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Integrated source-risk and uncertainty assessment for metals contamination in sediments of an urban river system in eastern China

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ABSTRACT

Integrated source apportionment and risk assessment of metals is of great importance for contamination source control and remediation at the regional watershed scale. To identify metal sources and source-specific ecological risks, sediments were collected in the Wen-Rui Tang urban watershed for metal analysis. Risk assessment showed considerable and extremely high risk for Cu and Cd with large spatial variation. Positive matrix factorization model extracted three main sources with reasonable prediction efficacy for metal concentrations. Due to different toxicity coefficients for various metals, the low concentration contribution of source factor 2 (27.2%) contributed 83.7% of total risk, while a high concentration loading for factor 3 (40.8%) only contributed 4.6% to total risk. Predicted source-specific risk was similar to determined risk level for Cr, Ni and Pb; however, Cu and Cd were predicted with decreased risk, while Zn had increased risk. Triangular fuzzy number (TFN) coupled with stochastic simulation showed elevated trend in risk simulation for Cd and Cu when compared with determined risk. The uncertainties for risk evaluation appear to result from spatial variations in metal concentrations. Source apportionment and specific-risk assessment results suggest that different strategies may be required to address mitigation of elevated metal concentrations versus ecological risk.

1. Introduction

Metal contamination in urban aquatic ecosystems originates from various anthropogenic activities related to industrialization and urbanization, such as industrial/domestic wastewater, runoff/gas emissions and solid-waste disposal. Sediments receive metal contaminations from the overlying water column (dissolved and particulate forms) and act as a source/sink of metals in aquatic ecosystems (Fan et al., 2020; Ge et al., 2021). Many studies have reported metal pollutions and sources in aquatic ecosystems worldwide, such as Dongting Lake in China (Long et al., 2020), Mediterranean coast in Egypt (Keshta et al., 2020) and Lake Wigry in Poland (Kostka & Leśniak, 2020). Due to the lack of effective removal pathways in riverine sediments, metals tend to accumulate over time thereby increasing toxicological risks in aquatic sediments. Risks to benthic aquatic organisms and humans occur when sediment metals are released to the water column or transferred to food web where they are subject to bioaccumulation/biomagnification (Geffard et al., 2007).

Metals are systemic toxicants known to induce multiple organ damage, even at low levels of exposure (Tchounwou et al., 2012). Long-term exposure to toxic metals causes cell injury and inflammation, which may lead to nervous system and brain trauma (Zhao et al., 2018). Adverse impacts of metal contamination have been reported worldwide and affect millions of humans (Wang et al., 2015). Several studies have demonstrated ecological and health risks of metal pollution in recent decades. For example, Santos et al. (2020) investigated long-term metal contamination in sediments of the Guadiamar River basin (Spain) and found decreasing risk due to lower total metal concentrations and an increasing incorporation into the residual metal fractions; Jafarabadi et al. (2020) investigated toxic metals in the sediment cores of Persian Gulf and found decreasing contamination and risk trend towards the bottom due to anthropogenic activities. Thus, to support aquatic

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ecosystem risk management and pollution remediation, it is necessary to understand the spatial metal distribution, identify pollution sources and evaluate the associated risks of metals in aquatic sediment.

Metal contamination mainly originates from anthropogenic activities and comprises various sources such as industry, mining/smelting, agriculture, coal burning and traffic (Men, et al., 2020). Multiple methods are applied to qualitatively investigate metal source apportionment, which include correlation analysis, principal component analysis and regression (Yang et al., 2019; Zhao, et al., 2019). For example, Fei et al. (2019) employed a synthesis model using Bayesian Maximum Entropy theory and Geographically Weighted Regression to determine that Cd contamination in Shanghai soils was mainly derived from agricultural activities while Cr originated from natural sources; Principal component analysis-multiple linear regression extracted 4 factors for soil heavy metals in a electroplate factory area (Duan et al., 2020). These methods can capture common characteristics of potential sources; however, they cannot specifically quantify contributions originating from different sources.

Positive matrix factorization (PMF), a typical quantitative receptor model, has distinct advantage of non-negative constraint in identifying source categories and apportioning corresponding contributions for priority contaminants and remediation strategies (Yang et al., 2019), which has been widely applied for source apportionment of metal contamination in the atmosphere, sediment and soil (Jorquera & Barraza, 2013; Wang et al., 2020; Lv, 2019). contamination prevention For example, a modified PMF approach was used for source apportionment of metals in agricultural soil in Tianjin (China) where it identified irrigation and atmospheric deposition as the two main pollution sources having contributions of 26.6% and 19.6%, respectively (Wu et al., 2020); Duan et al. (2020) showed better prediction of soil heavy metals by PMF model than that of principal component analysis-multiple linear regression (PCA-MLR) due to mathematical constraints in PCA-MLR method. Previous studies have addressed source apportionment and quantify contributions from various sources; however, few have attempted to evaluate contributions for related risks when carrying out metal source apportionment using receptor models like PMF, especially for integrated estimation for a link between source apportionment and risk assessment. An integrated evaluation incorporating source apportionment and risk assessment using quantitative model is expected to address source-specific risk evaluation. This approach allows prioritization of source control and establishes effective risk mitigations based on the potential risk of each source.

Risk assessment is widely applied to evaluate ecological/health risks for metal contamination (Deng et al., 2020; Liu et al., 2020). Potential ecological risk assessment model (PER) is commonly utilized to evaluate sediment ecological risk for metal pollution. For example, Zhang et al. (2019) demonstrated high spatial variability among metals, with most sampling sites displaying moderate ecological risk and four sites having extremely high risk for Cd in Subei Shoal (China) sediments. Risk evaluation in conventional PER is dependent on metal concentrations and serves as the basis for ecological risk categorization (Caballero-Gallardo, et al., 2020). However, metal concentrations show large spatial uncertainty, especially at the watershed/regional scale due to inherent spatial heterogeneity, sampling limitations and analytical error (Liu et al., 2006; Yan et al., 2019). This uncertainty can result in considerable bias (underestimation/overestimation) for risk evaluation based on limited sampling for metal concentrations at the watershed scale (Mukherjee et al. 2020).

The objectives of this study are to: (i) develop an integrated source-specific risk approach incorporating source apportionment and ecological risk estimation; (ii) quantify contributions from different source categories to metal concentration and source-specific risk; (iii) evaluate the uncertainty in risk assessment by comparison of calculated and simulated results. Our previous study focused on spatial distribution and quantitative source apportionment for metal content (Xia et al., 2018). This study emphasizes both the link and difference of contributions for specific sources in metal concentrations and related ecological risks. In addition, the integrated uncertainty assessment is expected to address the limitation, accuracy and further implication for risk assessment. Results of this study is expected to provide systematic and integrated information on metal contamination sources and source-specific risks to guide metal pollution remediation and risk management at the watershed/regional scale.

2. Material and methods

2.1. Study area and sampling sites

This research was conducted in the urban Wen-Rui Tang River watershed, which is located in the rapidly industrializing city of Wenzhou, East China. The Wen-Rui Tang River has a drainage area of 740 km^2 and a river network of 1178.4 km. The river system plays an important role in irrigation, drainage, aquaculture, transportation and industrial water supply, thereby making an important contribution to the local economy. The industrial structure of small workshops in Wenzhou used to make essential contribution to local economy. However, distributed workshops produced a great deal of untreated waste water containing mass contaminants and have been discharged directly into native river system due to a lack of effective source control and legislative regulations, resulting in metal accumulation in sediments.

We selected 39 sites within the river system for surface sediment collection (range: 120°35′E ~ 120°47′E, 27°55′N ~ 28°2′N) and these sites were coordinated with provincial and municipal sites for water quality monitoring (Fig. 1). Surface samples (0–15 cm) were collected from mid-channel in March 2017 using a clamshell bucket sampler; three samples were collected, mixed and subsampled to obtain a single composite sample for each site. The well-mixed samples were sealed in clean polyethylene bags, transferred to the laboratory and stored at −80 °C. Samples were freeze-dried and ground to pass a 18-mesh nylon sieve in preparation for chemical analysis.

2.2. Metal analysis

Sediments were digested by a mixed acid (HNO_3-HCl-HF-$HClO_4$) for total metal determination (Jaworska et al., 2020). Total Cu and Zn contents in the digested extracts were determined by atomic absorption spectrometry (PinAAcle 900, Perkin-Elmer), while total Pb, Cd, Cr, Co, and Ni in the digested extracts were determined by inductively coupled plasma mass spectrometry (Agilent 8800 ICP-MS, Agilent Technologies). The GBW-07312 reference sediment was used (Chinese Academy of Geological Sciences) for quality control; recoveries for total metal were 89 ~ 107%. Duplicate samples were analyzed for all samples and had a relative standard deviation of ± 5%.

2.3. Positive matrix factorization

Positive matrix factorization (PMF) is a typical receptor models that is widely applied for pollution source apportionment (Dash et al., 2020; Saggu & Mittal, 2020). The original pollution data array is factorized into two matrices using the PMF model (Norris et al., 2014):

$$x_{nm} = \sum_{k=1}^{p} g_{nk} f_{km} + e_{nm}$$

wherex_{nm} is the total metal content matrix; n is nth sample; m is metal m; g_{nk} is kth contribution to the sample; f_{km} is the factor profile matrix; and e_{nm} is residual error matrix. The PMF model sets non-negative constraints for contributions and factor profiles.

To minimize the residual matrix and satisfy the optimal solution for obtaining the optimum number of source factors, object function Q was calculated to determine a minimum value (Capozzi et al., 2018):

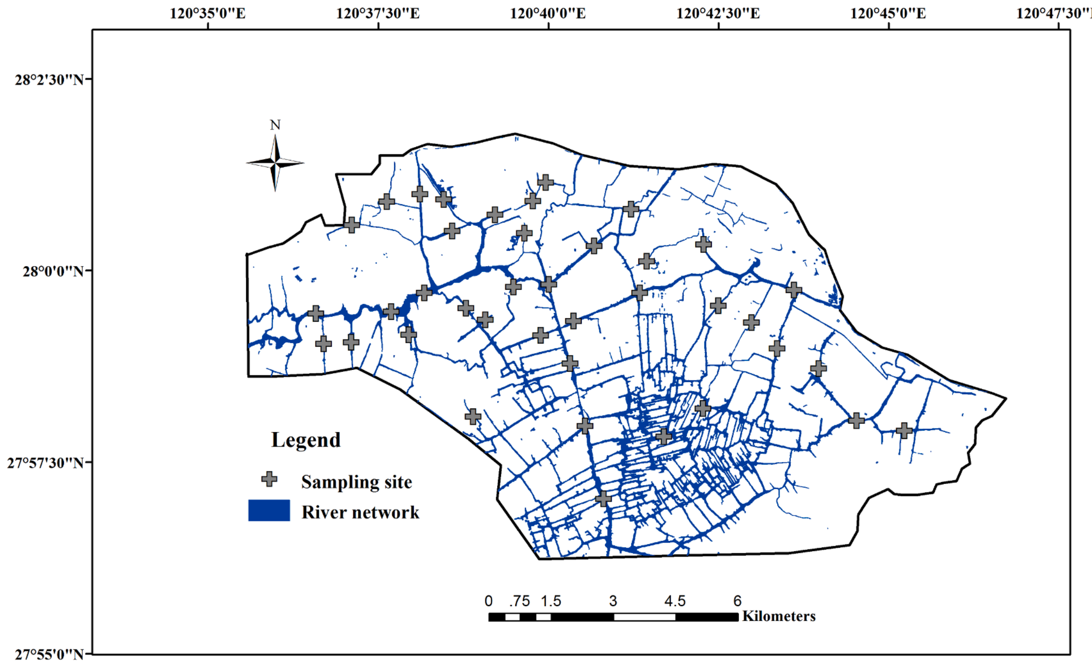

Fig. 1. The location of sampling sites (n = 39) in the Wen-Rui Tang River watershed.

$$\mathrm{Q} = \sum_{n=1}^{i}\sum_{m=1}^{j}\left(\frac{e_{nm}}{u_{nm}}\right)^2$$

where u_{nm} is the uncertainty for metal m for sample n, calculated as:

$$u_{nm} = \begin{cases} \frac{5}{6} \times MDL & x_{nm} \leq MDL \\ \sqrt{(\sigma_m \times x_{nm})^2 + (0.5 \times MDL)^2} & x_{nm} > MDL \end{cases}$$

where σ_m is the relative standard deviation for metal m.

We used PMF software from USEPA (ver. 5.0) (http://www.epa.gov) to quantify metal sources in the Wen-Rui Tang watershed.

2.4. Potential ecological risk assessment

Potential ecological risk index (PER) is used to evaluate metal ecological risk and the nth metal is calculated as (Hankson, 1980):

$$E_n = \frac{c_m}{b_m} \times t_m$$

where c_m and b_m are the concentrations of metal m in sample and background; t_m is the biological toxicity factor of metal m. Potential ecological risk is classified into five categories according to calculated E_n values (Negahban et al., 2021): low ($E_n < 40$), moderate ($40 \leq E_n < 80$), considerable ($80 \leq E_n \langle 160$), high ($160 \leq E_n \langle 320$), and very high ($E_n \geq 320$).

In this study, PMF result is incorporated with PER to achieve source-specific ecological risk, as well as quantitative contribution for risk assessment from each source.

2.5. Uncertainty analysis for risk assessment

Due to insufficient information and inaccuracies in sampling/analytical methods, there is inevitably uncertainty within risk assessments (Liu et al., 2006). We used the triangular fuzzy number (TFN) method to determine uncertainty information for risk assessment. A fuzzy number A is within real number field R, and its membership function is defined as (Yang et al., 2018):

$$\mathrm{A} = \begin{cases} 0 & x < a_1 or x > a_3 \\ \frac{x - a_1}{a_2 - a_1} & a_1 \leq x < a_2 \\ \frac{a_3 - x}{a_3 - a_2} & a_2 \leq x < a_3 \end{cases}$$

a_1, a_2 and a_3 are all real numbers and $a_1 \leq a_2 \leq a_3$. a_1, a_2 and a_3 are the lower, expected and upper value of the fuzzy number A. They are defined as follows:

$$a_1 = Max(\bar{x} - 2\sigma, minx), a_3 = \bar{x}, a_3 = Min(\bar{x} + 2\sigma, maxx),$$

where $\bar{x}$ and σ are the average and standard deviation of data x.

Then the triangular fuzzy number function was transformed as follows to obtain the probability density function for simple calculation:

$$f_{\mathrm{A}}(x) = \begin{cases} 0 & x < a_1 or x > a_3 \\ \frac{2(x - a_1)}{(a_2 - a_1)(a_3 - a_1)} & a_1 \leq x < a_2 \\ \frac{2(a_3 - x)}{(a_3 - a_2)(a_3 - a_1)} & a_2 \leq x < a_3 \end{cases}$$

An inverse transformation was used to provide stochastic simulation of × values, which were related to metal concentrations in this study. The possible values for metal concentration × were as follows:

$$x = \begin{cases} a_1 + \sqrt{[u(a_2 - a_1)(a_3 - a_1)]}\, u \leq \frac{a_2 - a_1}{a_3 - a_1} \\ a_3 - \sqrt{[(1 - u)(a_3 - a_2)(a_3 - a_1)]}\, u > \frac{a_2 - a_1}{a_3 - a_1} \end{cases}$$

where u belongs to the uniform random number [0, 1]. In this study, a Monte Carlo method was used for stochastic simulation of uniform random numbers for [0, 1] by Crystal Ball software (Oracle Inc. USA, version 11.1). Then stochastic simulation of metal concentrations for × values can be obtained. Finally, simulated potential ecological risk was calculated according to E_n and compared to determined values to assess risk uncertainty in this study.

3. Results and discussion

3.1. Metal concentrations and potential ecological risk (PER) assessment in sediments

Mean and median concentrations of metals in riverine sediment all exceeded local soil background concentrations in this region (Table S1). Relative to background concentrations, mean and median concentrations were highest for Cd (~100 × times and ~ 10 × times, respectively), followed by Zn and Cu (~10 × times and ~ 5 × times, respectively) and Pb, Cr and Ni (both 2 ~ 3 × times). The coefficient of variation (CV), reflecting the spatial variations of metal concentrations was greater than 200% for Cd and Cu, indicating some extreme 'hot spots' for these metals in the study region. The summary indicates that riverine sediments in the Wen-Rui Tang watershed were heavily contaminated by metals.

Based on total metal concentrations, potential ecological risks (PER) were assessed. The overall PER values for Cu, Zn, Pb, Cd, Cr and Ni in the riverine sediments ranged as 5–779, 2–70, 5–84, 60–55338, 2–10, and 5–30, respectively (Fig. 2). E_{Cr} and E_{Ni} values were all<40, indicating low risks for these two metals. For E_{Pb}, 38 of the 39 samples were identified as low risk and a single sample showed moderate risk. Zn was similar Pb with only 2 samples showing moderate risk. Cu had 28 sites with low risk, 10 with moderate risk and 1 site with very high ecological risk. All site showed moderate to very high risk for Cd, and more than half were identified as very high risk. The mean values for PER ranked as follows: Cd (3121.0) > Cu (47.4) > Pb (15.0) > Zn (12.5) > Ni (11.9) > Cr (4.4).

The combined metal concentration statistics and risk assessment results identified Cd as severely contaminated rendering it a priority for risk management. Although Zn was detected with high concentrations in sediment, it was classified by PER as low risk due to its low biological toxicity coefficient. This is similar to the findings of Fang et al. (2019) that found high Zn concentrations showed low risk in an urban watershed. Cu was identified with high contamination and showed moderate risk in the study region. Although, Cu concentration was much lower than Zn, it was assigned a moderate toxicity coefficient of 5, which resulted in a higher risk than Zn. Combined with previous spatial investigation of metal distribution (Xia et al. 2018), the primary sources of metal pollution in the Wen-Rui Tang watershed were identified as industrial wastes and wastewater derived from electroplating, printing/dyeing, and chemical and synthetic leather manufacturing. Research has demonstrated that industrial emissions are a dominant source of metal contaminations in riverine sediments worldwide (Tian et al., 2020; Lopes et al., 2014). The high CV value for metals, especially for Cd and Cu with high risk factors, strongly implicated anthropogenic activities as the source of metal contamination (Laribi et al., 2017).

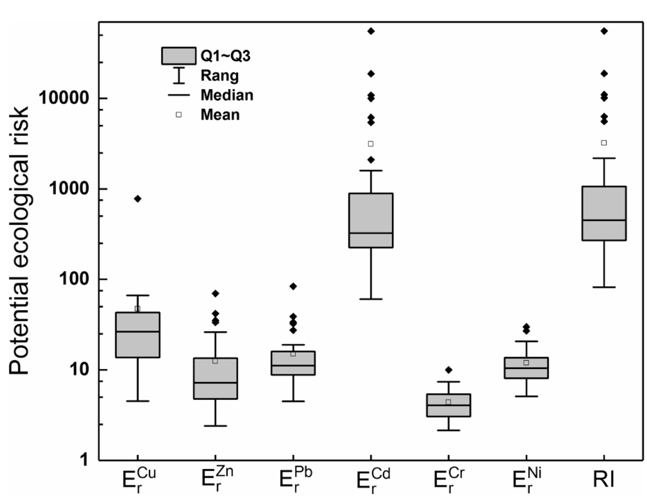

Fig. 2. Potential ecological risk for metals in sediment.

3.2. Source apportionment for metal concentrations and ecological risk by PMF model

The PMF model was used to predicate metal concentrations and model efficacy was assessed by comparing predicted versus measured metal concentrations. The r^2 coefficient between measured and predicted concentrations ranged from 0.521 to 0.999, indicating a reasonable prediction ability of the PMF model (Table 1). Cd, as the most prominently contaminated metal in riverine sediments, was determined with an r^2 coefficient of 0.999, which was followed by Cu (0.961), Zn (0.895), Pb (0.883), Ni (0.563), and Cr (0.521). These r^2 coefficients are similar to the results from previous studies using PMF model for metal concentration prediction (Yang et al., 2019; Kolakkandi et al., 2020). Combined with the pollution levels and risk assessment results, metals identified with high pollution levels and risks had a stronger predictability in the study region. This was similar with Hu et al. (2020), who found high Cd concentrations in sediments showed high r^2 with predicted values by the PMF model. As a result, the PMF model was deemed applicable for metal contamination prediction in the Wen-Rui Tang watershed.

We extracted three optimal factors with minimum Q value characterizing the metal pollution sources by PMF and the factor contributions to each metal are summarized in Fig. 3. Overall, Factor 1, 2 and 3 accounted for 32.0%, 27.2% and 40.8% of the metal contents in the riverine sediments (Table 2). Factor 1 was dominant for Cu (74.1%) along with an appreciably contribution for Zn (42.5%) and lower contributions for Pb, Cr and Ni (~20.0%). Notably, only a 6.5% proportion of Factor 1 was identified for Cd concentration. Factor 2 was dominantly loaded by Cd and the contribution reached more than 90%. In contrast, Factor 2 showed only ~ 6% loading for Cr and Ni concentrations. Lead, Cr and Ni showed a predominant loading on factor 3 with proportions exceeding 50%. We interpret the metal source contributions for Factor 1 as originating from agricultural sources, while Factor 2 showed a stronger relationship to industrial source, as our previous result showed similar spatial distribution between source factors and land use in this region (Xia et al., 2020). Due to the low contaminations and risk levels for Cr and Ni, we speculate that the Factor 3 related source is from a mixture of natural and traffic (Dong et al., 2019). More detailed information about PMF input/output and source profiles in the study area is available in Xia et al. (2020).

Factor contributions to potential ecological risk (PER) were different from contributions to metal concentrations by the PMF factors (Table 2). Factor 2 was the dominant contribution to risk comprising 83.7% of the total contribution, while it only contributed 27.2% to metal concentrations. In contrast, Factor 1 and Factor 3 contributed only 11.7% and 4.6% to ecological risk, respectively. Notably, Factor 3 provided the largest contribution to metal concentration (40.8%), but the lowest contribution to ecological risk (4.6%).

Based on PMF results, the predicted risk was calculated and compared to determined risks (Fig. 2 and Table S2). The determined versus predicted risks for Cr, Ni and Pb were consistent; Cu, Zn and Cd showed some difference. Predicted risk for Cu was reduced due to an

Table 1
Linear regression results for concentrations of selected metals by Positive Matrix Factorization.

Heavy metal	r^2	Intercept	Slope
Cu	0.961*	−0.176	0.984
Zn	0.895	−90.624	0.976
Pb	0.883	21.354	0.654
Cd	0.999	−0.033	1.023
Cr	0.521	79.837	0.505
Ni	0.563	38.671	0.465

* An outlier (~30 × mean value) was excluded in the regression.

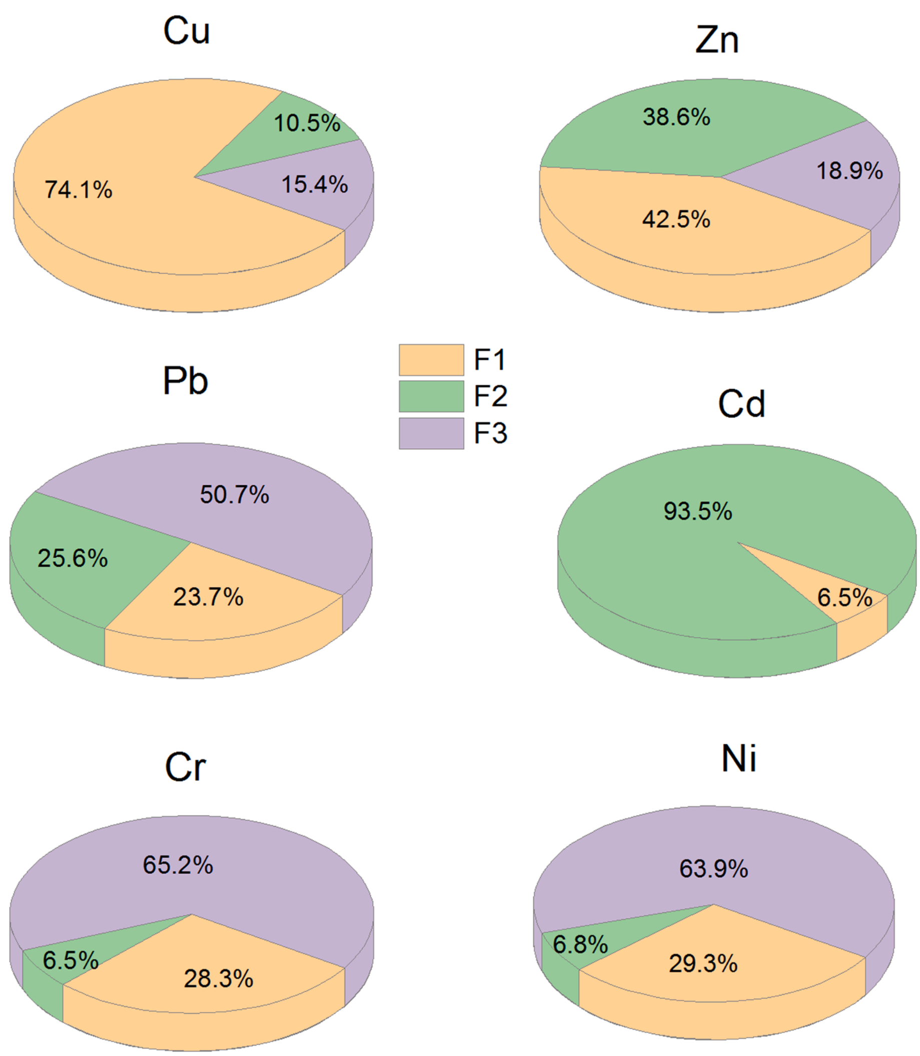

Fig. 3. Contributions from three extracted factors by PMF model for various metals.

Table 2
Source contributions to metal concentrations and potential ecological risk in riverine sediments (%).

	Factor 1	Factor 2	Factor 3
Metal concentrations	32.0	27.2	40.8
Potential ecological risk	11.7	83.7	4.6

appreciable underestimation for one site having very high risk. Similarly, one site determined to have very high risk for Cd was predicted to have high risk based on the PMF model. The risk level for Zn was increased due to one site receiving an elevated risk level, from moderate to considerable.

Spatial distribution of predicted PER values providing a useful tool for prioritizing metal pollution remediation (Fig. 4). Medium risk was predicted for Cu in the southwest portion of the watershed, while the remaining region displayed low risk. Notably, the spatial variation in PER values showed some differences compared to the spatial distribution in Cu concentration. An extremely high Cu concentration (5092 mg kg^{-1}) was identified at Site B18, but the model predicted concentration was reduced to 346.5 mg kg^{-1}, resulting in the difference between concentration and predicted risk distribution. Only a single site showed moderate/considerable predicted risk for Pb/Zn in the southwest portion, and the remaining showed low risks. There was low risk for Cr and Ni predicted across the entire study region. In contrast, a large portion of the watershed received high to very high predicted risk for Cd. The relatively high toxicity coefficient assigned to Cd was the primary basis for its high risk in the watershed.

Due to the contrasting metal toxicity coefficients, the high proportion of source Factor 1 (32%) and Factor 3 (40.8%) for metal concentrations showed a contrastingly low contribution to ecological risk (11.7% and 4.6% respectively). In contrast, while Factor 2 (27.2%) demonstrated a low contribution for metal concentration, it was the dominant contribution to ecological risk (83.7%). For example, Factor 2 showed a predominant contribution to Cd, which was assigned a high toxicity coefficient (30), resulting in the high contribution for predicted ecological risk (Fig. 3). In contrast, Factor 3 made significant contributions to Pb, Cr and Ni concentrations, but the low toxicity coefficients for these metals lead to a low contribution of Factor 3 for the predicted ecological risk. These results were similar to Yang et al. (2020), who identified low contributions for metal concentration but high contributions to total cancer risk due to Cd. When combined with our previous work (Xia et al., 2018), Zn and Cu were determined to display severe contamination within the Wen-Rui Tang watershed, but only presented moderate risks in the western portion based on PMF prediction. As a result, special attention should focus on source control for reducing both metal concentrations and ecological/human risks from different metal sources. The PMF model results for source apportionment provide an effective tool to facilitate determination of appropriate predictive metrics at the watershed scale.

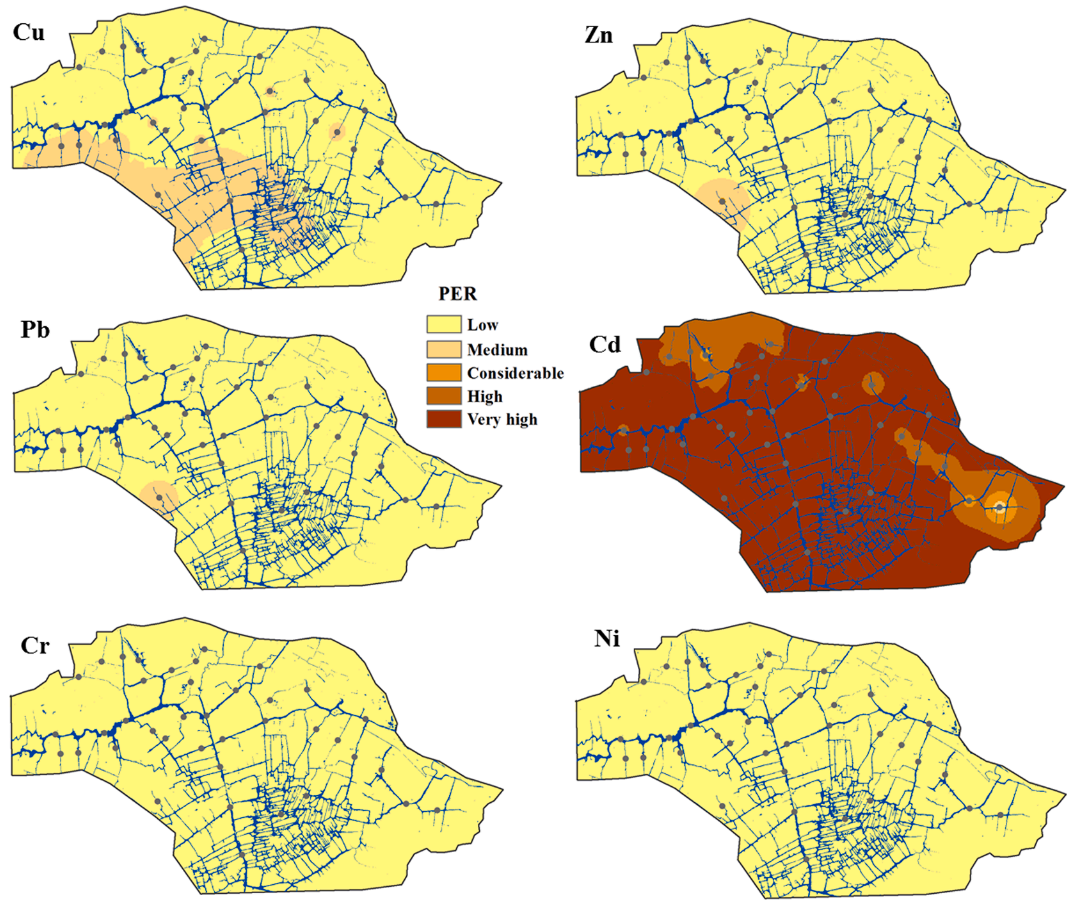

Fig. 4. Spatial distribution of predicted potential ecological risk (PER) for metals in riverine sediments from PMF model.

Our previous studies have quantitatively showed metal sources in the Wen-Rui Tang watershed and also evaluated the regional ecological risks. These studies revealed various metal origins and each contribution to metal pollutions in sediments. However, these results can provide little reference for reasonable risk assessment and management according to the contribution to metal content. The integrated source-risk assessment in this study is a supplement for metal source apportionment in regional scale to better understand source originated ecological risks.

3.3. Uncertainty analysis for ecological risk assessment

Due to inevitable sampling and analytical limitations/errors, the measured metal concentrations were parsed into concentration intervals by TFN to reduce uncertainty in risk assessment (Table 3). The fuzzification of metal concentrations were stochastically simulated by Oracle Crystal Ball software with 100,000 Monte Carlo simulation to acquire convergent results. The PER analysis using TFN-simulated ecological risk was compared with determined result (Table S3). Cr and Ni, which were identified with low risk, showed little difference between determined and TFN simulated results. The simulated and determined mean values for Zn all showed low risk; however, the simulated maximum value for Zn (39.2) indicated low risk while the determined maximum value implied moderate risk. A similar inconsistency occurred for Pb with the determined maximum value classified as considerable risk while the simulated risk was moderate. Although, determined and simulated showed similar extremely high ecological risk levels for Cd showed, the statistics showed some uncertainty for Cd. As showed in Table S3, mean and median values for ecological risk was highly elevated after TFN simulation. A considerable difference was identified for Cu, with the determined mean and median values identified as moderate and low risk, respectively, compared to considerable risk based on the simulated values. Similarly, the determined maximum Cu value was identified as very high risk compared to a simulated high risk.

The frequency distribution for each risk level was further analyzed for each metal (Table 4 and Fig. 5). Overall, the integrated ecological risk level for investigated metals by TFN simulation followed: Cd > Cu > Pb ≈ Zn = Cr = Ni. Zn, Pb, Cr and Ni were simulated with low risk, due to their dominance of values falling in the low risk level. Cu was

Table 3
Triangular fuzzy numbers for metal concentrations in riverine sediments of the Wen-Rui Tang River watershed (mg kg^{-1}).

Metal	Sample	Background
Cu	(29.5, 310.1, 1899.3)	32.7
Zn	(263, 1362, 4285)	109
Pb	(34.5, 115.3, 326.3)	38.4
Cd	(0.34, 17.7, 123.8)	0.17
Cr	(94.2, 192.7, 345.3)	88.1
Ni	(38.1, 89.0, 167.8)	37.4

Table 4
Potential ecological risk evaluation results for TFN simulation.

Metal	Percentage for each risk level (%)(low, moderate considerable, high, very high)	Category
Cu	(10.3, 26.1, 39.3, 24.3, 0)	considerable
Zn	(100, 0, 0, 0, 0)	low
Pb	(99.4, 0.6, 0, 0, 0)	low
Cd	(0, 0, 0, 0.1, 99.9)	very high
Cr	(100, 0, 0, 0, 0)	low
Ni	(100, 0, 0, 0, 0)	low

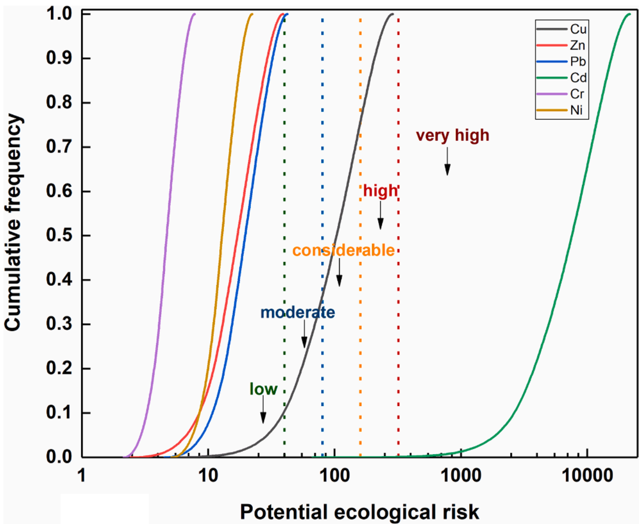

Fig. 5. Potential ecological risk simulated by TFN method for metals in riverine sediment of the Wen-Rui Tang watershed.

simulated with a 10.3%, 26.1%, 39.3%, and 24.3% distribution among the low, moderate, considerable and high risk categories. Based on a simple calculation (percentage × risk level threshold) for each metal risk category, Cu was categorized as considerable risk by TFN simulation. Cd was unique among metals showing 99.9% proportion at very high risk, leading to a very high risk level by TFN simulation.

The ecological risk for Cu and Cd were elevated after TFN simulation, demonstrating some uncertainty in the risk assessment for these two metals. This uncertainty may be associated with the high spatial variation (CV) of Cd (300%) and Cu (257%). In contrast, the remaining metals had similar risk frequency distributions between determined and simulated risk, as well as much lower spatial variability in metal concentrations (CV = 44 ~ 107%). This indicates that the uncertainty for ecological risk assessment is primary related to the large spatial variation of metal concentrations within the watershed. Researchers have reported that the spatial variability can be affected by intrinsic and extrinsic factors, leading to uncertainty in risk assessment (Liu et al., 2006; Zhao et al., 2020). Although, none to low ecological risk was simulated for Zn throughout the watershed, risk management for metal pollution hotspot is still needed, along with considerations for differences in metal fractions that affect metal bioavailability to organisms.

3.4. Limitation and prospect

Metal in sediments are complex due to its spatial and temporal migration process from various sources to sediments, which are both controlled by natural and anthropogenic activities. Based on metal contents in sampling sites, this study incorporated the PMF model and PER risk assessment to explore source specific ecological risk for watershed scale. These results help to understand the spatial variation of source originated risk, as the supplementary of source apportionment for metal concentrations. However, the limited observations seem inadequate for spatial source originated risk. Thus, regional emission inventory is of great importance to demonstrate the accuracy of spatial distribution from source-specific risk assessment by the PMF model. In addition, long-term monitoring is in need to have insight into temporal variation for source specific risk, which would prove efficiency of environmental policy and metal pollution management.

4. Conclusions

PER analysis for sediments in the Wen-Rui Tang watershed demonstrated variable levels of metal contamination risk, with Cd identified as having extremely high ecological risk. The PMF model provided reasonable predictions for metal concentration and three main source factors were extracted as Factor 1 (32%, agricultural source), Factor 2 (27.2%, industrial source) and Factor 3 (40.8%, a mixture source of nature and traffic). However, the source-specific risk evaluation results were inconsistent with the source contribution factors for metal concentration; risk contribution factors were Factor 1 (11.7%), Factor 2 (83.7%) and Factor 3 (4.6%). Cd showed a 93.5% loading on Factor 2 for concentration and was assigned a high toxicity coefficient, resulting in an 83.7% contribution to total potential ecological risk. The predicted source-specific risk from the PMF model showed similar levels with determined risk for Cr, Ni, and Pb. However, Cu and Cd had decreased predicted risk, while Zn had increased predicted risk. Source-specific risk for Cr, Ni, Zn and Pb showed similar spatial distributions with low risk. In contrast, predicted results for Cd showed extremely high risk throughout most of the watershed. Cu was identified with moderate risk in the southwest portion of the watershed with the remaining region having a low risk. TFN simulated results for Cr and Ni were similar to determined risks, and were consistent with the PMF predicted result. In contrast, the large spatial variation associated with Cu and Cd resulted in TFN simulated risks showing some inconsistency with determined results. These differences highlight potential uncertainties with metal risk assessment at the watershed scale. Results from this integrated specific-risk analysis provide important information for prioritization of metal source control and remediation at the watershed scale.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catena.2021.105277.

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