Copper Contamination in the Sediments of Love River Mouth, Taiwan

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

***Abstract*—This study was conducted using the data collected at the mouth of Love River to investigate and analyze Copper (Cu) contained in the sediments, and to evaluate the accumulation of Cu and the degree of its potential risk. The results show that samples collected at all monitoring stations near the mouth of Love River contain 84–300 mg/kg of Cu with average of 193±63 mg/kg. The spatial distribution of Cu reveals that the Cu 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 Love River mouth has the most serious degree of Cu accumulation and the ighest ecological potential risk.**

***Index Terms*—Copper, sediment, river mmouth, enrichment factor**

I. Introduction

The metals generated by anthropogenic activities cause 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]. Copper (Cu) is extremely toxic and highly bio-accumulative [3] and [4], its presence threatens the water ecological environment. Therefore, much research effort has been directed toward the distribution of Cu in water environment. Anthropogenic activities including municipal wastewater discharges, agriculture, mining, incineration, and discharges of industrial wastewater are the major source of Cu pollution [5]. Copper has low solubility in aqueous solution; it is easily adsorbed on water-borne suspended particles. After a series of natural processes, the water-borne Cu finally accumulates in the sediment, and the quantity of Cu contained in the sediment reflect the degree of pollution for the water body [6].

Love River is 12 km long with watershed of 56 km^2 that covers about 40% of total Kaohsiung City. Originated near Hu-Di channel, Love 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. Love 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 Love River have dense population with prosperous business and industrial establishments. The major pollution source includes 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. The objective of this study is to investigate the Cu distribution in the surface sediment near Love River mouth so that the degree of Cu accumulation and potential ecological risk can be evaluated.

II. Materials and Methods

A. Sampling and Analytical Methods

Surface sediment samples were collected at 10 stations near Love 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 *μm*), silt (2 *μm* < *dia* < 63 *μm*), and sand (*dia* >63 *μm*).

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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), Cu, 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 Cu analyses, 0.5 g dry weight of the sediment sample was mixed with a mixture of ultra-pure acids (HNO_3:*HCl*:*HF* = 5:2:5), and was then 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 Cu contents were determined using flame atomic absorption spectrophotometers (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 ($n = 3$).

TABLE I: SEDIMENT CHARACTERISTICS, COPPER CONTENTS AND ENRICHMENT FACTOR IN THE SEDIMENTS OF LOVE RIVER MOUTH

Station	Clay (%)	Silt (%)	Sand (%)	Water content (%)	OM (%)	TG (mg/kg)	Al (%)	Cu (mg/kg)
L1	10.6	81.4	8.0	64	5.7	5951	4.96	84
L2	9.0	73.5	17.5	86	7.3	4518	5.80	208
L3	9.7	87.8	2.5	79	7.5	11739	4.30	226
L4	11.3	79.5	9.2	101	7.3	5276	5.03	191
L5	8.8	86.1	5.1	55	4.5	2141	5.05	300
L6	11.1	79.0	9.9	87	6.2	4260	5.50	99
L7	7.5	77.0	15.5	83	6.8	3151	4.88	211
L8	9.5	87.5	3.0	67	4.3	5194	4.93	233
L9	12.6	80.2	7.2	98	5.9	3163	3.34	186
L10	12.2	85.9	1.9	94	6.8	7500	5.71	194
Mean	10.2	81.8	8.0	81.4	6.2	5,289	4.95	193
SD	1.6	4.8	5.3	15.2	1.1	2,741	0.72	63

TABLE II: PEARSON CORRELATION COEFFICIENTS AMONG SEDIMENT CHARACTERISTICS AND COPPER CONCENTRATIONS (N = 10)

	Clay	Silt	Sand	Water content	OM	TG	Al
Silt	0.129						
Sand	-0.422	-0.954[a]					
Water content	0.557	-0.428	0.222				
OM	0.097	-0.438	0.371	0.692(*)			
TG	0.170	0.468	-0.479	0.103	0.480		
Al	-0.229	-0.202	0.255	-0.098	0.128	-0.028	
Cu	-0.446	0.366	-0.199	-0.251	-0.206	-0.098	-0.101

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

TABLE III: EF AND I_{GEO} CLASSES OF COPPER FOR EACH STATION STUDIED AT LOVE RIVER MOUTH

Station	EF	EF class[1]	I_{geo}	I_{geo} class[2]
L1	2.5	1	0.0	1
L2	5.4	3	1.3	2
L3	7.8	3	1.5	2
L4	5.7	3	1.2	2
L5	8.9	3	1.9	2
L6	2.7	1	0.3	1
L7	6.5	3	1.4	2
L8	7.1	3	1.5	2
L9	8.3	3	1.2	2
L10	5.1	3	1.2	2
mean	5.8	3	1.2	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].

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

TABLE IV: POLLUTION INDEX AND POTENTIAL ECOLOGICAL RISK INDEX OF COPPER IN SEDIMENTS OF LOVE RIVER MOUTH

Station	PI	PERI [1]	Risk level
L1	6	28	low
L2	14	71	moderate
L3	15	77	moderate
L4	13	65	moderate
L5	20	102	higher
L6	7	34	low
L7	14	72	moderate
L8	16	79	moderate
L9	13	63	moderate
L10	13	66	moderate
mean	13	66	moderate

[1] 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].

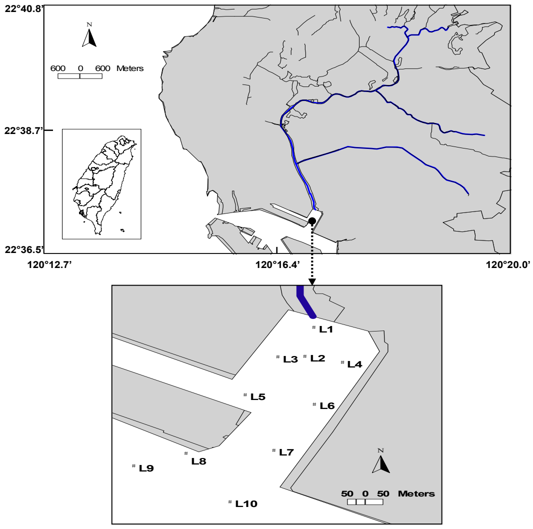

Fig. 1. Map of the study area and sampling locations.

A. 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 Cu 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 Cu pollution and the associated potential ecological risk index (PERI). EF is defined as: EF = $(X/Al)_{sediment}/(X/Al)_{crust}$, where (X/Al) is the ratio of Cu 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: $I_{geo} = log_2(C_n/1.5B_n)$ [11], where C_n is the measured content of Cu, and B_n is the background content of Cu in the average shale. The potential ecological risk index PERI is defined as: PERI = PI × Ti [12], where PI is the pollution index of *Cu* (C_i/C_f); T_i is its corresponding coefficient, i.e. 5 for *Cu [13]*; C_i is the measure concentration of Cu in sediment; C_f is the background concentration of *Cu*. In this study, the average Cu concentration in the bottom core sediment (80 cm) of 15 mg/kg [14] was taken as the Cu background concentration.

III. RESULTS AND DISCUSSION

A. Distribution of Copper in Sediments

Table 1 lists the location of sampling Love River mouth sediment, characteristics of the sediment, and Cu 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 μm to 63 *μm*. The percentage compositions are 73.5–87.8% for silt, 7.5–12.6% for Clay (<2 *μm*), and 1.9–17.5% for sand. Fine particles (dia. <63 *μm*) that can easily adsorb and accumulate pollutants are the major component of particles found in the Love River mouth sediment. The average water content of Love River mouth sediment is 81.4±15.2%; the organic matter content and total grease are 6.2±1.1% and 5,289±2,741, respectively. These results are similar to those reported earlier [8].

All sediment samples collected at Love River mouth contain 84–300 mg/kg of Cu with an average of 193±63 mg/kg. Concentration distributions of Cu in Love River mouth sediment shown in Fig. 2 reveal that the sediment Cu content is relatively higher near the boundary of the river mouth, and gradually decreases in the direction toward the harbor. Because Love 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].

Coefficient of the Pearson correlation between the sediment characteristics and Cu content was carried out (Table 2). The sediment Cu content is not obviously correlated to either OM or particle size (p>0.05) indicating that OM and particle size are not major factors to control the Cu 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 Cu concentration and other sediment characteristics is observed to exist.

B. Enrichment Factor and index of geo-accumulation

The extent of sediment contamination was assessed using the enrich factor (EF) and geo-accumulation index (I_{geo}). 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 show EF values of the sediment Cu for the Love River mouth region; the Cu concentration is consistent with the Cu EF value for all sampling stations, and all EF values are greater than 1. This indicates that the sediment Cu has enrichment phenomenon with respect to the earth crust and that all Cu originates from man-made sources. Except Stations L1, and L6 that has minor enrichment of Cu, all other sampling stations are classified as moderately severe enrichment.

The I_{geo} values for the metals studied were calculated using the Muller's (1979) expression: $I_{geo} = \log_2 (C_n/1.5B_n)$, where C_n is the measured content of element Cu, and B_n is the background content of Cu in the average shale. Based on the I_{geo} data and Muller's geo-accumulation indexes, the contamination level with respect to Cu at each station is ranked in Table 3. Based on the above observations, sediments at the Love River mouth was moderate polluted. These results point out that the sediment near Love River experiences moderately accumulation of Cu that originates from the upstream sources of pollution.

Additionally, the average EF value of 5.8±2.2 obtained in this study is lower than the average EF value of 7.1 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 Love 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 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 calculated PERI values can be categorized into 5 classes of potential ecological risks: 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 4 lists the PI value, PERI value, and risk classification for the Cu contained in the surface sediment samples collected near Love River mouth. Except Stations L1, and L6 that is classified as low risk, all other stations are classified between moderate to higher risk with respect to Cu pollution. The above evaluation results indicate that the Cu contained in surface sediments at Love 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.

IV. Conclusions

The sediment samples collected at all sampling stations at Love River mouth contain 84–300 mg/kg of Cu with an average of 193±63 mg/kg. The distribution of Cu in sediment reveals that the Cu 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 I_{geo} analyses indicate that the Love River mouth sediments were moderately contaminated with Cu. Compared to the EF value of 7.1 reported earlier [8], the degree of Cu enrichment at Love 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 Cu at Love River mouth is "high 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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