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Evaluating the leachable metals in Kaohsiung Harbor sediment using the toxicity characteristic leaching procedure (TCLP)

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ABSTRACT

The toxicity characteristic leaching procedure (TCLP) method was used to analyze the contaminants in the sediment materials of Kaohsiung Harbor as to evaluate the pollution potential associated with the Kaohsiung Harbor. A total of 80 sediment samples were collected at 20 locations and characterized for water content, organic matter (OM), total nitrogen (TN), total phosphorus (TP), and total grease (TG) as well as the leachable and total metals. The results indicated that the leachable metal concentrations were below the low detectable levels for mercury (Hg), lead (Pb), cadmium (Cd), chromium (Cr), and silver (Ag), between 0.005 and 0.281 mg/L, 0.07 and 24.0 mg/L, and 0.013 and 0.221 mg/L for Cu, Zn, and Ni, respectively. The leachable metal concentration at the river mouth vicinity was higher than that at other locations indicating that upstream industrial and domestic wastewater discharges were the main pollutant sources. Results of correlation studies revealed that the OM concentration in the sediment was highly correlated with TN, TP, TG, and total metal as well as the leachable Cu, Zn, and Ni. The above observation indicates that the OM present in the sediment mainly comes from man-made pollutants. All leachable metals in the Kaohsiung Harbor sediment were blown by the US Environmental Protection Administration standard. Hence, the dredged sediment from Kaohsiung Harbor can be a useful sea-filling material for land reclamation; however, the continuing leaching of metals and its impact on the aquatic environment need to be studied further.

Keywords: Toxicity characteristic leaching procedure (TCLP); Metals; Leachability; Sediments

1. Introduction

Harbor is a sink for the continuous deposit of silt and sand carried in riverine inflows, which reduce the harbor channel depth and may seriously affect the safety of navigation. Therefore, the harbor channel must be dredged regularly to maintain a proper navigation depth. The incoming stream flows often contain anthropogenetic pollutants, especially the hydrophobic pollutant particles, e.g. metals, from upstream industrial and

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domestic wastewater discharges [1–3]. These particles tend to settle in the harbor; hence, the harbor sediment often shows the accumulation of metals. When the harbor is dredged, the sediment is usually disposed of by ocean dumping or used for sea filling for land reclamation [3,4]. However, sediment dredging and dredged material disposal may perturb the environment, such as changes in redox potential (ORP), pH, and dissolved oxygen, which can alter the state and distribution of metals in the sediment and cause adverse impact to the aquatic environment of the harbor or spoil the disposal site [5–7].

Kaohsiung Harbor, the largest commercial harbor in Taiwan, is located on the southeastern seashore of Taiwan and is adjacent to the Greater Kaohsiung City, the largest industrial metropolitan in Taiwan. There are four streams feeding to the harbor causing a large quantity of settleable particles, which causing accumulation of pollutants in the harbor, and reducing channel depth that seriously threatens the navigation safety of its water way. About one million cubic meter of bottom sediment must be dredged from the harbor channel and disposed of, usually by ocean dumping [3]. Since the dredged harbor sediment is a potential natural resource, the Kaohsiung Harbor Authority gradually has applied the dredged sediment for sea filling to reclaim land for harbor expansion. However, the mobility and pollution potential of metals in the sediment must be evaluated as to assure that such practice does not cause adverse ecological impact on the aquatic environment of disposal sites [8,9].

Toxicity characteristic leaching procedure (TCLP) method has been used to simulate the time-dependent movement of metals in wastes disposed at sanitary landfill [10]. In the present study, in order to evaluate the mobility and polluting characters of metals, TCLP was used to determine the leachable concentration of metals in the harbor sediment. Additionally, the results were compared with the TCLP standards of US Environmental Protection Agency as to determine the hazard status of the dredged material and its suitability for uses filling sea for land reclamation.

2. Materials and methods

2.1. Monitoring station and on-site sampling

Twenty stations were installed for sampling Kaohsiung Harbor sediment (Fig. 1) based on the following considerations: (1) evenly distributed in the harbor to cover the harbor waters, (2) possible pollution sources, and (3) capable of evaluating the overall extent of sediment pollution. On-site sampling of all 80 surface sediment was conducted in February, May, August, and October, 2013 by fishing boat at the 20 locations in Kaohsiung Harbor. The precise location of each sampling site was pinpointed by using global positioning system (GPS). Samples were collected from the sediment surface (0–15 cm) using $6 \times 6 \times 6$ in Ekman Dredge grab sampler (Jae Sung International Co., Taiwan). The collected samples were placed in double-layer zipped sample bags and temporarily stored in a cooler filled with crushed ice before being transported back to laboratory for analyses.

2.2. Pretreatment and analyses of samples

In the laboratory, the samples were placed on a plastic dish to be divided into two portions. One portion was used to determine the water content, organic matter (OM), and particle size distribution; another portion was air-dried first in a dark and cool place. The air-dried sample was then placed in an agate pestle and mortar and ground to powder, and then stored in plastic bag. The weight difference between before and after drying was taken as the water content expressed as percent dry weight. The oven-dried sample was then ignited at a temperature of 550˚C for 4 h. After drying, the sample was placed in a desiccator and weighed. Igniting (30 min), cooling, desiccating, and weighing steps were repeated until the weight loss was less than 0.05 g. The weight difference with respect to dry weight was defined as the OM [11]. The particle size distribution was analyzed using the Coulter LS Particle Size Analyzer, and the particles were classified into three groups of clay (<2 μm), silt (2–63 μm), and sand (>63 μm) [12]. Total nitrogen (TN) and total phosphorus (TP) were analyzed following US EPA method 351.1 and US EPA method 365.2, respectively [13]. The Standard Method 503.D was used to analyze total grease (TG).

For analyses of total metal in sediments, a sediment sample of about 1.0 g dry weight was digested with a mixture of concentrated acids (HNO_3 65%: HCl 37%, 1:3, v:v) [14]. The MHS-10 technique was used for mercury (Hg) analysis (US EPA method 7471A) [15]. The leachable concentrations (mobility) of metals in the sediment were analyzed using the TCLP method developed by the US EPA (US EPA method 1311) [15]. The leaching liquid obtained by digesting the sample with acid were analyzed using a flame atomic absorption spectrophotometer (Hitachi Z–6000, Japan) to determine concentration of the leached metals including lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), zinc (Zn), nickel (Ni), and silver (Ag) in the leaching liquid. Mercury (Hg) was analyzed using the MHS-10 technique (US EPA method 7471B) [16].

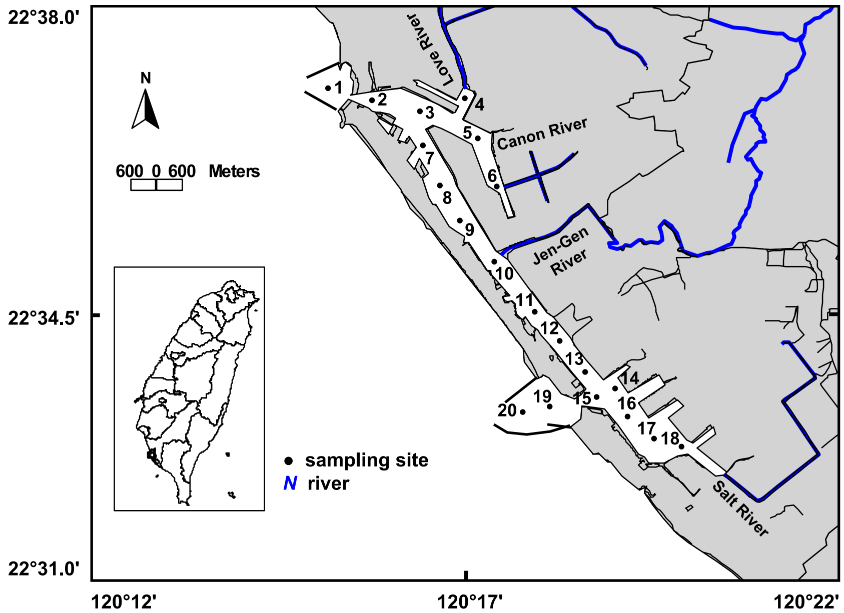

Fig. 1. Map of study area and sampling locations.

In this study, the maximum, minimum, average, and standard deviation of the results were analyzed statistically. Correlations between the sediment sample characteristics and concentration of the leachable metal were analyzed using the Pearson linear correlation coefficient available in the SPSS 12.0 software.

3. Results and discussion

3.1. Properties of Kaohsiung Harbor sediment

Table 1 lists the particle composition (clay, silt, and sand), water content, OM, TN, TP, and TG of sediment samples collected at the 20 selected sampling stations. The distributions of particle sizes in sediments at Stations 13, 15, and 16 were accounted for by sand (51.1, 63.7, and 64%, respectively), while fine particles (<63 μm) were dominant at the other stations (>55.6%). These fine particles would exhibit significant metal adsorption capacity. For the spatial distribution of WC, OM, TN, TP, and TG; stations in the vicinity of the river mouth (Stations 4, 6, 10, and 18) had obviously higher concentrations than the other stations. This observation was consistent with other studies [12,17], which demonstrated that the river mouth region was the receiver of discharges of domestic and industrial wastewater upstream; hence, relatively more OM and nutrients were accumulated in this region. Sediments rich in organics and nutrients would cause a decrease in dissolved oxygen and result in anaerobic condition.

3.2. Total metal content

The total metal content in sediments for each station is shown in Fig. 2. Of the metals measured, Zn was present at the highest concentration (ranging from 67 to 3,200 μg/g dw), while Ag was the lowest (ranging from <0.2 to 1.2 μg/g dw) from all sampling sites. Metal concentration followed the order: Zn > Cu > Cr > Pb > Ni > Hg > Cd > Ag. The results were similar to those reported in a previous study [6,12]. In the vicinity of Canon River and Salt River mouth (Stations 6 and 18), the Zn concentration was high 1,636 and 1,808 mg/kg, respectively, which was at least two to ten times that of other stations. This might imply a significant Zn contribution from upstreams. Like Zn, the highest concentrations for the other metals were found in the vicinity of the river mouth (Stations 4, 6, 10, and 18). The rivers received high-strength untreated industrial wastewater and domestic wastewater from upstream and thus had the highest concentrations of metals [3,12]. This result indicated that in the vicinity of the river mouth, the metal sinks rendering the metals immobilized once they arrived at the sediment [12]. However, the distribution of metals in the river mouths was varying. The Love River mouth (Station 4) showed the highest concentration of Ag; the Canon River mouth (Station 6) showed Hg and Cd; the Jen-Gen River mouth (Station 6) showed Cr; and the Salt River mouth (Station 10) showed Pb, Cu, Zn, and Ni (Fig. 2). This difference in metal distribution at different river mouth could be attributed to

Table 1
Sediment characteristics in the sediment of Kaohsiung Harbor

Site	Clay (%)	Silt (%)	Sand (%)	Water contents (WC) (%)	Organic matter (OM) (%)	Total grease (TG) (mg/kg)	Total nitrogen (TN) (mg/kg)	Total phosphorus (TP) (mg/kg)
1	10.4 ± 4.0	63.6 ± 14.5	26.0 ± 13.7	53±20	4.0 ± 0.7	163 ± 133	929 ± 149	259 ± 57
2	10.2 ± 4.8	57.3 ± 11.4	32.5 ± 12.4	52 ± 18	4.5 ± 0.2	237 ± 60	894 ± 77	299 ± 70
3	9.1 ± 2.2	70.5 ± 17.6	20.5 ± 16.1	67 ± 7	4.8 ± 0.4	292 ± 199	1,085 ± 88	296 ± 91
4	6.7 ± 2.3	64.2 ± 8.1	29.1 ± 10.1	114 ± 21	12.2 ± 2.7	688 ± 119	2,068 ± 340	511 ± 49
5	9.6 ± 3.3	68.4 ± 10.8	22.0 ± 7.5	92 ± 16	5.6 ± 0.4	322 ± 113	1,486 ± 214	362 ± 43
6	7.7 ± 2.2	59.0 ± 6.1	33.3 ± 4.4	100 ± 14	6.1 ± 0.8	305 ± 57	2,156 ± 318	541 ± 62
7	10.9 ± 3.7	66.8 ± 14.8	22.2 ± 13.6	65 ± 12	4.3 ± 0.5	127 ± 41	1,013 ± 204	297 ± 37
8	10.2 ± 2.7	63.8 ± 17.3	26.1 ± 15.0	68 ± 10	4.5 ± 0.6	246 ± 140	1,215 ± 141	332 ± 37
9	9.0 ± 1.8	61.2 ± 16.4	29.7 ± 15.7	60 ± 20	4.3 ± 0.4	117 ± 67	1,447 ± 263	309 ± 32
10	9.2 ± 3.1	67.4 ± 9.5	23.4 ± 7.3	70 ± 18	5.4 ± 0.6	420 ± 283	1,887 ± 299	440 ± 60
11	8.2 ± 2.2	54.1 ± 5.3	37.8 ± 5.8	40 ± 17	3.4 ± 0.3	124 ± 99	1,159 ± 129	360 ± 31
12	9.8 ± 2.0	62.3 ± 9.8	27.9 ± 7.9	55 ± 9	4.1 ± 0.4	287 ± 132	1,040 ± 146	375 ± 9
13	7.8 ± 5.8	41.1 ± 14.3	51.1 ± 19.5	36 ± 5	3.1 ± 0.7	161 ± 61	1,062 ± 122	343 ± 55
14	6.9 ± 4.1	48.7 ± 23.9	44.4 ± 27.9	41 ± 14	3.9 ± 0.1	175 ± 41	934 ± 251	269 ± 36
15	5.2 ± 3.2	31.0 ± 13.4	63.7 ± 16.5	34 ± 7	2.9 ± 0.2	157 ± 56	984 ± 241	285 ± 48
16	5.5 ± 3.9	30.4 ± 12.5	64.0 ± 16.3	33 ± 5	3.1 ± 0.2	145 ± 56	1,554 ± 166	458 ± 27
17	10.7 ± 1.7	62.8 ± 14.7	26.5 ± 13.1	72 ± 27	5.3 ± 0.4	212 ± 50	1,535 ± 282	397 ± 83
18	11.4 ± 3.9	65.9 ± 12.6	22.7 ± 9.4	74 ± 22	11.0 ± 5.2	300 ± 99	1,713 ± 227	419 ± 55
19	10.2 ± 2.1	60.2 ± 18.8	29.7 ± 20.2	33 ± 10	3.7 ± 0.7	154 ± 30	910 ± 120	279 ± 33
20	10.2 ± 2.8	62.2 ± 22.6	27.5 ± 25.4	62 ± 21	4.7 ± 0.5	145 ± 76	871 ± 163	278 ± 49

the various upstream domestic and industrial wastewater discharges into the water ways.

3.3. TCLP concentration of metals

The TCLP results are listed in Table 2. Among the 8 metals analyzed, Hg, Pb, Cd, Cr, and Ag in the samples collected at all 20 stations had leachable concentrations of less than of the detection limit (Hg: 0.001 mg/L, Pb: 0.025 mg/L, Cd: 0.005 mg/L, Cr: 0.025 mg/L, and Ag: 0.015 mg/L) (Table 2). However, Cu, Zn, and Ni showed detectable leaching concentrations at all stations. For all 80 sediment samples, the leachable concentration of Cu was between 0.005 and 0.281 mg/L with an average of 0.063 ± 0.040 mg/L. The highest Cu leachable concentration between 0.068 ± 0.100 and 0.149 ± 0.106 mg/L was measured at north of Kaohsiung Harbor (Stations 2–9) and the mouth of Salt River (Station 18). The leachable concentration of Zn was between 0.07 and 24.0 mg/L with an average of 3.78 ± 3.13 mg/L; Stations 4–10 and 17–18 had higher concentration between 4.55 ± 1.95 and 11.4 ± 8.5 mg/L than 0.32 ± 0.15 and 2.64 ± 2.54 mg/L for all other stations. The leachable concentrations of Ni was between 0.013 and 0.221 mg/L with an average of 0.060 ± 0.028 mg/L; the highest leachable concentration appeared in the sample collected at the mouths of the Salt River, Jen-Gen River, Canon River, and Love River.

Fig. 3(a)–(c) shows the spatial distribution of the TCLP leachable concentration of Cu, Zn, and Ni in sediments at 20 stations in Kaohsiung Harbor. Sediment samples collected at the vicinity of the First Harbor (Station 1) and the Second Harbor (Stations 19 and 20) had relatively low leachable Cu. This is probably due to frequent dredging of the harbor entrance and exit that disturbs the sediment surface and release the Cu to the water phase. In contrast, samples collected near the river mouth showed relatively higher concentration of leachable Cu probably because of the low frequency of dredging and the tendency of accumulating the upstream pollutants near the river mouth. Zn and Cu had similar spatial distribution; samples collected at the river mouth, especially the mouth of Salt River (Station 18) and Canon River (Station 6), apparently had higher leachable Zn concentrations than other stations. Relatively higher leachable Ni concentration was observed with the samples collected at the mouth of Salt River, Jen-Gen River, and Love River; the river mouth of Canon River had similar leachable Ni concentration as samples collected at other stations.

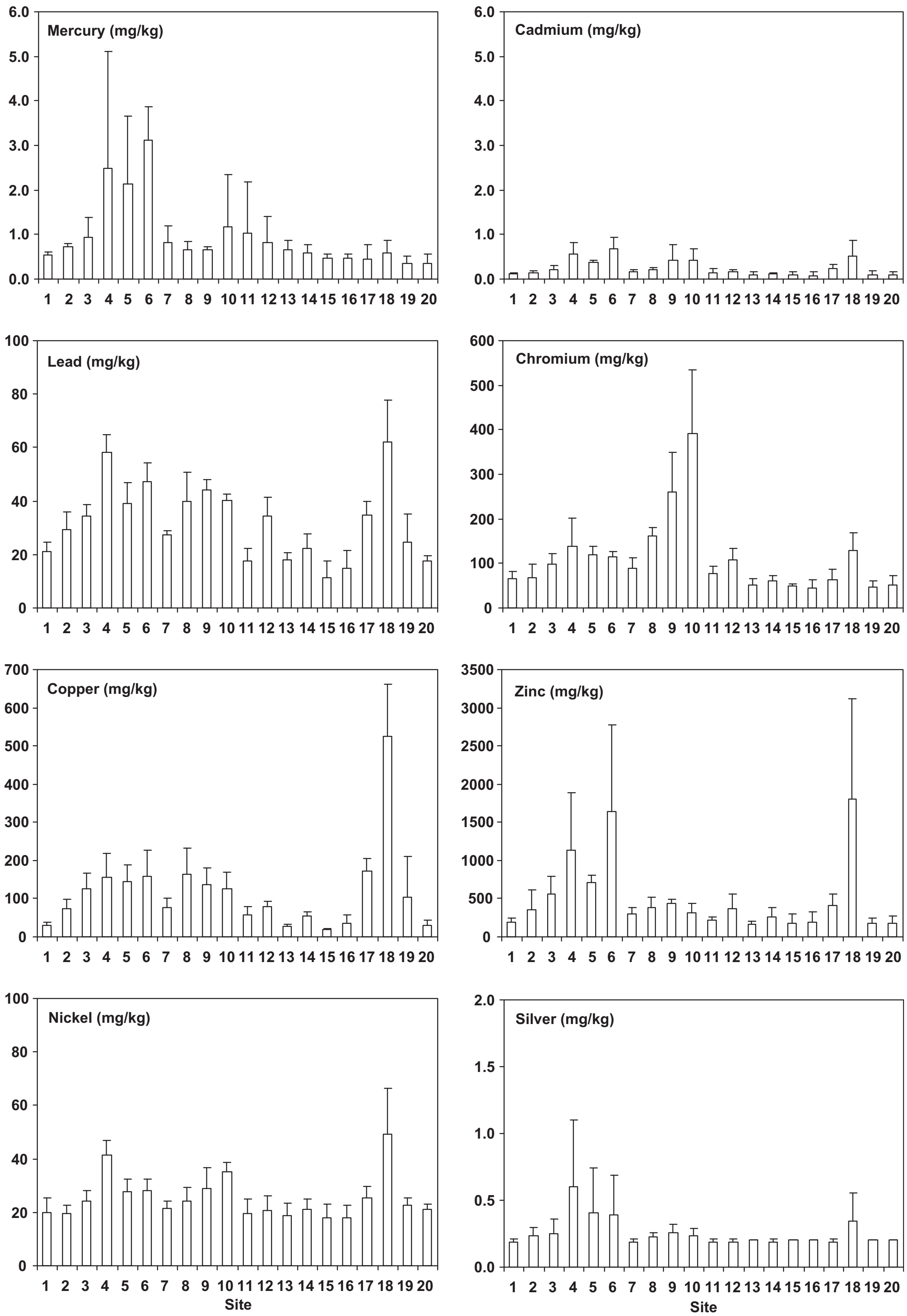

Fig. 2. The distribution of total metals in sediments of Kaohsiung Harbor.

Table 2
The metal concentrations in TCLP leachate of sediments from Kaohsiung Harbor

Sampling time	Site	Concentrations of metals in TCLP leachate (mg/L)								Sampling time	Site	Concentrations of heavy metals in TCLP leachate (mg/L)							
		Hg	Pb	Cd	Cr	Cu	Zn	Ni	Ag			Hg	Pb	Cd	Cr	Cu	Zn	Ni	Ag
Feb 2013	1	<0.001	<0.025	<0.0005	<0.025	0.013	1.25	0.013	<0.015	Aug 2013	1	<0.001	<0.025	<0.0005	<0.025	0.010	0.14	0.028	<0.015
	2	<0.001	<0.025	<0.0005	<0.025	0.156	4.56	0.032	<0.015		2	<0.001	<0.025	<0.0005	<0.025	0.008	0.11	0.025	<0.015
	3	<0.001	<0.025	<0.0005	<0.025	0.160	5.78	0.029	<0.015		3	<0.001	<0.025	<0.0005	<0.025	0.010	0.57	0.044	<0.015
	4	<0.001	<0.025	<0.0005	<0.025	0.022	13.3	0.221	<0.015		4	<0.001	<0.025	<0.0005	<0.025	0.015	7.53	0.116	<0.015
	5	<0.001	<0.025	<0.0005	<0.025	0.040	10.8	0.097	<0.015		5	<0.001	<0.025	<0.0005	<0.025	0.021	6.35	0.049	<0.015
	6	<0.001	<0.025	<0.0005	<0.025	0.048	24.0	0.064	<0.015		6	<0.001	<0.025	<0.0005	<0.025	0.041	6.26	0.041	<0.015
	7	<0.001	<0.025	<0.0005	<0.025	0.138	2.07	0.074	<0.015		7	<0.001	<0.025	<0.0005	<0.025	0.077	5.61	0.060	<0.015
	8	<0.001	<0.025	<0.0005	<0.025	0.065	2.66	0.035	<0.015		8	<0.001	<0.025	<0.0005	<0.025	0.126	6.72	0.076	<0.015
	9	<0.001	<0.025	<0.0005	<0.025	0.229	4.02	0.063	<0.015		9	<0.001	<0.025	<0.0005	<0.025	0.071	1.94	0.040	<0.015
	10	<0.001	<0.025	<0.0005	<0.025	0.068	5.29	0.107	<0.015		10	<0.001	<0.025	<0.0005	<0.025	0.074	2.38	0.047	<0.015
	11	<0.001	<0.025	<0.0005	<0.025	0.023	0.75	0.052	<0.015		11	<0.001	<0.025	<0.0005	<0.025	0.059	2.02	0.044	<0.015
	12	<0.001	<0.025	<0.0005	<0.025	0.044	2.95	0.098	<0.015		12	<0.001	<0.025	<0.0005	<0.025	0.055	1.86	0.047	<0.015
	13	<0.001	<0.025	<0.0005	<0.025	0.038	0.48	0.027	<0.015		13	<0.001	<0.025	<0.0005	<0.025	0.074	0.35	0.036	<0.015
	14	<0.001	<0.025	<0.0005	<0.025	0.013	2.33	0.076	<0.015		14	<0.001	<0.025	<0.0005	<0.025	0.063	1.34	0.051	<0.015
	15	<0.001	<0.025	<0.0005	<0.025	0.005	0.61	0.109	<0.015		15	<0.001	<0.025	<0.0005	<0.025	0.054	1.55	0.043	<0.015
	16	<0.001	<0.025	<0.0005	<0.025	0.006	1.08	0.047	<0.015		16	<0.001	<0.025	<0.0005	<0.025	0.089	1.68	0.061	<0.015
	17	<0.001	<0.025	<0.0005	<0.025	0.020	5.28	0.127	<0.015		17	<0.001	<0.025	<0.0005	<0.025	0.018	4.07	0.068	<0.015
	18	<0.001	<0.025	<0.0005	<0.025	0.017	5.39	0.152	<0.015		18	<0.001	<0.025	<0.0005	<0.025	0.158	19.4	0.186	<0.015
	19	<0.001	<0.025	<0.0005	<0.025	0.038	0.56	0.084	<0.015		19	<0.001	<0.025	<0.0005	<0.025	0.015	0.30	0.039	<0.015
	20	<0.001	<0.025	<0.0005	<0.025	0.007	0.31	0.027	<0.015		20	<0.001	<0.025	<0.0005	<0.025	0.011	0.12	0.031	<0.015
May 2013	1	<0.001	<0.025	<0.0005	<0.025	0.048	0.96	0.025	<0.015	Oct 2013	1	<0.001	<0.025	<0.0005	<0.025	0.018	3.87	0.038	<0.015
	2	<0.001	<0.025	<0.0005	<0.025	0.049	2.76	0.045	<0.015		2	<0.001	<0.025	<0.0005	<0.025	0.016	0.50	0.033	<0.015
	3	<0.001	<0.025	<0.0005	<0.025	0.173	3.62	0.059	<0.015		3	<0.001	<0.025	<0.0005	<0.025	0.036	0.58	0.033	<0.015
	4	<0.001	<0.025	<0.0005	<0.025	0.218	6.83	0.034	<0.015		4	<0.001	<0.025	<0.0005	<0.025	0.018	3.42	0.038	<0.015
	5	<0.001	<0.025	<0.0005	<0.025	0.234	1.83	0.125	<0.015		5	<0.001	<0.025	<0.0005	<0.025	0.032	6.42	0.114	<0.015
	6	<0.001	<0.025	<0.0005	<0.025	0.281	9.05	0.120	<0.015		6	<0.001	<0.025	<0.0005	<0.025	0.019	6.27	0.058	<0.015
	7	<0.001	<0.025	<0.0005	<0.025	0.252	0.07	0.047	<0.015		7	<0.001	<0.025	<0.0005	<0.025	0.055	16.7	0.034	<0.015
	8	<0.001	<0.025	<0.0005	<0.025	0.062	5.65	0.065	<0.015		8	<0.001	<0.025	<0.0005	<0.025	0.056	3.16	0.037	<0.015
	9	<0.001	<0.025	<0.0005	<0.025	0.250	11.2	0.037	<0.015		9	<0.001	<0.025	<0.0005	<0.025	0.045	3.84	0.045	<0.015
	10	<0.001	<0.025	<0.0005	<0.025	0.012	3.45	0.146	<0.015		10	<0.001	<0.025	<0.0005	<0.025	0.019	5.82	0.120	<0.015
	11	<0.001	<0.025	<0.0005	<0.025	0.021	1.23	0.044	<0.015		11	<0.001	<0.025	<0.0005	<0.025	0.033	1.13	0.027	<0.015
	12	<0.001	<0.025	<0.0005	<0.025	0.010	0.31	0.099	<0.015		12	<0.001	<0.025	<0.0005	<0.025	0.039	2.38	0.035	<0.015
	13	<0.001	<0.025	<0.0005	<0.025	0.020	1.26	0.030	<0.015		13	<0.001	<0.025	<0.0005	<0.025	0.031	1.29	0.032	<0.015
	14	<0.001	<0.025	<0.0005	<0.025	0.015	2.43	0.092	<0.015		14	<0.001	<0.025	<0.0005	<0.025	0.039	2.48	0.037	<0.015
	15	<0.001	<0.025	<0.0005	<0.025	0.035	2.89	0.030	<0.015		15	<0.001	<0.025	<0.0005	<0.025	0.030	0.88	0.031	<0.015
	16	<0.001	<0.025	<0.0005	<0.025	0.047	1.03	0.026	<0.015		16	<0.001	<0.025	<0.0005	<0.025	0.032	1.28	0.035	<0.015
	17	<0.001	<0.025	<0.0005	<0.025	0.141	4.84	0.075	<0.015		17	<0.001	<0.025	<0.0005	<0.025	0.029	4.38	0.043	<0.015
	18	<0.001	<0.025	<0.0005	<0.025	0.158	2.92	0.063	<0.015		18	<0.001	<0.025	<0.0005	<0.025	0.215	9.79	0.095	<0.015
	19	<0.001	<0.025	<0.0005	<0.025	0.006	0.62	0.017	<0.015		19	<0.001	<0.025	<0.0005	<0.025	0.020	0.92	0.035	<0.015
	20	<0.001	<0.025	<0.0005	<0.025	0.010	0.45	0.021	<0.015		20	<0.001	<0.025	<0.0005	<0.025	0.027	0.40	0.044	<0.015
TCLP criteria		0.2	5.0	1.0	5	–	–	–	5	TCLP criteria		0.2	5.0	1.0	5	–	–	–	5

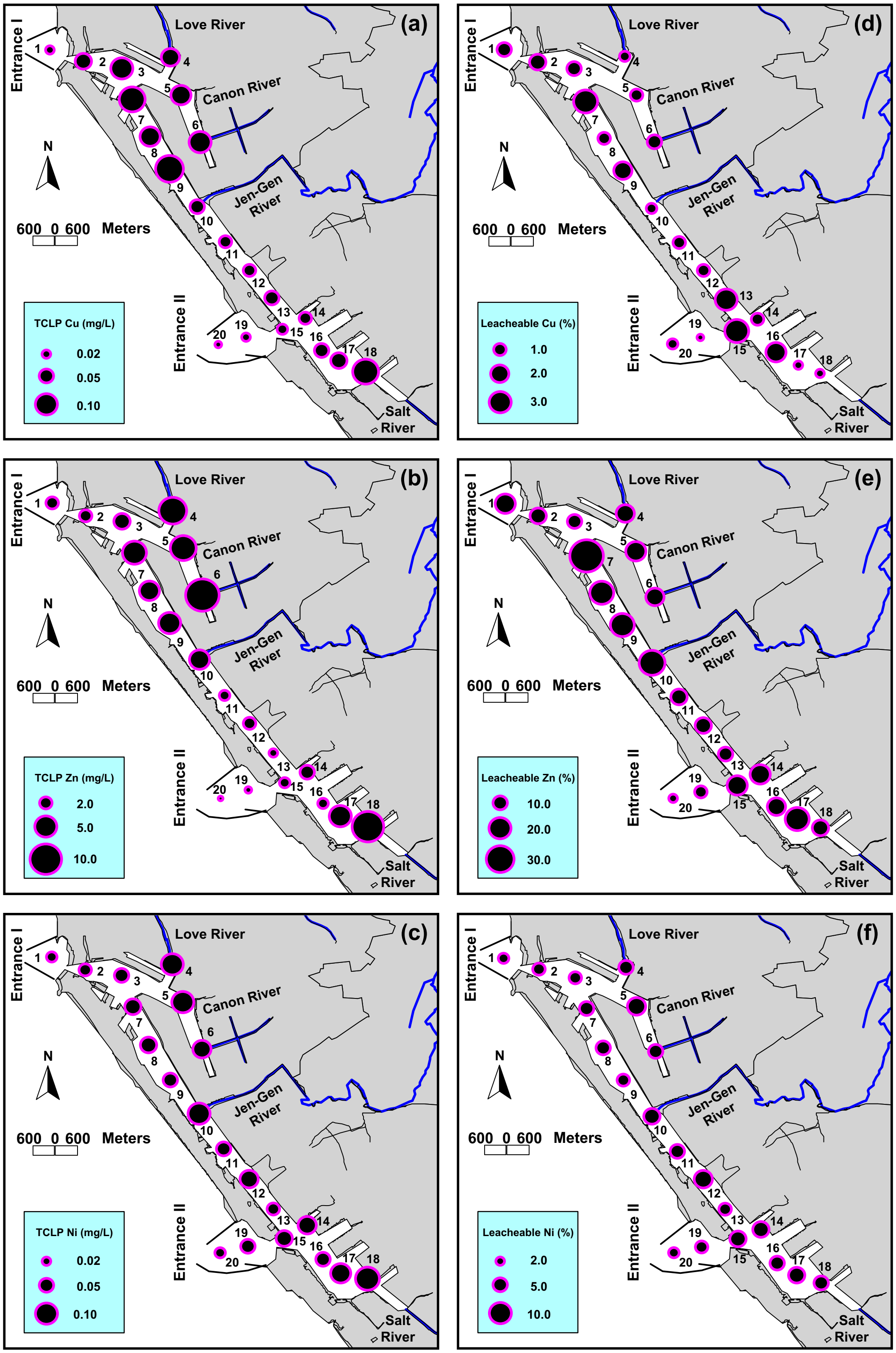

Fig. 3. The distribution of the TCLP leachability of copper (Cu), nickel (Ni), and zinc (Zn) in sediments of Kaohsiung Harbor.

Table 3
Pearson correlation coefficients among sediment characteristics, total metal, and TCLP leachable metals ($n = 80$)

Item[c]	Clay	Silt	Sand	OM	WC	TG	TN	TP	Hg	Pb	Cd	Cr	Cu	Zn	Ni	Ag	TCLPCu	TCLPZn
Silt	0.32[a]																	
Sand	−0.48[a]	−0.99[a]																
OM	0.01	0.30[a]	−0.28[b]															
WC	0.21	0.28[b]	−0.29[a]	0.55[a]														
TG	−0.05	0.35[a]	−0.32[a]	0.59[a]	0.52[a]													
TN	−0.19	0.25[b]	−0.20	0.57[a]	0.56[a]	0.50[a]												
TP	−0.15	0.14	−0.11	0.44[a]	0.48[a]	0.45[a]	0.83[a]											
Hg	−0.22	0.15	−0.10	0.35[a]	0.55[a]	0.36[a]	0.59[a]	0.56[a]										
Pb	0.23[b]	0.32[a]	−0.34[a]	0.72[a]	0.64[a]	0.55[a]	0.55[a]	0.44[a]	0.32[a]									
Cd	0.11	0.33[a]	−0.33[a]	0.48[a]	0.68[a]	0.46[a]	0.75[a]	0.64[a]	0.58[a]	0.65[a]								
Cr	0.07	0.32[a]	−0.31[a]	0.25[b]	0.31[a]	0.42[a]	0.50[a]	0.28[b]	0.26[b]	0.46[a]	0.51[a]							
Cu	0.23[b]	0.24[b]	−0.26[b]	0.64[a]	0.43[a]	0.28[b]	0.43[a]	0.32[a]	0.18	0.76[a]	0.54[a]	0.27[b]						
Zn	0.09	0.19	−0.19	0.43[a]	0.52[a]	0.32[a]	0.49[a]	0.51[a]	0.32[a]	0.64[a]	0.67[a]	0.06	0.66[a]					
Ni	0.02	0.17	−0.16	0.68[a]	0.54[a]	0.40[a]	0.56[a]	0.44[a]	0.32[a]	0.80[a]	0.62[a]	0.42[a]	0.76[a]	0.60[a]				
Ag	0.10	0.02	−0.03	0.40[a]	0.54[a]	0.36[a]	0.33[a]	0.31[a]	0.39[a]	0.51[a]	0.42[a]	0.13	0.31[a]	0.38[a]	0.53[a]			
TCLP Cu	0.28[b]	−0.02	−0.03	0.24[b]	0.30[a]	0.06	0.09	0.06	−0.00	0.53[a]	0.27[b]	0.16	0.40[a]	0.34[a]	0.43[a]	0.50[a]		
TCLP Zn	−0.01	0.24[b]	−0.22	0.52[a]	0.47[a]	0.37[a]	0.50[a]	0.43[a]	0.35[a]	0.58[a]	0.51[a]	0.25[b]	0.48[a]	0.57[a]	0.42[a]	0.10	0.29[b]	
TCLP Ni	0.19	0.19	−0.21	0.50[a]	0.31[a]	0.46[a]	0.37[a]	0.35[a]	0.07	0.53[a]	0.40[a]	0.32[a]	0.41[a]	0.28[b]	0.41[a]	0.09	0.13	0.47[a]

[a]Correlation is significant at the 0.01 level (2-tailed).
[b]Correlation is significant at the 0.05 level (2-tailed).
[c]OM: organic matter, WC: water content, TG: total grease, TN: total nitrogen, TP: total phosphorus, Hg: mercury, Pb: lead, Cd: cadmium, Cr: chromium, Cu: copper, Zn: zinc, Ni: nickel and Ag: silver.

Fig. 3(e)–(f) shows the spatial distribution of the leachability of Cu, Zn, and Ni in sediments [TCLP leachable content (mg/kg)/total metal content (mg/kg) × 100%] in Kaohsiung Harbor. Sediment samples collected at all 20 stations showed relatively lower percentage of TCLP leachable Cu (average: 1.6%), Zn (average: 18.9%), and Ni (average: 5.0%), which indicated that these metals were associated with the other sediment matrixes, such as organic matter fraction, Fe–Mn oxides fractions, and/or residual fractions [6,7,9,18,19].

3.4. Correlation among sediment characteristics, total metal, and leached metal

The Pearson correlation coefficients among sediment properties, total metal, and leaching concentration of metals in the harbor sediment are listed in Table 3. The sediment that has high OM content usually has high water content. Therefore, these two factors show significant positive correlation ($r = 0.55$, $p < 0.01$). Total metal, TN, TP, and TG usually originate from upstream discharges of industrial or domestic wastewater, carried over by stream water to the harbor, and finally deposit in the harbor [12]. Therefore, the OM shows significant correlation with total metal content ($r = 0.25$ (Cr, $p < 0.05$)—0.72 (Pb, $p < 0.01$)), TN ($r = 0.57$, $p < 0.01$), TP ($r = 0.44$, $p < 0.01$), and TG ($r = 0.59$, $p < 0.01$), whereas the sediment particle composition had relatively low or no significant correlation with the pollutants (Table 3). The results revealed that the OM was an important control parameter for the distribution of total metal, TN, TP, and TG in the sediment [12]. In other words, distribution of the man-made pollutants in the harbor will be different depending on the content of OM.

The Cu leached out of the sediment had significant correlation with WC ($r = 0.24$, $p < 0.05$), OM ($r = 0.30$, $p < 0.01$), and clay ($r = 0.28$, $p < 0.05$). The leachable concentration of Zn and Ni were correlated with WC ($r = 0.31$–0.47, $p < 0.01$), OM ($r = 0.50$–0.52, $p < 0.01$), TG ($r = 0.37$–0.46, $p < 0.01$), TN ($r = 0.37$–0.50, $p < 0.01$), and TP ($r = 0.35$–0.43, $p < 0.01$). The leachable concentration of Cu, Zn, and Ni showed low or no significant correlation with the sediment particle size including clay, silt, and sand (Table 3). The above observation indicated that except particle size, the property of sediment was an important factor controlling the leachable concentration of metal of the sediment [20]. The leachable concentration of Cu, Zn, and Ni showed significant correlation with the total metals.

Significant positive correlations were observed between the leachable concentration of Zn and Cu ($r = 0.29$, $p < 0.05$) as well as that between Zn and Ni ($r = 0.47$, $p < 0.01$), whereas the leachable concentration of Ni and Cu showed no significant correlation ($r = 0.13$, $p > 0.05$). The results revealed that Zn, Cu, and Ni had the same or similar sources and that Cu and Ni were originated from different sources.

3.5. The characteristics of metals in the leaching solution

Table 2 shows that leaching concentrations of all 8 metals in Kaohsiung Harbor sediments were lower than the TCLP standard published by the US EPA. This indicates that the dredged materials of the Kaohsiung Harbor can be used for sea filling and reclaim of land. However, the leachable Cu concentration of 59% sediment samples was higher than 0.03 mg/L as established by Taiwan Environmental Protection Administration (TEPA), whereas the leachable Zn concentration of 86% sediment samples were higher than the TEPA standard of 0.50 mg/L. Therefore, before the dredged harbor sediment is used as sea-filling material, the impact caused by the leachable metals on the ocean environment needs to be evaluated. Additionally, changes of environmental conditions such as pH, ORP, microbial activities, among others, may lead to higher mobility or leaching capability of metals in the filling material as well as increasing the bioavailability of the OM [5,6]. Therefore, the reclaimed land and its surrounding environment must be monitored in order to avoid any adverse impact on the environment.

4. Conclusions

Results of TCLP carried out on Kaohsiung Harbor sediment revealed that leachable concentrations of metals in the sediment samples were between 0.005 and 0.281, 0.07 and 24.0, and 0.013 and 0.221 mg/L for Cu, Zn, and Ni, respectively, whereas the leachable concentrations of Hg, Pb, Cd, Cr, and Ag were lower than the detection limits. The river mouth vicinity had higher leachable concentration of Cu, Zn, and Ni than other stations indicating that the major pollution sources were upstream domestic and industrial wastewater discharges. Results of correlation analyses showed that the sediment OM content was highly correlated with the sediment TN, TP, TG, and total metal as well as the leachable concentrations of Cu, Zn, and Ni. This indicated that the OM content was an important parameter controlling the distribution of the man-made pollutants in the harbor sediment. Comparison of the leachable metal concentrations with the US EPA standard revealed that the dredged harbor sediment was not hazardous material; hence, the Kaohsiung

Harbor sediment can be used as sea-filling material for reclaiming land. However, possible adverse impact caused by the leaching metals and changing environmental conditions on the seashore ecological environment should be evaluated.

References

[1] Y.C. Lin, G.P. Chang-Chien, P.C. Chiang, W.H. Chen, Y.C. Lin, Multivariate analysis of heavy metal contaminations in seawater and sediments from a heavily industrialized harbor in Southern Taiwan, Mar. Pollut. Bull. 76 (2013) 266–275.

[2] L. Huang, X. Pu, J.F. Pan, B. Wang, Heavy metal pollution status in surface sediments of Swan Lake lagoon and Rongcheng Bay in the northern Yellow Sea, Chemosphere 93 (2013) 1957–1964.

[3] C.F. Chen, C.D. Dong, C.W. Chen, Evaluation of sediment toxicity in Kaohsiung Harbor, Taiwan, Soil Sediment Contam. 22 (2013) 301–314.

[4] V. Kapsimalis, I. Panagiotopoulos, T. Kanellopoulos, I. Hatzianestis, P. Antoniou, C. Anagnostou, A multi-criteria approach for the dumping of dredged material in the Thermaikos Gulf, Northern Greece, J. Environ. Manage. 91 (2010) 2455–2465.

[5] R. Liu, D. Zhao, The leachability, bioaccessibility, and speciation of Cu in the sediment of channel catfish ponds, Environ. Pollut. 147 (2007) 593–603.

[6] C.F. Chen, C.D. Dong, C.W. Chen, Metal speciation and contamination in dredged harbor sediments from Kaohsiung Harbor, Taiwan, Soil Sediment Contam. 22 (2013) 546–561.

[7] A. Guevarariba, A. Sahuquillo, R. Rubio, G. Rauret, Assessment of metal mobility in dredged harbour sediments from Barcelona, Spain, Sci. Total Environ. 321 (2004) 241–255.

[8] P. Adamo, M. Arienzo, M. Imperato, D. Naimo, G. Nardi, D. Stanzione, Distribution and partition of heavy metals in surface and sub-surface sediments of Naples city port, Chemosphere 61 (2005) 800–809.

[9] E.D. Passos, J.C. Alves, I.S. dos Santos, J.D.H. Alves, C.A.B. Garcia, A.C. Spinola Costa, Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis, Microchem J. 96 (2010) 50–57.

[10] C.E. Halim, R. Amal, D. Beydouna, J.A. Scott, G. Low, Evaluating the applicability of a modified toxicity characteristic leaching procedure (TCLP) for the classification of cementitious wastes containing lead and cadmium, J. Hazard. Mater. 103 (2003) 125–140.

[11] APHA (American Public Health Association), Standard Methods for the Examination of Water and Wastewater, twenty-first ed., APHA-AWWA-WEF, Washington, DC, 2005, pp. 2–57.

[12] C.W. Chen, C.M. Kao, C.F. Chen, C.D. Dong, Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan, Chemosphere 66 (2007) 1431–1440.

[13] USEPA (United States Environmental Protection Agency), 1979, Methods for Chemical Analysis of Water and Wastes, United States Environmental Protection Agency, Cincinnati, OH, Publ. 600/4-79-020, rev, March 1983.

[14] G. Rauret, J.F. López-Sánchez, A. Sahuquillo, R. Rubio, C. Davidson, A. Ure, P. Quevauviller, Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials, J. Environ. Monit. 1 (1999) 57–61.

[15] USEPA (United States Environmental Protection Agency), Method 1311: Toxicity characteristic leaching procedure, 1992. Available from: http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/1311.pdf.

[16] USEPA (United States Environmental Protection Agency), Method 7471B: Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique), 2007. http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/7471b.pdf.

[17] C.F. Chen, C.W. Chen, C.D. Dong, C.M. Kao, Assessment of toxicity of polycyclic aromatic hydrocarbons in sediments of Kaohsiung Harbor, Taiwan, Sci. Total Environ. 463–464 (2013) 1174–1181.

[18] J. Morillo, J. Usero, I. Gracia, Heavy metal distribution in marine sediments from the southwest coast of Spain, Chemosphere 55 (2004) 431–442.

[19] D.T. Cuong, J.P. Obbard, Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure, Appl. Geochem. 21 (2006) 1335–1346.

[20] U. Chuangcham, W. Wirojanagud, P. Charusiri, W. Milne-Home, R. Lertsirivorakul, Assessment of heavy metals from landfill leachate contaminated to soil: A case study of Kham Bon landfill, Khon Kaen province, NE Thailand, J. Appl. Sci. 82 (2008) 1383–1394.