

Assessing the heavy metal contamination of soils in the water-level fluctuation zone upstream and downstream of the Manwan Dam, Lancang River

Shiliang Liu · Cong Wang · Juejie Yang · Qinghe Zhao

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Abstract

Purpose The intersections of the terrestrial and aquatic systems (water-level fluctuation zones, WLFZs) suffer from the increasing pressure of hydroelectric construction and operation. Taking WLFZs upstream and downstream of Manwan Dam (first dam completed in Lancang River) as an example, the dam operation impacts on the heavy metals in soils in WLFZs were assessed.

Materials and methods In December 2011, 117 soil samples were collected in the WLFZs and infralittoral reference zones (IRZs) with respect to heavy metal (Cd, Cr, Cu, Ni, Pb and Zn) and metalloid (As) concentrations. Their concentrations were determined with the application of inductively coupled plasma atomic absorption spectrometry, ICP-AES. Enrichment factor (EF), ecological risk index (RI) and principal component analysis (PCA) were employed for element contamination and ecological risk assessment and source identification, respectively. The multivariable statistic approaches, an analysis of variance (ANOVA) and a paired-samples *T* test were performed in the data analysis.

Results and discussion Parts of element concentrations in the upstream were significantly higher than those in the downstream and significant differences existed between the WLFZs and IRZs. No significant difference was detected between the different water elevations in the WLFZs. Compared to the soil quality guidelines, As and Cd exceeded the standard in both the WLFZs and IRZs. In addition, the water-level fluctuation during the submergence increased the enrichment degree and risk level in the WLFZs. The sources of the studied elements could be divided into natural factors and anthropogenic inputs. In addition, the submergence changed the major contaminants in the upstream WLFZs.

Conclusions The results verified that dam operation had an effect on the heavy metals in the soils in WLFZs. In addition, this study proposed a useful tool (modified enrichment factor) to assess the enrichment degree caused by the water-level fluctuation. Assessing the heavy metal contamination of soils in WLFZs could be an important first step to the rational management of the dam operation.

Keywords Ecological risk · Enrichment factors · Heavy metal · Infralittoral reference zone · Manwan Dam · Water-level fluctuation zone

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S. Liu (✉) · C. Wang · J. Yang · Q. Zhao
School of Environment, State Key Laboratory of Water Environment of Simulation, Beijing Normal University, Beijing 100875, China
e-mail: shiliangliu@bnu.edu.cn

C. Wang
State Key Laboratory of Urban and Regional Ecology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

J. Yang
School of Environment, Tsinghua University, Beijing 100084, China

Q. Zhao
College of Environment and Planning, Henan University, Kaifeng 475004, China

1 Introduction

Hydroelectric dam construction has become a major driving force for social and environmental problems (Fearnside 2005). Terrestrial and aquatic systems suffer from the increasing pressure of hydroelectric construction (Bai et al. 2009). Heavy metals widely exist in the water, soil and plants in the riparian zone, which is the intersection of the terrestrial and aquatic ecosystems on earth's surface (Ye et al. 2013). In the non-flood season, the sources of heavy metals in the riparian zone are divided into two categories: natural weathering and

anthropogenic activities, such as riverine discharge, domestic sewage and industrial wastewater (Feng et al. 2004; Zhang et al. 2007a). In the flood season, the inputs from human activities in the uplands and the aquatic environment heavy metals could be delivered to the riparian zone by flooding (Loska and Wiechula 2003) in addition to the natural origins. In different seasons, the load of these two sources might be different. Human activities have easily altered the heavy metal concentrations in the riparian environment (Mays and Edwards 2001; Zhang et al. 2009). Therefore, the heavy metal contamination in the riparian zone has attracted increasing concern in recent years.

Persistence, toxicity and non-degradability make the heavy metals serious pollutants in the environment (Tam and Wong 2000; Yuan et al. 2004). The toxicity and mobility of heavy metals in soils depend on the total concentration, their specific chemical form, their binding state, the metal properties, environmental factors and soil properties, redox conditions and root exudates acting as chelates (Nyamangara 1998; Rodríguez et al. 2009). Many research projects have been mainly focused on the spatial variation and assessing the heavy metals in the sediments and fresh water in the reservoir (Audry et al. 2004; Avila-Pérez et al. 1999; Karadede and Ünlü 2000; Loska and Wiechula 2003). In fact, the riparian zones have also been of great concern, as they can be an effective sink for heavy metals because of the integration and accumulation of pollutants from both the aquatic and terrestrial environments (Tam and Wong 2000). However, relatively few studies have centred on the riparian zones in river systems that were planned or constructed with cascade hydropower dams in which the riparian zones have been affected by regulating the reservoir water level and a prolonged water renewal time (Kummu and Varis 2007). In addition, some of the most widely used indicators for the estimation of anthropogenic inputs in the soils are enrichment factor (EF) and geoaccumulation index (Igeo) (Covelli and Fontolan 1997; Ghrefat and Yusuf 2006; González-Macías et al. 2006). Based on this technique, metal concentrations were normalized to metal concentrations of average shale (Mwamburi 2003; Ghrefat and Yusuf 2006) or average crust (González-Macías et al. 2006). However, the EF and Igeo method could only assess the difference between the concentration in the soils and background value, which could be considered as the overall impacts by the human activities. In other words, they could not specialize the heavy metal accumulation caused by water-level fluctuation.

The Lancang River is the largest international river in Asia. It originates from the eastern Tibetan Plateau in China and enters the South China Sea in the southern part of Vietnam (Zhang et al. 2007b). Cascade hydropower dams have been constructed on the mainstream of the Lancang River. The Manwan Dam was completed and began operation in 2000. The reservoir water level fluctuates from 982 m in summer

(June–September) to 984 m in winter (October–May), leading to the formation of the reservoir water-level fluctuation zones (WLFZs) (Gan et al. 2008; Zhao et al. 2011). WLFZs also exist downstream of the Manwan Dam, as the Dachaoshan Dam is located downstream of the Manwan Dam along the Lancang River. Previous studies have assessed the heavy metal contamination in riverine soils upstream and downstream of the Manwan Dam (Bai et al. 2009). Nevertheless, little information is available regarding the heavy metal contamination in the WLFZs and their variations between different elevations upstream and downstream. In this study, the adjacent zones above the WLFZs that were not subjected to submergence were considered as were the infralittoral reference zones (IRZs); thus, we could examine the impact of the water-level fluctuation on the WLFZs heavy metals by comparing the heavy metal conditions in the WLFZs and in the IRZs.

The goals of this study are as follows: (1) to explore the spatial variation of heavy metals in WLFZs upstream and downstream and at different water elevations; (2) to assess the extent of contamination of the heavy metals using soil quality guidelines, enrichment factors and the ecological risk index; (3) to identify sources of contamination; and (4) to propose a convenient method to assess the water-level fluctuation impact on heavy metal accumulation.

2 Materials and methods

2.1 Study area

In the upper Lancang River Basin, the river elevation drops dramatically with an average gradient of 0.15 %. The study area is subject to a monsoon climate and periodic rainstorms in which the overall rainfall is plentiful, and approximately 70 % of precipitation occurs in the summer (He et al. 2006). The Manwan Dam was the first dam of the Lancang mainstream cascade development project, as well as the first multimillion kilowatt hydropower station in the Yunnan Province; the station is located in the middle reaches of the Lancang River (Fig. 1). Recently, some negative effects have been detected in both upstream and downstream areas of the Manwan Dam, such as landscape devastation and potential geological hazards (He et al. 2006; Xu and Chen 2005).

2.2 Sampling and analytical methods

To investigate the heavy metals in the WLFZs upstream and downstream of the Manwan Dam, soil samples were collected in December 2011, when the WLFZs were exposed to the air after submergence. A total of 39 sampling sites (pairwise in the WLFZs and corresponding IRZs) were selected upstream (S1–S21) and downstream (X1–X18) of the Manwan Dam

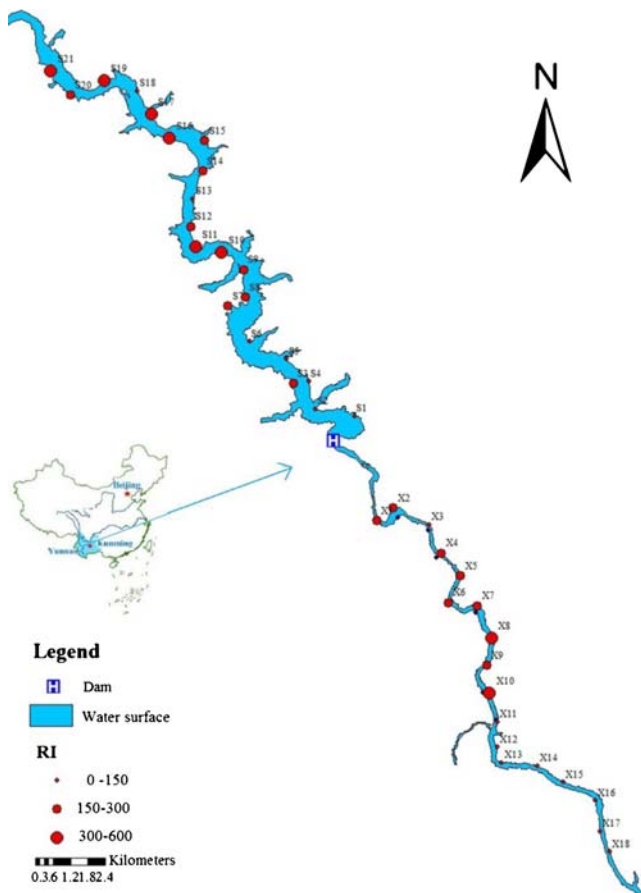


Fig. 1 Location of the Manwan Dam and the sample sites, Yunnan Province, China. The red solid circles describe the sampling sites, and the size indicates the potential ecological risk

(Fig. 1). At each site, three sampling plots (1 m×1 m) were selected with an interval of 1 m in elevation. At each plot, we collected five top soil samples (i.e. 0–20 cm), and the samples were well mixed to form a composite sample. All samples were sealed in plastic bags and stored at 4 °C for analysis. Before determining the soil heavy metals, all samples were air dried at room temperature, and the air-dried samples were ground until all particles passed a 100-mesh nylon sieve after the coarse debris was removed. The dried sediment sample was placed into a closed Teflon vessel with 3-mL HNO₃ (1.42 g/mL), 2-mL HClO₄ (1.49 g/mL), and 1-mL HF (1.68 g/mL) acids. Then, the vessels were placed inside a well-closed stainless steel block and heated on a thermostatically controlled hot plate at 70 °C for approximately 12 h (Oregioni and Aston 1984). After the HF was eliminated with 2-mL H₂SO₄ (1.07 g/mL), the residue was redissolved to a specific volume with diluted HNO₃ in vinyl-chloride bottles and filtered. For each digestion programme, a blank was prepared using the same procedure. The heavy metal concentrations (i.e. As, Cd, Cr, Cu, Fe, Ni, Pb and Zn) in the solutions were determined using the SEPAC method HJ/T 166-2004 (inductively coupled plasma atomic absorption spectrometry,

ICP-AES) (SEPAC 2004). Quality control was performed by a parallel analysis of the standard reference material (GBW07401) obtained from the Chinese Academy of Measurement Sciences, and a good agreement was observed (the analytical precision was within ±5 %).

2.3 Data analysis

To assess the level of contamination within the WLFZs and IRZs, an enrichment factor (EF) was used. The EF concept was developed to evaluate the degree of anthropogenic contribution to heavy metal contamination (Zoller et al. 1974). The formula is

$$EF = \frac{E_s/Fe_s}{E_a/Fe_a} \tag{1}$$

where E_s/Fe_s is the examined element to Fe ratio in the WLFZs sample and E_a/Fe_a is the examined element to Fe ratio in the reference environment. Because Fe is inert in the migration process and originates mainly from natural lithogenic sources, Fe was selected as the reference element. In the present study, the background concentrations in the Yunnan Province were used as the reference (Table 1). The Fe background concentration was 52,200 mg/kg. According to Birch’s suggested criteria (Birch 2003), $EF < 1$ was considered as no enrichment; $1 \leq EF < 3$, as minor enrichment; $3 \leq EF < 5$, as moderate enrichment; $5 \leq EF < 10$, as moderately severe enrichment; and $10 \leq EF < 25$, as severe enrichment.

To assess the ecological risks caused by heavy metals in the WLFZs, the ecological risk index (RI) suggested by Hakanson (1980) was applied in the present study. This index considers the toxicity of the heavy metals and the response of the environment by using a toxic response factor for a given substance (Hakanson 1980). The RI is defined as follows:

$$RI = \sum_{i=1}^n (T_i \times C_f i) = \sum_{i=1}^n \left(T_i \times \frac{C_s^i}{C_n^i} \right) \tag{2}$$

where T_i is the toxic response factor for a given substance, and $C_f i$ is the contamination factor (a ratio between preindustrial soil records (C_n^i) and present concentration values (C_s^i)). The toxic response factor (T_i) for Cr, Cu, Ni, Zn, Pb, As and Cd is 2, 5, 5, 1, 5, 10 and 30, respectively (Qiao et al. 2005). The reference values for the background records were obtained from the background values of soils in the Yunnan Province (Table 1). According to Hakanson (1980), the following definitions are suggested for the RI value: $RI \leq 150$, low ecological risk; $150 < RI \leq 300$, moderate ecological risk; $300 < RI \leq 600$, high ecological risk; and $RI > 600$, significantly high ecological risk.

In addition, multivariable statistic approaches were performed for further analysis. The paired-samples *T* test was

Table 1 Soil heavy metal concentrations (micrograms per gram) in the water fluctuating zone upstream and downstream of the Manwan Reservoir

Location	Zone	Contents	As	Cd	Cr	Cu	Ni	Pb	Zn	Fe
Upstream	WLFZ	Range	2.82–85.53	0.01–3.93	49.5–113.47	2.62–188.94	17.6–65.23	7.51–163.05	28.07–456.95	27,050.72–49,885.92
		Mean±SD	37.00±21.38	1.31±1.07	68.77±14.07	43.22±29.67	34.05±8.57	49.79±37.76	148.12±101.23	35,104.83±4,790.86
Downstream	IRZ	Range	2.80–67.90	0.01–2.94	54.4–102.42	2.61–188.97	20.75–65.29	7.52–91.35	28.81–257.84	30,703.22–43,638.91
		Mean±SD	28.82±24.1	0.98±1.16	74.88±14.18	40.96±43.28	37.12±10.55	34.46±32.05	108.02±90.85	36,415.03±4,109.92
Downstream	WLFZ	Range	4.6–59.7	0.13–3.11	13.26–80.24	15.24–113.05	5.78–44.46	10.43–125.77	50.82–301.73	22,149.31–42,068
		Mean±SD	25.49±11.55	0.87±0.67	55.86±9.52	29.83±12.79	25.81±5.22	44.39±20.62	120.64±57.80	27,967.90±3,662.41
Guide values of soil quality in China ^a	IRZ	Range	9.73–59.74	0.13–1.86	44.03–80.25	20.04–52.57	15.82–44.14	10.44–69.77	53.04–207.07	22,548.42–42,068.96
		Mean±SD	24.2±12.6	0.67±0.57	56.7±9.08	30.64±9.39	26.2±6.06	36.1±17.32	103.6±47.52	28,757.90±5,643.78
Elemental background concentration in Yunnan Province ^b			25	0.60	300	100	50	300	250	–
			18.4	0.22	65.2	46.3	42.5	40.6	89.7	52,200

^a Chinese environmental quality standard for soils (GB 15618–1995) (SEPAC 1995)^b Chinese element background values for soils (SEPAC 1990)

performed to compare the metal concentrations in the WLFZs and IRZs. A one-way ANOVA was used to examine the spatial variation of the metals. Principal component analysis (PCA) was used to identify their sources. The Kaiser-Meyer-Olkin (KMO) and Bartlett's sphericity tests were performed to examine the suitability of the data. All data analyses were conducted using SPSS 15.0.

3 Results and discussion

3.1 Heavy metal concentrations in WLFZs and IRZs upstream and downstream of the Manwan Dam

The statistical characteristics of the average As, Cd, Cr, Cu, Ni, Pb, Zn and Fe concentrations in the upstream and downstream WLFZs and IRZs of the Manwan Dam are shown in Table 1. As shown in Table 1, there was a distinct change in the contents of heavy metals among the sampling soils, Cd and Zn had relatively higher coefficients of variation, and Cr and Ni had relatively lower coefficients of variation, both in the WLFZs and IRZs. As the soil quality guidelines reflect the importance of contaminated soils as a possible cause for adverse environmental effects (Youssef and El-Said 2011), we compared the observed heavy metal concentrations in the samples with the second grade of Chinese soil quality standards (GB15618-1995) (SEPAC 1995), as class II was for safeguarding human health. The results showed that the As and Cd sampled in both the IRZs and WLFZs in the study area exceeded the second grade and could be related to the high emission from anthropogenic activities. Moreover, the average Cu and Ni concentrations in the downstream WLFZs and IRZs were relatively lower than the Yunnan Province background concentrations, while Cd concentrations in the WLFZ and IRZ and the Zn concentration in the WLFZ were obviously higher upstream (SEPAC 1990).

The spatial variation of heavy metals in the upstream and downstream WLFZs and IRZs is shown in Fig. 2. The average concentrations of As, Cd, Cr, Cu, Ni, Pb, Zn and Fe were higher in the upstream WLFZ than those in the downstream WLFZ. In addition, the ANOVA results showed that As, Cr, Cu, Ni and Fe levels in the upstream WLFZ were significantly different ($P < 0.05$, $P < 0.01$) from those in the downstream WLFZ (Fig. 2a), which means that these heavy metals revealed spatial variation, as the lithology type was the same and classified as rhyolite (Fang 1998) and the soil type was latosolic red soil (NSSO 1995) in the study area. In addition, no evidence revealed that heterogeneous parent materials existed there, and it might be concluded that spatial variation did not relate with the local geochemical background of heavy metal. Thus, the spatial variation could be attributed to the Manwan Dam trapping the heavy metals and the fast flow velocity in the adjacent downstream waters (Bai et al. 2009; Zhang et al.

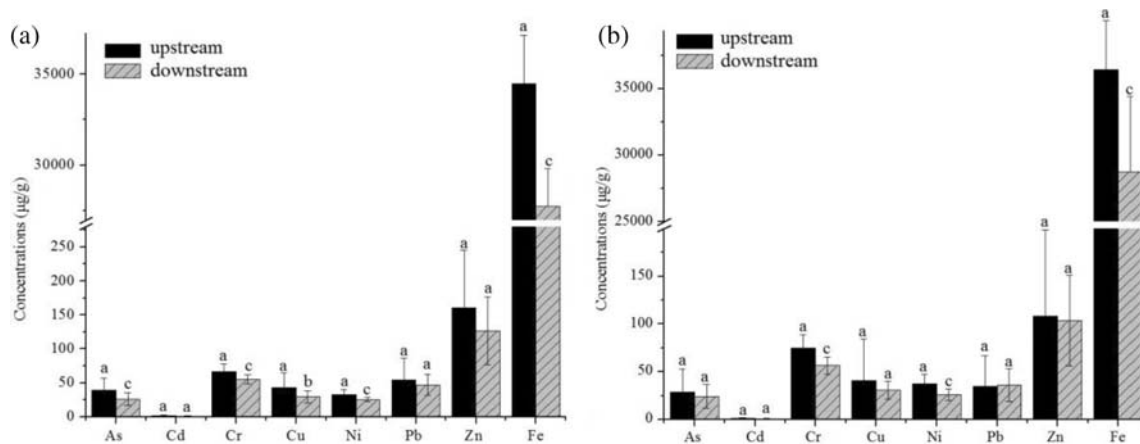


Fig. 2 **a** Average concentrations of heavy metals in WLFZs upstream and downstream of the Manwan Dam (micrograms per gram). **b** Average concentrations of the heavy metals in IRZs upstream and downstream of the Manwan Dam (micrograms per gram). *a* indicates that there is no

significant difference between upstream and downstream; *b* indicates a significant difference at the 0.05 level; *c* indicates a significant difference at the 0.01 level

2005). The concentrations of the studied heavy metals (except Pb) were higher in the upstream IRZ than those in the downstream IRZ. The ANOVA results revealed that the Cr, Ni and Fe concentrations showed significant variations between the upstream and downstream IRZs; such variations might be related to different sources and land use changes, as more crop lands existed in the upstream compared with those in the downstream, resulting in more use of fertilizer containing Fe in the upstream, relatively.

3.2 Variation between the WLFZs and IRZs

A paired-samples *T* test was applied to compare the heavy metals in the WLFZs and IRZs in the upstream and downstream regions of the Manwan Dam. The results indicated that the As, Cd, Cu, Pb and Zn concentrations increased, while the Cr and Ni decreased in the upstream WLFZ compared with those in the IRZ. Furthermore, Cr showed a significant variation ($P < 0.01$) between the WLFZ and IRZ upstream of the Manwan Dam (Fig. 3a). Additionally, heavy metals in the downstream region showed similar patterns to those in the upstream. Chromium, Pb and Zn ($P < 0.01$, $P < 0.05$) concentrations in the WLFZ were significantly different from those in the IRZ downstream of the Manwan Dam (Fig. 3b). These results partly demonstrated the impacts of water-level fluctuations during the submergence period on the heavy metal concentrations in the WLFZs, which could be further explained as the heavy metal deposition from the water in the reservoir (Ye et al. 2011).

Heavy metal variations between different water elevations in the upstream and downstream WLFZs were also evaluated by the paired-samples *T* test. The results showed that there were no significant differences between different water elevations in both the upstream and downstream WLFZs (Fig. 4). These results are in accordance with the study in the Three

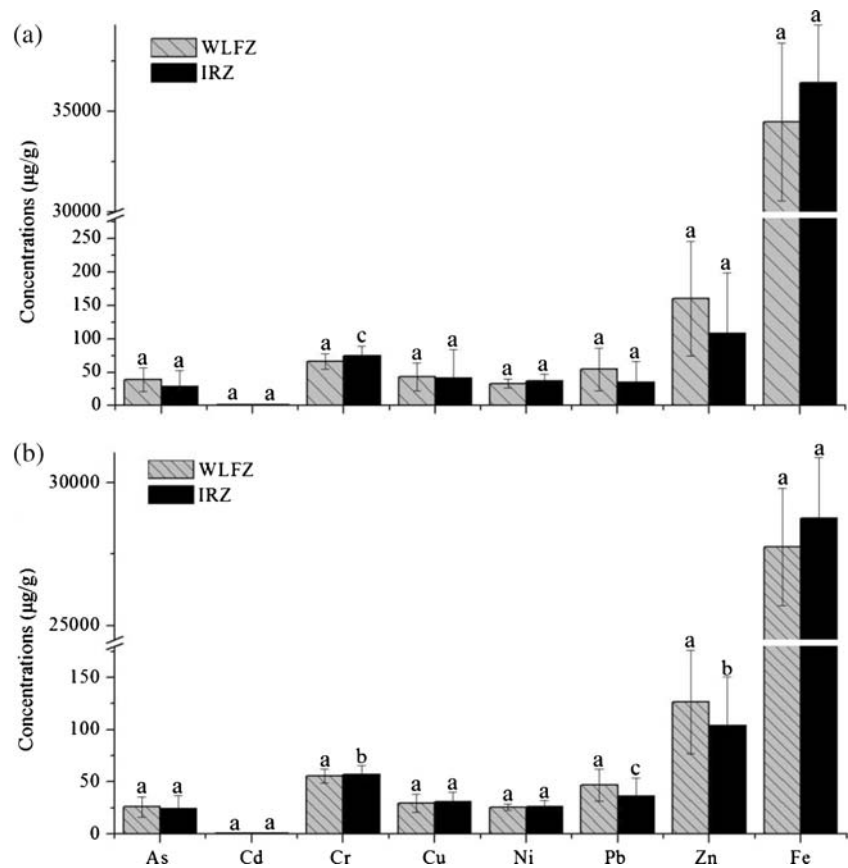
Gorges Reservoir by Wang (2012b); this result could be due to the insufficient flooding time to impact the heavy metal variations in different water levels (Wang et al. 2010, 2012b), or because the water elevation interval in this study area was too small to reveal significant variations.

3.3 Enrichment degree assessment

The enrichment factors for this study were calculated for the upstream and downstream WLFZs and IRZs. The EF values are shown in Table 2. The order of the average enrichment degree for different metals in the upstream WLFZ was $Cd > As > Zn > Pb > Cr > Cu > Ni$, and the order was $Cd > As = Zn > Pb > Cr > Cu > Ni$ downstream. In the upstream WLFZ, Cd fell into the moderately severe enrichment group; As fell into the moderate enrichment group; and Cr, Cu, Ni, Pb and Zn fell into the minor enrichment group. In the downstream WLFZ, Cd belonged to the moderately severe enrichment group; and As, Cr, Cu, Ni, Pb and Zn belonged to the minor enrichment group. Overall, the enrichment level in the upstream WLFZ was higher than that in the downstream WLFZ. Comparing the EF values in the WLFZ and those in IRZ (Table 2), results showed that the enrichment level in the WLFZs was relatively higher than that in the IRZs for almost all of the studied elements both upstream and downstream, suggesting that the water-level alteration caused by the dam operation brought additional sources of heavy metals into the WLFZs soils (Ye et al. 2011).

The distributions of the heavy metal enrichment factors in the upstream and downstream WLFZs of the Manwan Dam are presented in Fig. 5. As shown in Fig. 5, the enrichment factors of elements As, Cd, Pb and Zn revealed quite similar trends in both the upstream and downstream WLFZs; this similarity could be related to their similar anthropogenic sources and the similar properties of some metals (Wang

Fig. 3 **a** Average heavy metal concentrations in the WLFZ and IRZ upstream of the Manwan Dam (micrograms per gram). **b** Average heavy metal concentrations in the WLFZ and IRZ downstream of the Manwan Dam (micrograms per gram). *a* indicates that there is no significant difference between the WLFZs and IRZs; *b* indicates a significant difference at the 0.05 level; *c* indicates a significant difference at the 0.01 level



et al. 2012a). In addition, the above elements in the upstream WLFZ had relatively higher EF values at S9 and S21, as the residential area located at S21 led to more untreated sewage discharge and the tributaries adjacent to S9 contributed heavy metals to the mainstream. In the downstream WLFZ, higher EF values for As, Cd, Pb and Zn were found at X8 and X10; these higher values could be attributed to the chemical fertilizer application in the adjacent farmlands (Srinivasa Gowd et al. 2010, Zhao 1996). As for Cr, Cu and Ni, the EF values were relatively lower, ranging from 1.1 to 1.6, both in the upstream and downstream WLFZs; therefore, these metals might come from crustal materials or natural weathering (Acevedo-Figueroa et al. 2006).

3.4 Source identification

PCA identifies the correlations among the original variables in a data set and leads to an easier interpretation. PCA was performed for the heavy metals in the WLFZs upstream and downstream of the Manwan Dam. The results showed that heavy metal concentrations in the upstream WLFZs could be represented with two main components, which accounted for 76.92 % of the total variance (Table 3). The first component, with a variance of 46.48 %, was highly correlated with As, Cd, Pb and Zn. This component could be identified as an

“anthropogenic factor” and might originate from a common source due to hydroelectric development (Bai et al. 2009). The second component accounted for 30.44 % of the total variance with high loadings on Cr, Ni and Fe. We can label this component the “natural factor”, as Fe belongs to the lithogenous components; therefore, their metal concentrations might be controlled by the parent rock composition (Rubio et al. 2000; Wang et al. 2012a). Copper was divided between the two components, suggesting that Cu was contributed by both natural and anthropogenic sources. On the other hand, in the downstream WLFZs (Table 3), 73.98 % of the cumulative variance was explained by the first two principal components. PC1 accounted for 47.86 % of the total variance; had the highest loadings of As, Cd, Pb and Zn; and could also be identified as an “anthropogenic factor”. PC2 accounted for approximately 26.12 % of the total variance with the highest loadings of Cr and Ni and could be considered as a “natural factor”, as the background concentrations in this study area were relatively higher (Table 1) (SEPAC 1990). Cu and Fe revealed intermediate loadings of PC1 and were also represented in PC2, indicating that their sources could be both natural and anthropogenic.

Comparing the heavy metal source identification results of the upstream and downstream WLFZs, results showed that the heavy metal sources in the upstream and downstream WLFZs

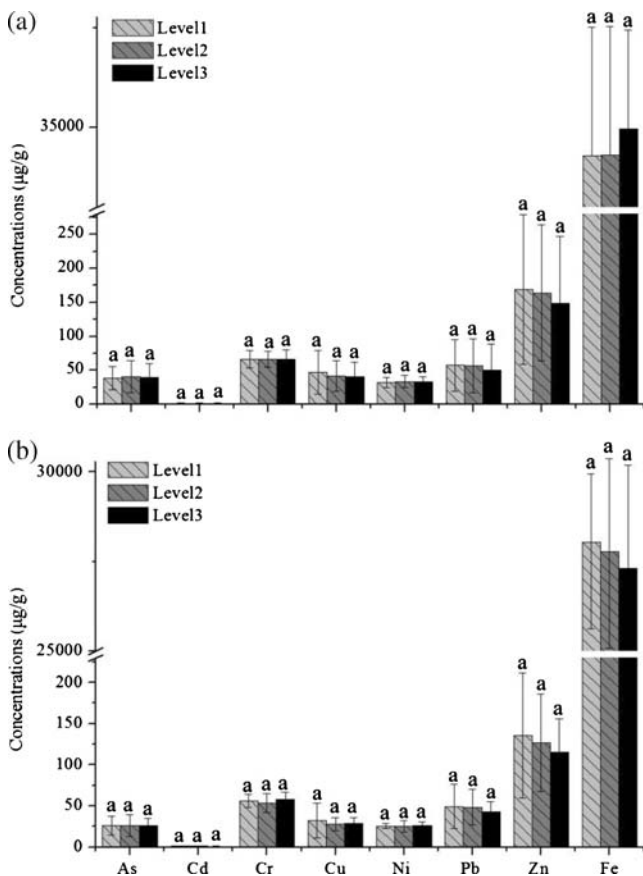


Fig. 4 a Average heavy metal concentrations at different elevations in the WLFZ upstream of the Manwan Dam (micrograms per gram). b Average heavy metal concentrations at different elevations in the WLFZ downstream of the Manwan Dam (micrograms per gram); a indicates that there is no significant difference among the three elevation levels

were basically consistent, indicating that the Manwan Dam did not impose significant impacts. In addition, the anthropogenic sources could be further specified. The application of fertilizers or pesticides in agricultural activities (Tongke 1996), the metal mining and smelting industries (Li 1999; Yanqun et al. 2005), the pigment and electroplating industries (Lin et al. 2002) and the exploitation of the Heihui River (located upstream of the Manwan Reservoir) (Zhao et al. 2012) mainly contributed to the relatively higher concentrations of As, Cd, Pb and Zn.

The IRZs represented the conditions that were not subject to submergence. The possible sources of heavy metals in IRZs were

Table 2 Mean values of each element EF at upstream and downstream WLFZs and IRZs of Manwan Dam

	EF	As	Cd	Cr	Cu	Ni	Pb	Zn
Upstream	WLFZ	3.23	9.76	1.54	1.41	1.18	2.03	2.70
	IRZ	2.25	6.39	1.65	1.27	1.25	1.22	1.73
Downstream	WLFZ	2.66	8.13	1.60	1.20	1.13	2.18	2.66
	IRZ	2.39	5.51	1.58	1.20	1.12	1.62	2.10

also identified through PCA (Table 4), and the results were compared with those of the WLFZs. In the IRZs, two factors were obtained, accounting for 80.59 % of the total variance in the upstream region and 80.96 % in the downstream region. In the upstream IRZ, factor 1, accounting for 62.25 % of the total variance, has the highest loadings of As, Cd, Cr, Pb and Zn, medium loadings of Ni and Fe and can be considered as an anthropogenic factor. Factor 2, accounting for 18.34 % of total variance with the highest loadings of Cu and intermediate loadings of Fe and As, could be identified as a natural factor. In the downstream IRZ, factor 1, accounting for 40.92 % of the total variance, has the highest loadings of Cr, Cu and Ni and medium loadings of As, and Fe and can be considered as a natural factor. Factor 2, which accounts for 40.04 % of the total variance with the highest loadings of Cd, Pb and Zn and intermediate loadings of As, could be considered a anthropogenic factor.

Comparing the heavy metal source identification results in the IRZs with those in the WLFZs, results showed that the primary pollutants changed from As, Cd, Cr, Pb and Zn to As, Cd, Pb and Zn after submergence upstream, while the primary pollutants were basically consistent after submergence downstream. The transformation could be partly attributed to material exchange due to the submergence in the WLFZ (Censi et al. 2006; Qiao et al. 2007; Ye et al. 2011).

3.5 Potential ecological risk assessment

The RI values for all sample sites in the upstream and downstream WLFZs of the Manwan Dam were calculated and plotted in Fig. 1 using the geographic information system software. The results showed that six sites revealed high ecological risk (S10, S11, S16, S17, S19 and S21), eight sites revealed moderate ecological risk (S3, S7, S8, S9, S12, S14 and S15), and the remaining revealed a low ecological risk in the upstream WLFZ. In addition, two sites revealed a high ecological risk (X8 and X10), seven sites revealed moderate ecological risk (X1, X2, X4, X5, X6, X7 and X9) and the rest revealed a low ecological risk in the downstream WLFZ. The distribution plot was quite conducive for identifying the sites that need more attention and monitoring in our study area.

Comparing the RI values in upstream and downstream WLFZs (Fig. 1), results showed that the upstream WLFZ revealed a higher ecological risk, which could be partly related to the dam trap of the heavy metals in the river. In addition, the average RI values in the WLFZs and IRZs upstream and downstream were also calculated. The average RI values in upstream and downstream WLFZs were 234 and 166, respectively. The average RI values in upstream and downstream IRZs were 159 and 118, respectively. The results showed that the WLFZs had relatively higher ecological risks than the IRZs, which indicated that the water-level fluctuation increased the risk level in the WLFZs during the submergence period.

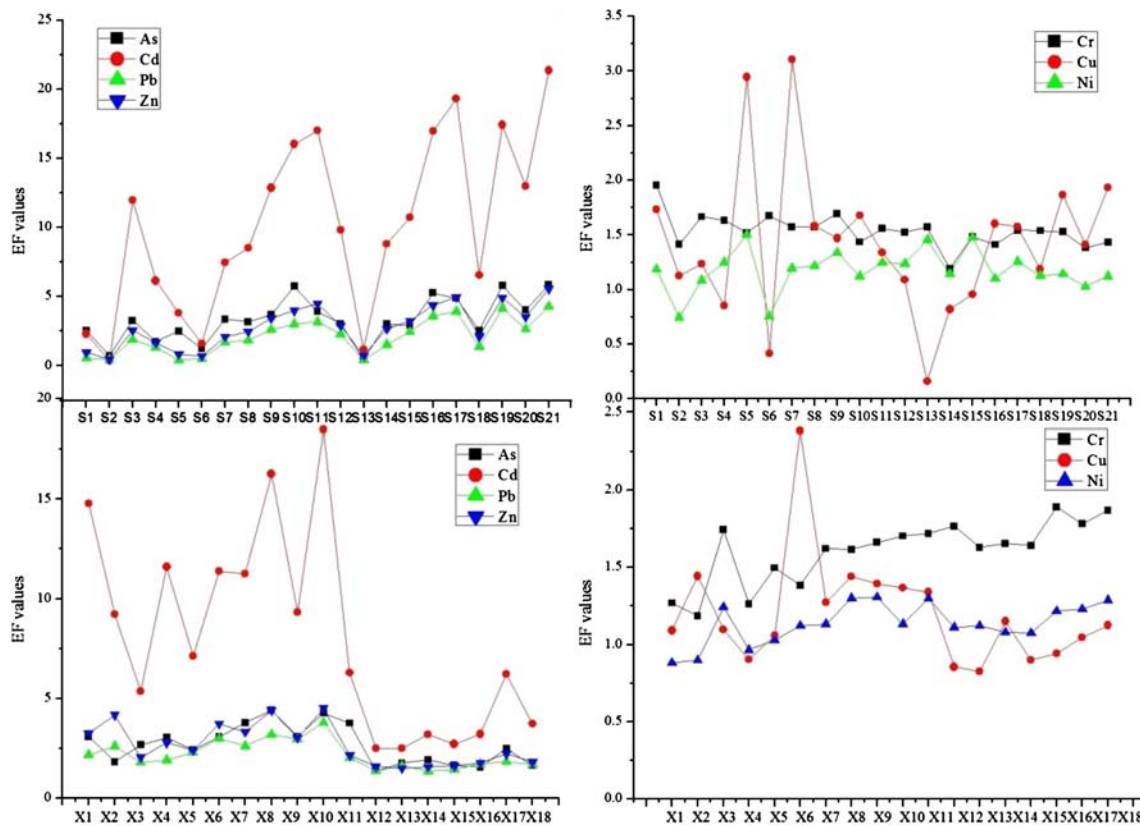


Fig. 5 EF values of the elements in the sample sites in the upstream and downstream WLFZs of the Manwan Dam. The upstream sites are represented *above*, and the downstream sites are represented *below*

3.6 A modified enrichment factor equation

Calculating the EF for heavy metals above uncontaminated background levels is a common approach for estimating the

anthropogenic impact on soils (Dickinson et al. 1996). This research attempted to plot geochemical trends in the WLFZs induced by the water-level fluctuation. A modified form of the enrichment factor equation was presented to calculate the

Table 3 Varimax-rotated factor loading (PCA) and identified sources of heavy metals in soils of the upstream and downstream WLFZs of the Manwan Reservoir, China

Upstream			Downstream		
Variable	Factor 1	Factor 2	Variable	Factor 1	Factor 2
As	0.93	-0.15	As	0.79	0.26
Cd	0.92	-0.29	Cd	0.96	-0.01
Cr	-0.20	0.87	Cr	-0.14	0.92
Cu	0.43	0.24	Cu	0.59	0.15
Ni	-0.05	0.78	Ni	0.18	0.91
Pb	0.92	-0.29	Pb	0.92	0.17
Zn	0.93	-0.26	Zn	0.97	-0.04
Fe	-0.20	0.87	Fe	0.32	0.55
Eigenvalue	4.45	1.71	Eigenvalue	4.03	1.89
Percent of variance	46.48	30.44	Percent of variance	47.86	26.12
Cumulative percentage	46.48	76.92	Cumulative percentage	47.86	73.98
Possible source	Anthropogenic factor	Natural factor	Possible source	Anthropogenic factor	Natural factor

Table 4 Varimax-rotated factor loading (PCA) and identified sources of heavy metals in soils of the upstream and downstream IRZs of the Manwan Dam, China

Upstream			Downstream		
Variable	Factor 1	Factor 2	Variable	Factor 1	Factor 2
As		0.84	As		0.72
Cd		0.96	Cd		-0.03
Cr		-0.85	Cr		0.88
Cu		0.22	Cu		0.84
Ni		-0.56	Ni		0.92
Pb		0.96	Pb		0.06
Zn		0.94	Zn		0.07
Fe		-0.66	Fe		0.64
Eigenvalue	5.07	1.37	Eigenvalue	3.82	2.66
Percent of variance	62.25	18.34	Percent of variance	40.92	40.04
Cumulative percentage	62.25	80.60	Cumulative percentage	40.92	80.96
Possible source	Anthropogenic factor	Natural factor	Possible source	Anthropogenic factor	Natural factor

contamination level in the WLFZs caused by the water-level fluctuation as follows:

$$mEF = \frac{E_{WLFZ}/Fe_{WLFZ}}{E_{IRZ}/Fe_{IRZ}} \quad (3)$$

where E_{WLFZ} and Fe_{WLFZ} are the soil sample concentrations of the heavy metals and Fe (or other normalizing element) in the WLFZs, respectively, and E_{IRZ} and Fe_{IRZ} are their concentrations in the corresponding IRZs. For the classification and description of the modified degree of contamination (mEF) in the WLFZ soils, the following gradations are proposed: $mEF \leq 1$, nil to a very low degree of enrichment; $1 < mEF \leq 3$, minor enrichment; and $3 < mEF \leq 5$, moderate enrichment.

The mEFs for the heavy metals in the WLFZs were calculated according to Eq. 3 and are shown in Fig. 6. The results showed that most heavy metals in the upstream WLFZ revealed similar patterns (except Ni in the upstream) in most sample sites and that they are more conspicuous in the downstream WLFZ, indicating that their distribution patterns were mainly affected by one major factor: the water-level fluctuation. The above results validated the proposed modified equation. However, some different trends at some of the sites are detected in Fig. 6. These different trends might be attributed to the differences in the topography and management practices at these sites.

Overall, this study proposed a convenient tool to assess the heavy metal accumulation caused by the water-level fluctuation induced by the reservoir regulation. This tool was also helpful in assessing the environmental impacts of the dam operation.

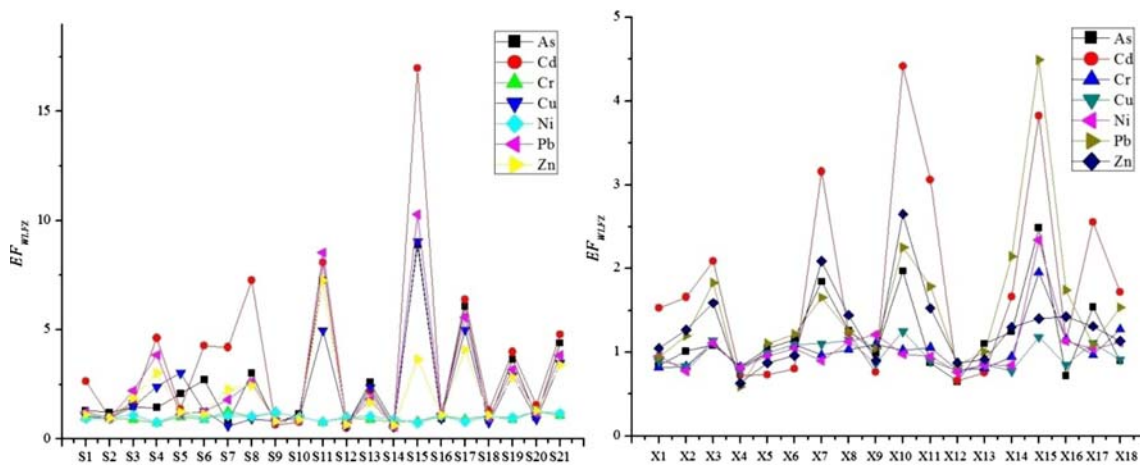


Fig. 6 WLFZ_{EF} values of the elements at the sample sites in upstream and downstream WLFZs of the Manwan Dam. The sites upstream are represented to the left, and the sites downstream are represented to the right

4 Conclusions

To investigate the heavy metals in the WLFZs upstream and downstream of the Manwan Dam, soil samples were collected and analysed in this study. Results showed that spatial variation of heavy metals existed in WLFZs upstream and downstream. Most of the studied element concentrations in the upstream WLFZ were significantly higher than those in the downstream WLFZ due to the Manwan Dam trap and the fast water flow velocity adjacent to the downstream waters; only Cr, Ni and Fe revealed significant variations between upstream and downstream IRZs. Chromium upstream and the Cd, Pb and Zn downstream revealed significant differences between the WLFZs and IRZs, which could be partly related to the deposition and material exchange among those metals caused by water-level fluctuation during submergence. In addition, heavy metal concentrations at different water elevations revealed no significant differences, which could be attributed to insufficient flooding time or the small elevation interval.

Most of the studied element concentrations in the soil in WLFZs and IRZs upstream and downstream of Manwan Dam did not exceed guidelines of Chinese quality standard, except for As and Cd. The EF indices showed that most of the studied elements were slightly enriched in the WLFZs and that Cd and As revealed moderately severe enrichment degrees. Fourteen of 21 sites in the upstream revealed moderate ecological risk and above, and half of the sites in the downstream revealed moderate ecological risk and above. Higher enrichment levels in the WLFZs than in the IRZs could indicate that the water-level fluctuation during the submergence period brought additional sources. The higher ecological risk in the WLFZs indicated that submergence increased the risk level.

As for the sources of the heavy metals in the sampling sites, PCA results revealed that the heavy metal sources in the WLFZs could be divided into two categories: natural factors and anthropogenic factors. The anthropogenic inputs mainly came from the application of fertilizers and pesticides, the pigment and electroplating industries, the metal mining and smelting industries and tributary exploitation. The PCA comparative results indicated that the upstream primary pollutants were different in the WLFZs than in the IRZs, which could be related to the submergence.

In order to assess the enrichment degree caused by the water-level fluctuation after submergence, a modified enrichment factor index was proposed and applied in this study, and the results confirmed the applicability of the formula. These results examined the contamination, sources and distribution of the heavy metals in the upstream and downstream WLFZs of the Manwan Dam and could contribute to reservoir management and maintenance. This study suggests strict administration over the discharge of industrial and agricultural inputs is needed to reduce the contamination and risk levels in the WLFZs. Assessing the heavy metal contamination of soils

in WLFZs could be an important first step to the rational management of the dam operation. However, more research is needed to (1) explore the water-level fluctuation impacts on the soil quality in the WLFZs and (2) analyse the riparian habitat changes due to the water regulation by Manwan Dam.

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