Evaluation of Chromium Contamination in the Sediments of Jen-Gen River Mouth, Taiwan

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Abstract—This study was conducted using the data collected at the mouth of Jen-Gen River to investigate and analyze chromium (Cr) contained in the sediments, and to evaluate the accumulation of Cr and the degree of its potential risk. The results show that samples collected at all monitoring stations near the mouth of Jen-Gen River contain 92–567 mg/kg of Cr with average of 366±166 mg/kg. The spatial distribution of Cr reveals that the Cr concentration is relatively high in the river mouth region, and gradually diminishes toward the harbor region. This indicates that upstream industrial and municipal wastewater discharges along the river bank are major sources of pollution. The accumulation factor and potential ecological risk index indicate that the sedimentation at Jen-Gen River mouth has the most serious degree of Cr accumulation and the highest ecological potential risk

Keywords—chromium, sediment, river mouth, enrichment factor.

I. INTRODUCTION

THE metals generated by anthropogenic activities cause I more environmental pollution than naturally occurring metals [1]. After entering a water body, heavy metals will be carried over to sea so that the river mouth and regions along seashore become the ultimate resting place for these metals being transported in the environment. Hence, the river mouth region, harbor and seashore with dense population and industries usually become heavily polluted by toxic metals [2]. Chromium (Cr) is extremely toxic and highly bio-accumulative [3]-[4]; its presence threatens the water ecological environment. Therefore, much research effort has been directed toward the distribution of Cr in water environment. Anthropogenic activities including municipal wastewater discharges, agriculture, mining, incineration, and discharges of industrial wastewater are the major source of Cr pollution [5]. Chromium has low solubility in aqueous solution; it is easily adsorbed on water-borne suspended particles. After a series of natural processes, the water-borne Cr finally accumulates in the sediment, and the quantity of Cr contained in the sediment reflect the degree of pollution for the water body [6].

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Jen-Gen River flows through a southern Taiwan industrial city (Kaohsiung City). In previous years, the river received untreated municipal and industrial wastewater discharges causing serious deterioration of the river water quality and the environmental quality near the river mouth to threaten the water environmental ecological system seriously. The objective of this study is to investigate the Cr distribution in the surface sediment near Jen-Gen River mouth so that the degree of Cr accumulation and potential ecological risk can be evaluated.

II. MATERIALS AND METHODS

A. Study area

Jen-Gen River is 19 km long with watershed of 54 km² that covers about 40% of total Kaohsiung City. Originated near Hu-Di channel, Jen-Gen River flow through the downtown area of Kaohsiung City and finally discharged into Kaohsiung Harbor (Fig. 1). Kaohsiung City is the largest industrial city in Taiwan with 1.5 million residents. During earlier years, the lack of sanitary sewer system causes un-treated raw wastewater to be discharged directed into adjacent water bodies that leads to serious deterioration of river water quality. Although in recent years, Kaohsiung City actively promotes the construction of wastewater collection and treatment systems, in 2009, the wastewater system only serves 56% of the city in 2009 [7]. Additionally, Kaohsiung City also actively involves in public projects on renovating rivers (e.g. Jen-Gen River) by constructing river intercepting stations near the middle section of the river to divert the upstream polluted river water to a wastewater treatment for alleviating the downstream pollution problem. However, during the wet season, the river water intercepting gate is opened for by-passing the sudden surge of river flow brought over by storms that will discharge the upstream pollutants to downstream sections. Regions along Jen-Gen River have dense population with prosperous business and industrial establishments. The major pollution source domestic wastewater discharges, industrial wastewater discharges (e.g. tanneries, paint and dye, chemical production, metal processing, electronic and foundry), municipal surface runoff, and transportation pollution [8]. All the pollutants will eventually be transported to the river mouth to deposit and accumulate in the bottom sediment.

B. Sampling and analytical methods

Surface sediment samples were collected at 11 stations near Jen-Gen River mouth (Fig. 1) in May, 2009 with Ekman Dredge Grab aboard a fishing boat. The collected samples were

temporarily placed in polyethylene bottles that had been washed with acid; the bottles were stored in a dark ice chest filled with crushed ice. 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 subject to particle size analyses using a Coulter LS Particle Size Analyzer; the particles were classified into three groups, i.e. clay (dia $<2 \mu m$), silt (2 $\mu m < dia < 63$ 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), total grease (TG), Cr, and aluminum (Al). OM was determined using the LOI (loss-on-ignition) method at 550°C; TG was determined according to procedures 5520E published in Standard Method [9]. For Al and Cr analyses, 0.5 g dry weight of the sediment sample was mixed with a mixture of ultra-pure acids (HNO₃:HCl:HF = 5:2:5), and was then heated to digest. The digested sample was filter through 0.45 um filter paper; the filtrate was diluted with ultra-pure water to a pre-selected final volume. The Al and Cr 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 91.7±1.9 mg/kg in our lab that is close to the certified values of 90.7 ± 4.6 mg/kg (n = 3).

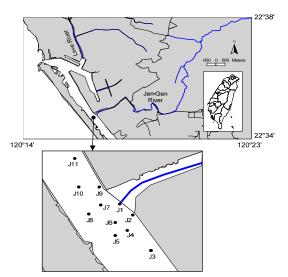


Fig. 1 Map of the study area and sampling locations

C.Data analyses

Statistical data analyses include average, standard deviation,

maximum and minimum. The linear correlation of Pearson technique was used to analyze the correlation between sediment characteristics and Cr concentration implemented with the SPSS 12.0 software. In this study, the enrichment factor (EF) and geo-accumulation index (I_{geo}) were applied to evaluate the degree of Cr pollution and the associated potential ecological risk index (PERI). EF is defined as:

$$EF = \frac{(X/AI)_{sediment}}{(X/AI)_{crust}}$$
 (1)

Where (X/Al) is the ratio of Cr to Al. The average Al content in the earth crust was excerpted from the data published by Taylor (1964) [10].

The I_{geo} is defined as [11]:

$$I_{geo} = log_2 (C_n/1.5B_n)$$
 (2)

Where C_n is the measured content of Cr, and B_n is the background content of Cr in the average shale.

The potential ecological risk index PERI is defined as [12]:

$$PERI = PI \times T_{i} \tag{3}$$

$$PI = C_i / C_f$$
 (4)

Where PI is the pollution index of Cr; T_i is its corresponding coefficient, i.e. 2 for Cr [13]; C_i is the measure concentration of Cr in sediment; C_f is the background concentration of Cr. In this study, the average Cr concentration in the bottom core sediment (80 cm) of 15 mg/kg [14] was taken as the Cr background concentration.

III. RESULTS AND DISCUSSION

A. Characteristics and Distribution of chromium in Sediments

Table I lists the location of sampling Jen-Gen River mouth sediment, characteristics of the sediment, and Cr concentration. Results of sediment particle diameter analyses show that except the station J10, the major particles in all sediment samples are silt with diameter between 2 μ m to 63 μ m. The percentage compositions are 26.7–87.8% for silt, 5.6–17.5% for Clay (<2 μ m), and 0.1–67.7% for sand. Fine particles (dia. <63 μ m) that can easily adsorb and accumulate pollutants are the major component of particles found in the Jen-Gen River mouth sediment. The average water content of Jen-Gen River mouth sediment is 82.5±26.9%; the organic matter content and total grease are 5.1±1.1% and 3,522±1,340, respectively. These results are similar to those reported earlier [8].

All sediment samples collected at Jen-Gen River mouth contain 92–567 mg/kg of Cr with an average of 366±166 mg/kg. Concentration distributions of Cr in Jen-Gen River mouth sediment shown in Fig. 2 reveal that the sediment Cr content is relatively higher near the boundary of the river mouth, and gradually decreases in the direction toward the harbor. Because

TABLE I SEDIMENT CHARACTERISTICS, CHROMIUM CONTENTS AND ENRICHMENT FACTOR IN THE SEDIMENTS OF JEN-GEN RIVER MOUTH

Station	Clay (%)	Silt (%)	Sand (%)	Water content (%)	OM (%)	TG (mg/kg)	Al (%)	Cr (mg/kg)
J1	11.5	84.4	4.1	102	6.3	4,933	4.25	534
J2	12.8	87.0	0.2	57	3.9	4,526	5.71	241
J3	13.0	84.3	2.7	96	5.9	3,274	5.20	411
J4	9.9	84.6	5.5	113	5.9	3,864	5.06	567
J5	9.9	87.8	2.3	56	5.5	4,346	4.49	386
J6	10.4	86.6	3.0	119	6.8	4,926	5.14	464
J7	12.9	83.9	3.2	83	5.3	3,452	5.01	539
J8	17.5	82.4	0.1	69	4.5	1,770	4.15	124
J9	12.1	86.6	1.3	98	4.5	4,170	5.16	251
J10	5.6	26.7	67.7	32	3.3	6,67	4.11	92
J11	15.3	82.0	2.7	82	4.6	2,819	4.31	419
Mean	11.9	79.7	8.4	82.5	5.1	3,522	4.78	366
SD	3.1	17.7	19.7	26.9	1.1	1,340	0.54	166

TABLE II
SEDIMENT CHARACTERISTICS, CHROMIUM CONTENTS AND ENRICHMENT FACTOR IN THE SEDIMENTS OF JEN-GEN RIVER MOUTH

	Clay	Silt	Sand	Water content	OM	TG	Al
Silt	0.613*						
Sand	-0.707*	-0.992**					
Water content	0.200	0.614^{*}	-0.582				
OM	0.022	0.576	-0.519	0.806^{**}			
TG	0.037	0.763**	-0.689*	0.613*	0.659^{*}		
Al	0.024	0.465	-0.420	0.345	0.164	0.568	
Cr	-0.003	0.540	-0.483	0.712^{*}	0.809^{**}	0.636^{*}	0.232

**Correlation is significant at the 0.01 level (2-tailed); *Correlation is significant at the 0.05 level (2-tailed).

Jen-Gen River is subject to upstream discharges of un-treated domestic and industrial wastewaters, 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 [8].

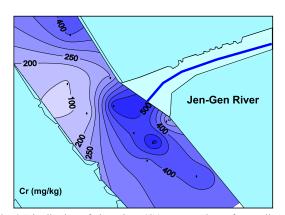


Fig. 2 Distribution of chromium (Cr) contents in surface sediment of Jen-Gen River mouth

Coefficient of the Pearson correlation between the sediment characteristics and Cr content was carried out. The sediment Cr content are obviously correlated to water content (r = 0.712, p < 0.05), OM (r = 0.809, p < 0.01), and TG (r = 0.636, p < 0.05) but not to particle size (p > 0.05) indicating that particle size are not major factors to control the Cr distribution [15]. The

environmental condition of the river mouth in this study region such as discharges of upstream pollutants, and alternation between fresh water and sea water may be very complicated so that very little correlation between the sediment Cr concentration and other sediment characteristics is observed to

B. Enrichment Factor and index of geo-accumulation

The enrichment factor (EF) is a useful tool for differentiating the man-made and natural sources of metal contamination [16]-[18]. 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 [8], [19]. 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 [20]: no enrichment for EF <1, minor for EF <3, moderate for EF = 3-5, moderately severe for EF = 5-10, severe for EF = 10-25, very severe for EF = 25-50, and extremely severe for EF >50. Table 3 and Fig. 3 show EF values of the sediment Cr for the Jen-Gen River mouth region; the Cr concentration is consistent with the Cr EF value for all sampling stations, and all EF values are greater than 1. This indicates that the sediment Cr has enrichment phenomenon with respect to the earth crust and that all Cr originates from

 $\begin{tabular}{ll} TABLE III \\ EF AND I_{GEO} CLASSES OF CHROMIUM FOR EACH STATION STUDIED AT ITS GEN PAGE MOUTH. \\ \end{tabular}$

Station	EF	EF class ¹	I_{geo}	Igeo class ²
J1	10.3	4	1.8	2
J2	3.5	2	0.7	1
J3	6.5	3	1.5	2
J4	9.2	3	1.9	2
J5	7.1	3	1.4	2
J6	7.4	3	1.6	2
J7	8.9	3	1.8	2
J8	2.5	1	-0.3	0
Ј9	4.0	2	0.7	1
J10	1.8	1	-0.7	0
J11	8.0	3	1.5	2
mean	6.3	3	1.9	2

 1 0: EF <1 (no enrichment), 1: EF <3 (minor), 2: EF = 3–5 (moderate), 3: EF = 5–10 (moderately severe), 4: EF = 10-25 (severe), 5: EF = 25-50 (very severe), and 6: EF >50 (extremely severe) [20].

TABLE IV
POLLUTION INDEX AND POTENTIAL ECOLOGICAL RISK INDEX OF CHROMIUM
IN SEDIMENTS OF IENLIGEN RIVER MOUTH

IN SEDIMENTS OF JEN-GEN RIVER MOUTH					
Station	PI	PERI ¹	Risk level		
J1	36	71	moderate		
J2	16	32	low		
J3	27	55	moderate		
J4	38	76	moderate		
J5	26	51	moderate		
J6	31	62	moderate		
J7	36	72	moderate		
Ј8	8	17	low		
J9	17	33	low		
J10	6	12	low		
J11	28	56	moderate		
mean	24	49	moderate		

¹PERI < 40 indicates low risk, $40 \le PERI < 80$ is moderate risk, $80 \le PERI < 160$ is higher risk, $160 \le PERI < 320$ is high risk, and $PERI \ge 320$ is serious risk [12].

man-made sources. Except Stations J8 and J10 that has minor enrichment of Cr, and Station J1 that has severe enrichment, all other sampling stations are classified as either moderate or moderate severe enrichment. Based on the $I_{\rm geo}$ data and Muller's geo-accumulation indexes, the contamination level with respect to Cr at each station is ranked in Table 3. Based on the above observations, sediments at the Jen-Gen River mouth was moderate polluted. These results point out that the sediment near Jen-Gen River experiences moderate accumulation of Cr that originates from the upstream sources of pollution.

Additionally, the average EF value of 6.3±2.9 obtained in this study is lower than the average EF value of 8.4 reported earlier [8] 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 Jen-Gen River flow and dredging the river mouth.

C. Assessment of 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) [12] can be used to evaluate the potential risk of one metal or combination of multiple metals. The calculated PERI values can be categorized into 5 classes of potential ecological risks: low risk (PERI < 40), moderate risk ($40 \le PERI < 80$), higher risk ($80 \le PERI < 160$), high risk ($160 \le PERI < 320$), and serious risk (PERI ≥ 320). Table 4 and Fig. 4 lists the PI value, PERI value, and risk classification for the Cr contained in the surface sediment samples collected near Jen-Gen River mouth. Except Stations J2, J8, J9, and J10 that are classified as low risk, all other stations are classified as moderate risk with respect to Cr pollution. The above evaluation results indicate that the Cr contained in surface sediments at Jen-Gen River mouth has moderate potential ecological risks. Therefore, effective management and control of upstream pollution should be immediately implemented in order to improve the river mouth sediment quality and lower the associated ecological risk.

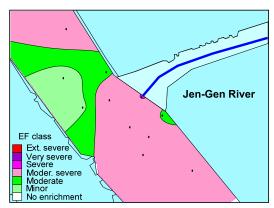


Fig. 3 EF class in sediments of Jen-Gen River mouth

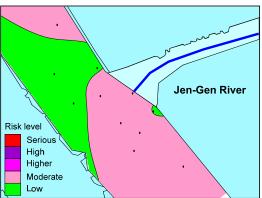


Fig. 4 PERI risk level in sediments of Jen-Gen River mouth

 $^{^2}$ 0: $I_{\rm geo}$ <0 (none), 1: $I_{\rm geo}$ = 0–1 (none to medium), 2: $I_{\rm geo}$ = 1–2 (moderate), 3: $I_{\rm geo}$ = 2–3 (moderately to strong), 4: $I_{\rm geo}$ = 3–4 (strongly polluted), 5: $I_{\rm geo}$ = 4–5 (strong to very strong), and 6: $I_{\rm geo}$ >5 (very strong) [11].

IV. CONCLUSIONS

The sediment samples collected at all sampling stations at Jen-Gen River mouth contain 92-567 mg/kg of Cr with an average of 366±166 mg/kg. The distribution of Cr in sediment 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 of EF and Igeo analyses indicate that the Jen-Gen River mouth sediments were moderately contaminated with Cr. Compared to the EF value of 8.4 reported earlier [8], the degree of Cr enrichment at Jen-Gen River mouth has been obviously reduced. This may be associated with river renovation and river mouth dredging. Results of potential ecological risk evaluation show that the classification of potential ecological risk for the sediment Cr at Jen-Gen River mouth is between "low risk" to "moderate risk". 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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