Total nitrogen and pH-controlled chemical speciation, bioavailability and ecological risk from Cd, Cr, Cu, Pb and Zn in the water level-fluctuating zone sediments of the Three Gorges Reservoir

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ABSTRACT

We investigated the distribution and chemical speciation of Cd, Cr, Cu, Pb and Zn in the water level-fluctuating (WLF) zone of the main stream (MS) and tributaries (ZX and MX) of the Three Gorges Reservoir. We evaluated the ecological risk and pollution level from heavy metals based on the Potential Ecological Risk Index (RI), Risk Assessment Code (RAC), and Ratio of Secondary Phase and Primary Phase (RSP). Our results indicated that the total and bio-available heavy metal contents were higher in the tributaries than in the MS. Moderate pollution from Cd and light pollution from Pb were observed both at the MS and ZX sites, whereas the MX site exhibited a pattern of heavy Cd pollution and light Cr and Pb pollution. In our study area, the results indicated that Cd exhibited a higher ecological risk than did the other heavy metals. Finally, the pH and nitrogen content of sediments may play a key role in controlling the amount of heavy metal bioavailability, further inducing a higher potential ecological risk.

1. Introduction

Heavy metals are non-biodegradable and bioaccumulative and have been closely studied in recent decades [1,2]. The WLF zone of reservoirs plays a key role as an interface between terrestrial and aquatic ecosystems. The WLF zone of the Three Gorges Reservoir Area (TGRA) covers more than 400 km² [3]. Due to periodic water fluctuation in the riparian zone, fast turnover rates of nutrients and heavy metals have been observed [4]. Following the manipulation of the water storage regimen, the WLF zone of the TGRA commonly exhibits a dry period followed by a period of flooding from October to April of the following year [5]. Therefore, when the riparian zone was used as agricultural land during the dry period, the period of flooding that followed resulted in a potential risk from the use of improper fertilizer rates during the dry period [6]. The heavy metals associated with fertilizer use accumulate in the sediment of the riparian zone during the dry periods and are released into the water during the flooding period. This periodic fertilizer-based heavy metal loading in the sediment has been observed since 2003 in fluctuating water levels between 145 and 175 m [7]. Thus, there is a potential risk of heavy metals in the TGRA riparian zone that could detrimentally affect the water quality.

Currently, numerical methods to estimate the potential risk from heavy metals in the sediment of the riparian zone have been reported, such as the Enrichment Factor [7], the Index of Geo-accumulation [8] and RI [9]. However, these risk assessment methods have been based only on the total heavy metal content. Thus, including the available content of individual heavy metals into ecological risk assessments is necessary. As previous studies have shown, the potential ecological risk from heavy metals is positively correlated with their effective chemical speciation [10]. Thus, evaluating the contribution of various chemical fractions from heavy metals requires a reliable ecological risk assessment approach. Therefore, available heavy metal-based methods have been developed, e.g. the RAC and RSP [11–13]. These assessment methods relate the free ion [12] and sediment surface to the weakly bound phase of heavy metals [13–15].

Therefore, the aim of the current study was to estimate the ecological risk from heavy metals in the riparian...
(0–10 cm) sediments were collected from the WLF zone during the dry season (Figure 1).

2.2. Pre-treatment and analytical procedures

The soil samples were sieved through a 1-mm mesh filter after removing plant residues and were then air-dried at room temperature and stored in a brown glass bottle. Then, 0.5 g samples were digested in a microwave oven (Mars-5, CEM Co., Matthews, NC, USA) with an acid mixture (9 ml of 14.0 M HNO₃, 3 ml of 11.7 M HCl, 2 ml of 23.0 M HF and 2.5 ml of 8.8 M H₂O₂) and then condensed to 1–2 ml for total metal analysis on an inductively coupled plasma mass spectrometer (Agilent Technologies Co. Ltd., USA). The speciation of metals, including acid-soluble (F₁), reducible (F₂), oxidisable (F₃) and residual (F₄) metals, was conducted with a modified BCR [13]. Quality control was assured by using a reference material (GSS-14, from Chinese Environmental Monitoring Center) that was analysed in the same way as the samples in both duplicate and parallel. The duplicates exhibited a difference of <9%, and satisfactory recoveries were obtained for Cd (94–105%), Cu (96–106%), Pb (98–104%), Cr (95–99%) and Zn (95–102%).

Organic matter (OM) was determined by using the modified Walkley–Black procedure [16]. The pH was analysed in deionized water extracts (1:2.5 w/w). The cation

2. Materials and methods

2.1. Study sites and sampling

The present study was carried out on the Yangtze River’s Wanzhou Section (MS) and its two tributaries, called ZX and MX (N30.85372° – 30.80282°, E108.33517° – 108.44072°) in the northeastern Chongqing municipality in China (Figure 1). The WLF zone typically comprises bench terraced valley slopes that were previously used as farmland. The region is characterized by a north subtropical humid monsoon climate with an average annual temperature of 18.2 °C, average annual precipitation of 1053.15 mm, average annual effective solar radiation of between 3600 and 3700 MJ/m², and average annual sunshine duration of approximately 1400 h. Surface

![Figure 1. Geographical distribution of the study sampling sites.](image-url)
exchange capacity (CEC) was determined using the bar-
ium chloride method adjusted to the pH [17]. The total N
was determined using the Kjeldahl method [18].

2.3. Risk assessment
The RSP, RAC and RI methods were used to assess the
potential ecological risk from, and bioavailability of,
heavy metals [11–13].

2.4. Statistical analysis
A two-way ANOVA was used to determine the differences
in the heavy metal contents and their risk among the
three study areas. All of the statistical analyses and the
correlations between heavy metals were performed by
using IMB SPSS Statistics for Windows version 20.0 at a
significance level of 0.05.

3. Results and discussion
3.1. Edaphic factors and the total heavy metal
content
Edaphic factors are important for the bioavailability of
heavy metals. As shown in Table 1, the physicochemical
characteristics in MS, ZX and MX were as follows:
the SOM content was 64.24 ± 6.01a, 65.04 ± 4.08a, and
68.11 ± 6.25a g·kg⁻¹; the TN content was 0.28 ± 0.06a, 0.41 ± 0.09b, and 0.40 ± 0.03b g·kg⁻¹; and the TP was
0.28 ± 0.06a, 0.41 ± 0.09b, and 0.40 ± 0.03b g·kg⁻¹, respectivel
compared. With the two tributaries, the
MS had low SOM and TN, with a higher pH and CEC.
The sediment particle size composition indicated that clay < silt < sand in the three study areas, and the propor
portion of sand was higher in the tributaries than in MS.
The higher TN in MX and ZX might result from the accu
mulation of aquatic organisms and terrestrial plant
residues on a gentler sloping floodplain in the WLF zone
of the tributaries [19]. The lower CEC in the tributaries
might result from the higher proportion of sand in the tributaries [20].

The descriptive statistics of the heavy metals in the
WLF zone of the MS and its tributaries (ZX and MX)
exhibited a distinct change (Table 2). The Cd, Cr, Cu, Pb
and Zn contents varied between 4.58 and 6.47, 91.23
and 137.93, 18.38 and 18.50, 125.96 and 137.36, 85.68
and 91.93 mg/kg, respectively, and their average con
ents were 5.85, 114.76, 18.43, 133.34 and 89.66 mg/kg,
respectively. The heavy-metal background values from
Sichuan were used as reference values [21]. The contents
of Zn, Cr, Pb and Cd were 1.04, 1.45, 4.32 and 73.13-
fold higher than the background values, respectively.
The pattern of increase in the total Cd, Cr, Zn and Pb
contents across the three study sites was MX > ZX > MS,
whereas, for total Cu, it was MS > ZX > MX. The aver-
genent contents of Cd, Cr, Cu, Pb and Zn in the WLFZ of
MX were 6.47, 137.93, 18.38, 137.36 and 91.93 mg/kg,
respectively, which were higher than those in the other
two regions. The gently sloping tributaries had more
farming activities than MS [22]. The water flow in the
tributaries was also much slower, which could lead to
heavy metal accumulation [23].

3.2. Heavy metal fractions in the WLFZ sediments
As shown in Figure 2, both Cu and Zn were predomi
antly associated with the residual fraction (F₄), whereas
a relatively higher proportion of Cu bound to F₄ occurred in
the MS than in its tributaries. By contrast, a higher propor
ion of Zn bound to F₄ occurred in the tributaries than in the MS. Pb was mainly bound to both the oxi
disable (F₅) and residual fraction (F₄), which exhibited
no significant difference between MS and its tributaries.
By contrast, a higher proportion of Cd existed in the
acid-soluble fraction (F₅), which was more prevalent in
the tributaries than in the MS. The complexity of the
heavy metals with the dissolved organic matter [24,25]
and redox conditions influenced by water fluctuations.
Thus, Cd transformation was mainly controlled by pH and TN. For Cr, F1 and total content were negatively correlated with pH and CEC \((p < 0.05)\). The F2 and F3 fractions were negatively correlated with TN and pH \((p < 0.05)\). The F4 fraction was positively correlated with TN \((p < 0.05)\). Thus, the controlling factor for Cr transformation was TN.

For Cu, the F1 and F3 fractions were negatively correlated with pH \((p < 0.01)\), whereas the F2 and F3 were positively correlated with TN \((p < 0.01)\). Furthermore, the total Cu content was negatively correlated with TP \((p < 0.05)\). Therefore, TP has a strong impact on Cu transformation.

For Pb, the F2 fraction was correlated with pH and TN, whereas the F3 fraction was correlated with pH, organic matter and TN \((p < 0.05)\). F4 was negatively related with pH, and the total Pb was positively correlated with TN \((p < 0.05)\). Given that the main fractions of Pb were F3 and F4, pH, organic matter and TN mainly affected the transformation of Pb.

For Zn, the F1 and F2 fractions were negative correlated with TN, whereas F3 was positively correlated with both organic matter and TN \((p < 0.05)\). The F4 fraction of Zn had no correlation with any of the above-mentioned factors.

We found that the heavy metal fractions and their release were controlled by the pH and TN content. The pH is believed to be the key factor affecting the speciation of heavy metals [31]. Laboratory simulation has shown that exotic heavy metals are mostly bonded to oxides under alkaline conditions and onto organic matter in acidic conditions in soil [32]. The pH is positively correlated with the reducible fraction \((F_2)\) of heavy metals [32]. Wang et al. found that, with increasing pH, the speciation of heavy metals in sludge was transformed to oxidisable and residual fractions [33]. However, the negative correlation between pH and the oxidisable fraction reported in the current study are contrary to those of Wang et al. This was probably caused by microbial processes that occur

### Table 3. Relationship between the heavy metal fractions and physicochemical characteristics.

| Element | pH | OM | TN | TP | CEC  |
|---------|----|----|----|----|------|
| Pb-F1   | 0.40 | −0.16 | 0.08 | −0.27 | 0.57** |
| Pb-F2   | 0.50* | −0.35 | −0.52* | −0.13 | 0.29 |
| Pb-F3   | −0.46* | 0.48* | 0.55** | 0.04 | −0.27 |
| Pb-F4   | −0.48* | 0.21 | 0.30 | 0.20 | −0.35 |
| Pb-total | −0.38 | 0.31 | 0.52* | 0.01 | −0.10 |
| Cd-F1   | −0.49* | 0.40 | 0.56* | 0.23 | −0.33 |
| Cd-F2   | 0.48* | −0.47* | −0.50* | −0.31 | 0.41 |
| Cd-F3   | −0.59** | 0.33 | 0.68** | 0.31 | −0.19 |
| Cd-F4   | 0.26 | −0.12 | 0.29 | 0.03 | 0.45* |
| Cd-total | −0.45* | 0.35 | 0.63** | 0.24 | −0.21 |
| Cr-F1   | −0.52* | 0.37 | 0.42 | 0.23 | −0.46* |
| Cr-F2   | 0.23* | −0.21 | −0.65** | 0.00 | −0.12 |
| Cr-F3   | −0.48* | 0.32 | 0.66** | 0.25 | −0.26 |
| Cr-F4   | −0.22 | 0.16 | 0.46* | −0.08 | 0.03 |
| Cr-total | −0.51* | 0.35 | 0.41 | 0.22 | −0.46* |
| Cu-F1   | −0.61* | 0.45 | 0.52* | 0.22 | −0.36 |
| Cu-F2   | 0.41 | −0.38 | −0.68* | −0.17 | 0.19 |
| Cu-F3   | −0.67* | 0.29 | 0.60* | 0.32 | −0.06 |
| Cu-F4   | 0.29 | 0.14 | −0.22 | −0.35 | 0.27 |
| Cu-total | 0.05 | −0.24 | 0.08 | −0.49* | 0.49* |
| Zn-F1   | 0.57** | −0.29 | −0.48* | −0.22 | 0.36 |
| Zn-F2   | 0.41 | −0.35 | −0.56* | −0.16 | 0.32 |
| Zn-F3   | −0.48* | 0.47* | 0.46* | −0.07 | −0.34 |
| Zn-F4   | −0.21 | 0.44 | 0.39 | 0.03 | 0.41 |
| Zn-total | 0.09 | 0.37 | 0.08 | −0.16 | −0.29 |

\(p < 0.05\); \(p < 0.01\).

Figure 2. Heavy metal fractions in the WLFZ sediment.

3.3. The factors influencing the distribution of heavy metal fractions

The relationships between heavy metal contents and physicochemical characteristics (pH, SOM, TN, TP, and CEC) in the WLF zone are shown in Table 3. For Cd, F1, F2, F3 and the total content were significantly correlated with pH and TN \((p < 0.05)\). The F1 fraction was negatively correlated with OM \((p < 0.05)\), whereas the F4 fraction was positively correlated with CEC \((p < 0.05)\). The F1 fraction was the major speciation of Cd. Thus, Cd transformation was mainly controlled by pH and TN.

For Cr, F1 and total content were negatively correlated with pH and CEC \((p < 0.05)\). The F2 and F3 fractions were negatively correlated with TN and pH \((p < 0.05)\). The F4 fraction was positively correlated with TN \((p < 0.05)\). Thus, the controlling factor for Cr transformation was TN.

For Cu, the F1 and F3 fractions were negatively correlated with pH \((p < 0.01)\), whereas the F2 and F3 were positively correlated with TN \((p < 0.01)\). Furthermore, the total Cu content was negatively correlated with TP \((p < 0.05)\). Therefore, TP has a strong impact on Cu transformation.

For Pb, the F2 fraction was correlated with pH and TN, whereas the F3 fraction was correlated with pH, organic matter and TN \((p < 0.05)\). F4 was negatively related with pH, and the total Pb was positively correlated with TN \((p < 0.05)\). Given that the main fractions of Pb were F3 and F4, pH, organic matter and TN mainly affected the transformation of Pb.

The F1 and F2 fractions of Zn were negative correlated with TN, whereas F3 was positively correlated with both organic matter and TN \((p < 0.05)\). The F4 fraction of Zn had no correlation with any of the above-mentioned factors.

We found that the heavy metal fractions and their release were controlled by the pH and TN content. The pH is believed to be the key factor affecting the speciation of heavy metals [31]. Laboratory simulation has shown that exotic heavy metals are mostly bonded to oxides under alkaline conditions and onto organic matter in acidic conditions in soil [32]. The pH is positively correlated with the reducible fraction \((F_2)\) of heavy metals [32]. Wang et al. found that, with increasing pH, the speciation of heavy metals in sludge was transformed to oxidisable and residual fractions [33]. However, the negative correlation between pH and the oxidisable fraction reported in the current study are contrary to those of Wang et al. This was probably caused by microbial processes that occur
Metals can be dissolved and transformed into acid-soluble fractions, resulting in an increase in the mobility and bioavailability of heavy metals [36,37]. In addition, the oxidizable and residual fractions of heavy metals can form from the chelation, complexation, adsorption, and ion exchange of all the humification products during the microbial processes of the organic carbon and nitrogen cycles [38–40]. In addition to pH, TN is also a controlling factor of the heavy metal fraction and mobility.

### 3.4. Potential ecological risk

The RI was assessed to illustrate the potential risk caused by heavy metal pollution in sediments and the sensitivity of various organisms to toxic substrates. Cd seriously polluted the sediments and had a much greater potential ecological risk than the other heavy metals (Table 4). The RI values of the study sites were ranked as follows: MX > ZX > MS. A similar pattern was also found by Lin [8].

The RAC results indicated that the percentages of the exchangeable and carbonate fractions of Cu and Zn were less than 10% for all of the study areas. Thus, both Cu and Zn had low ecological risk over the whole study area (Figure 3). Pb and Cr had RACs between 10 and 30%, and thus, exhibited medium ecological risk in ZX and MS. By contrast, in MX, the RAC value of Pb was less than 10%, which represents a low risk, whereas the value of Cr was between 30 and 50%, representing a high risk. Moreover, the RAC values of Cd in ZX and MX were higher than 50%, representing an extremely high risk, as did the Cd RAC of 42% in MS.

In general, the calculated mean K\textsubscript{RSP} values of the heavy metals were ranked as follows: Cd > Pb > Cr > Zn > Cu, where Cd had the highest K\textsubscript{RSP} value of 2.8, which suggests that the sediments studied were seriously polluted by Cd (Figure 4). The average values of K\textsubscript{RSP} for Pb and Cr...
were 1.5 and 1.3, respectively, representing a medium degree of pollution. However, the mean $K_{\text{RSP}}$ values of Zn and Cu were less than 1, indicating that Zn and Cu were not polluting. Furthermore, the mean $K_{\text{RSP}}$ values from Cd in the study areas were ranked as follows: MX > ZX > MS. The mean $K_{\text{RSP}}$ value from Cr in MX was higher than in MS and ZX. Meanwhile, the $K_{\text{RSP}}$ value of Pb in ZX was the highest among the three study areas.

The MX is an important tributary of the Yangtze River’s Wanzhou sections and covers a basin area of 4.71 km$^2$. The population of this area has gradually increased to 0.05 million, and the river passes through the city centre. Thus, a huge volume of wastewater from increasing industrial activities drains into the river in MX [42]. Furthermore, the slow water flow may also be decreasing the diffusion of heavy metals [43,44]. Therefore, the geographical distribution of heavy metals around the river indicated that the anthropogenic sources of heavy metals contributed a higher fraction of the heavy metal pollution in sediment around the WLFZ. The Cr of the $F_2$ fraction also exhibited an increasing trend in MX. This indicated that the $F_2$ fraction of both Cd and Cr in the tributaries exhibited a higher potential risk of transforming from a solid phase into a liquid phase. A similar phenomenon was also reported in a recent study by Chen [45]. The reducible fraction ($F_1$) of Cd and Cr could be transformed to an acid soluble fraction ($F_A$) due to submerged conditions and higher organic matter inputs into the tributaries [28,46]. The organic matter could be gradually degraded into small-molecule organic acids, resulting in the dissociation of a reducible fraction of heavy metals [47].

4. Conclusions

In summary, the total contents of Cd, Cr, and Pb were ranked in the following decreasing order: MX > ZX > MS. The pollution levels from heavy metals followed a ranking of Cd > Pb > Cr > Zn > Cu. Among these heavy metals, Cd, Cr, and Pb were considered to pose a serious threat to residents’ health and to the aquatic ecosystem because they accounted for a significant proportion of the non-residual fractions. The pollution from Cd was higher, and Cr and Pb were relatively low in MX, whereas the MS and ZX only received moderate pollution from Cd, and light pollution from Cr. The pH and TN in the sediments were the core factors affecting the transformation of these heavy metals. Furthermore, RI and RAC revealed that Cd was the primary pollutant and determined that it had the highest risk among the heavy metals evaluated. Overall, the risk levels in the study areas from heavy metals were ranked as follows: MX > ZX > MS. Therefore, due to wastewater inputs and the slow water flow, accumulation of heavy metals in the surface sediments may occur. Thus, the potential ecological risk from the fluctuating water level zone should play a key role in the water level management of the Yangtze River tributaries in the Wanzhou section.

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Disclosure statement

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