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Spatiotemporal Variation and Ecological Risk Assessment of Heavy Metals in Industrialized Urban River Sediments: Fengshan River in Southern Taiwan as a Case Study

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Abstract: The sediment pollution index acts as a useful indicator for assessing anthropogenic pollution within river drainage basins. An industrialized urban river, Fengshan River in Kaohsiung City, southern Taiwan has been suffering heavy metal pollution from surrounding factories. In this study, spatial and seasonal variations in heavy metals in sediments from seven sampling sites of Fengshan River were determined to assess sediment pollution status and potential ecological risk using multiple sediment pollution indices. Results showed that the heavy metal concentrations displayed large spatial variations. Severe contamination of heavy metals, especially for Cr, Hg, and Zn in the lower reaches of Fengshan River, may attribute to wastewater discharges from leather processing and metal finishing factories along the river drainage basin. An increase in metal concentrations from upstream to downstream indicated that heavy metals tend to accumulate in tidal reaches, probably as a result of the flocculation effect. Frequent heavy rainfall in the wet season can enhance surface runoff to discharge metal pollutants from non-point sources (scattered factories) into the river. Assessment of multiple pollution indices showed moderately polluted (mCd = 3.9, PLI = 2.6) and considerable ecological risk (RI = 540, mERM = 0.55), indicating Fengshan River sediments, particularly in the lower reaches, are considered toxic and can cause adverse effects to benthic organisms. Organic matters showed a good correlation with heavy metals, which play an important role in the spatiotemporal variations in heavy metal pollutants in the Fengshan River sediments. This study can provide valuable information for river pollution remediation, and urban planning and management.

Keywords: heavy metal; river sediment; pollution index; ecological risk

1. Introduction

Heavy metal contamination in aquatic environments has attracted massive attention due to its toxicity, persistence, and accumulation, causing potential adverse effects on the ecosystems [1]. Those heavy metal pollutants such as cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), and lead (Pb) can be discharged into a river system through anthropogenic sources through industrialization and distributed between aqueous and solid phases [2]. In river systems, suspended solids settling may cause the transfer of heavy metal pollutants from water to sediments [3]. The heavy metal pollutants in contaminated river habitats may enter into the food chain and pose a threat to human health [4]. Depending on the difference in particle size distribution, mineralogical composition, and organic matter content, river sediments may create anomalously heavy metals contamination depending on the river hydrological processes (e.g., weathering, erosion, and transport.
conditions) [5]. Moreover, heavy metal pollutants are not fixed permanently in the sediments, which may be desorbed/dissolved and released into the water column through the remobilization processes, negatively affecting water quality [6]. Thus, sediments act both as sinks and sources for heavy metals and strongly affect their distribution in river environments, playing an essential role in determining the pollution pattern of river systems [7,8]. Therefore, river sediments are valuable indicators for assessing anthropogenic pollution within river watersheds.

However, direct determination of heavy metal concentrations in sediments may not be suitable to assess the heavy metal pollution status and potential risks to exposed aquatic organisms; as heavy metals may be of natural or anthropogenic origin [9,10]. Therefore, the assessment of the sediment pollution level depends on sediment quality guidelines (SQGs) derived from numerous data of biological responses from aquatic organisms, including threshold-effects-level (TEL), probable-effects-level (PEL), effects-range-low (ERL), and effects-range-median (ERM) guidelines [11,12]. The SQGs can provide quick information on identifying the sediment quality and probability of biological toxicity. Based on the SQGs, many derived ecological and chemical approaches, such as mean ERM quotient (mERM$\_Q$) and the contamination severity index (CSI), have been used to evaluate the ecological risk of toxic metals for aquatic lives and the potential adverse effects on infaunal animals [13,14]. Furthermore, several contamination indices such as contamination factor (CF), geo-accumulation index ($I_{geo}$), and pollution load index (PLI) have also been widely used to distinguish anthropogenic pollutants from the natural background [15,16].

Therefore, whether it is a large natural river or a small river in an urban area, the heavy metal pollution level can be assessed using the sediment quality guidelines and the sediment pollution indices. Even though the actual ecological impacts of river sediment may vary with the water environment condition and sediment characteristics, which need to be confirmed by laboratory or on-site toxicity experiments, those sediment pollution indices can provide a simple and integrated judgement of river contamination levels and potential ecological risks of heavy metal pollution.

*Case Study*

Kaohsiung City is an important industrial city in Taiwan with the third-largest population of over 2.7 million. So far, over 55% of domestic wastewaters in Kaohsiung City are still directly discharged to rivers without treatment due to the uncompleted construction and household connection of sewage systems. Moreover, a lot of industries and factories, such as electronic industries, chemical manufacturing factories, metal processing plants, foundries, paint and dye industries, motor vehicle plating and finishing plants, and paper and board mills, are located in or around Kaohsiung City [13]. Those industries may discharge a considerable amount of untreated and minimally treated wastewaters into the adjacent rivers. Fengshan River, one of the most important rivers flowing through the downtown of Kaohsiung City, receives domestic, industrial, agriculture, and husbandry wastewater from the residential areas, factories, and stock farming in the watershed. In terms of the total amount of pollution, industrial wastewater accounts for the most contribution. The characteristics of heavy metal contamination strongly depend on the industries along the river. The situation leads to the need to evaluate the heavy metal contamination in the Fengshan River sediments and assess the potential environmental risk. Despite this great need, no studies have studied the heavy metal contamination in Fengshan River sediments and its associated ecological impacts.

Therefore, this study investigated spatial and temporal variations in heavy metals in the surface sediments of Fengshan River to assess the degree of heavy metal contamination and the potential ecological risk using multiple sediment pollution indices. The relationship between sediment properties and heavy metals, and the major factors controlling the spatiotemporal variations in sediment heavy metal concentrations were also determined.
2. Materials and Methods

This study focused on an industrialized urban river, Fengshan River, in Kaohsiung City southern Taiwan, and assessed the river sediment pollution status using a multivariate approach. The sediment pollution indices applied in this study includes the contamination factor (CF), geo-accumulation index (I_{geo}), modified degree of contamination (mCd), pollution load index (PLI), potential ecological risk index (RI), mean ERM quotient (mERM_Q), sum of the toxic units (ΣTU), and contamination severity index (CSI), which were widely used in sediment heavy metal pollution assessment [13–17].

2.1. Study Area

Fengshan River originates from the Jiuqutang Mountain area and flows through Dashu, Daliao, Niaosong, and Fengshan District of Kaohsiung City. As the river flows southwest into Qianzhen District, it is renamed Qianzhen River and finally injected into Kaohsiung Port. Fengshan River (including the Qianzhen River) is approximately 20 km, with a drainage area of ~53.85 km². The primary pollutant sources in the Fengshan River drainage basin include 43% of industrial wastewater, 40% of domestic sewages, 15% of husbandry wastewater, and 2% agricultural wastewater [18]. Industrial wastewater can be regarded as the primary source of pollution in the river due to the distribution of many small factories along and within the river basin, such as metal finishing, basic metal manufacturing, electroplating, printed circuit board manufacturing, and leather processing, especially the pollution from leather processing and metal finishing factories in the upstream area [19]. In the past, while the pollution prevention and control legislation were not complete and the sewage system was not popularized, most of the wastewater from leather processing was untreated or limitedly treated and discharged directly into Fengshan River, extremely polluting the river and causing environmental risk.

2.2. Sample Collection and Analysis

In this study, surface sediment samples (0–15 cm) from seven sampling sites (Figure 1) were collected from the main channel and river mouth of Fengshan River using a Van Veen dredge in the dry season (December 2015) and the wet season (May 2016). The sampling sites are situated upstream (F1, F2), midstream (F3, F4, F5), and downstream (F6, F7). Among them, site F3 is located nearby the effluent outfall of the Fengshan Water Resources Center. Sites F6 and F7 are situated at the tidal river reach, of which site F7 is located at the river mouth. Sites F1–F6 were sampled at the center of the river channel on bridge, and site F7 was sampled on a boat. According to Taiwan Central Weather Bureau [20], the accumulated precipitation in Kaohsiung City were 94 mm and 359 mm on October–December 2015 (dry season) and March–May 2016 (wet season), respectively.

After the sediment samples were air-dried, ground, and homogenized, approximately 1 g of dry sediments was digested in a Teflon digestion vessel with nitric acid (HNO₃), hydrogen peroxide (H₂O₂), and hydrochloric acid (HCl) by referring to protocols of the standard method of the Taiwan Environmental Protection Administration (NIEA M353.02C). Firstly, the sediment sample was digested with 15 mL HNO₃ at 95 ± 5 °C (not boiling) for 20 min. Then, the sediment sample was digested with 10 mL H₂O₂ at 95 ± 5 °C (not boiling) for 10 min. Finally, the sediment sample was digested with 10 mL HCl at 95 ± 5 °C (not boiling) for 15 min. After digestion, the digested solution was diluted to 50 mL with deionized water (~18 MΩcm). The concentrations of Cr, Cu, Ni, Pb, Zn, As, and Hg in the digested solution were analyzed by an inductively coupled plasma atomic emission spectrometer (Thermo Scientific iCAP 7400, Waltham, MA, USA) based on the standard method of the Taiwan Environmental Protection Administration (NIEA M104.02C). The standard reference material of sediment (NIST SRM 1646a, Gaithersburg, MD, USA) was analyzed using the same digestion and measurement procedures to validate the results.
2.3. Assessment of Sediment Contamination Level and Ecological Risk

2.3.1. Contamination Factor (CF)

The contamination factor (CF) was calculated using the following equation:

\[
CF = \frac{M_{\text{sample}}}{M_{\text{background}}}
\]

where \(M_{\text{sample}}\) and \(M_{\text{background}}\) are heavy metal concentrations of the studied sediment sample and the background, respectively. The \(M_{\text{background}}\) was acquired from the continental upper crust average, i.e., 92, 28, 47, 17, 67, 4.8, and 0.05 mg/kg for Cr, Cu, Ni, Pb, Zn, As, and Hg, respectively [21]. Based on the CF value, the sediment heavy metal contamination status can be interpreted as very high (CF > 6), considerable (3–6), moderate (1–3), and low contamination (<1) [22].

2.3.2. Geo-Accumulation Index (Igeo)

The geo-accumulation index (Igeo) was calculated using the following equation:

\[
I_{\text{geo}} = \log_2 \left( \frac{M_{\text{sample}}}{1.5M_{\text{background}}} \right)
\]

where \(M_{\text{sample}}\) and \(M_{\text{background}}\) are heavy metal concentrations of the studied sediment sample and the background, respectively. Based on the Igeo value, the sediment heavy metal contamination status can be classified as extremely polluted (Igeo > 5), strongly to extremely polluted (4–5), strongly polluted (3–4), moderately to strongly polluted (2–3), moderately polluted (1–2), unpolluted to moderately polluted (0–1), and unpolluted (<0) [23].

2.3.3. Modified Degree of Contamination (mCd)

The modified degree of contamination (mCd) was calculated using the following equation:
mCd = \frac{\sum_{i=1}^{n} CF_i}{n} \quad (3)

where \( CF_i \) and \( n \) are the contamination factor of each heavy metal obtained using the Equation (2) and the number of heavy metals studied, respectively. Based on the mCd value, the sediment heavy metal contamination level can be categorized into ultra-high degree (mCd > 32), extremely high degree (16–32), very high degree (8–16), high degree (4–8), moderate degree (2–4), low degree (1.5–2), and nil to very low degree of contamination (<1.5) [24].

2.3.4. Pollution Load Index (PLI)

The pollution load index (PLI) was calculated using the following equation:

\[ PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n} \quad (4) \]

where \( CF_i \) and \( n \) are the contamination factor of each heavy metal, and the number of heavy metals studied, respectively. The sediment heavy metal contamination level can be ranked based on the PLI value and classified as strongly polluted (>3), moderately (2–3), and slightly (1–2). The simple interpretation of PLI value was no pollution for PLI < 1 and polluted for PLI > 1 [25].

2.3.5. Potential Ecological Risk Index (RI)

The potential ecological risk index (RI) was calculated using the following equation:

\[ RI = \sum_{i=1}^{n} (CF_i \times Tr_i) \quad (5) \]

where \( CF_i \) and \( Tr_i \) are the contamination factor and biological toxicity factor of each heavy metal, respectively. The \( Tr_i \) value was suggested by Håkanson [22] as 2, 5, 5, 5, 1, 10, and 40 for Cr, Cu, Ni, Pb, Zn, As, and Hg, respectively. Based on the RI value, the ecological risk of the studied sediment can be classified into very high (RI > 600), considerable (300–600), moderate (150–300), and low ecological risk (<150) [22].

2.3.6. Mean ERM Quotient (mERM\( _Q \))

The mean ERM quotient (mERM\( _Q \)) was calculated using the following equation:

\[ mERM_Q = \frac{\sum_{i=1}^{n} \left( \frac{M_{sample}}{M_{ERM}} \right)_i}{n} \quad (6) \]

where \( M_{sample} \) and \( M_{ERM} \) are heavy metal concentrations of the studied sediment sample and the effect-range-median (ERM) criteria value, respectively, and \( n \) is the number of heavy metals studied. The \( M_{ERM} \) are 145, 390, 50, 110, 270, 85, and 1.3 mg/kg for Cr, Cu, Ni, Pb, Zn, As, and Hg, respectively [26]. Based on the mERM\( _Q \) value, the toxicity probability of the studied sediment for benthic organisms can be categorized into high toxic (76% probability of being toxic for mERM\( _Q \) > 1.5), considerable toxic (49%, 0.5–1.5), moderate toxic (21%, 0.1–0.5), and slightly toxic (9%, <0.1) [27].

2.3.7. Sum of the Toxic Units (\( \Sigma TU \))

The sum of the toxic units (\( \Sigma TU \)) was calculated using the following equation:

\[ \Sigma TU = \sum_{i=1}^{n} \left( \frac{M_{sample}}{M_{PEL}} \right)_i \quad (7) \]
where $M_{\text{sample}}$ and $M_{\text{PEL}}$ are heavy metal concentrations of the studied sediment sample, and the probable-effects-level (PEL) criteria value, respectively. According to MacDonald et al. [26], the $M_{\text{PEL}}$ are 90, 197, 36, 91.3, 315, 17, and 0.486 mg/kg for Cr, Cu, Ni, Pb, Zn, As, and Hg, respectively. The potential acute toxicity of the studied sediment for benthic organisms can be ranked based on the $\Sigma$TU value, of which high $\Sigma$TU means high acute toxicity and vice versa [28].

### 2.3.8. Contamination Severity Index (CSI)

The contamination severity index (CSI) was calculated using the following equation:

$$CSI = \sum_{i=1}^{n} W_i \left[ \left( \frac{M_{\text{sample}}}{M_{\text{ERL}}} \right)^{1/2} + \left( \frac{M_{\text{sample}}}{M_{\text{ERM}}} \right)^2 \right]$$

where $M_{\text{sample}}$, $M_{\text{ERL}}$, and $M_{\text{ERM}}$ are heavy metal concentrations of the studied sediment sample, the effect-range-low (ERL) and the effect-range-median (ERM) criteria values, respectively. The $W_i$ value was calculated by the eigenvalue and loading value obtained from principal component analysis/factor analysis (PCA/FA) based on the following Equation (9), which the only factor attributed to anthropogenic pollution source was computed [29].

$$W_i = \frac{(\text{Loading Value}_i \times \text{Eigenvalue})}{\sum_i (\text{Loading Value}_i \times \text{Eigenvalue})}$$

Based on the CSI value, the severity levels of ecological risk for sediment contamination can be classified into ultra-high (CSI > 5), very high (4–5), high (3–4), moderate to high (2.5–3), moderate (2–2.5), low to moderate (1.5–2), low (1–1.5), and very low severity of contamination (0.5–1), respectively [29].

### 2.4. Multivariate Statistical Analyses

The multivariate statistical analyses, including the Spearman correlation coefficient matrix and PCA/FA, were performed on the whole data set (13 variables) using IBM SPSS Statistics software version 20. The grain size composition (clay, silt, sand), organic matter (OM), total nitrogen (TN), and total phosphorus (TP) contents of the Fengshan River sediments in same study sites were obtained from our previous study [18].

### 3. Results and Discussion

#### 3.1. Spatial and Seasonal Variations in Heavy Metals

Table 1 shows the concentrations of heavy metals in Fengshan River sediments. The spatial and seasonal variations in trace metals concentrations in the studied sediments are shown in Figure 2. The distribution of heavy metals in the sediments showed large variations with a range of 15.8–352.7, 17.3–175.3, 17.3–64.3, 11.6–72.8, 119–533, 11.2–44.1, and 0.18–1.44 mg/kg for Cr, Cu, Ni, Pb, Zn, As, and Hg, respectively. The average concentrations of those heavy metals (Cr, Cu, Ni, Pb, Zn, As, and Hg) were 118.2, 78.4, 39.1, 33.0, 277.3, 24.9, and 0.6 mg/kg, respectively. In particular, the concentrations of Cr, Cu, Ni, Pb, and Zn displayed a similar trend of spatial variations. During the dry season, Cr, Cu, Ni, Pb, and Zn all showed the highest concentrations at site F6, which were 294.9, 142.6, 57.1, 49.9, and 501 mg/kg, respectively. The second-highest concentration was observed at the river mouth (F7), which was 234.6, 117.7, 39.1, 33.5, and 343 mg/kg for Cr, Cu, Ni, Pb, and Zn, respectively. Those metal concentrations at other stations (F1–F4) were relatively low and gradually increased from upstream to downstream during the dry season. During the wet season, the highest concentration was found at site F6, which was 352.7, 175.3, 64.3, 72.8, 533 mg/kg for Cr, Cu, Ni, Pb, and Zn, respectively. The second-highest concentration was observed at the river mouth (F7) except for Ni, which was 292.6, 148.0, 49.5, and 431 mg/kg for Cr, Cu, Pb, and Zn, respectively. Similarly, other stations also showed an increasing trend from upstream to downstream during the wet season. The mercury concentration in the dry season rose from the upstream to the maximum of 1.44 mg/kg at site F5 and
then decreased toward site F7, whereas the highest concentration was found at site F6 of 1.30 mg/kg in the wet season. There was no significant variation in the concentration of arsenic along the river in both dry and wet seasons.

Table 1. The concentrations (mg/kg) of heavy metals (As, Hg, Cr, Cu, Ni, Pb, Zn) in the sediments of Fengshan River in dry and wet season.

| Station | As      | Hg   | Cr        | Cu         | Ni   | Pb   | Zn  |
|---------|---------|------|-----------|------------|------|------|-----|
| F1      | 24.3    | 0.21 | 15.8      | 17.3       | 17.3 | 19.6 | 148 |
| F2      | 37.8    | 0.39 | 58.7      | 32.7       | 26.7 | 22.7 | 200 |
| F3      | 28.5    | 0.36 | 28.6      | 18.6       | 24.0 | 18.6 | 251 |
| F4      | 37.7    | 0.72 | 31.9      | 77.8       | 31.9 | 31.3 | 353 |
| F5      | 25.2    | 1.44 | 91.3      | 64.6       | 34.0 | 26.0 | 218 |
| F6      | 13.1    | 0.99 | 295       | 143        | 57.1 | 49.9 | 501 |
| F7      | 12.6    | 0.39 | 235       | 118        | 39.1 | 33.5 | 343 |

Dry season (December 2015)

| Station | As      | Hg   | Cr        | Cu         | Ni   | Pb   | Zn  |
|---------|---------|------|-----------|------------|------|------|-----|
| F1      | 19.5    | 0.18 | 26.0      | 31.2       | 27.2 | 11.6 | 119 |
| F2      | 41.1    | 0.33 | 81.9      | 79.4       | 37.7 | 28.0 | 144 |
| F3      | 18.4    | 0.29 | 46.6      | 48.1       | 32.5 | 29.3 | 139 |
| F4      | 44.1    | 0.66 | 46.4      | 91.6       | 62.1 | 44.0 | 292 |
| F5      | 21.1    | 0.31 | 53.1      | 53.2       | 51.8 | 24.9 | 211 |
| F6      | 14.3    | 1.30 | 353       | 175        | 64.3 | 72.8 | 533 |
| F7      | 11.2    | 0.40 | 293       | 148        | 41.1 | 49.5 | 431 |

Wet season (June 2016)

| Station | As      | Hg   | Cr        | Cu         | Ni   | Pb   | Zn  |
|---------|---------|------|-----------|------------|------|------|-----|
| ERL     | 33      | 0.15 | 80        | 70         | 30   | 35   | 120 |
| ERM     | 85      | 1.3  | 145       | 390        | 50   | 110  | 270 |
| TEL     | 5.9     | 0.174| 37.3      | 35.7       | 18   | 35   | 123 |
| PEL     | 17      | 0.486| 90        | 197        | 36   | 91.3 | 315 |
| SEL     | 33      | 2    | 110       | 110        | 75   | 250  | 820 |
| UCC     | 4.8     | 0.05 | 92        | 28         | 47   | 17   | 67  |

Criteria values for effect range low (ERL), effect range median (ERM), threshold effect level (TEL), probable effect level (PEL), and severe effect level (SEL) of sediment quality guideline for heavy metals in freshwater ecosystem [26]. Average contents of the upper continental crust (UCC) [21].

Overall, the spatial distribution of heavy metals in the Fengshan River sediments showed a relatively high concentration in the lower reaches (F6, F7). The maximum was frequently found at site F6 where the boundary of tidal river reach is located, probably as a result of the flocculation effect [30,31]. The salinity of river water serves as an important controlling factor for the partitioning of heavy metals to sediments, particularly the flocculation process in the lower reaches and estuary of rivers affected the distribution of heavy metals in the river sediments [31]. The concentration at the river mouth (F7) slightly decreased compared with site F6, probably because of resuspension and transportation of contaminated sediments seaward.

The seasonal variation in precipitation plays an important role in the fate of anthropogenic pollutants in the aquatic environment, especially for the river basin with distinct wet and dry seasons, such as the Fengshan River in Kaohsiung City, Taiwan. As shown in Figure 2, most heavy metals showed relatively high concentrations in the sediments during the wet season compared with those collected during the dry season. During the wet season, frequent and heavy rainfall can induce the discharge of pollutants from non-point sources to the Fengshan River through surface runoff. Moreover, the river sediment in the upper reaches may be resuspended by a strong river stream when a heavy rainfall occurs, causing sediments to scour from upstream to downstream and estuaries. Some studies have also shown similar findings that the higher concentration of heavy metals in river sediments during the rainy season resulted from heavy rainfall-induced water erosion and runoff of heavy metals-containing materials from the upper catchment [32,33].

The comparison of the heavy metals (Cr, Cu, Ni, Pb, Zn, As, and Hg) concentrations in Fengshan River sediments and the sediment quality guidelines are shown in Figure 2 and Table 1. The heavy metal concentrations in the studied sediments were mostly higher.
than the criteria value of ERL. As exceeded the ERL at two sites (F2 and F4), Pb exceeded the ERL at three sites (F4, F6, and F7), both Cr and Cu exceeded the ERL at four sites (F2, F5, F6, and F7 for Cr, and F2, F4, F6, and F7 for Cu), Ni exceed the ERL at six sites (except F1), and both Hg and Zn exceeded the ERL at all the sampling sites. Moreover, Hg, Cr, Ni, Zn showed concentrations exceeding the criteria value of ERM, where Hg exceeded the ERM at one site (F5), Cr exceeded the ERM at two sites (F6 and F7), and both Ni and Zn exceeded the ERM at three sites (F4, F5, F6 for Ni and F4, F6, F7 for Zn). These findings indicated that the concentrations of Hg, Cr, Ni, and Zn were severely contaminated in Fengshan River sediments, leading to the frequent occurrence of adverse biological effects. Those kinds of heavy metals pollution may attribute to wastewater discharges from leather processing and metal finishing factories within the river watershed, particularly along the river upstream and tributaries [19,34].

Figure 2. Spatial and seasonal variations in heavy metals (As, Hg, Cr, Cu, Ni, Pb, Zn) and organic matter contents in the sediments of Fengshan River. The horizontal dot lines and dash lines represent the ERL and ERM values, respectively.

3.2. Sediment Pollution Status

The sediment heavy metal contamination levels in this study were assessed using the contamination factor (CF), geo-accumulation index ($I_{geo}$), modified degree of contamination (mCd), and pollution load index (PLI). The CF and $I_{geo}$ are often applied to differentiate...
the metal source between natural terrestrial and anthropogenic pollution in sediments. Both the mCd and the PLI were comparative indices for assessing overall heavy metals contamination level in a simple way.

As shown in Figure 3a, As, Hg, Zn, and Cu have CF values greater than 6, which denotes “very high contamination”. The CF value for Hg shows the highest among all metals and reveals the highest number of sites with CF > 6 among all studied metals. The second-highest occurrence of “very high contamination” is As, which appeared at the F2 and F4 both in the dry and wet seasons. Both Zn and Cu have CF > 6 at site F6, which appeared in the wet season for Zn and in each of the wet and dry seasons for Cu. The CF value of “considerable contamination” mainly came from As, Hg, Zn, and Cu. Other than the sites showing “very high contamination”, the CF value for Hg at other sites showed “considered contamination”. The CF value of “considered contamination” for As were shown at sites F1, F3, and F5 both in the dry and wet seasons, while those CF values for Zn were shown at sites F3–F5 and F7 in the dry season and sites F4–F5 in the wet season, and those for Cu were shown at site F7 in the dry season and site F4 and F7 in the wet season. In addition, the CF value with “considered contamination” for Cr also had one site (F6) in the dry season and two sites (F6 and F7) in the wet season, and those for Pb only appeared at site F7 in the wet season. In contrast, none of the sites showed “considered contamination” in Ni. Overall, the sediment contamination degree of heavy metals is ranked in the following order of Hg > As > Zn > Cu > Pb > Cr > Ni.

Figure 3. (a) Contamination factor (CF), (b) geo-accumulation index (I\text{geo}), (c) modified degree of contamination (mCd), and (d) pollution load index (PLI) for heavy metals (As, Hg, Cr, Cu, Ni, Pb, Zn) in the sediments of Fengshan River. The CF is classified as low (<1), moderate (1–3), considerable (3–6), and very high contamination (>6); the I\text{geo} is classified as unpolluted (<0), unpolluted to moderately (0–1), moderately (1–2), moderately to strongly (2–3), strongly (3–4), and strongly to extremely polluted (4–5); the mCd is classified as nil to very low (<1.5), low (1.5–2), moderate (2–4), and high degree of contamination (4–8); the PLI is classified as unpolluted (<1), slightly (1–2), moderately (2–3), and strongly polluted (>3).

The geo-accumulation index (I\text{geo}) results are shown in Figure 3b. The I\text{geo} classes of the Fengshan River sediments were ranked from “moderately polluted” to “strongly to extremely polluted” for Hg, “unpolluted to moderately polluted” to “moderately to strongly polluted”
for As and Zn, “unpolluted” to “moderately to strongly polluted” for Cu, “unpolluted” to “moderately polluted” for Pb and Cr, and “unpolluted” for Ni. Similar to the result of contamination factors (CF), the contamination degree of heavy metal in the Fengshan River based on the \( I_{\text{geo}} \) value followed the order of Hg > As > Zn > Cu > Pb > Cr > Ni.

The mCd is an overall assessment of the degree of contamination for all studied metals. According to the mCd assessment (Figure 3c), the mCd values classified as “high degree contamination” were shown at sites F4 and F6 in both the dry and wet seasons, at site F5 in the dry season and site F7 in the wet season. Both sites F2 and F3 in the dry and wet seasons, site F5 in the wet season, and site F7 in the dry season showed “moderate degree contamination”. In contrast, site F1 only indicated “low degree contamination” in both dry and wet seasons.

The PLI values ranged from 1.1 to 5.07 (Figure 3d), indicating that heavy metal pollution existed (PLI > 1) in Fengshan River sediments. Most sites in the Fengshan River showed “moderate degree polluted” to “strongly polluted” except sites F1 and F2 were “slightly polluted”, which further indicated that the industrial effluent discharge might be responsible for the accumulation of heavy metals in sediments of the Fengshan River. Overall, the degree of heavy metal contamination in Fengshan River can be classified as “moderate degree polluted,” mainly attributed to the industrial effluent discharge. The degree of heavy metal contamination showed an increasing trend from the upper reaches to the lower reaches. It slightly decreased in the river mouth, probably because of resuspension and transportation of contaminated sediments seaward.

A comparison between the heavy metal concentrations of sediments in Fengshan River and those from other regions is shown in Table 2. The concentrations of heavy metals in the Fengshan River sediments were mostly higher than those of river sediments from other countries, especially for Hg, Cr, Cu, and Zn. It highlighted the seriousness of heavy metal pollution in the Fengshan drainage area, which needs to pay more attention to this critical issue by the government and related organizations.

### Table 2. Comparison among the heavy metal concentrations (mg/kg) of sediments in Fengshan River and those from other regions.

| Station                        | As     | Hg     | Cr     | Cu     | Ni     | Pb     | Zn     |
|--------------------------------|--------|--------|--------|--------|--------|--------|--------|
| Fengshan River, Taiwan         | 11–44  | 0.18–1.44 | 16–353 | 17–175 | 17–64  | 12–73  | 119–533|
| Keelung River, Taiwan [35]     | na     | na     | na     | 3.5–120| na     | 9.3–200| 41–390 |
| Changjiang River, China [36]   | 9.0–34 | 0.01–0.09| 14–37  | 26–34  | 17–42  | 72–131 |
| Yellow River, China [37]       | 14–48  | na     | 41–128 | 30–102 | na     | 26–78  | 90–202 |
| Xijiang River, China [38]      | 4.9–60 | 0.01–0.48| 6–119  | 6–120  | na     | 11–155 | 28–479 |
| River Ganges, India [39]       | na     | na     | 1.8–6.4| 1.0–4.4| na     | 4.3–8.4| 10–20  |
| Korotoa River, Bangladesh [40] | 2.6–52 | na     | 55–183 | 35–118 | 37–163 | 36–83  | na     |
| River Soan, Pakistan [41]      | na     | na     | 2.9–19 | 4.8–59 | 19–35  | 7.5–78 | 7.3–189|
| Nile River Branches, Egypt [42]| na     | na     | na     | 12–68  | 1.0–3.7| 15–30  | 30–80  |
| Bormida River, Italy [43]      | 9.0–59 | 0.09–0.96| 63–392 | 16–77  | 28–231 | 13–77  | 48–228 |
| Brisbane River, Australia [44] | 8.9–13 | 1–2    | 82–332 | 20–110 | 20–34  | 25–126 | 142–257|

na: not available.

### 3.3. Potential Biological Risk

The potential biological risk of the Fengshan River sediments for benthic organisms was assessed by the potential ecological index (RI), mean ERM quotient (mERM\(_Q\)), the sum of the toxic units (ΣTU), and contamination severity index (CSI). As shown in Figure 4a, the sediments in Fengshan River exhibited RI values ranging between 199 and 1233 with an average of 542, showing a considerable ecological risk according to the classification reported by Håkanson [22]. In particular, sites F4, F5, and F6 showed “very high ecological risk” with an average RI value up to 670. The mERM\(_Q\) values varied from 0.24 to 1.14 with an average of 0.55, indicating that the contamination level of heavy metals in Fengshan River sediments may be considerably toxic (49% probability of being toxic) to benthic organisms (Figure 4b). A relatively high mERM\(_Q\) value was found at site F6.
(\text{mERM}_Q = 1.14 \text{ in the wet season and } \text{mERM}_Q = 0.97 \text{ in the dry season}), \text{ followed by site F7 (mERM}_Q = 0.82 \text{ in the wet season and } \text{mERM}_Q = 0.67 \text{ in the dry season}). \text{ It is indicated that the sediments in the lower reaches and the river mouth were highly toxic (76\% probability of being toxic), which may be harmful to the growth of local benthic organisms. Similarly, the } \Sigma \text{TU values ranged between 3.2 and 12.6, with an average of 6.7. The highest } \Sigma \text{TU value was observed at site F6 (\Sigma \text{TU} = 12.6 \text{ in the wet season and } \Sigma \text{TU} = 10.5 \text{ in the dry season}), indicating a high risk of potential acute toxicity effects of the river sediments on the benthic community, especially for those in the lower reaches (Figure 4c).}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{(a) Potential ecological risk index (RI), (b) mean ERM quotient (mERM}_Q), (c) the sum of the toxic units (\Sigma \text{TU}), and (d) contamination severity index (CSI) for heavy metals (As, Hg, Cr, Cu, Ni, Pb, Zn) in the sediments of Fengshan River. The RI is classified into low (<150), moderate (150–300), considerable (300–600), and very high ecological risk (>600); the mERM}_Q is classified into 9\% (<0.1), 21\% (0.1–0.5), and 49\% probability of being toxic (0.5–1.5); the CSI is classified into uncontaminated (<0.5), very low (0.5–1), low (1–1.5), low to moderate (1.5–2), moderate (2–2.5), moderate to high (2.5–3), and high severity of contamination (3–4).}
\end{figure}

In addition, the CSI value was calculated by the eigenvalues of 6.387 and loading values of 0.776, 0.910, 0.881, 0.915, 0.819, 0.175, and 0.711 for Cr, Cu, Ni, Pb, Zn, As, and Hg, respectively. The eigenvalues and loading values adopted the VF1 obtained from PCA/FA, which can be interpreted as anthropogenic sources. As shown in Figure 4d, the CSI values ranged between 0.86 and 3.88, with a mean of 1.8. A similar trend to the mean ERM quotient was observed, which showed the highest value at site F6 (CSI = 3.9 in the wet season and CSI = 3.2 in the dry season), followed by site F7 (CSI = 2.7 in the wet season and CSI = 2.2 in the dry season). This indicated moderate to high severity of heavy metal contamination in the lower reaches and the river mouth.

3.4. Relationship among Sediment Properties and Heavy Metals

As shown in Table 3, significantly positive relationships between heavy metals (Cr, Cu, Ni, Pb) and organic matters (OMs) were observed in Fengshan River sediments, showing a correlation coefficient of 0.56–0.65 at a confidence level of 95\%. It is indicated that OMs is an important factor affecting the sediment heavy metal distribution in Fengshan River. Moreover, the sediment metal concentrations were also well correlated with total nitrogen.
(TN) and total phosphorus (TP) contents. Due to TN and TP being mainly derived from organic compounds, a good correlation of heavy metals with TN and TP strongly indicated that the organic compounds play an essential role in the spatiotemporal variations in heavy metals in the Fengshan River sediments. However, relatively low correlation coefficient values were observed for heavy metals with grain size (either sand, silt, or clay), indicating that the influence of grain size composition on the sediment heavy metal distribution was less critical than the organic matter.

**Table 3.** Spearman correlation matrix for the sediment grain size, organic matter (OM), total nitrogen (TN), total phosphorus (TP), and heavy metals contents (As, Hg, Cr, Cu, Ni, Pb, Zn) in the sediments of Fengshan River.

|            | Clay | Silt | Sand | OM | TN | TP | As | Hg | Cr | Cu | Ni | Pb |
|------------|------|------|------|----|----|----|----|----|----|----|----|----|
| Silt       | 0.911 ** | -0.911 ** | -1.00 ** |    |    |    |    |    |    |    |    |    |
| Sand       |        | 0.534 * | -0.534 * |    |    |    |    |    |    |    |    |    |
| OM         | 0.422  | 0.697 ** | -0.697 ** | 0.763 ** |    |    |    |    |    |    |    |    |
| TN         | 0.477  | 0.697 ** | -0.697 ** | 0.763 ** |    |    |    |    |    |    |    |    |
| TP         | 0.163  | 0.433  | -0.433 | 0.688 ** | 0.842 ** |    |    |    |    |    |    |    |
| As         | -0.255 | -0.363 | 0.363  | -0.407 | -0.538 * |    |    |    |    |    |    |    |
| Hg         | 0.218  | 0.332  | -0.332 | 0.497 | 0.673 ** | 0.376 | -0.057 |    |    |    |    |    |
| Cr         | 0.343  | 0.534 * | -0.534 * | 0.622 * | 0.815 ** | 0.749 ** | -0.495 | 0.651 * |    |    |    |    |
| Cu         | 0.165  | 0.385  | -0.385 | 0.648 * | 0.829 ** | 0.807 ** | -0.402 | 0.682 ** | 0.842 ** |    |    |    |
| Ni         | -0.073 | 0.152  | -0.152 | 0.635 * | 0.657 * | 0.741 ** | -0.301 | 0.535 * | 0.714 ** | 0.866 ** |    |    |
| Pb         | 0.134  | 0.297  | -0.297 | 0.556  | 0.771 ** | 0.714 ** | -0.390 | 0.680 ** | 0.754 ** | 0.938 ** | 0.820 ** |    |
| Zn         | 0.244  | 0.371  | -0.371 | 0.314  | 0.631 * | 0.486 | -0.358 | 0.801 ** | 0.622 * | 0.763 ** | 0.600 * | 0.780 ** |

* Grain size, OM, TN, and TP data obtained from Lin et al. [18]. ** significant at p < 0.01, expressed in bold; * significant at 0.01 < p < 0.05; n = 14.

In general, grain size and organic matter serve as two primary factors to affect the variations in heavy metal concentrations in sediments. The grain size effect has been documented in previous studies [45,46]. Muddy sediments, mainly consisting of aluminosilicate minerals (i.e., clay minerals), have high cation exchange capacity and large specific surface area [47], which are prone to adsorb anthropogenic pollutants (e.g., heavy metals). Consequently, heavy metals are accumulated in the muddy sediments [48]. On the contrary, sandy sediments commonly consist of coarse-grained biogenic carbonates and quartz. The carbonate or quartz sands with relatively low cation exchange capacity and specific surface area are not easy to adsorb heavy metal pollutants compared with clay minerals [49].

On the other hand, high concentrations of heavy metals are often associated with high organic matter content in sediments [17,50]. Most organic matters have large specific surface areas with negatively-charged sites, leading to the adsorption of anthropogenic heavy metals [51]. Chen et al. [17] reported that the influence of organic matter content on the distribution of heavy metals in sediments was more significant than the effect of sediment grain size, especially for the aquatic environments with rich organic matter (e.g., estuaries and harbors).

Furthermore, good relationships among the heavy metals (Hg, Cr, Cu, Ni, Pb, and Zn) in the studied sediments were observed with a correlation coefficient ranging between 0.53 and 0.94 at a confidence level of 95% (p < 0.05). This indicated that those heavy metals were probably derived from similar pollution sources, which may attribute to industrial wastewater discharges from leather processing and metal finishing factories within the river basin.

According to the results of PCA/FA, three factors with eigenvalues > 1 were extracted from our data set. The corresponding VFs, variable loadings, eigenvalues, and the explained variance are shown in Table 4. The VF1 displays strong positive loadings (>0.70) on OM, TN, TP, Hg, Cr, Cu, Ni, Pb, and Zn, which accounts for 49% of the total variance. This is consistent with the results of the Spearman correlation analysis, where good correlation among OM, TN, TP, and heavy metals (Cr, Cu, Ni, Pb) were observed (Table 2). Therefore, the VF1 can be interpreted as anthropogenic pollution sources. In contrast, the VF2 displays strong positive loadings on grain size composition (i.e., clay, silt, and sand) with 24.1% of the total variance, which can be interpreted as lithogenic sources (i.e., natural origin).
The difference of PCA/FA factors obtained from grain size and heavy metals indicated grain size appears to be not a major controlling factor for the heavy metals’ spatiotemporal variations in the river sediments. This is consistent with the results of the Spearman correlation analysis. The VF3 displays strong positive loadings on As only with 13.6% of the total variance, probably indicating the source of As was different from the other metals (Hg, Cr, Cu, Ni, Pb, and Zn).

Table 4. Corresponding variable loadings, eigenvalues, and explained variance obtained from PCA/FA for the entire data set.

|       | VF1      | VF2      | VF3      |
|-------|----------|----------|----------|
| Clay  | −0.096   | 0.938    | −0.043   |
| Silt  | 0.275    | 0.917    | 0.232    |
| Sand  | −0.217   | −0.951   | −0.191   |
| OM    | 0.762    | 0.317    | 0.331    |
| TN    | 0.865    | 0.365    | 0.292    |
| TP    | 0.823    | 0.165    | 0.315    |
| As    | −0.175   | −0.192   | −0.901   |
| Hg    | 0.711    | 0.111    | −0.187   |
| Cr    | 0.776    | 0.342    | 0.507    |
| Cu    | 0.910    | 0.122    | 0.319    |
| Ni    | 0.881    | −0.201   | 0.031    |
| Pb    | 0.915    | 0.042    | 0.229    |
| Zn    | 0.819    | 0.141    | 0.352    |
| Eigenvalue | 6.387 | 3.130 | 1.768 |
| % of Total variance | 49.1% | 24.1% | 13.6% |

*Grain size, OM, TN, and TP data obtained from Lin et al. [18]. Bold values indicate strong loadings (>0.7).

4. Conclusions

The results of this study clearly showed that Fengshan River sediments were extremely contaminated with Hg, Cr, Ni, and Zn. Those heavy metal pollutants were mainly attributed to the leather processing and metal finishing factories around the river upstream. The contaminated river sediments pose a considerable ecological risk based on the assessment of multiple pollution indices, especially for the sediments in the lower tidal reaches and river mouth, which may cause adverse effects on the benthic organisms. Even though the ecological impacts of river sediments on the local benthic organisms may depend on the water environment condition and sediment characteristics, the results of this study can provide a warning to the government, who should pay attention to river remediation and improve the current pollution status. Further laboratory and on-site toxicity experiments are needed to be conducted to understand the actual adverse effects on local organism in Fengshan River. This study can provide valuable information for river pollution remediation and urban planning and management.

Author Contributions: Conceptualization, C.-D.D. and C.-M.K.; methodology, C.-F.C.; validation, K.-N.L. and Y.-C.L.; formal analysis, K.-N.L.; investigation, Y.-C.L.; data curation, C.-W.C.; writing—original draft preparation, K.-N.L.; writing—review and editing, C.-W.C., C.-M.K. and C.-D.D.; visualization, K.-N.L.; supervision, C.-M.K.; project administration, C.-M.K.; funding acquisition, C.-D.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.
Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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