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Human and Ecological Risk Assessment: An International Journal

ISSN: 1080-7039 (Print) 1549-7860 (Online) Journal homepage: http://www.tandfonline.com/loi/bher20

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**Cr and Ni in sediments of Three Gorges Reservoir**

# Distribution and potential eco-risk of chromium and nickel in sediments after impoundment of Three Gorges Reservoir, China

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**Abstract**

The impoundment of the Three Gorges Reservoir (TGR) altered the hydrodynamic conditions and would modulate the accumulation and behaviors of heavy metals in the sediments. In this study, the sediments from the riparian and submerged areas of the entire TGR mainstream were collected in 2014 to investigate the spatial distribution of chromium (Cr) and nickel (Ni), and to assess their contamination state and potential eco-risk to aquatic environment by multiple


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indices. Results showed that the concentrations of Cr and Ni in the sediments increased towards the dam. The concentrations of Cr were significantly higher in the riparian sediments than in the submerged sediments, whereas the Ni concentrations were comparable. The relatively high storages of Cr and Ni in the sediments existed near the dam. The sediment physiochemical properties and local human activities controlled the spatial variations of Cr and Ni in the sediments. Currently, the TGR sediments were not heavily contaminated by Cr and N and showed low eco-risk. Nevertheless, considering the decrease in sediment loads from the upper Yangtze River and the rapid urbanization in the TGR catchment, much more attentions should be paid to the geochemical behaviors and the eco-risk of Cr and Ni in the sediments.

**Key words**

Heavy metals; spatial distribution; eco-risk; sediments; Three Gorges Reservoir



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## 1 INTRODUCTION

The rapid industrialization and urbanization with the increasing population have discharged large amounts of heavy metals in aquatic ecosystems through direct industrial discharge, city sewage, agricultural and domestic run-off, and so on (Järup, 2003; Bing et al., 2011; Gao et al., 2016b). Chromium (Cr) and nickel (Ni) are essential micronutrients for the proper functions of living organisms, whereas they will exert toxic effects on biota and human health when reaching an acceptable concentration. The anthropogenic Cr is generally from industrial processes including chrome plating, dyes and pigments, leather tanning, and wood preserving (Kotaś and Stasicka, 2000). The main anthropogenic sources of Ni are emissions of metal processing operations and combustion fumes of coal and oil, and the applications of sludge and phosphate fertilizer are also important sources of Ni in water and soils (Gonnelli and Renella, 2013).

Riverine systems, especially the dam-constructed rivers, have been altered through impoundments and diversions due to the increasing demands on water resources. Dams are physical barriers that limit the natural transfer of water and decrease the water flow velocity. Consequently, the residence time of sediments increases, which will change the fates of heavy metals in riverine systems (Friedl and Wüest, 2002; Frémion et al., 2016). Sediment is a major sink of heavy metals in the riverine systems. The particle-reactive metals in water will eventually be incorporated into the bottom sediment (Han et al., 2015a, b). The construction of dams favors the accumulation of heavy metals in sediments through the continuous sediment deposition


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(Frémion et al., 2016). However, the sediment physicochemical conditions (e.g., temperature, pH, solid/liquid ratio, redox conditions, and biological effects) may be altered with various environmental changes related to reservoir management. This can affect the mobilization and transformation of heavy metals in the sediments (Foster and Charlesworth, 1996; Sin et al., 2001), and thus cause potential threat to aquatic biota and human health.

Various methods have been widely applied to assess the contamination of heavy metals in the sediments, including the index of geoaccumulation ($I_{geo}$), enrichment factor (EF), contamination index ($P_i$), potential eco-risk ($E_r^i$), etc. (Muller, 1969; Hakanson, 1980; Bricker, 1985; Varol, 2011; Bing et al., 2013). These indices can not only evaluate the contamination level and potential eco-risk of heavy metals in the sediments, but also reflect the anthropogenic contribution after the anthropogenic metal sources are well-defined. Multivariable statistical analysis, such as principal component analysis, cluster analysis, and correlation analysis, screens the elements with the similar properties or sources, which has been used to reveal the natural and anthropogenic contributions to heavy metals in sediments (Mamat et al., 2016). Therefore, it is necessary to apply multiple methods to assess heavy metal contamination by human activity in the sediments.

The Three Gorges Reservoir (TGR) is the world largest hydroelectric project. It covers a total water surface area of $1.08\times10^3$ km$^2$ and a storage capacity of 39.3 billion m$^3$ when the water level reaches 175 m above sea level (a.s.l.) (Bao et al., 2015). The water-level fluctuation zone, with

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the area of 349 $km^2$, was formed after the full anti-seasonal operation of the TGR in 2010. After the impoundment, approximately 70% of sediment discharge from the upper reaches of the Yangtze River was trapped in the TGR (Yang et al., 2006), and the initial distribution of the sediments has changed markedly (Hu et al., 2013). Moreover, the contents of suspended particles and heavy metals in the water column decreased towards the Three Gorges Dam (TGD) (Ding et al., 2013; Gao et al., 2016b). The TGR operation alters the transportation and distribution of heavy metals in the sediments.

In recent years, as the significant influences of the TGR region in the local and downstream water safety, more attentions have been paid on the sediments contamination and its effect on water environment. However, these studies were mainly carried out in the soils and sediments of some tributaries and also several reaches of the TGR (Ye et al., 2011; Li et al., 2015; Han et al., 2015a; Han et al., 2015b), and lacked the investigation of the temporal and lager spatial variation and storage of heavy metals in the sediments. In addition, these studies highlighted the most toxic metals (cadmium, lead, etc.), and ignored other metals like Cr and Ni (Han et al., 2015b; Bing et al., 2016). Therefore, in this work, the entire TGR mainstream was selected to analyze the concentrations of Cr and Ni in the riparian and submerged sediments. The main objectives are: 1) to investigate the spatial distribution and storages of Cr and Ni in the sediments; 2) to decipher the main factors modulating the accumulation of Cr and Ni; and 3) to assess the contamination and potential eco-risk of Cr and Ni by multiple indices.

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## 2 MATERIALS AND METHODS

### 2.1 Study Area

The Three Gorges Reservoir (29°16′-31°25′N, 106°20′-111°50′E) is located between Jiangjin District, Chongqing Municipality, and Zigui County, Hubei Province, the upper reach of the Yangtze River (Fig. 1). The climate in the TGR region is mainly controlled by the humid subtropical monsoon. The mean annual temperature and mean annual precipitation are 16-19°C and 1000-1200 mm, respectively.

A unique geomorphological unit, the water-level fluctuation zone, is formed after the full operation of the TGR in 2010 with water level of 175 m a.s.l. in summer and 145 m a.s.l. in winter (Bao et al., 2015). The information about the water-level fluctuation zone has been introduced in details by Tang et al. (2016). The fluctuant backwater zone (FBZ, from Jiangjin (S1) to Changshou (S5)) and the permanent backwater zone (PBZ, from Changshou (S5) to Zigui (S23)) depend on the water level fluctuation (Wu et al., 2016).

### 2.2 Sample Collection

Twenty-three sites in the riparian zone and eight sites in the submerged area were selected to collect the surface sediments in July-August 2014 (Fig. 1, Table S1). At each riparian site, three sediments profiles were hand-dug, and the sediments from 0 to 30 cm in each profile were collected and mixed for one sample in the field. Given the sediment depositions were small in


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Wushan (S20), Badong (S21), and Zigui (S22-23), the surface riparian sediments in 0-10 cm were collected. It was difficult to collect the submerged sediment due to the coarse texture in the FBZ. Therefore, only eight sites in the PBZ were chosen to collect submerged sediment cores. Three sediments cores were collected using a gravity sampler (length: 100 cm, φ 6 cm) at each site. The water depth was more than 30 m at all core sediments sampling sites. Each core was directly sliced, and the top 30 cm were kept with a plastic sheet. All samples were kept at 4°C in the laboratory before the analysis.

**2.3 Chemical Analysis**

The sediment sample (ca. 0.5 g) for grain size analysis was successively pretreated with 10 mL of 30% $H_2O_2$ over 24 h to remove organic matters and with 5 mL of 5% HCl for 10 min to remove carbonates. The grain size (Clay: <4 μm; Silt: 4-64 μm; Sand: >64 μm) was determined using a Mastersizer 2000 laser diffraction granulometer.

The content of sediment organic matters was determined by loss on ignition (LOI), consisting of burning 1 g sediment sample for 4 h at 550°C in a muffle furnace. The sediment pH was measured in a 1:2.5 sediments/water suspension using a glass electrode and a potentiometer (HACH Co., HQ30d, U.S., with the accuracy of 0.01 pH).

The sediment samples for analysis of major and trace elements concentrations were digested with HCl-$HNO_3$-HF-$HClO_4$. The concentrations of Al, Ca, Fe, Mg, Mn, K, and P were measured


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by an Inductive Coupled Plasma Atomic Emission Spectrometer (ICP-AES), and the concentrations of Cr and Ni were detected by an Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). The relative standard deviation was below 3% and 5% for ICP-AES and ICP-MS, respectively.

**2.4 Calculations**

The enrichment factors (EFs), geoaccumulation index ($I_{\mathrm{geo}}$), contamination index ($P_i$), and potential eco-risk index ($E_r^i$) of Cr and Ni in the sediments were calculated following previous researchers (Muller, 1969; Hakanson, 1980; Bricker, 1985; Varol, 2011). The storages of Cr and Ni in the sediments were calculated by the equation:

$$Q = S \cdot C \cdot 100 \quad (1)$$

where $Q$ is the storage of Cr and Ni in the sediments, $S$ represents the sediments loads (surface 30 cm or 10 cm based on the field sediment depth), and $C$ is the Cr and Ni concentration in the sediments.

**2.5 Statistical Analysis**

One-way ANOVA was performed to identify the significant differences of Cr and Ni concentrations and other variables in the sediments. Spearman correlation analysis was applied to establish the correlation of Cr and Ni with other parameters in the sediments. The statistical


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analysis was performed by the software SPSS 16.0 and Origin 8.0, and the distribution of Cr and Ni storages in the sediments were performed by ArcGIS 9.3.

## 3 RESULTS AND DISCUSSION

### 3.1 Sediment Physiochemical Properties

The riparian sediments in the FBZ were dominant by sand (60-78%), whereas those in the PBZ featured high silt contents (50-93%) (Fig. S1a). Silt, accounting for 59-92% of the total contents, dominated the grain size compositions in the submerged sediments (Fig. S1b). The contents of clay and silt in the riparian sediments increased towards the TGD, whereas the variations of the grain size compositions in the submerged sediments were not significant spatially. The spatial variation of the particle size in the riparian sediments reflected the changes of the hydrological regimes. Since the full impoundment of the TGR in 2010, the water flow velocity decreased and the residence time of the sediments was much longer (Bao et al., 2015; Tang et al., 2016), which facilitated the deposition of fine particles (Ding et al., 2013; Yuan et al., 2013; Gao et al., 2016b). However, the relatively stable hydrodynamic conditions in the PBZ did not induce significant variation of the grain size compositions in the submerged sediments.

The pH in the riparian sediments (mean ±SD: 8.04 ±0.3) was significantly lower than that in the submerged sediments (8.61 ±0.3) ($p < 0.05$). The spatial variation of pH was not marked in the riparian and submerged sediments except for several fluctuations at some sites (Fig. S1c, d).


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The LOI contents ranged between 0.49% and 6.43% (2.27 ±1.4%) in the riparian sediments and between 3.51% and 3.79% (3.64 ±0.1%) in the submerged sediments (Fig. S1c, d). Spatially, the higher LOI in the riparian sediments was observed at Yubei (S3), Changshou (S4), and the areas from Fengdu (S11) to Zhongxian (S16). In contrast, the spatial variation of the LOI was not significant in the submerged sediments.

The concentrations of major elements in the sediments are presented in Table 1. There were no significant differences in the concentrations of these elements (expect for Al) between the riparian and submerged sediments. However, compared with the submerged sediments, a larger variation range of the element concentrations was observed in the riparian sediments (see the SD). The concentrations of Al, Fe, K, Mn, and P in the riparian sediments showed an increasing trend towards the TGD with fluctuations, whereas those of Ca showed an opposite case generally (Fig. S2). The Mg concentrations in the riparian sediments did not display a marked spatial trend. However, in the submerged sediments, the concentrations of Ca, Mg and P showed marked high values at Wanzhou (S17) and Badong (S21), those of Fe, K, and Mn peaked at Wanzhou (S17), whereas those of Al were generally constant except the markedly lower concentration at Badong (S23) (Fig. S2).

**3.2 The Concentrations of Cr and Ni in the Sediments**

The concentrations of Cr were significantly higher in the riparian sediments than in the submerged sediments ($p < 0.01$), whereas no significant difference for Ni was observed between the riparian and submerged sediments ($p$ = 0.09). Specifically, the metal concentrations in the riparian sediments ranged between 62.0 and 129 mg/kg for Cr and between 25.3 and 54.5 mg/kg for Ni, with the means of 91.8 and 40.0 mg/kg, respectively. The concentrations of Cr and Ni in the submerged sediments varied between 80.6 and 98.1 mg/kg and between 39.8 and 50.5 mg/kg, with the means of 86.8 and 42.7 mg/kg, respectively (Table 2).

The concentrations of Cr and Ni in the TGR sediments were clearly higher than those in the upper continental crust. Compared with the existing sediment quality criteria in China and the world, the concentration of Cr exceeded the low contamination levels, and that of Ni was close to the low contamination threshold value. Furthermore, the concentrations of Cr and Ni were comparable to those in the suspended particles in the TGR, whereas they exceeded the concentrations in the purple soils of the TGR and the soils in Chongqing and China (Table 2). The differences indicated that after the impoundment of the TGR the Cr and Ni accumulated markedly in the sediments, which induced their contamination with different levels.

Spatially, no clear variation trend for Cr concentrations were found in the riparian sediments, and they were higher at Jiangjin (S1), Changshou (S5), Fuling (S11), Zhonxian (S15), Wanzhou (S17), Fengjie (S19), Wushan (S20), and Zigui (S22-23) (Fig. 2). A gradual increase trend of Ni in the riparian sediments was observed towards the TGD. Nevertheless, in the submerged sediments, the Cr and Ni concentrations showed the same variations, and the higher concentrations displayed at Wanzhou (S17).


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### 3.3 Factors Controlling the Distribution of Cr and Ni in the Sediments

The Cr and Ni concentrations of the riparian sediments revealed different spatial variations towards the dam (Fig. 2). A gradual increase trend for Ni in the riparian sediments was remarkable compared with Cr, which was mainly attributed to the decrease of grain size towards the TGD (Figs. 2b, S1). Fine particle plays an important role in the adsorption of trace metals in sediments due to the large surface area and high contents of clay minerals and metal oxides/hydroxides (Fernandes and Nayak, 2016). Clay minerals in the TGR region mainly consist of goeschwitzite, kaolinite, and chlorite, which featured high contents of Fe/Al oxides or hydroxides (He et al., 2011; Fan et al., 2012; Li et al., 2012, Yao et al., 2016). Compared with Cr, Ni showed much more significant correlation with Al, Fe, and silt in the riparian sediments (Table 3), indicating the Ni distribution in the riparian sediments was mainly controlled by the fine particles. However, the spatial variations of the Cr and Ni concentrations in the submerged sediments did not correlate with fine particles (Table 3). This was probably attributed to the transportation and mixture of the sediments after the impoundment of the TGR, which altered the initial grain size fractions of the sediments.

Except the grain size compositions, the anti-seasonal desiccation and rewet processes of sediments in the riparian zone affected the geochemistry cycles of Cr and Ni in the riparian sediments through changing the sedimentary environment (e.g., pH, redox condition). The positive correlation was only observed between Cr and pH in the riparian sediments (Table 3).

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This implied that the alkaline environment favored the enrichment of Cr in the riparian sediments. Moreover, Cr and Ni in the riparian sediments correlated significantly with Fe and Mn, whereas this was not observed in the submerged sediments (Table 3). The Fe and Mn are metals very sensitive to the changes of redox conditions in sediments (Foster and Charlesworth, 1996). The desiccation of the riparian sediments could induce the oxidization of Fe and Mn and form Fe/Mn oxides and/or hydroxides, which increased the absorption of Cr and Ni and then enriched them in the riparian sediments. On contrast, the rewet processes in the riparian zone changed the sedimentary environment from the oxidation to reduction conditions, which tended to release Cr and Ni from the sediments. In addition, the significant correlations among Ni, Cr, Ca, and Mg in the submerged sediments (Table 3) revealed that the Cr and Ni were probably from the rock stratum with high Cr and Ni contents in the karst area of the TGR region (Huang et al., 2009; Zhang et al., 2015).

The nonpoint source pollution was responsible for the spatial distribution of Cr and Ni in the sediments. The loss of P in the TGR region has been reported positively correlated with the amount of water and soil erosion (Shen et al., 2014), and thus the significant correlation between the heavy metals studied and P (Table 3) indicated the contribution of nonpoint source emissions to these metals in the sediments. On the other hand, the loads of agricultural pollution sources in the TGR region were markedly higher at Jiangjin, Fuling, Zhongxian, Wanhou, and Fengjie (Xiao et al., 2014), which was coincident with the spatial distribution of Cr and Ni in the


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sediments (Fig. 2). In addition, the correlation of Cr and Ni with P in the riparian sediments was much more significant than that in the submerged sediments (Table 3). This further confirmed that the particles from the local nonpoint pollution source under the impacts of bank soil erosion and runoff enriched Cr and Ni in the riparian zone.

The local industry inputs increased the accumulation of Cr and Ni in the sediments. With the fast development of the economy in the TGR region, many industrial districts have been established along the Yangtze River, such as the areas of Jiangjin, Changshou, Zhongxian, and Wanzhou. According to the *Chongqing Statistical Yearbook* (http://www.cqtj.gov.cn), the total discharged waste water by Chongqing industry in 2013 was about 0.3 billion tons. The hotspots for the Cr accumulation emerged at Jiangjin (S1), Changshou (S5), Fuling (S11), Zhonxian (S15), and Wanzhou (S17). The dominant industries at Jiangjin (S1), Changshou (S5), and Fuling (S11) are machine-building industry, chemical industry, and so on, which features a large discharge of pollutants and a high concentration of Cr (Wu and Jiang, 2012; Fan and Luo, 2013). This revealed that human activities in the local catchment played a key role in the spatial variations of Cr in the riparian sediments (Fig. 2a). For Ni, the highest concentration in the riparian sediments appeared at Zigui (S22), and the lowest was at Changshou (S4). However, the hotspots of Ni were not remarkable at Jiangjin (S1), Changshou (S5), and Fuling (S11), indicating the different sources of Ni compared with Cr. In the submerged sediments, the spatial variations of Cr and Ni were also controlled by the local inputs, especially at Wanzhou (S17)


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where exists many industrial plants, such as the chemical industry, textile and garment industry, mechanical and electrical industry.

The temporal variation of the Cr and Ni concentrations in the sediments from 1985 to 2014 (Table S4) was closely related to the socioeconomic development of the TGR region. The annual industry and agriculture inputs in the TGR catchment have been increasing quickly since the impoundment in 2003 (Zhang et al., 2016). The longer water residence time facilitates the sediments deposition and the adsorption of Cr and Ni. The changes of hydrodynamic and sedimentary conditions after the operation of the TGR (Tang et al., 2016) further accelerated the accumulation of Cr and Ni in the sediments in recent years.

**3.4 The Storages of Cr and Ni in the Sediments**

The total storages of Cr and Ni in the riparian sediments were 2441 and 1106 tons, respectively (Fig. 3). Spatially, the storages of Cr and Ni in the riparian sediments were mainly distributed at Fuling (S11), Zhongxian (S15), Wanzhou (S17), and Yunyang (S18), accounting for approximately 80% of their total storages. The storages of Cr and Ni in the submerged sediments were 9545 and 4694, respectively. The higher storages were observed in the areas from Zhongxian (S16) to Zigui (S23).

The spatial distribution of Cr and Ni storages was mainly related to the variations of sediment inputs (Fig. 3, Table S3). After the impoundment of the TGR, the decreasing flow velocity and

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longer residence time of the water accelerated the deposition of sediments (Bao et al., 2015; Tang et al., 2016). Compared with other areas, the broader reaches with slow water flow and more gentle slopes from Fuling (S11) to Fengjie (S19) favored the accumulation of sediments in the riparian zones (Wang et al., 2016). This was the major reason for the high storages of Cr and Ni in the riparian sediments in these areas (Fig. 3a). However, the submerged sediments were mainly distributed in the reaches from Wanzhou (S16) to Zigui (S23) (Wu et al., 2012; Hu et al., 2013). Therefore, the storages of Cr and Ni were high from Wanzhou (S16) to Zigui (S23) in the submerged sediments.

**3.5 Contamination and Potential Eco-risk of Cr and Ni in the Sediments**

The concentrations of heavy metals are direct indicator of their pollution in the environment. The concentrations of Cr and Ni in the sediments of the TGR were clearly higher than those in the local and Chinese soils (Table 2). The concentration of Cr exceeded the low contamination level, but below the high contamination level according to Chinese, Hong Kong and French sediment quality guidelines, whereas it exceeded the high contamination levels according to the Canadian and US sediment quality guidelines. The pollution of Ni reached the low-moderate level based on the sediment quality guidelines.

The contamination and potential eco-risk states of Cr and Ni in the sediments of the TGR were assessed by the multiple geochemical indices (Fig. 4, Table S2). The EF values were in the ranges of 2.30 - 5.00 for Cr, and 1.90 - 2.90 for Ni. In general, the EF values of Cr and Ni in the


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sediments, higher than 1.5, indicated their marked enrichment. The $I_{geo}$ varied in values of 0.24 - 1.29 for Cr, and -0.24 - 0.86 for Ni. The $P_i$ was in the ranges of 0.70 - 1.40 for Cr, and 0.60 - 1.70 for Ni. Comprehensively, the values of $I_{geo}$ and $P_i$ revealed a low contamination level of Cr and Ni in the sediments of the TGR, though hotspots were observed at Jiangjin (S1), Changshou (S5), Zhongxian (S15), Wanzhou (S17), Fengjie (S19), and Zigui (S22) in the riparian sediments, and also at Wanzhou (S17) in the submerged sediments. Contrastingly, the EF, $I_{geo}$, and $P_i$ of Cr were higher in the riparian sediments compared with those in the submerged sediments, indicating that the local inputs increased the Cr contamination in the riparian sediments. Nevertheless, in comparison with the riparian sediments, the $I_{geo}$ and $P_i$ of Ni were higher in the submerged sediments. This probably resulted from the flushing of fine particles from the riparian zone to the submerged sediments by the rainfall in summer.

The $E_r^i$ levels of Cr and Ni in the riparian and submerged sediments were less than 40.0, which indicated the low eco-risk of Cr and Ni in the TGR sediments (Fig. 4, Table S2). The $E_r^i$ values of Cr and Ni were higher in the riparian sediments than those in the submerged sediments, which suggested that the desiccation and rewet processes of the riparian sediments would cause the potential release of Cr and Ni and then threat the ecological safety of the TGR. Spatially, the $E_r^i$ for Cr showed no clear spatial variations in both the riparian and submerged sediments, while the $E_r^i$ for Ni in the riparian sediments showed an increase trend. The increased $E_r^i$ for Ni was attributed to the increased Ni absorption ability of the fine particles towards the dam.

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## 4 CONCLUSIONS

After the impoundment of the TGR, the concentrations of Cr and Ni increased slightly. There was a spatially increasing trend in the Cr and Ni concentrations towards the dam. The concentrations and multiple geochemical indices of Cr and Ni in the sediments showed the higher enrichment levels from Zhongxian to Zigui. The storages of the Cr and Ni in the riparian sediments were mainly distributed in the reaches of from Fuling to Fengjie, whereas those in the submerged sediments were from Wanzhou to Zigui. Site-specific human activities (e.g., industrial sewage, agricultural pollution) in the catchment and sediment physiochemical properties, such as the grain size and Al/Fe/Mn oxides, notably had a marked impact on the Cr and Ni distribution in the sediments of the TGR. Since the reduction of sediments loads from the upper reaches of Yangtze River and the increasing inputs of contaminated sediments from local soil erosion and water loss, the geochemistry cycle of heavy metals in the sediments need to be further studied.

**Acknowledgments**

This work was supported by Key Laboratory of Mountain Surface Processes and Ecological Regulation, Chinese Academy of Sciences, Science and Technology Service Network Initiative of Chinese Academy of Sciences (KFJ-EW-STS-008), and Chinese Academy of Sciences (CAS "Light of West China" Program).

**References**

Bao Y, Gao P, He X, 2015. The water-level fluctuation zone of Three Gorges Reservoir-A unique geomorphological unit. Earth-Sci. Rev. 150, 14-24.

Bing H, Wu Y, Liu E *et al*., 2013. Assessment of heavy metal enrichment and its human impact in lacustrine sediments from four lakes in the mid-low reaches of the Yangtze River, China. Journal of Environmental Sciences 25, 1300-1309.

Bing H, Wu Y, Zhou J *et al*., 2016. Historical trends of anthropogenic metals in Eastern Tibetan Plateau as reconstructed from alpine lake sediments over the last century. Chemosphere 148, 211-219.

Bricker O P, 1985. Metals in the Hydrocycle . Eos, Transactions American Geophysical Union, 66(33), 593-593.

CCME, 1999. Canadian sediments quality guidelines for the protection of aquatic life: summary tables. Canadian Environmental Quality Guidelines. Canadian Council of Ministers of the Environment Winnipeg.

Chen H, Teng Y, Lu S *et al*., 2015. Contamination features and health risk of soil heavy metals in China . Sci. Total Environ. 512–513, 143-153.

 

Dai S, Lu X, 2014. Sediment load change in the Yangtze River (Changjiang): A review. Geomorphology 215, 60-73.

Ding T, Gao J, Shi G *et al.*, 2013. The contents and mineral and chemical compositions of suspended particulate materials in the Yangtze River, and their geological and environmental implications. Acta Geologica Sinica 87, 634-660. (in Chinese)

Dong J, Yang D, Zhou B *et al.*, 2006. Change of trace element contents of purple soil in the Three Gorges Reservoir region. Scientia Geographica Snica 26, 592-596. (in Chinese)

Fan D, Wang Y, Wu Y, 2012. Advances in provenance studies of Changjiang riverine sediments. Advances in Earth Science 27, 515-528. (in Chinese)

Fan X S, Luo H, 2013. Spatial and industrial distribution pattern of heavy metals emission in industrial waste water. China Environ. Sci. 33, 655-662. (in Chinese)

Fernandes M C, Nayak G N, 2016. Role of sediments size in the distribution and abundance of metals in a tropical (Sharavati) estuary, west coast of India . Arab. J. Geosci. 9, 1-13.

Foster I, Charlesworth S M, 1996. Heavy metals in the hydrological cycle: trends and explanation. Hydrol. Process. 10, 227-261.

 ACCEPTED MANUSCRIPT

Fernandes M C, Nayak G N, 2016. Role of sediment size in the distribution and abundance of metals in a tropical (Sharavati) estuary, west coast of India. Arabian Journal of Geosciences 9, 1-13.

Friedl G, Wüest A, 2002. Disrupting biogeochemical cycles - Consequences of damming. Aquat. Sci. 64, 55-65.

Gao J M, Sun X Q, Jiang W C *et al.*, 2016a. Heavy metals in sediments, soils, and aquatic plants from a secondary anabranch of the three gorges reservoir region, China. Environ. Sci. Pollut. Res. 23, 1-11.

Gao Q, Li Y, Cheng Q *et al.*, 2016b. Analysis and assessment of the nutrients, biochemical indexes and heavy metals in the Three Gorges Reservoir, China, from 2008 to 2013 . Water Res. 92, 262-274.

Gonnelli C, Renella G, 2013. Chromium and Nickel. Heavy Metals in Soils. Springer Netherlands, pp. 313-333.

Hakanson L, 1980. An ecological risk index for aquatic pollution control. A sedimentological approach. Water Res. 14, 975-1001.

 ACCEPTED MANUSCRIPT

Han L, Gao B, Wei X *et al.*, 2015a. The characteristic of Pb isotopic compositions in different chemical fractions in sediments from Three Gorges Reservoir, China. Environ. Pollut. 206, 627-635.

Han L, Gao B, Zhou H *et al.*, 2015b. The spatial distribution, accumulation and potential source of seldom monitored trace elements in sediments of Three Gorges Reservoir, China. Scientific reports 5.

He M, Zhang H, Huang X *et al.*, 2011. Clay mineral assemblages in the Yangtze drainage and provenance implications. Acta Sedimentologica Sinica 29, 544-552. (in Chinese)

Hu J, Yang S, Wang X, 2013. Sedimentation in Yangtze River above Three Gorges Project since 2003. Journal of Sediment Research, 39-40. (in Chinese)

Huang J, Chu X, Chang J *et al.*, 2009. Trace element and rare earth element of cap carbonate in Ediacaran Doushantuo Formation in Yangtze Gorges . Chinese Sci. Bull. 54, 3498-3506. (in Chinese)

Järup L, 2003. Hazards of heavy metal contamination. Brit. Med. Bull. 68, 167-182.

Kotaś J, Stasicka Z, 2000. Chromium occurrence in the environment and methods of its speciation . Environ. Pollut. 107, 263-283.

 ACCEPTED MANUSCRIPT

Li G, Xiao S, Wang Y *et al.*, 2012. Distributional characteristics of grain size and mineral composition in sediments of Yangtze River in Three Gorges Reservoir. Journal of China Three Gorges University (Natural Sciences) 34, 9-13. (in Chinese)

Li J, Zhou Q, Yuan G *et al*., 2015. Mercury bioaccumulation in the food web of Three Gorges Reservoir (China): Tempo-spatial patterns and effect of reservoir management. Sci. Total Environ. 527, 203-210.

Mamat Z, Haximu S, Zhao Y Z *et al*., 2016. An ecological risk assessment of heavy metal contamination in the surface sediments of Bosten Lake, northwest China. Environ. Sci. Pollut. Res. 23, 1-11.

Muller G, 1969. Index of geoaccumulation in sediments of the Rhine River. Geojournal 2, 108-118.

National Standard of China Marine Sediments Quality (GB18668-2002). Standards Press of China, 136 Beijing, 2002.

Peart M R, Fok L, Chen J, 2012. Sediments and water quality in the Kam Tin River, Hong Kong. International Association of Hydrological Sciences.

Reverey F, Grossart H, Premke K *et al.*, 2016. Carbon and nutrient cycling in kettle hole sediments depending on hydrological dynamics: a review. Hydrobiologia 775, 1-20.

 ACCEPTED MANUSCRIPT

Shen Z Y, Qiu J L, Hong Q, *et al.*, 2014. Simulation of spatial and temporal distributions of non-point source pollution load in the Three Gorges Reservoir Region. Sci. Total Environ. 493, 138-146.

Sin S N, Chua H, Lo W *et al.*, 2001. Assessment of heavy metal cations in sediments of Shing Mun River, Hong Kong . Environ. Int. 26, 297-301. (in Chinese)

Tang M, Yang C, Lei B, 2013. Spatial distribution investigation on the Water-Level-Fluctuating Zone slopes in Three Gorges Reservoir areas based on GIS. Environment and Ecology in the Three Gorges 35, 8-20. (in Chinese)

Tang Q, Bao Y, He X *et al*., 2016. Flow regulation manipulates contemporary seasonal sedimentary dynamics in the reservoir fluctuation zone of the Three Gorges Reservoir, China. Sci. Total Environ. 548-549, 410-420.

Tang Q, Bao Y, He X *et al*., 2014. Sedimentation and associated trace metal enrichment in the riparian zone of the Three Gorges Reservoir, China. Sci. Total Environ. 479–480, 258-266.

Taylor S R, McLennan S M, 1995. The geochemical evolution of the continental crust. Rev. Geophys. 33, 241-265.


ACCEPTED MANUSCRIPT

U.S. Environmental Protection Agency, 1995. Proposed Sediments Quality Criteria, In: Quality Assurance Technical Document 7 - Compilation of Sediments & Soil Standards, Criteria & Guidelines. The Resources Agency Department of Water Resource State of California.

Varol M, 2011. Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. J. Hazard. Mater. 195, 355-364.

Wang B, Wen A, Yan D, 2016. Factors influencing sedimentation in the riparian zone of the Three Gorges Reservoir, China. Science of Soil and Water Conservation 14, 12-19. (in Chinese)

Wei F, Yang Z, Jiang D *et al.*, 1991. Basic statistics and characteristics of the background values of soil elements in China. Environmental Monitoring in China 7, 1-6. (in Chinese)

Wu L, Long T Y, Cooper W J, 2012. Simulation of spatial and temporal distribution on dissolved non-point source nitrogen and phosphorus load in Jialing River Watershed, China. Environ. Earth Sci. 65, 1795-1806.

Wu W J, Jiang H Q, 2012. Equal standard pollution load of heavy metals from industrial wastewater in China. Environ. Sci. Technol. 35, 180-185.


ACCEPTED MANUSCRIPT

Wu Y, Wang X, Zhou J *et al.*, 2016. The fate of phosphorus in sediments after the full operation of the Three Gorges Reservoir, China. Environ. Pollut. 214, 282-289.

Xiao X, Ni J, He B *et al.*, 2014. Estimation of agricultural nonpoint source pollution loads and its regional differentiation in Chongqing section of the Three Gorges Reservoir Region. Journal of Basic Science and Engineering 22, 634-646. (in Chinese)

Yang Z, Wang H, Saito Y *et al.*, 2006. Dam impacts on the Changjiang (Yangtze) River sediment discharge to the sea: The past 55 years and after the Three Gorges Dam. Water Resour. Res. 42, 1-10.

Yao Q, Wang X, Jian H *et al.*, 2016. Behavior of suspended particles in the Changjiang Estuary: Size distribution and trace metal contamination. Mar. Pollut. Bull. 103, 159-167.

Ye C, Li S, Zhang Y *et al*., 2011. Assessing soil heavy metal pollution in the water-level-fluctuation zone of the Three Gorges Reservoir, China. J. Hazard. Mater. 191, 366-372.

Yuan J, Xu Q, Tong H, 2013. Study of sediment deposition in region of Three Gorges reservoir after its impoundment. Journal of Hydroelectric Engineering 32, 139-145. (in Chinese)


ACCEPTED MANUSCRIPT

Zhang L, Ji H, Gao J *et al.*, 2015. Geochemical characteristics of major, trace and rare earth elements in typical carbonate weathered profiles of Guizhou Plateau. Geochim. Cosmochim. Ac. 44, 323-336. (in Chinese)

Zhang T, Ni J, Xie D, 2016. Assessment of the relationship between rural non-point source pollution and economic development in the Three Gorges Reservoir Area. Environ. Sci. Pollut. Res. 23, 8125-8132.


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**Table 1** Physicochemical properties of the sediments in the TGR

| | Riparian sediment (n = 81) | | | | | Submerged sediment (n = 24) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | Median | MIN | MAX | SD | Mean | Median | MIN | MAX | SD |
| Al (mg/g) | 68.0 | 69.6 | 47.3 | 91.3 | 13.2 | 80.8 | 81.8 | 67.8 | 85.4 | 5.5 |
| Ca (mg/g) | 43.7 | 43.2 | 31.2 | 60.5 | 8.5 | 39.8 | 38.9 | 28.9 | 58.3 | 9.0 |
| Fe (mg/g) | 40.9 | 42.6 | 32.3 | 46.6 | 4.3 | 44.5 | 44.3 | 42.2 | 47.1 | 1.6 |
| K (mg/g) | 20.3 | 20.4 | 14.7 | 27.4 | 3.7 | 23.8 | 23.9 | 20.5 | 25.6 | 1.6 |
| Mg (mg/g) | 19.1 | 17.9 | 14.3 | 25.9 | 3.2 | 17.8 | 17.1 | 15.6 | 21.2 | 1.8 |
| Mn (mg/g) | 0.950 | 0.891 | 0.581 | 1.34 | 0.2 | 0.910 | 0.902 | 0.831 | 1.03 | 0.1 |
| P (mg/g) | 0.810 | 0.823 | 0.580 | 0.981 | 0.1 | 0.753 | 0.723 | 0.703 | 0.85 | 0.1 |
| Clay (%) | 9.28 | 5.61 | 1.00 | 31.3 | 8.7 | 23.5 | 24.5 | 19.5 | 27.2 | 2.9 |
| Silt (%) | 64.9 | 68.8 | 20.3 | 93.1 | 23.8 | 71.5 | 71.1 | 69.6 | 75.2 | 2.0 |
| Sand (%) | 25.7 | 15.4 | 2.26 | 78.4 | 26.9 | 4.93 | 3.96 | 3.15 | 10.6 | 2.5 |
| LOI (%) | 2.27 | 1.71 | 0.992 | 6.43 | 1.4 | 3.64 | 3.60 | 3.51 | 3.79 | 0.1 |


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| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| pH | 8.04 | 7.97 | 7.65 | 8.56 | 0.3 | 8.61 | 8.76 | 8.01 | 8.90 | 0.3 |


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**Table 2** Comparison of the concentrations of Cr and Ni in the sediments of the TGR with sediment quality guidelines around the world (Units: mg/kg)

| | | Cr | Ni | References |
|---|---|---|---|---|
| Riparian sediment (n = 81) | Range | 62.0-129 | 25.3-54.5 | This study |
| | Mean±SD | **91.8±19** | **40.0±8** | |
| Submerged sediment (n = 24) | Range | 80.6-98.1 | 39.8-50.5 | This study |
| | Mean±SD | **86.8±5** | **42.7±3** | |
| UCC | | 35 | 20 | Taylor and McLennan (1995) |
| TGR suspended particles | Range | 101-125 | 48-68 | Ding et al. (2013) |
| TGR purple soil | Mean | 67 | 33 | Dong et al. (2006) |
| Chongqing soils | Range | 60-91 | 25-45 | Chen et al. (2015) |
| | Mean | 76 | 34 | |
| China soils | | 61 | 26 | Wei et al. (1991) |

 

| | | | | |
|---|---|---|---|---|
| Chinese marine sediment quality crieria | Level 1 | 80 | -- | National Standard of China (2002) |
| | Level 2 | 150 | -- | |
| Canadian sediment quality guidelines | Level 1 | 37 | -- | CCME (1999) |
| | Level 2 | 90 | -- | |
| Hong Kong sediment quality critetia | Level 1 | 80 | 40 | Peart et al. (2012) |
| | Level 2 | 160 | 40 | |
| US sediment quality guidelines | Level 1 | 25 | 20 | U.S. Environmental Protection Agency (1995) |
| | Level 2 | 75 | 50 | |
| French sediment quality guidelines | Level 1 | 90 | 37 | Frémion et al. (2016) |
| | Level 2 | 180 | 74 | |

UCC: upper continental crust.


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**Table 3** Spearman correlation of Cr and Ni with sediment physicochemical properties

| **Riparian sediment (n = 81)** | **Sediment physicochemical** |
|---|---|
| Cr | pH$^{**}$, Fe$^{*}$, K$^{*}$, Mg$^{*}$, Mn$^{**}$, P$^{**}$, Ni$^{**}$, -Clay$^{*}$ |
| Ni | Al$^{**}$, Fe$^{**}$, K$^{**}$, Mn$^{**}$, P$^{**}$, Cr$^{**}$, Silt$^{**}$, |
| **Submerged sediment (n = 24)** | |
| Cr | Ca$^{*}$, Mg$^{*}$, Ni$^{**}$ |
| Ni | -LOI$^{*}$, Ca$^{**}$, Mg$^{**}$, P$^{*}$, Cr$^{**}$ |

$^{**}$Correlation is significant at the 0.01 level (2-tailed);

$^{*}$Correlation is significant at the 0.05 level (2-tailed).

The minus represents negative correlation.


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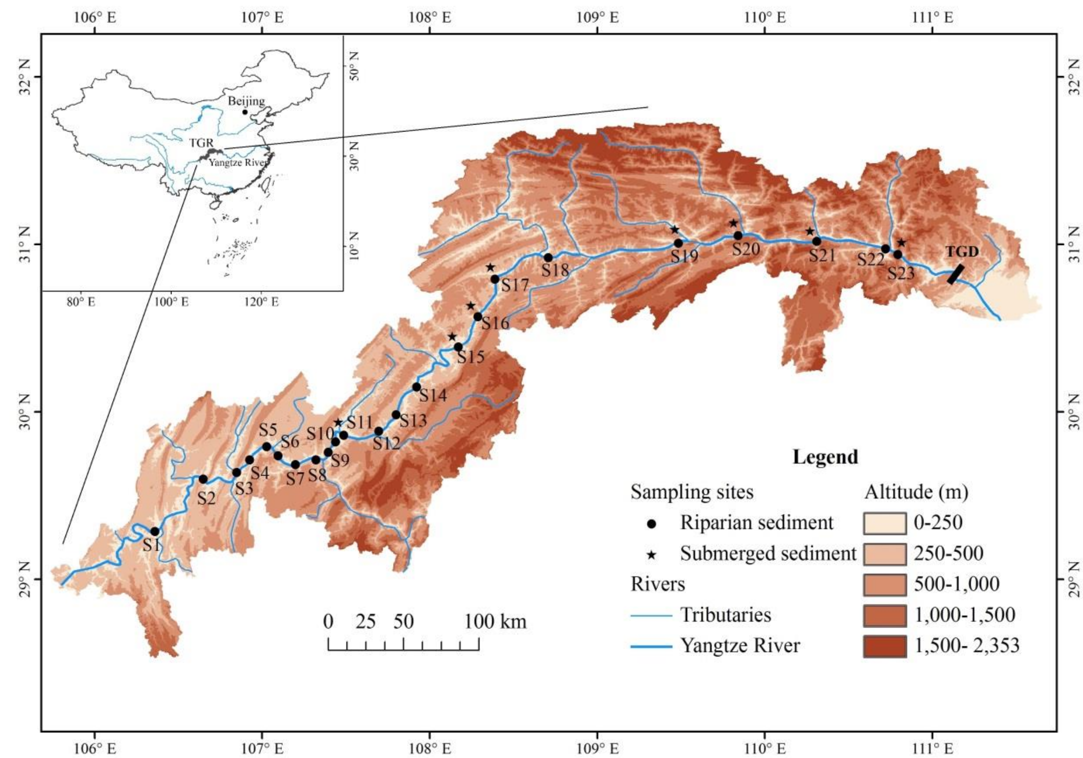


**Fig. 1** The study area and sampling sites in the TGR region


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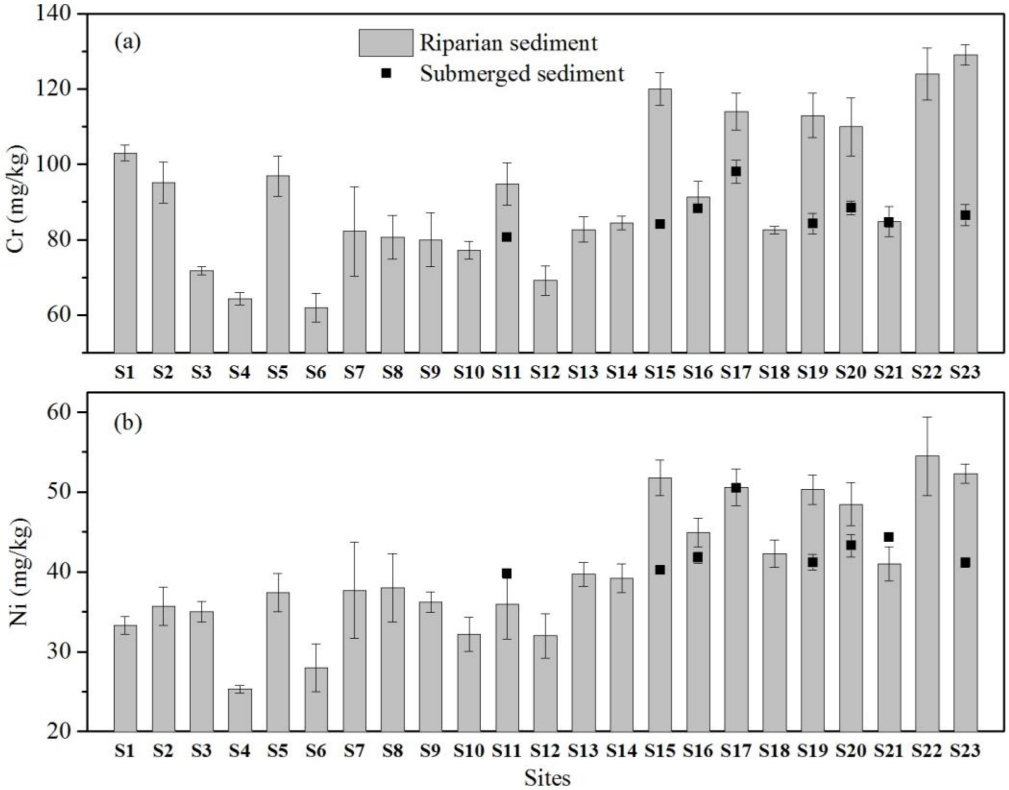


**Fig. 2** The concentrations (mean + standard deviation) of Cr and Ni in the riparian and submerged sediments

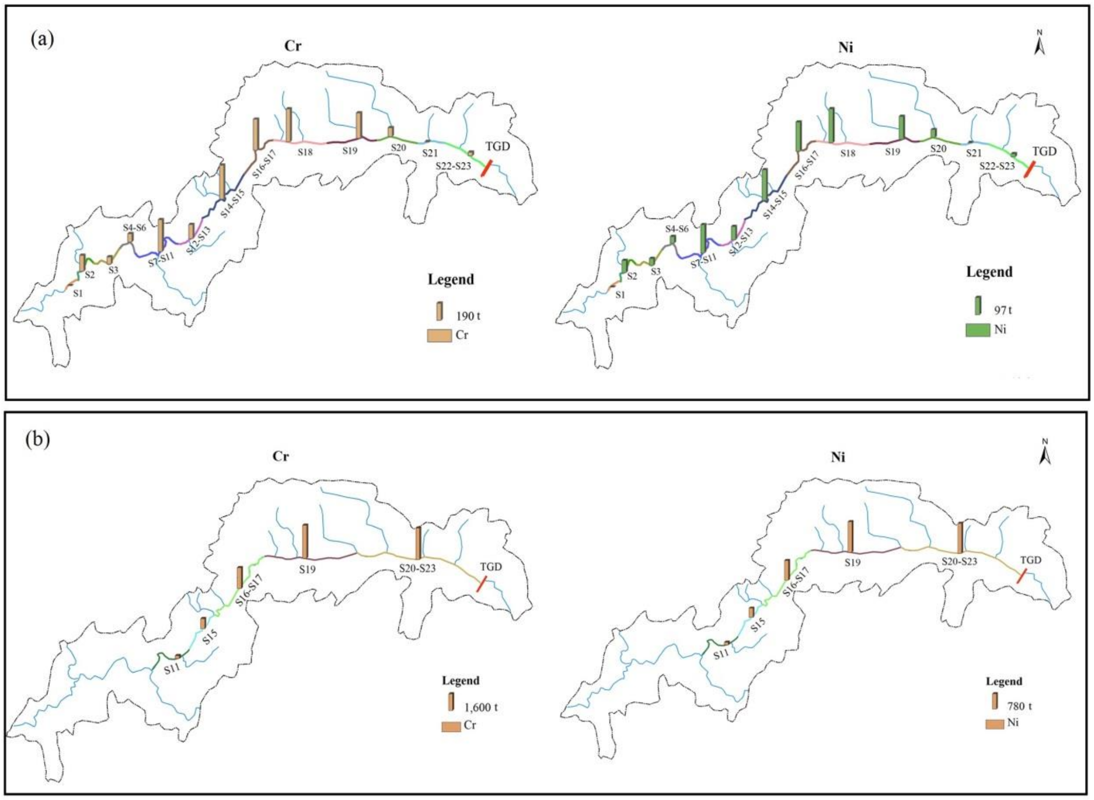

**Fig. 3** The storages of Cr and Ni in the riparian (a) and submerged (b) sediments


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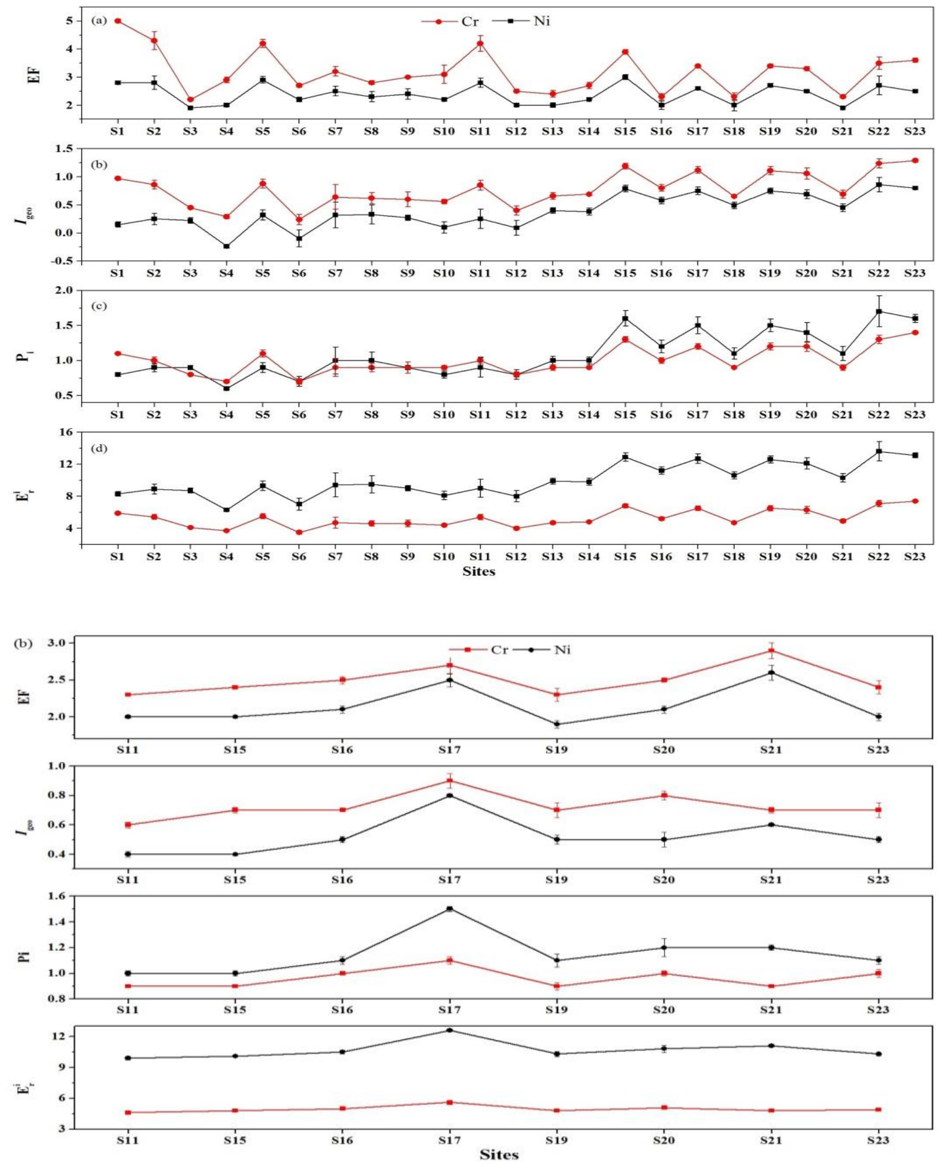


**Fig. 4** Spatial distribution of EF, $I_{geo}$, $P_i$, and $E_r^i$ of Cr and Ni in the riparian (a) and submerged (b) sediments


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