



Ecological risk assessment of heavy metals sampled in sediments and water of the Houjing River, Taiwan

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Abstract

The Houjing River flows through Kaohsiung, the most industrialized city in southern Taiwan. In this study, heavy metal concentrations in water and sediments from samples along the river were investigated to illustrate metal contamination levels and call for the awareness of industrial pollution prevention. The heavy metal concentrations in the water samples were low and appear to pose little direct risk to aquatic life and irrigation, but heavy metal concentrations in the sediments are locally very high and present an environmental risk. Cadmium, Cu, and Zn were found in higher concentrations in the river sediments than those recommended in some sediment quality guidelines and findings of river sediments in similar studies worldwide. Hence, the ecological risk of heavy metal contamination in sediments was assessed using the pollution load index (PLI) and potential ecological risk index (RI). Three of the eleven sites sampled were found to have PLI values higher than 1 and 8 of them had ‘considerable’ to ‘very high’ RI values, suggesting a considerable ecological risk. These findings provide an insight into elemental metal contamination of the Houjing River and present a baseline data set, which will be critical for future development and environmental protection plans devised for the region.

Keywords Water quality parameters · Sedimentary heavy metal contamination · Monitoring and pollution control plans

Introduction

Although heavy metals naturally occur in the environment, they are considered environmental contaminants when they are introduced into an environment where they are not common or are artificially concentrated. Their persistence, non-biodegradability, bio-accumulation, and toxicity in the ecosystem have attracted wide attention in both public and scientific communities (Tessier and Campbell 1987; Tomlinson et al. 1980). Heavy metals can enter ecosystems through various processes, including dissolution,

precipitation, sorption, and complexation (Dhanakumar et al. 2015; Pejman et al. 2015). At elevated levels, they are harmful to organisms (e.g., some of benthic invertebrates and fish species) and pose different negative effects to human and ecosystem health (Chapman et al. 1998; Eeva and Lehtikoinen 2000; Kiffney and Clements 1993; Vu et al. 2017b). Although heavy metals can occur naturally, industrial manufacturing, transportation, and agricultural irrigation often lead to elevated or excess heavy metal concentrations (El Nemr et al. 2016a; Venkatramanan et al. 2015; Yan et al. 2016).

Industrialization has led to numerous sites contaminated by heavy metal through the release of chemical products used in different industrial processes (Dhanakumar et al. 2015; Pejman et al. 2015). Metals entering aquatic ecosystem are rapidly deposited, connected to organic and inorganic compounds, including complexation, and eventually settled out in sediments. Since the mobility and bio-availability of heavy metals in aquatic environment can be altered, heavy metals can be accumulated in the bodies of aquatic organisms and enter the food chain (Tessier and Campbell 1987). Heavy metals are difficult to degrade and/or excrete and excessive amounts of them may cause

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negative effects on the growth and physiological functions of organisms, including humans (Deniseger et al. 1990). Therefore, understanding the distribution and ecological risk of heavy metals is important for the management of the environment.

The rapid industrial transformation from an agricultural society in Taiwan has created high environment pressure (Huang et al. 2016; Vu et al. 2017a). One of the most noticeable environmental problems on the island is the widespread heavy metal pollution of water bodies (Huang 2003; Lin et al. 2009, 2010; Williams and Chang 2008). Kaohsiung City, the most industrialized area in Taiwan, is where heavy industries concentrated over the last 40 years. Located in the northern part of Kaohsiung City, the Houjing River has a long pollution history due to the industrial plants situated along its banks (Lin et al. 2017; Vu et al. 2017b). Many widely known incidents of illegal discharge from metal-utilizing companies into the river over the years have drawn wide attention from the public and resulted in a demand for risk assessment and frequent monitoring of heavy metal pollution (Chen 2016; Tsai 2014). Therefore, we investigated the heavy metal contamination at 11 sampling sites along the Houjing River and assessed environmental and ecological risks. The results of the current contamination status of the Houjing River are essential for guiding city development plans and restoration studies or plans for land-use changes, and are, thus, paramount for the city's future economic and environmental development.

Materials and methods

Location

The Houjing River, situated in north–west Kaohsiung City in southern Taiwan (Latitude 22°69'21.63"N–22°73'17.74"N and Longitude 120°25'74.36"E–120°33'74.70"E), has two upstream origins: one from the north-east in Dashe District and one from the south-east in Renwu District (Fig. 1). The waters meet near the Si-Chingpu Landfill and flow from there through the city and into the Taiwan Strait. The river is about 13 km long. Southern Taiwan has long winters and summers, and short springs and autumns. The basins main water supply is a composite of rainfall and effluent discharges from industrial wastewater treatment plants along the river. In the past, the river water was the main source for agricultural activities in the area, but recent urbanization and industrialization have impacted water and sediments (Lin et al. 2010). The previous studies showed that the river is polluted with the elevated levels of organic compounds including di-(2-ethylhexyl) phthalate (DEHP) in sediments (Lin et al. 2009), benzene, toluene, ethylbenzene, xylene (BTEX) in water (Lin et al. 2007), and emerging contaminants in water (Jiang et al. 2015).

Sampling

Figure 1 shows a map of the 11 sites which we sampled from September 2014 to September 2015. The sites

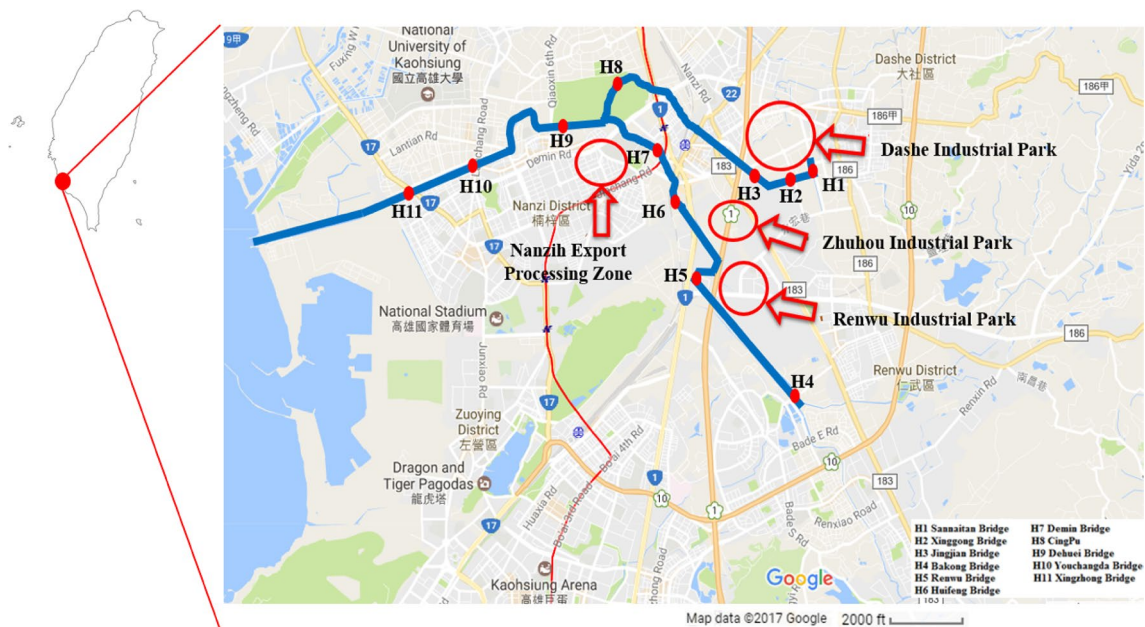


Fig. 1 Study area (overview map) of the sampling sites and major pollution sources of the Houjing River, Taiwan (Google map 2017)

Sannaitan (H1), Xinggong (H2), and Jingjian (H3) were chosen to investigate the potential heavy metal influx and contamination caused by different anthropogenic activities in the upstream Dashe District that includes a large petrochemical manufacturing complex and some metal-surface-coating processes. Sites H1 and H2 are upstream from the industrial facilities of Dashe Industrial Park with wastewater discharged between sites H2 and H3. Sites Bakong (H4), Renwu (H5), and Huifeng (H6) were selected to investigate pollution caused by industrial activities upstream in Renwu District, where plastic resin and traditional metal-surface-processing industries are located. Site H4 is upstream of the Renwu Industrial Park with wastewater discharged between sites H4 and H5, while Zhuhou Industrial Park's wastewater is discharged between sites H5 and H6. Sites Demin (H7), CingPu (H8), and Dehuei (H9) focused on industrial activities in the midstream Nanzih Export Processing Zone (NEPZ). The NEPZ has various heavy metal-processing plants, including computer chip, packaging, electroplating, and surface-coating manufacturing. Youchangda (H10) and Xingzhong (H11) are downstream sites before the water masses join the Taiwan Strait. The heavy industrial activities are putting the environmental health of the river and ocean systems under a significant pressure as wastewater discharge of plants is poorly managed. Kaohsiung's Environmental Protection Bureau only monitors and mandates the discharge of NEPZ, Dashe, and Renwu Industrial Parks. These Industrial Parks have two discharge options, either directly into the Houjing River (limit 20,000 m³/day) or into the ocean through an ocean outflow pipe constructed in 1989 (5 km away from the coastal line, limit 74,800 m³/day). More importantly, the discharge management only focuses on the level of total chemical oxygen demand (COD), i.e., limit of 100 mg/L for the Houjing River and 300 mg/L for the ocean outflow (Lin et al. 2010) and not the level of individual contaminants. Sadly, illegal discharge activities through deep-water pipeline or wastewater trucks also take place (Lin et al. 2009, 2007). Hence, a study of heavy metal concentrations and contaminations of water and sediments of the Houjing River is long overdue.

In this study, we followed the standard US Environmental Protection Agency methods of water (USEPA 2013) and sediment sampling (USEPA 2014). A total of 88 sediment and 88 water samples were collected. An Ekman Dredge was used to collect sediment samples, which were then stored in polyethylene bags. Water samples were collected with a bucket and transferred into plastic bottles. Samples were collected in the middle of the river, approximately 5 m from the river banks. The samples were stored at 4 °C until they were analyzed.

Instrumental analysis

Temperature, salinity, dissolved oxygen (DO), pH, turbidity, and conductivity in water samples were assessed on-site using a Multi-Parameter Water Quality Sonde (YSI 6600 V2-4). Biochemical oxygen demand (BOD₅) (Winkler's method) and chemical oxygen demand (COD) were measured using the standard methods (APHA 1999)

For heavy metal analysis, water samples were first acidized with HNO₃ (Zhang et al. 2016a) and aliquots of 20 mL were then filtered through Whatman[®] filter paper. Sediment samples were homogenously mixed, and rock fragments were removed manually before 0.2 g of the samples were taken and lyophilized in a vacuum freeze dryer (Eyela FDU-1200) at -50 °C and 10 Pa for 24 h. Acids (3 mL HCl and 1 mL HNO₃) were added to both water and sediment samples before microwave digestion (Topex, Preekem) according to the instruction of the manufacturer. After the digestion, the samples were filtered and analyzed using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES Optima 2100 DV, PerkinElmer) and a Mercury Analyzer (NIC MA-2, Systematic). ICP-OES was used to quantify As, Cd, Cr, Cu, Pb, Ni, and Zn concentrations.

The plastic sample containers and glassware used for ICP analysis were treated with 5% HNO₃ prior to sampling and analysis. Similarly, ship-shaped ceramic sample containers used for mercury analysis were soaked in 5% HNO₃ and baked in an oven at 500 °C for 18 h before the analysis. Standard ICP and mercury solutions were purchased from High-Purity Standards (Charleston, USA) and J.T.Baker (Avantor Performance Materials, USA), respectively. For all analyses, analytical grade reagents and deionized water were used.

Minimum detection limits (MDL) were set based on triple standard deviations of the analysis results of seven samples at the same concentration. A calibration curve was constructed using the seven levels of standard concentrations. Relative standard deviation (RSD) was less than 10%. The acceptable correlation coefficient (*r* value) for each element was greater than 0.995. A set of quality control (QC) samples was required for every batch of ten samples analyzed. Average deviation of continuing calibration recovery was assured to be less than 10%. Blanks (laboratory blank, field blank, and trip blank) were less than MDL. Spike sample recovery fell within the 80–120% range. Relative percent differences (RPD) of all duplicate samples were below 20%.

Risk assessment methods

Pollution load index

Pollution load index (PLI) is an important index that is often used to describe the severity of the heavy metal contamination. PLI is calculated as follows:

$$PLI = (C_{f1} \times C_{f2} \times C_{f3} \times \dots \times C_{fn})^{\frac{1}{n}}, \quad \text{where } C_f^i = C^i / C_{ref}^i,$$

where C_{fi} is the contamination factor; n the number of heavy metals, which is 8 in this study, C^i the heavy metal concentration in sediment and water samples; C_{ref}^i the reference value of the element (Hakanson 1980; Yan et al. 2016), and C_f^i the contamination factor of each element for the local site. If PLI value equals 0, the site is not polluted. If it is less than 1, the site is considered 'unpolluted'. If the value equals or is greater than 1, the site is considered 'polluted' (Tomlinson et al. 1980). The greater the value, the more polluted the site.

Potential ecological risk index

Potential ecological risk index (RI), proposed by (Hakanson 1980), is a commonly used index to evaluate the potential risk of one or multiple heavy metals to the ecological system:

$$RI = \sum_{i=1}^n E_f^i, \quad \text{where } E_f^i = C_f^i \times T_f^i,$$

where C_f^i is the contamination factor; T_f^i is the toxicity response coefficient of each element (As = 10, Cd = 30, Cr = 2, Cu = Pb = Ni = 5, Zn = 1 and Hg = 40) (Yan et al. 2016), and E_f^i is the potential ecological risk factor of each element.

The values of C_d and RI were simplified using the scale displayed in Table S1.

Results and discussion

Ecological risk of heavy metal concentrations in water samples

Table 1 shows the results of heavy metal concentrations of the water samples and the water quality parameters. At the time of sampling, heavy metal concentrations in the waters were low. Copper was found at slightly elevated concentrations at the sites H3 (0.0655 mg/L), H9 (0.0700 mg/L), H6 (0.0903 mg/L), and H10 (0.0523 mg/L), while Zn had marginally high concentrations at the sites H5 (0.0710 mg/L), H7 (0.0640 mg/L), and H11 (0.0503 mg/L). Other metals, including As, are found in negligible concentrations at all sites.

Unlike heavy metal ecological risk assessment methods for sediments which have been well established (El Nemr et al. 2016b), heavy metal ecological risk assessment for water has rarely been addressed. However, the contamination factor and potential ecological risk factor for heavy metals in water can be calculated following the approach of

Sharifi et al. (2016). Similar to the calculation of contamination factor and potential ecological risk factor for heavy metals in sediments, Sharifi et al. (2016) used the reference values (C_{ref}^i) of different water quality guidelines to calculate contamination and potential ecological risk factors for heavy metals in water. In the current study, we used the values of C_{ref}^i taken from heavy metal water quality indices issued by the Canadian Council of Ministers of the Environment (CCME 2007), the National Resource Management Ministerial Council, the Commonwealth of Australia (NRMCA 2011), and the Australian and New Zealand Environment and Conservation Council & Agriculture and Resource Management Council of Australia and New Zealand (ANZECC and ARMCANZ 2000).

The risk factors of the metal concentrations in the water are several orders of magnitude lower than the reference values issued by the above organizations (Table S2). This implies that the ecological risk of the Houjing River is relatively small, but more detailed monitoring or more frequent sampling of the water masses is suggested to confirm the findings.

Ecological risk heavy metal contamination in sediment

Heavy metal content in sediment

The analytical results of the heavy metal concentrations in sediments of the Houjing River are provided in Table 2. Sites H1 and H2 are upstream of the Dashe Industrial park and provide some background measurements, although the area is fully developed. In comparison to sites H1 and H2, site H3 near Dashe Industrial Park (petrochemical resin production) had 4–5 times the concentrations of Pb (110.94 ± 103.78 mg/kg), 3 times the concentration of Zn (642.75 ± 424.67 mg/kg), and 6 times the concentrations of Hg (0.63 ± 0.61 mg/kg). Site H8, situated on Dashe upstream reach near Si-Cingpu Landfill and after sites H1 to H3, showed lower metal concentrations compared to site H3. For example, concentrations of Pb, Zn, and Hg at site H8 were 18.95 ± 6.55 , 345.05 ± 186.30 , and 0.16 ± 0.16 mg/kg, which are much lower than the above-mentioned concentrations of these metals at site H3. Probably, the dilution of the flow caused the heavy metal concentrations to decrease from site H3 to site H8. Site H4, the upstream background site for Renwu Park, had highly elevated levels of As, Cr, Ni, and Zn compared to sites H1 and H2, probably due to the recently rapid growth of the Renwu urban district. Ever since the establishment of the industrial parks in Renwu district, the commercial and residential area here has grown rapidly and become increasingly crowded, making the management of solid-waste disposal and wastewater collection and treatment a difficult task for the local government. Illegal discharge

Table 1 Heavy metal concentrations in water samples and other water quality parameters in the Houjing River, Taiwan (mean \pm SD; $n = 8$; ND not detected)

	Samaitan H1	Xinggong H2	Jingjian H3	Cingpu H8	Bakong H4	Renwu H5	Huifeng H6	Demin H7	Dehwei H9	Youchangda H10	Xingzhong H11
As (mg/L)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cd (mg/L)	0.0095 \pm 0.0165	0.0120 \pm 0.0208	0.0055 \pm 0.0096	0.0025 \pm 0.0043	ND	0.0035 \pm 0.0061	ND	0.0030 \pm 0.0052	0.0028 \pm 0.0048	0.0028 \pm 0.0044	0.0055 \pm 0.0095
Cr (mg/L)	ND	0.0025 \pm 0.0043	ND	0.0025 \pm 0.0043	0.0025 \pm 0.0043	0.0025 \pm 0.0043	ND	0.0023 \pm 0.0039	ND	ND	ND
Cu (mg/L)	0.0328 \pm 0.0974	0.0360 \pm 0.0515	0.0655 \pm 0.0912	0.0483 \pm 0.0388	0.0360 \pm 0.0467	0.0330 \pm 0.0417	0.0903 \pm 0.0681	0.0333 \pm 0.0382	0.0700 \pm 0.0731	0.0523 \pm 0.0435	0.0473 \pm 0.0483
Pb (mg/L)	0.0233 \pm 0.0234	0.0248 \pm 0.0154	0.0148 \pm 0.0162	0.0183 \pm 0.0184	0.0143 \pm 0.0143	0.0050 \pm 0.0087	0.0138 \pm 0.0147	0.0135 \pm 0.0137	0.0108 \pm 0.0108	0.0153 \pm 0.0149	0.0170 \pm 0.0204
Ni (mg/L)	ND	0.0320 \pm 0.0498	0.0030 \pm 0.0052	ND	ND	0.0040 \pm 0.0069	0.0515 \pm 0.0317	0.0035 \pm 0.0061	0.0200 \pm 0.0212	0.0245 \pm 0.0105	0.0033 \pm 0.0056
Zn (mg/L)	0.0393 \pm 0.0414	0.0320 \pm 0.0498	0.0480 \pm 0.0579	0.0313 \pm 0.0351	0.0375 \pm 0.0492	0.0710 \pm 0.1064	0.0178 \pm 0.0307	0.0640 \pm 0.0801	0.0370 \pm 0.0483	0.0448 \pm 0.0716	0.0503 \pm 0.0508
Hg (mg/L)	0.0035 \pm 0.0061	0.0048 \pm 0.0082	0.0042 \pm 0.0091	0.0020 \pm 0.0035	0.0020 \pm 0.0035	0.0025 \pm 0.0043	0.0020 \pm 0.0035	0.0018 \pm 0.0030	0.0015 \pm 0.0026	0.0040 \pm 0.0064	0.0020 \pm 0.0035
Temp (°C)	27.01 \pm 2.46	28.89 \pm 2.79	29.22 \pm 3.22	28.99 \pm 1.73	26.86 \pm 2.95	27.87 \pm 2.51	28.06 \pm 2.42	28.71 \pm 2.62	28.55 \pm 2.52	28.46 \pm 1.88	29.15 \pm 3.08
Salinity (‰)	0.5 \pm 0.03	0.66 \pm 0.50	0.46 \pm 0.08	0.45 \pm 0.06	0.21 \pm 0.21	1.3 \pm 0.46	1.16 \pm 0.42	1.13 \pm 0.32	0.99 \pm 0.27	1.44 \pm 0.24	0.95 \pm 0.24
DO (mg/L)	0.17 \pm 0.08	4.58 \pm 1.47	7.8 \pm 3.07	8.38 \pm 4.39	3.52 \pm 0.70	3.24 \pm 1.07	3.88 \pm 0.40	6.7 \pm 3.10	4.76 \pm 2.08	5.64 \pm 0.49	6.8 \pm 2.73
pH	7.67 \pm 0.05	7.63 \pm 0.10	8.06 \pm 0.23	7.85 \pm 0.20	7.49 \pm 0.07	7.31 \pm 0.07	7.48 \pm 0.07	7.61 \pm 0.16	7.62 \pm 0.09	7.48 \pm 0.26	7.77 \pm 0.16
Turbidity (NTU)	277.5 \pm 64.78	207.23 \pm 103.71	171.78 \pm 51.89	204.96 \pm 96.06	208.59 \pm 71.15	221.86 \pm 99.21	206.35 \pm 88.98	205.11 \pm 74.99	203.75 \pm 91.94	157.03 \pm 61.40	203.29 \pm 99.22
Conductivity (µS/cm)	1014.25 \pm 37.64	1969 \pm 606.55	955.25 \pm 123.43	923 \pm 87.89	829.25 \pm 37.08	2529.5 \pm 877.50	2436.75 \pm 792.06	2248.25 \pm 603.52	1946.25 \pm 543.53	2625 \pm 596.05	1906.25 \pm 480.47
BOD (mg/L)	59.08 \pm 9.18	11.51 \pm 3.41	31.03 \pm 3.93	14.67 \pm 3.93	15.78 \pm 3.26	13.15 \pm 2.41	12.17 \pm 4.54	11.48 \pm 2.21	12.2 \pm 2.92	12.99 \pm 3.08	11.48 \pm 3.19
COD (mg/L)	125.2 \pm 4.59	29.83 \pm 8.92	72.68 \pm 6.58	67.75 \pm 46.85	36.28 \pm 9.14	36.8 \pm 9.43	37.05 \pm 6.16	34.65 \pm 4.88	47.18 \pm 22.57	22.15 \pm 3.45	29.68 \pm 9.73

Table 2 Heavy metal concentrations in sediments at the 11 sampling sites of the Houjing River, Taiwan (mg/kg dry weight) (mean \pm SD; $n = 8$)

	As	Cd	Cr	Cu	Pb	Ni	Zn	Hg
H1	2.67 \pm 2.67	5.58 \pm 4.06	45.00 \pm 19.15	124.63 \pm 50.28	20.98 \pm 8.85	28.24 \pm 8.72	275.20 \pm 97.94	0.10 \pm 0.11
H2	2.15 \pm 1.84	16.05 \pm 27.80	54.25 \pm 24.70	130.48 \pm 71.38	24.16 \pm 18.59	37.70 \pm 16.18	476.50 \pm 327.24	0.12 \pm 0.06
H3	4.31 \pm 4.37	1.85 \pm 3.00	80.80 \pm 29.52	184.15 \pm 94.71	110.94 \pm 103.78	47.13 \pm 17.07	642.75 \pm 424.67	0.63 \pm 0.61
H4	183.81 \pm 311.89	3.05 \pm 5.28	76.73 \pm 35.15	261.80 \pm 129.07	41.56 \pm 28.81	94.39 \pm 91.04	619.58 \pm 533.30	0.07 \pm 0.05
H5	3.29 \pm 2.91	17.61 \pm 29.56	29.00 \pm 14.66	82.08 \pm 25.33	63.40 \pm 82.50	33.94 \pm 12.50	268.50 \pm 115.48	0.17 \pm 0.10
H6	6.09 \pm 4.31	1.69 \pm 2.92	54.86 \pm 20.21	86.40 \pm 33.17	20.58 \pm 10.89	38.34 \pm 5.27	376.70 \pm 74.85	0.14 \pm 0.18
H7	46.41 \pm 75.48	43.75 \pm 72.92	97.88 \pm 86.55	677.83 \pm 924.75	60.81 \pm 70.56	110.48 \pm 82.11	389.43 \pm 154.48	0.09 \pm 0.11
H8	1.90 \pm 3.30	8.90 \pm 15.42	69.77 \pm 39.98	87.65 \pm 20.23	18.95 \pm 6.55	32.32 \pm 5.56	345.05 \pm 186.30	0.16 \pm 0.16
H9	2.94 \pm 1.81	7.13 \pm 9.48	49.24 \pm 8.73	126.00 \pm 65.43	22.36 \pm 8.23	153.54 \pm 188.45	391.65 \pm 282.30	0.09 \pm 0.06
H10	4.50 \pm 4.55	1.49 \pm 1.70	67.84 \pm 36.50	384.48 \pm 319.08	38.60 \pm 29.56	101.15 \pm 58.84	571.75 \pm 330.90	0.08 \pm 0.05
H11	2.36 \pm 1.93	10.86 \pm 11.11	37.68 \pm 12.11	65.04 \pm 22.52	19.43 \pm 13.48	26.24 \pm 3.81	187.73 \pm 81.03	0.05 \pm 0.04

is sometimes observed, although the local authority has made series of propaganda campaigns to raise the awareness of the local inhabitants about the negative impacts of that action. Probably, stricter regulations and higher penalties are needed to address this problem. Site H5, situated near Renwu Industrial Park (including Formosa Plastics and other companies mostly involved with metal, chemical and plastic production), had high concentrations of Pb (63.40 \pm 82.50 mg/kg). Site H6 showed high concentrations of Zn (376.70 \pm 74.85 mg/kg). From site H5 to site H6, there is no clear increasing or decreasing pattern of metal concentrations. High concentrations of Cd (43.75 \pm 72.92 mg/kg), Pb (60.81 \pm 70.56 mg/kg), Ni (110.48 \pm 82.11 mg/kg), Cu (677.83 \pm 924.75 mg/kg), and Cr (97.88 \pm 86.55 mg/kg) occurred at the site H7. High concentrations of Ni (153.54 \pm 188.45 mg/kg) appeared at the site H9. The sites H7 and H9 are situated next to the discharges of NEPZ-Kaoshiung's semiconductor manufacturing center. The related inputs from NEPZ also supported by the concentrations increase from H6 to H7; thus, intensive monitoring and regulatory enforcement are warranted. The downstream site H10 showed high concentrations of Cr (67.84 \pm 36.50 mg/kg), Cu (384.48 \pm 319.08 mg/kg), Ni (101.15 \pm 58.84 mg/kg), and Zn (571.75 \pm 330.90 mg/kg). The heavy metal concentrations at the next site (site H11) are mostly lower heavy metal concentrations than those at site H10. Site H11 only showed high concentrations of Zn (187.73 \pm 81.03 mg/kg) and Cu (65.04 \pm 22.52 mg/kg).

Next, average concentrations of heavy metals, which are calculated by the total concentration of each metal divided by the number of sediment samples collected throughout the whole river basin during the entire sampling period, are compared with average metal concentrations of other water bodies in south-east Asia in order to have an overview over the seriousness of sediment contamination in the Houjing River (Table 3). Although the heavy metal concentrations vary between sampling sites, the average concentrations of

Cd, Cu, Zn, and Hg in sediment samples of the Houjing River are higher than those of other coastal or river sediments in the comparison. Noticeably, the concentration of Ni in this study was considerably higher than those of the Bangshi River, the Ganga River, the Shuangtaizi River, the Bortala River, and rivers in Eastern China.

The data can also be shown in comparison with limits determined by various environmental management organizations (Table 4), such as the Taiwan EPA, the New Zealand, and Australian environmental conservation council or NOAA. The comparison shows that the metal concentrations in the sediment of the Houjing River are very high, and often fall between the lower and upper values of the selected guidelines. The ecological effects of the heavy metals are deemed "rarely observed" concerning the lower limit value, but "frequently observed" concerning the upper limit. It would succeed that, when concentrations of the metals are either equal to or greater than the lower limit but below the upper limit, their effects would be realized as "occasionally observed" (Duodu et al. 2017; Vu et al. 2017a). Although As concentrations were only high at sites H4 and H7, our average As value fell between the low and high levels of Taiwan EPA, ANZECC and ARMCANZ and NOAA, suggesting a need for consideration by future monitoring and pollution control plans, especially at sites H4 and H7. Most alarming were our findings for average concentrations of Cd (10.72 mg/kg), Cu (200.96 mg/kg), and Zn (413.17 mg/kg), which exceeded the upper concentrations of most guidelines. Hence, the sites with such high metal concentrations along the Houjing River are clearly at high ecological risk and further or future metal contributions at these sites or remediation action have to be very carefully considered. Average concentrations of Cr (60.28 mg/kg) and Pb (40.16 mg/kg) are within the guidelines and only slightly above the lower limit of CCME ISQG. For Ni, although our average concentration exceeded the upper levels established by ANZECC and ARMCANZ and NOAA, it only fell between the upper

Table 3 Average sediment heavy metal concentrations (mg/kg dry weight) of different riverine areas (NA not available)

Geographical areas	As	Cd	Cr	Cu	Pb	Ni	Zn	Hg	References
Bangshi River, Bangladesh	1.93	0.61	98.10	31.01	59.99	25.67	117.15	NA	Rahman et al. (2014)
Rivers in Eastern China	NA	0.925	142	54.7	61.9	60.5	192	NA	Tang et al. (2014)
Ganga River, India	NA	NA	72	33	NA	52	NA	NA	Pandey et al. (2014)
Korotoa River, Bangladesh	25	1.2	109	76	58	25^a	NA	NA	Islam et al. (2015)
Shuangtaizi River, China	NA	0.498	NA	6.501	6.888	NA	58.653	0.011	Li et al. (2015)
Karnaphuli River, Bangladesh	81.09^a	2.01	20.3	NA	43.69	NA	NA	NA	Ali et al. (2016)
Bortala River, China	9.67	0.17	51.55	30.09	31.98	23.32	99.19	0.018	Zhang et al. (2016b)
Houjing River, Taiwan	23.67^b	10.72^a	60.28	200.96^a	40.16	63.95 ^{b,c}	413.17^a	0.16^a	This study

^aBold and italics are the highest concentration of the specific element

^bBold are the second highest concentration of the specific element

^cThe noticeable Ni concentration (third highest of the Houjing River)

Table 4 Comparison of data of this study (the Houjing River, Taiwan) to sediment standard guidelines worldwide (values in mg/kg dry weight)

Elements	Average current data	Taiwan EPA upper limit ^a	Taiwan EPA lower limit ^a	CCME ISQG ^b	CCME PEL ^b	ANZECC and ARMCANZ low ^c	ANZECC and ARMCANZ high ^c	NOAA ERL ^d	NOAA ERM ^d
As	23.67	33	11	5.9	17	20	70	8.2	70
Cd	10.72	2.5	0.65	0.6	3.5	1.5	10	1.2	9.6
Cr	60.28	233	76	37.3	90	80	370	81	370
Cu	200.96	157	50	35.7	197	65	270	34	270
Pb	40.16	161	48	35	91.3	50	220	46.7	218
Ni	63.95	80	24	–	–	21	52	20.9	51.6
Zn	413.17	384	14	123	315	200	410	150	410
Hg	0.16	0.87	0.23	0.17	0.486	0.15	1	0.15	0.71

^aTaiwan Environmental Protection Administration (Taiwan EPA)’s sediment quality guideline upper and lower limits (TEPA 2010)

^bCanadian Council of Ministers of the Environment (CCME)’s interim sediment quality guideline (ISQG) and probable effect level (PEL) (CCME 1999)

^cAustralian and New Zealand Environment and Conservation Council (ANZECC) and Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ)’s low and high levels (ANZECC and ARMCANZ 2000)

^dNational Oceanic and Atmospheric Administration (NOAA)’s effects range-low (ERL) and effects range-median (ERM) (Long et al. 1995)

and lower limits of Taiwan EPA. Therefore, Ni needs to be included in future monitoring plans and if possible, remediation projects.

Ecological risk assessment of heavy metals in sediments

Table 5 shows the results of the calculation of contamination factor (C_f^i) and pollution load index (PLI) for heavy metals in sediments. From the sites H1 and H2 to H3, all metals, except Cd, showed around 1.5–6 times increase in the values of C_f^i . The increasing trend implies the pollutants discharge and accumulation potentials while the water body entering Dashe Industrial Park. Although the values of C_f^i fluctuate mostly between 0.2 and 3.0 from site H4 to site H6, there are two noticeably high values of C_f^i , which are 12.24 for As at site H4 and 17.61 for Cd at site H5. At the site H7, Cd and Cu showed very high values of C_f^i , being 43.75 and 13.56

respectively. From site H8 to site H11, the values of C_f^i vary strongly and no clear patterns could be observed.

Regarding PLI, the values at sites H2 (PLI=0.99), H3 (PLI=1.43), and H5 (PLI=0.99) were high, probably because they were affected by the industrial discharges from Dashe and Renwu Industrial Parks. The site H4 showed a ‘very high’ value of PLI (1.83), which is due to the high value C_f^i of As (12.25) at this site. Although the site H4, which is located at the upstream Renwu origin, should be a background site, high values of contamination factors at this site imply that it could be affected by the rapid urbanization and the rapid development of small and medium businesses. As discussed above, due to the occurrence of Renwu and Zhuhou Industrial Parks, the area around site H4 has become a busy residential and commercial area with numbers of condominiums and shopping streets. Probably, the illegal discharge of wastewater and solid waste from the residential

Table 5 Contamination factor and pollution load index of heavy metals in sediments calculated for the Houjing River, Taiwan

Sites	Contamination factor ^a (C_f^i)								Pollution load index (PLI) ^b
	As	Cd	Cr	Cu	Pb	Ni	Zn	Hg	
H1	0.18	5.58	0.50	2.49	0.30	0.42	1.57	0.42	0.75
H2	0.14	16.05	0.60	2.61	0.35	0.55	2.72	0.50	0.99
H3	0.29	1.85	0.90	3.68	1.58	0.69	3.67	2.52	1.43
H4	12.25	3.05	0.85	5.24	0.59	1.39	3.54	0.26	1.83
H5	0.22	17.61	0.32	1.64	0.91	0.50	1.53	0.66	0.99
H6	0.41	1.69	0.61	1.73	0.29	0.56	2.15	0.56	0.78
H7	3.09	43.75	1.09	13.56	0.87	1.62	2.23	0.37	2.64
H8	0.13	8.90	0.78	1.75	0.27	0.48	1.97	0.65	0.84
H9	0.20	7.13	0.55	2.52	0.32	2.26	2.24	0.36	1.02
H10	0.30	1.49	0.75	7.69	0.55	1.49	3.27	0.32	1.11
H11	0.16	0.72	2.51	4.34	1.30	1.75	12.52	0.00	0.77

^aIn bold are $C_f^i > 10$ for a specific element at a specific site

^bIn bold are $PLI > 1$ for a specific element at a specific site

and busy commercial activities has contaminated site H4. The site H7, located at the discharge of NEPZ, had the highest PLI (2.64). The downstream sites H10 and H11 showed high PLI values (1.11 and 0.77, respectively). According to Tomlinson et al. (1980), if the PLI value equals or is greater than 1, the site is considered polluted. As shown on Table 5, H3, H4, H7, H9, and H10 are considered ‘polluted’ and are geographically associated with industrial parks along sides of the Houjing River. It also suggests that the Houjing River in its present state is a threat to aquatic life in the ocean, and further investigations and monitoring are required.

Table 6 shows the potential ecological risk index of the sites and highlights that 8 of 11 sites posed “considerable”-to-“very high” risk. These findings suggest that metal pollution needs to be curbed and reduced to reduce the ecological risks in the area. From site H1 to site H3, many metals showed increasing trends in the values of E_f^i . From

site H4 to site H6, the values of E_f^i varies greatly. At site H7, a very high value of E_f^i (1312.50) occurs. From site H7 onward, the values of E_f^i fluctuate strongly and no clear pattern is observed. The RI values of the sampling sites depend mostly on Cd levels with sites H2, H5, and H7 having “very high” RI values of 524, 574, and 1443, respectively, implying that the ecological system is at its highest threat at these sites. These sites are also located near the major industrial plants of Dashe Industrial Park, Renwu Industrial Park, and NEPZ. The sites H1 (204.24), H4 (265.90), H8 (310.33), H9 (259.31), and H11 (232.92) showed “considerable high” RI values, indicating a need for continued monitoring and future ecological risk assessment. Regarding to site H4 that has the highest E_f^i for As ($E_f^i = 122.54$) implies that a special forensic investigation on arsenic is warranted. It should be noticed that As is

Table 6 Potential ecological risk factor and potential ecological risk index of heavy metals in sediments calculated for the Houjing River, Taiwan

Sites	Potential ecological risk factor ^a (E_f^i)								Potential ecological risk index ^b (RI)	
	As	Cd	Cr	Cu	Pb	Ni	Zn	Hg		
H1	1.78	167.25	1.00	12.46	1.50	2.08	1.57	16.60	204.24	Considerable
H2	1.43	481.50	1.21	13.05	1.73	2.77	2.72	19.80	524.21	Very high
H3	2.87	55.58	1.80	18.42	7.92	3.47	3.67	100.68	194.40	Moderate
H4	122.54	91.50	1.71	26.18	2.97	6.94	3.54	10.52	265.90	Considerable
H5	2.19	528.30	0.64	8.21	4.53	2.50	1.53	26.40	574.30	Very high
H6	4.06	50.63	1.22	8.64	1.47	2.82	2.15	22.36	93.34	Low
H7	30.94	1312.50	2.18	67.78	4.34	8.12	2.23	14.92	1443.01	Very high
H8	1.27	267.00	1.55	8.77	1.35	2.38	1.97	26.04	310.33	Considerable
H9	1.96	213.98	1.09	12.60	1.60	11.29	2.24	14.56	259.31	Considerable
H10	3.00	44.78	1.51	38.45	2.76	7.44	3.27	12.96	114.15	Moderate
H11	1.57	7.24	25.12	43.36	12.96	17.49	125.15	0.03	232.92	Considerable

^aIn bold are $E_f^i > 100$ for a specific element at a specific site

^bIn bold are $RI > 200$; in bold and italics are $RI > 500$ for a specific element at a specific site

actually very toxic for certain species, i.e., fish, invertebrates, and humans (Eisler 1988).

As a summary for the Houjing River basin, Cd is obviously the most critical element, follows by Cu, Hg, and As, that need to be curbed and reduces. Therefore, strict regulations on these heavy metals discharge into the water body should be strictly established and enforced.

The rapid development of heavy industries has created wealth and improved economic status of Kaohsiung City and its citizens (Huang et al. 2016; Vu et al. 2017a; Williams and Chang 2008). However, those industries have also seriously destroyed the environment of the city (Vu et al. 2017a, b). The Houjing River is one of the most endured “victims” of those environmentally degrading industries. The main reason for those industries to continue damaging the environment is the lenient regulation of the government, who has entire authority to prevent the adverse impacts resulted from those environmentally damaging industrial activities. Kaohsiung City is a “typical” rapidly industrially developed city in Asia, where hundreds of other industrial cities reside, i.e., those in China, India, Bangladesh, and Vietnam. The lesson learned here from this study of the case of the Houjing River is that economic growth from rapid industrial development should not compromise the inherently natural environment; otherwise, the damage would be too immense and too costly to recover. Therefore, hopefully, the Kaohsiung City’s government and Taiwan EPA would recognize that and impose strict regulations on the environmentally damaging industrial activities. In addition, despite the possibly incurred great cost, regular monitoring plans and remediation projects are needed to prevent environmentally degrading activities and to reclaim the degraded environment of Kaohsiung City.

Conclusions

The concentrations of heavy metals (As, Cd, Cr, Cu, Pb, Ni, Zn, and Hg) in water and sediments of the Houjing River were between ND–0.09 mg/L and 0.05–677.83 mg/kg, respectively. Concentrations, contamination factors (C_f^i), and potential ecological risk factors (E_f^i) of heavy metals in collected water samples were low, and thus, a limited ecological risk is identified. In contrast, metal concentrations in sediments were elevated to high and occasionally above EPA guidelines depending on site and element. The study determined factors and indices to evaluate which element at which sites may pose “considerable” or “very high” potential ecological risks (as expressed by high values of C_f^i and E_f^i). The comparisons of our findings with other similar studies and sediment quality guidelines indicate that the heavy metal concentrations in sediments of the Houjing River exceeds recommended limits and thus place some site at high ecological risks which are recommended to be considered for

pollution control and remediation plans of the city’s government. The values of PLI and RI at sites H4 (Bakong) and H7 (Demin) were very high, which implies that pollution prevention needs to be carefully considered and planned while in the urbanization processes and that of the economic investment in the emerging semiconductor manufacturing industry. Since almost all sites show some sort of elevated metal concentrations or factors, the sediments of the Houjing River are clearly contaminated and require monitoring and pollution control programs if its negative impacts on the ecological system along the riverside, estuary, and the ocean are to be limited. The heavy metal contamination of the river is clearly a result of decades of poor environmental and wastewater management policies and guidelines and other rapid industrially developing countries should take notice of the lessons learned in Kaohsiung City as metal contamination could be limited, reduced, or even prevented. However, decades of negligence now result in very high risk and remediation costs.

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