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Authors

Wang, Zhenfeng
Zhou, Jiayu
Zhang, Chi
et al.

Publication Date

2019-02-01

DOI
10.1016/j.envpol.2018.11.078

Environmental Pollution 245 (2019) 1022–1030

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

A comprehensive risk assessment of metals in riverine surface sediments across the rural-urban interface of a rapidly developing watershed☆

Zhenfeng Wang [a], Jiayu Zhou [b], Chi Zhang [a], Liyin Qu [a], Kun Mei [a], Randy A. Dahlgren [a, c], Minghua Zhang [a, c], Fang Xia [a, *]

[a] Southern Zhejiang Water Research Institute, Zhejiang Provincial Key Laboratory of Watershed Science and Health, Wenzhou Medical University, Wenzhou, 325035, China
[b] Zhijiang College of Zhejiang University of Technology, Shaoxing, 312030, China
[c] Department of Land, Air, and Water Resources, University of California, Davis, CA, 95616, United States

ARTICLE INFO

Article history:
Received 10 July 2018
Received in revised form
22 November 2018
Accepted 24 November 2018
Available online 28 November 2018

Keywords:
Environmental risk assessment
Land use
Monte Carlo simulation
Uncertainty

ABSTRACT

Metal contamination in aquatic environments is a severe global concern to human health and aquatic ecosystems. This study used several risk assessment indices, to evaluate metal (Cu, Zn, Pb, Cd and Cr) environmental risk of riverine surface sediments across the rural-urban interface of the rapidly developing Wen-Rui Tang River watershed in eastern China. Risk assessments were determined for 38 sites based on the potential ecological risk index (RI), consensus-based sediment quality guidelines (SQGs) and risk assessment code (RAC). Land-use cluster analysis showed that sediments were severely contaminated, especially for Cd, whose concentrations were ~100 times higher than background levels and had a high proportion in the bioaccessible fraction. According to RI, E_r^{Cd} was identified with extremely high risk potential, resulting in the highest ecological risk of Cluster 4 (industrial). Similarly, risk within Cluster 4 (industrial) was also ranked highest by SQGs assessment due to the high proportion of industrial land use. Zinc was determined with high risk due to its high concentration compared to its effect range medium (ERM) value. Discrepancies in predicting environmental risks from metals among the three indices were mainly attributed to the contrasting definitions of these metrics. Environmental risk uncertainty derived from spatial variation was further estimated by Monte Carlo simulation and ranked as: Zn > Cd > Cr > Pb > Cu. This comprehensive environmental risk assessment provides important information to guide remediation strategies for management of metal contamination at the watershed scale.

1. Introduction

Metal contamination in sediments is mainly derived from anthropogenic activities associated with industrialization and urbanization (industrial discharge and domestic wastewater as point sources; waste gas emissions/deposition as non-point sources). Metals in sediments pose a severe threat to aquatic biota due to their toxicity and lack of an effective removal mechanism. Furthermore, metal contamination is a potential risk to human health because of its bioaccumulation/biomagnification in the aquatic food web (Authman et al., 2013).

Metal concentrations in riverine sediments can be disproportionately influenced by adjacent land-use types (Wu et al., 2017). For example, Nguyen et al. (2016) reported significant accumulation of metals in river sediments located in highly industrialized and urbanized areas; Karstens et al. (2016) identified significant enrichment of metal concentrations in coastal wetland sediments, which was attributed to adjacent fertilized cropland; and Zhang et al. (2017) ascribed different characteristics of metal contamination and their corresponding ecological risk to differences between urban and rural metal input sources. However, these studies were based on a coarse land-use classification, which may result in the

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☆ This paper has been recommended for acceptance by Joerg Rinklebe.
* Corresponding author. Southern Zhejiang Water Research Institute, Zhejiang Provincial Key Laboratory of Watershed Science and Health, Wenzhou Medical University, Wenzhou, China.
E-mail address: xiafangzju@126.com (F. Xia).

https://doi.org/10.1016/j.envpol.2018.11.078
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loss of specific details regarding variations in metal contamination as a function of land use.

Due to the potential risk of metal contaminated sediment to the overlying water column through chemical and biological exchange mechanisms, it is important to acquire information on sediment quality and its associated ecological risk status. Several risk assessment indices based on total metal concentration have been developed for evaluation of ecological risk, for example, the geo-accumulation index (Dai et al., 2018) and potential ecological risk index (Liu et al., 2018). Due to the importance of metal bioaccessibility (Li et al., 2018a, b, c), a metal-fractions based index was established to better understand the ecological risk related to specific metal associations (i.e., fractions). For example, Soliman et al. (2017) found a high risk for Cd toxicity in Lake Qarun (Egypt) by calculating the risk assessment code (RAC), which is based on the acid soluble fraction. Given the contrasting approaches utilized in various risk assessment indices, several discrepancies may arise between ecological risk predictions for a specific region. As a result, Venkatramanan et al. (2015) proposed using several independent indices to avoid bias from a single risk index and provide a comprehensive ecological risk assessment.

Most studies assign a certain value of ecological risk based on a deterministic calculation. The need to consider the uncertainties of the ecological risks originating from spatial-temporal variations and systematic parameters has also been recognized when risk assessments were carried out (Huang et al., 2018; Li et al., 2018a, b, c). Qu et al. (2016) compared simulated versus calculated metal risk assessment results from China's major aquatic bodies and advocated the advantage of using a joint approach of Hakanson risk index and probability analysis from Monte Carlo simulation to avoid overestimation/underestimation of ecological risk. Li et al. (2018a, b,c) constructed a probabilistic integrated ecological risk assessment model to synthetically assess integrated ecological risk degrees for sediments in Honghu Lake watershed. Qu et al. (2018) calculated the health risk uncertainty in surface water and documented the uncertainties arising from data deficiencies. Therefore, it is high warranted to perform uncertainty analysis in conjunction with ecological risk assessment when carrying out a comprehensive metal risk assessment.

Many river systems are currently suffering from metal contamination derived from anthropogenic activities associated with various land-use types. In addition, failure to evaluate uncertainties surrounding ecological risk assessments may result in either over- or under-estimation of risk potential for a specific region. Therefore, the objectives of this study were: (i) to investigate the magnitude of metal contamination associated with various land-use clusters; (ii) to perform a comprehensive risk assessment based on the synthesis of three risk assessment indices; and (iii) to determine the uncertainty of risk assessment by application of the Monte Carlo simulation method. This comprehensive risk assessment provides important information to prioritize and guide remediation of metal contamination at the watershed scale.

2. Materials and methods

2.1. Study area

The Wen-Rui Tang River watershed is located in the coastal city of Wenzhou, East China. It originates from the Lishui Mountains and flows eastward to the East China Sea. The river system plays an important role in aquaculture, agricultural irrigation, industrial activities and transportation. The watershed (~740 km^2) ranges from rural to urban area with large variation in population (31,300–223,700 (total in each town or sub-district)). The climate is sub-tropical monsoon with an annual average temperature of ~18 °C and annual precipitation of ~1800 mm, with 70% falling between April and September.

2.2. Sampling sites and metal analysis

Based on the river network and land-use distribution, a total of 38 surface sediments (0–10 cm) were collected in the mid-channel of the Wen-Rui Tang River and its tributaries during March 2017 (Fig. 1). These sites were located at provincial and municipal sites for water quality assessment as part of a water treatment project. Sediment samples were stored in a freezer (−80 °C) after transferred to the laboratory. After freeze-drying, samples were pulverized to sieve <100 μm. The average (range) sediment pH was 7.1 (6.6–7.9, water, M:V = 1:5) and organic carbon was 36.4 g kg^{-1} (7.8–90.4 g kg^{-1}, potassium dichromate oxidation).

Concentrations of Cu and Zn in sediment samples were determined by atomic absorption spectrometry (PinAAcle 900, PerkinElmer; detection limit: Cu = 0.01, Zn = 0.01 mg L^{-1}) and Pb, Cd, and Cr were detected by inductively coupled plasma mass spectrometry (Agilent 8800 ICP-MS, Agilent Technologies, internal standard method (Ge, In and Bi); detection limits: Pb = 0.005, Cd = 0.01, Cr = 0.01 mg L^{-1}) after digestion with mixed acid (HNO_3–HCl–HF–$HClO_4$). All samples were analyzed in duplicate and the relative standard deviation of all duplicate samples was ±5%. GBW-07312 reference sediment (Chinese Academy of Geological Science) was used for quality control (recovery percentage: 89–107%). To characterize the metal fractions, the Community Bureau of Reference sequential extraction procedure (BCR) was performed (Wang et al., 2017). The BCR method is briefly summarized as: Step 1, acid soluble fraction (F1) extracted by 0.1 M acetic acid; Step 2, reducible fraction (F2) extracted with 0.5 M hydroxylamine hydrochloride; Step 3, oxidizable fraction (F3) extracted by 30% hydrogen peroxide and 1 M ammonium acetate; and Step 4, residual fraction (F4) determined by the mixed acid method as described above for total metal concentrations.

2.3. Land-use clusters

The original 96 detailed land-use categories for the study region were amalgamated into four broad categories based on the similar land-use functions: agricultural, industrial, urban and ecological. According to Chen et al. (2016), the percentage of the four categories at each site was calculated using ArcGIS statistical tools. Based on the land-use characteristics for each sampling location, the 38 sites were classified into 5 clusters (hierarchical cluster method): Cluster 1 urban/industrial, Cluster 2 urban, Cluster 3 urban/ecological, Cluster 4 industrial, and Cluster 5 ecological.

2.4. Environmental risk assessment methods

Due to the different approaches utilized in environmental risk assessment, we used three independent methods to assess the environmental risk of metals in sediments: potential ecological risk index (RI), consensus-based sediment quality guidelines (SQGs) and risk assessment code (RAC) based on the bioaccessible metal fraction.

RI, aims to evaluate a single metal ecological risk at each site and the associated overall risk based on the selected metals (Krishna and Mohan, 2016). Ecological risk was divided into five levels (Table S1) based on the calculation of E_r^i and RI as follows:

$$RI = \sum_{i=1}^{n} E_r^i \tag{1}$$

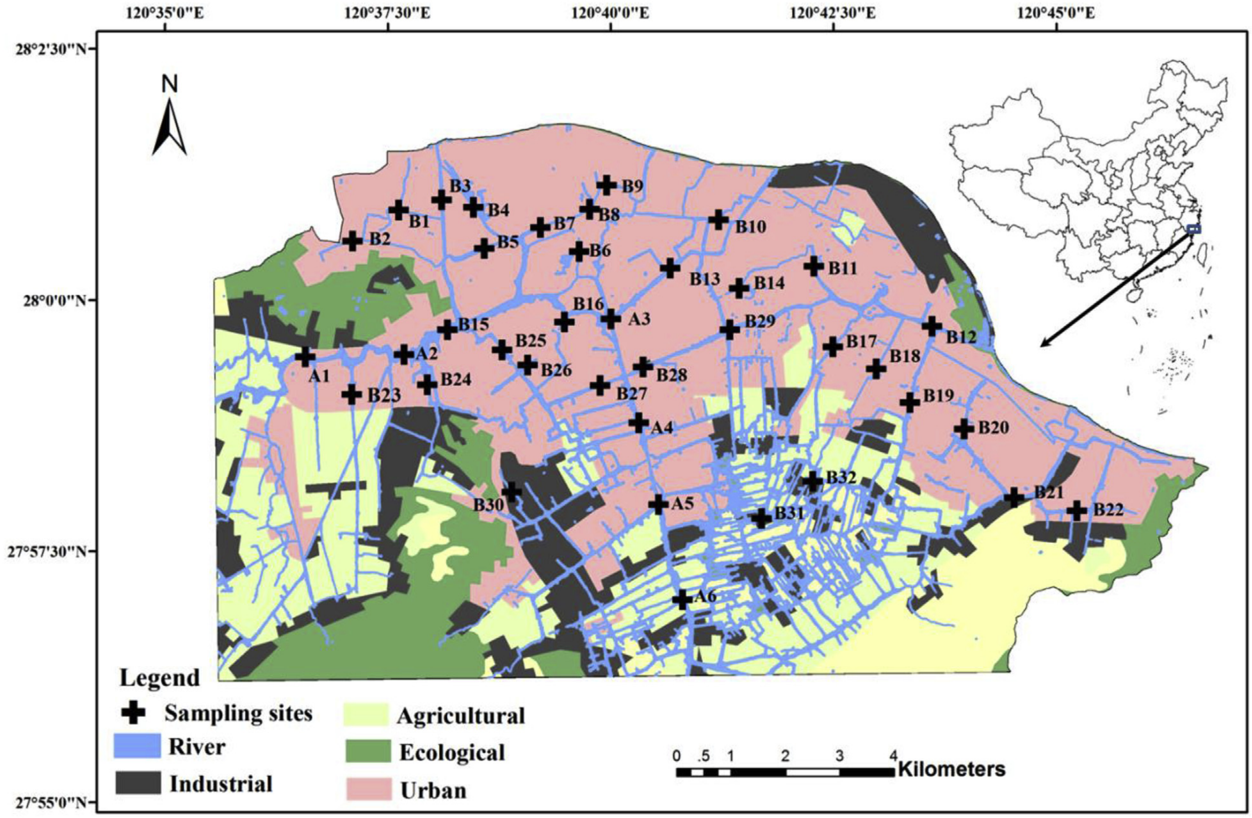

Fig. 1. Location of sampling sites in Wen-Rui Tang River watershed.

$$E_r^i = T_r^i \times \left(C_i \big/ C_f\right) \quad (2)$$

where C_i is the concentration of metal i, C_f is the reference value of metal i, T_r^i is the biological toxicity factor for metal i and n is the number of selected metals. Due to the lack of metal concentration standards for freshwater sediments, reference metal values in this study referred to soil background values in the Wen-Rui plain of Zhejiang Province (Wang et al., 2007).

SQGs, evaluate potential ecological toxicity for metals in freshwater ecosystems, based on the value of effect range medium (ERM). The effect range median quotient (ERM-Q) was introduced in this study to determine the possible biological effect of individual metals (Strady et al., 2017). In addition, the mean ERM-Q (mERM-Q) was calculated to assess the integrated biological effect of the selected metals. The index was calculated as follows:

$$\mathrm{mERM} - \mathrm{Q} = \left(\sum_{i=1}^{n} \mathrm{ERM} - \mathrm{Q}_i\right) \Big/ n \quad (3)$$

$$\mathrm{ERM} - \mathrm{Q}_i = C_i / \mathrm{ERM}_i \quad (4)$$

where ERM_i is the effect range medium of metal i, $\mathrm{ERM} - \mathrm{Q}_i$ is the effect range median quotient of metal i, and C_i and n are the same as described above for RI. Risks were classified into four levels: low priority (≤ 0.1), medium-low priority (0.1–0.5), high-medium priority (0.5–1.5), and high priority (>1.5).

RAC, which is based on the labile F1 fraction, was classified into five levels: none, low, medium, high and extremely high if F1 $\leq 1\%$, 1–10%, 10–30%, 30–50% and $>50\%$, respectively (Jain, 2004).

2.5. Uncertainty analysis by Monte Carlo simulation

Spatial variation and sampling randomness result in variable degrees of fuzziness and uncertainty in environmental risk assessment models. A Monte Carlo method, based on mathematical statistics and probability theory, was used to estimate the distribution of metal concentrations for the purpose of evaluating uncertainty in environmental risk models caused by random sampling (Qu et al., 2018). Combined with the consensus-based sediment quality guideline model, Monte Carlo analysis provided a probability distribution of ERM-Q values for the entire watershed. This allowed us to provide a measure of uncertainty for ecological risk of metals in the entire Wen-Rui Tang River watershed.

Monte Carlo simulation was carried out in Crystal Ball (Oracle Inc. USA, version 11.1). Distribution patterns for selected metal concentrations were determined before simulation to attain parameters for subsequent simulations. The distribution patterns for selected metals in surface sediments are summarized in Table S3.

3. Results

3.1. Land-use clusters

To better assess metal ecological risk in the watershed as a function of land use, sampling sites were grouped into five clusters according to land-use proportion (Fig. 2). Cluster 1 contained 8 sampling sites and was mainly comprised of urban (65.2%) and industrial (16%) land uses. Cluster 2 was comprised of 13 sites and dominated by urban lands (80.3%) that were mainly located in the northern part of the watershed. There were 6 sampling sites in Cluster 3 and 4, and 5 sampling sites in Cluster 5. Cluster 3 was dominated by urban (56.1%) and ecological (31.0%) lands, Cluster 4

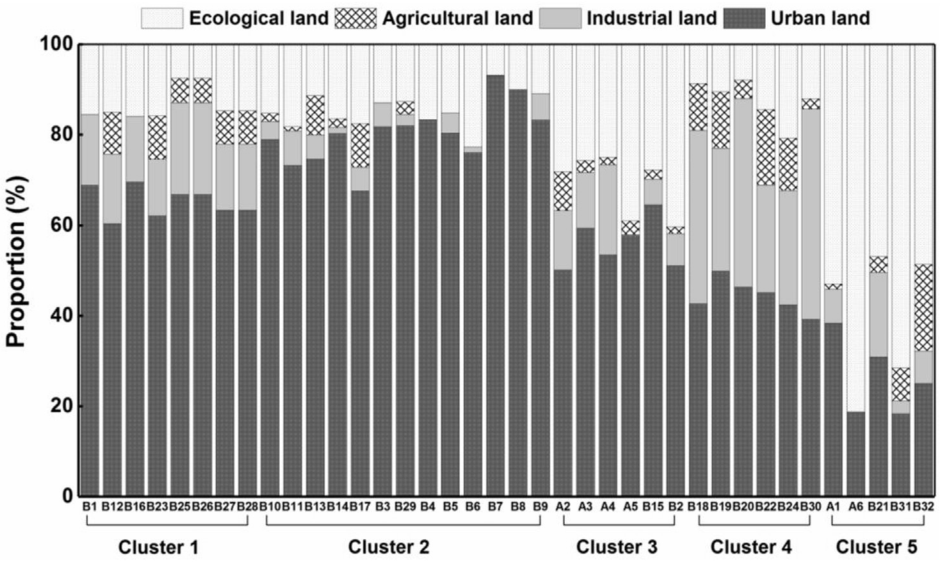

Fig. 2. Land-use proportion of sub-catchments for each sampling site.

by industrial land (33.8%), and Cluster 5 by ecological (60.3%) land.

3.2. Land-use based metal concentration and fractions in river sediments

In general, the river sediments were highly contaminated by metals compared to local background levels, especially Cd which was ~100 times higher than background. Metal concentrations in sediments of each cluster are summarized in Fig. 3. Cluster 4 (industrial) showed the highest concentrations of all metals, except Cr. The average (±std) concentrations of Cu, Zn, Pb, and Cd were 995 ± 2011, 2345 ± 2901, 217 ± 226 and 62 ± 125 mg kg^{-1},respectively, in Cluster 4 (industrial). The highest Cr concentration was identified in Cluster 5 (ecological), with an average of 248 ± 131 mg kg^{-1}. Cluster 2 (urban) showed the lowest metal concentrations.

In addition to comparisons with background levels, metal concentrations were evaluated with respect to threshold values for sediment quality guidelines (Table S2). The metal concentration exceedance rate of ERL followed: Zn = Cr > Pb > Cu > Cd. In total, ERL exceedance rates were more than 90% for Zn, Pb and Cr, and ~80% for Cu. In contrast, only ~25% of sediment samples showed higher concentrations of Cd than the ERL. There were some differences in the order of exceedance rate for ERM: Zn (97%) > Cr (71%) > Pb (32%) > Cd (21%) > Cu (11%).

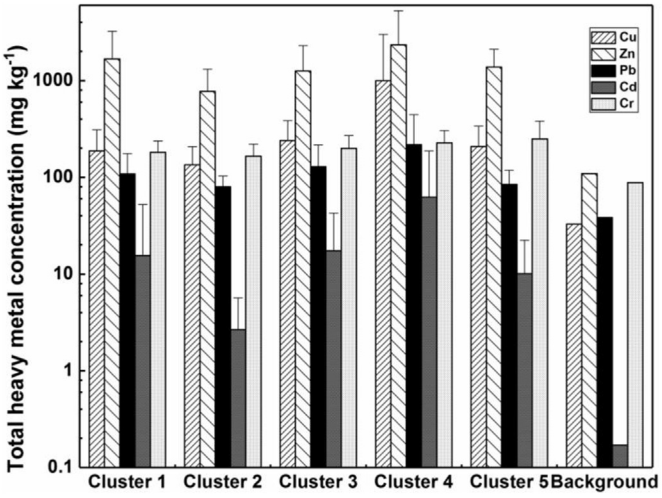

Fig. 3. Mean total heavy metal concentrations in each cluster.

Aside from total metal concentrations, chemical metal speciation is vital for assessing risk to aquatic ecosystems due to contrasting bioaccessibility among various extractable fractions, such as the most bioaccessible F1 fraction. The average contents of various metal fractions for the five land-use clusters are shown in Fig. 4. Generally, Zn and Cd were identified with higher F1 labile fractions, while Pb and Cr were found in the more stable F4 fraction. The F3 fraction was the dominant form of Cu in all five clusters. However, there was no consistent pattern in metal fraction distribution among the five clusters. In Clusters 1, 2, and 3, the dominant fraction was F4, while Clusters 4 and 5 had similar proportions of F2, F3 and F4.

3.3. Risk assessment of sediment metals in land-use clusters

Results of the ecological risk assessment for metals in the Wen-Rui Tang watershed are summarized for each land-use cluster in Table 1. The E_r^i values for Zn, Pb and Cr were lower than 40 in all clusters indicating a low ecological risk. The E_r^{Cu} of Cluster 4 (industrial) was 152 ± 308, which suggests a considerable ecological risk. The remaining 4 clusters were identified as having a low ecological risk from Cu due to their low E_r^{Cu} values. In contrast, Cd showed an extremely high ecological risk in all clusters due to its high value for the biological toxicity factor and its anomalously high concentrations at some sites. Because of the high contribution of Cd to the comprehensive ecological risk, the RI for the Wen-Rui Tang watershed showed an extremely high ecological risk, except for Cluster 2 (urban), which had a relatively low E_r^{Cd} value compared to the other four clusters. According to E_r^i values among clusters, Cluster 4 (industrial) showed the highest ecological risk and Cluster 2 (urban) the lowest risk.

Based on total metal concentrations, the ecological risk assessment was evaluated by comparison to the effect range low (ERL) and effect range medium (ERM) criteria. According to the average value of ERM-Q for each metal, the ecological risks ranked as

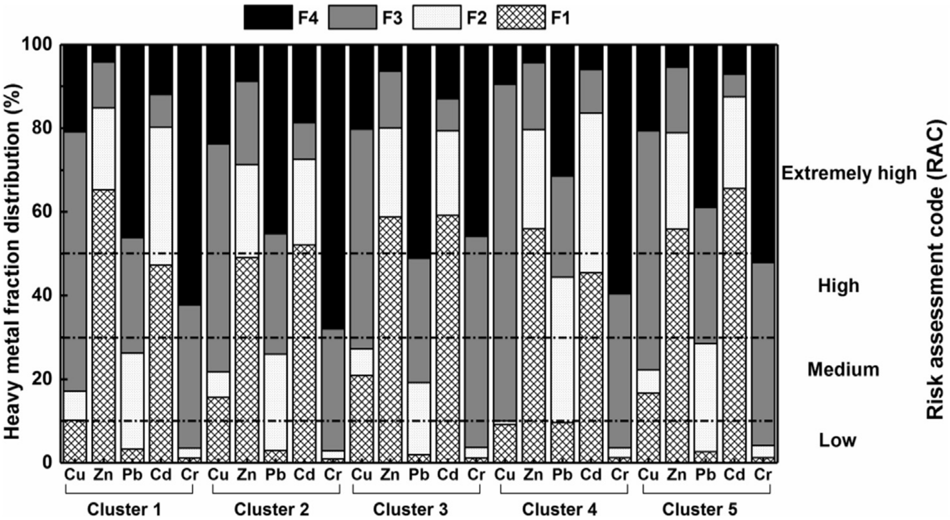

Fig. 4. Heavy metal fraction distribution and corresponding risk assessment code for each land-use cluster. The dashed horizontal lines indicate the qualitative risk based on the F1 fraction.

Table 1
Potential ecological risk (RI) for single and all selected metals in clusters (mean ± std).

	E_r^{Cu}	E_r^{Zn}	E_r^{Pb}	E_r^{Cd}	E_r^{Cr}	RI
Cluster 1	28.7 ± 18.6	15.4 ± 14.3	14.1 ± 8.8	2745 ± 6454	4.1 ± 1.3	2808 ± 6479
Cluster 2	20.5 ± 11.1	7.1 ± 4.9	10.4 ± 3.0	470 ± 532	3.7 ± 1.3	513 ± 545
Cluster 3	36.8 ± 22.0	11.5 ± 9.5	16.8 ± 11.3	3073 ± 4459	4.53 ± 1.6	3143 ± 4496
Cluster 4	152 ± 308	21.5 ± 26.6	28.3 ± 29.5	11,007 ± 22,069	5.1 ± 1.7	11,214 ± 22,066
Cluster 5	31.8 ± 19.8	12.7 ± 6.6	11.0 ± 4.5	1779 ± 2154	5.7 ± 3.0	1841 ± 2178

Cluster 1 = urban/industrial, Cluster 2 = urban, Cluster 3 = urban/ecological, Cluster 4 = industrial, Cluster 5 = ecological.

follows: Zn > Cd > Cr > Pb > Cu (Fig. 5). This ecological risk order showed some differences when compared to the ERM exceedance rates presented above. Based on ERM-Q values for individual metals, Cluster 4 (industrial) posed the highest risk for Cu, Zn, Pb, and Cd and displayed large variations, while Cluster 5 (ecological) was identified with a higher risk for Cr. Cluster 2 (urban) had the lowest risk levels for all selected metals. Finally, the mERM-Q was calculated to evaluate the integrated risk for each cluster. According to mERM-Q, ecological risk by clusters followed: Cluster 4 > Cluster 1 > Cluster 3 > Cluster 5 > Cluster 2. Except for Cluster 2 (urban), which showed high-medium priority, all other clusters posed high priority. Generally, the contribution of the ERM-Q_{Zn} to mERM-Q accounted for more than 50% of the total contribution based on the average for all clusters, while Cu and Cd contributed only 7% and 9%, respectively.

Unlike RI and ERM-Q, which are based on total metal concentrations in sediments, risk assessment by RAC is based on the F1 proportion (labile) (Fig. 4). According to RAC levels, the risk from metals in sediments of the Wen-Rui Tang watershed followed: Zn > Cd > Cu > Pb > Cr. The Pb and Cr in the five clusters showed low risk due to a low contribution from the F1 fraction for these two metals. While Cu was identified with low to medium risk, Zn and Cd showed high to extremely high risk due to their high F1 fractions (>50% of the total content). Though Cluster 4 (industrial) was identified with high total metal contents, Cluster 3 (urban/ecological) generally showed higher ecological risk when considering metal speciation.

3.4. Uncertainty analysis of risk assessment

Based on the distribution patterns for the metals examined in this study, a 100,000-iteration Monte Carlo simulation was carried out to obtain simulated ERM-Q values. Selected statistical values were compared with calculated ERM-Q values derived from the measured concentrations (Fig. 6). Generally, the ranges of simulated ERM-Q values for all selected metals were larger than the calculated ranges. Copper was the only metal to show a lower simulated median value than calculated value. The simulated medians for Pb and Cr were similar to the calculated values. In contrast, Zn and Cd had greater simulated medians than the calculated medians. Additionally, mERM-Q was identified to have a higher simulated median (1.45) than calculated median (1.11). However, median values for both calculated and simulated groups fell within the range of high-medium priority risk. The ecological risk probability of mERM-Q was calculated based on cumulative probabilistic risk curves (Fig. 7). The rate of high priority occurrence for the simulated group was 47.2%, higher than the calculated group (39.5%). In contrast, the rate of high-medium priority occurrence in the simulated group (52.8%) was lower than the calculated group (55.3%). The rate of medium-low priority occurrence accounted for 5.3% in the calculated group, which was 0.03% higher than the value for the simulated group.

4. Discussion

4.1. Land-use based metal contamination in river sediments

Metals in riverine surface sediments of the Wen-Rui Tang watershed were severely contaminated, especially for Cd and Zn (Fig. 3), which were 10–100 times higher than background levels. According to the metal concentrations in each cluster, Cluster 4 (industrial) was the most contaminated while Cluster 2 (urban) was least contaminated with metal pollution. Previous studies have confirmed industrial discharge as a primary source of metal

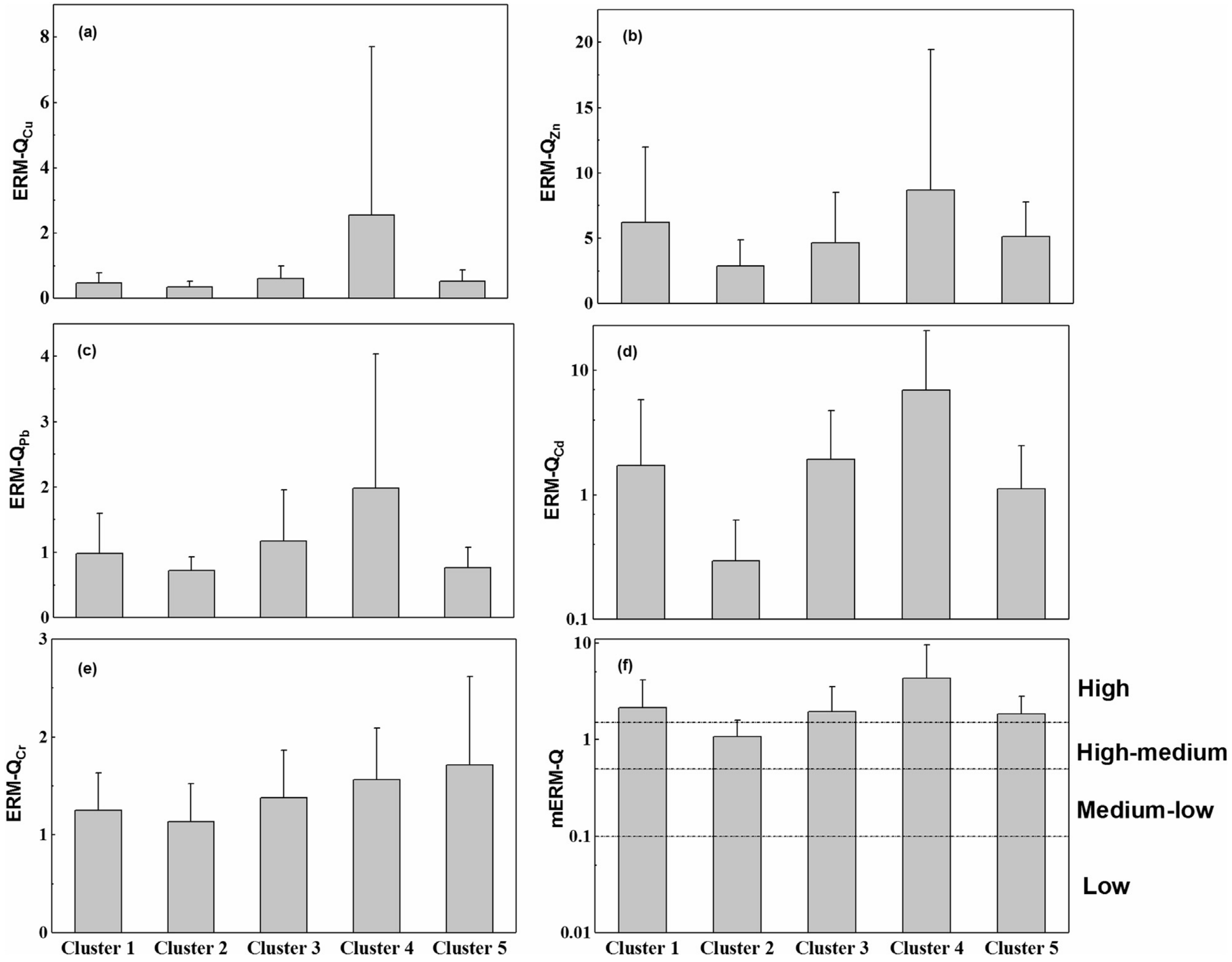

Fig. 5. Risk assessment of ERM-Q of heavy metals in sediments in Wen-Rui Tang River.

pollution (Varol, 2011; Khan et al., 2016). Small domestic workshops, such as those engaging in electroplating, printing and dyeing, synthetic leather and electronic manufacturing, have been active over the past several decades in the Wen-Rui Tang watershed. Due to the absence of strict legislation and enforcement of pollutant discharge during this period of rapid economic development, large emissions of untreated wastewater and industrial residues containing metals were discharged directly into the environment, resulting in extensive metal contamination at some locations within the Wen-Rui Tang watershed.

Although the contamination degree is closely related to total contents, the potential ecological risks from metals also depend on metal chemical speciation due to its effect on accessibility and availability to aquatic organisms. The F1 fraction was highest for Cd and Zn among the metals investigated. These results are consistent with Yang et al. (2014) findings of an extremely high acid extractable fraction of Cd in lake sediments. The large proportion of labile Cd in sediments might be associated with its strong affinity for the sediments. Previous studies reported that Zn and Cd were mainly bound and co-precipitated with carbonates in sediments (Yu et al., 2000; Ahdy and Youssef, 2011). The residual fraction was the dominant form of Pb and Cr, indicating that these metals might be strongly bound/trapped in the crystalline lattices of primary and/or secondary minerals making them less bioaccessible to aquatic organisms (Xiao et al., 2015). Copper showed a high proportion in the F3 fraction, which suggests a strong affinity with organic matter. Yu et al. (2000) also demonstrated a high proportion of organically complexed Cu in river sediments of Taiwan. The average content of organic matter in the Wen-Rui Tang River sediments was 62.7 g kg^{-1}, which could retain a high amount of Cu due to the strong binding affinity of organic matter for Cu (Latrille et al., 2003).

4.2. Comparison of various ecological risk indices for aquatic sediments

Comparison of contrasting ecological risk assessment metrics (E_r^i, ERM-Q and RAC) for metals in the Wen-Rui Tang River sediments showed some discrepancies (Table 1, Figs. 4 and 5). The RI method identified Cd as the highest risk metal and Cr as the lowest risk metal in the watershed. The E_r^i index is calculated from the ratio of metal concentration to the reference content. The background concentrations were selected as the reference and Cd and Cr were 0.17 and 88.1 mg kg^{-1}, respectively. In addition, Cd was assigned a biological toxicity factor of 30 compared to 2 for Cr (Hakanson, 1980). These two aspects contributed to a very high risk level for Cd and low risk level for Cr, similar to the findings of Hu et al. (2016) that identified moderate risk for Cd and low risk for Cr. Based on the SQGs of ERM-Q, the ecological risk followed: Zn > Cd > Cr > Pb > Cu. ERM-Q is an empirical index, which is derived from toxicity trials on specific aquatic amphipods (MacDonald et al., 2000). The ERMs for Zn and Cu were 390 and 270 mg kg^{-1}, compared to average Zn and Cu concentrations of

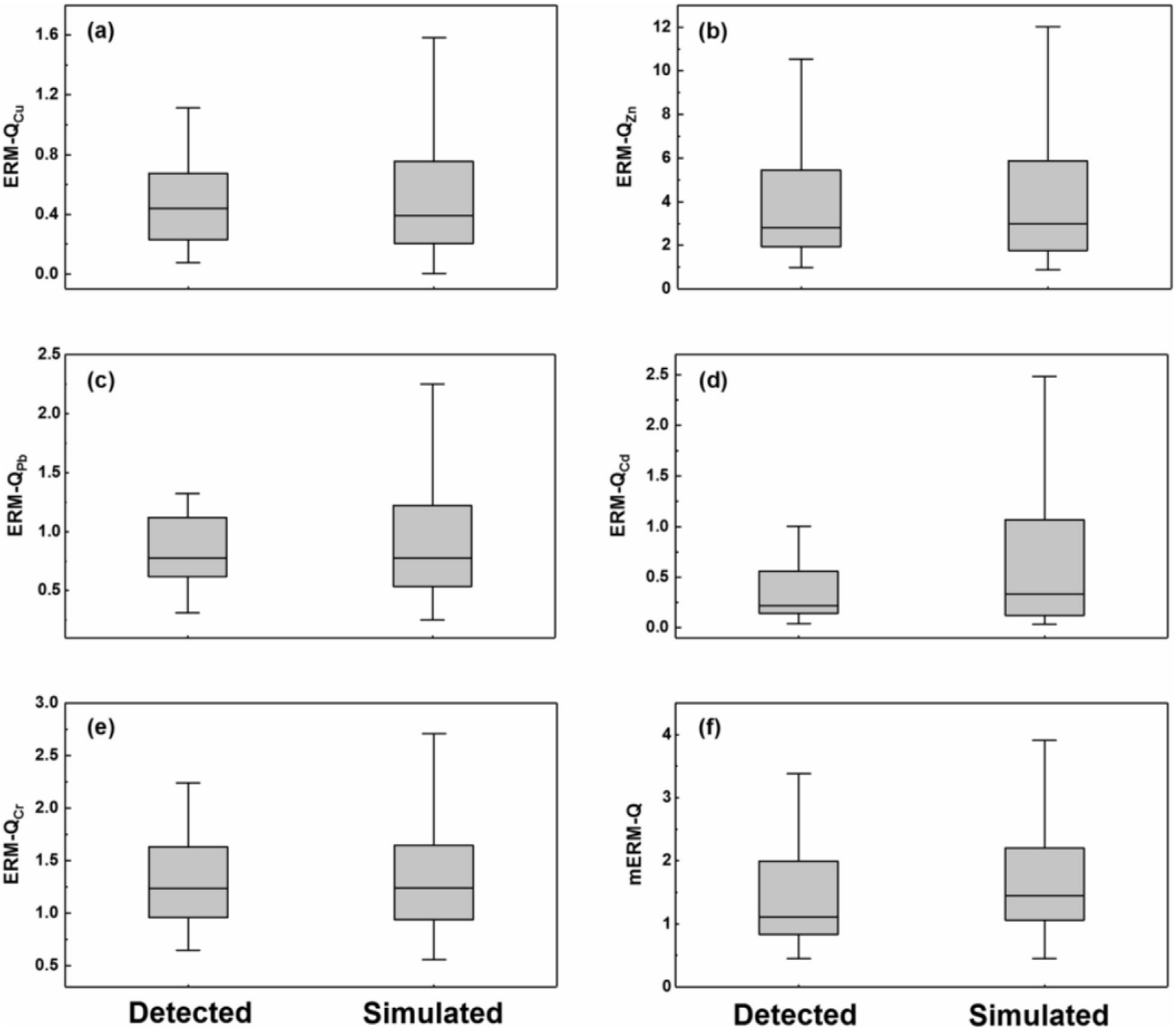

Fig. 6. Detected and simulated ERM-Q values for five metals in surface sediments of the Wen-Rui Tang River watershed.

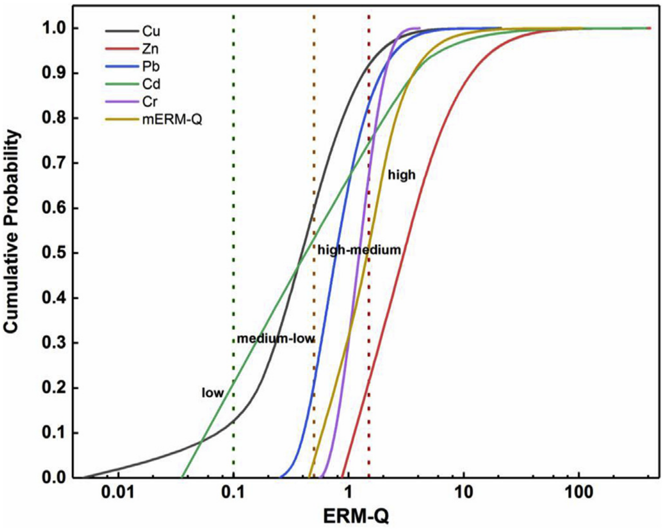

Fig. 7. Simulated risk assessment of ERM-Q for metals in sediments of the Wen-Rui Tang River.

1368 and 308 mg kg^{-1} across all sampling sites. This leads to a watershed risk assessment of high risk level for Zn and low risk level for Cu. In contrast to metrics based on total concentrations, RAC was proposed to evaluate ecological risk according to the bioaccessible fraction of metals. In the studied area, Zn and Cd had the highest F1 fraction with values of ~51.3% for Zn and ~51.9% for Cd when averaged across all sampling sites. This high proportion of potentially bioaccessible metal resulted in an extremely high risk ranking. Although most sampling sites had higher concentrations of Pb and Cr than Cd, the former two metals were identified as having low risk potential due to the low proportions of labile forms (F1 fraction).

The contrasting ecological risk assessment metrics also provided some differing results with regard to land-use clusters. Based on total concentrations, RI and mERM-Q of Cluster 4 (industrial) showed the highest ecological risk, while Cluster 2 (urban) ranked lowest. In this study, the high value of RI was primarily dependent on Cd risk, which was assigned a high biological toxicity factor. The extremely high ecological risk from Cd made a large contribution to the integrated potential risk in Cluster 4 (industrial). In contrast, the highest environmental risk based on mERM-Q in Cluster 4 (industrial) was associated with the large contribution from ERM-Q$_{Zn}$.

Based on RAC assessment, Cluster 3 (urban/ecological) posed the highest risk within the watershed, due to the high labile metal fraction (F1). The high risk indicated by RAC might be related to vehicle traffic in urban lands, which provides a readily labile source of metals accumulating in the F1 exchangeable fraction (Acosta et al., 2014).

4.3. Uncertainty analysis

According to simulation results, ecological risk estimated by Monte Carlo analysis was higher than detected results, demonstrated by the higher probability of high-priority risk. The uncertainty associated with the risk assessment metrics is mainly derived from spatial variation of metals at the watershed scale. The Monte Carlo simulation identified Cd as having largest uncertainty among the five metals examined in this study. This may result from the large spatial variation of Cd concentrations in sediments across the watershed ($CV = 296\%$). In contrast, little difference was found between the simulated and calculated groups for Zn. This contrasts with the fact that Zn had a moderate CV (108%) among the five metals. Based on the inconsistent relationship between the Monte Carlo uncertainty results and CV values, we infer that spatial variability in metal concentrations plays an important role in contributing to risk assessment variability at the watershed scale. In addition to metal concentration, Monte Carlo uncertainty simulation evaluated the geographical data distribution, which may therefore incorporate elements of spatial uncertainty. For the integrated mERM-Q assessment, the results were similar to that of Zn, which is attributed to the high value of ERM-Q_{Zn} and its disproportionate contribution to mERM-Q.

5. Conclusions

This study provided a comprehensive assessment of metal contamination and associated environmental risk from five metals (Cu, Zn, Pb, Cd and Cr) in surface sediments in the Wen-Rui Tang River watershed. The results generally showed that Cluster 4 (industrial) posed the highest risk based on total concentrations while Cluster 2 (urban) posed the lowest ecological risk. Risk assessment results diverged for the five metals according to the various metrics. Cd showed the highest risk from the calculation of E_r^{Cd}, while Zn was identified as the highest priority metal contaminant based on the SQGs method. According to RAC, Zn and Cd were determined to have extremely high environmental risk due to their high labile fractions, resulting in Cluster 3 (urban/ecological) having the highest ecological risk. Based on the Monte Carlo simulation, the risk of high priority (mERM-Q) was higher when compared with detected results. In conclusion, efforts to control and remediate extensive metal contamination in the Wen-Rui Tang watershed should focus on Zn and Cd. This comprehensive risk assessment provides vital information for risk assessment and remediation of metal contamination in surface sediments. Outcomes regarding food security and human health should focus on the worst-case scenario among the multiple assessment results to provide a margin of safety given their importance to human wellbeing.

Acknowledgements

This work was financially supported by the Science and Technology Project of Wenzhou (W20170019), Science Research Funding of Wenzhou Medical University (QTJ16011), and National Natural Science Foundation of China (41807495).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2018.11.078.

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