risk evaluation show that the classification of potential ecological risk for the sediment Zn at the Ocean Disposal Site is low risk. The results can provide regulatory valuable information to be referenced for developing future strategies to renovate and manage ocean disposal site.

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