Abundance and mobility of metal(loid)s in reservoir sediments of Singe Tsangpo and Yarlung Tsangpo in Tibet, China: Implications for ecological risk

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Abstract Geogenic arsenic enrichment in soil and river sediments of Tibet compared to its upper crustal abundance has been observed, raising the question whether other trace elements are also enriched and thus may pose ecological risks. Because human activities are limited, the reservoir sediments after the recent construction of the Shiquan dam on the Singe Tsangpo (ST) and the Zam dam on the Yarlung Tsangpo (YT) collect and thus represent material sourced from 14,870 km^2 and 157,668 km^2 of drainage areas, respectively. Bulk concentrations of the metalloid (As) and 13 metals (Li, Be, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Cs, and Pb) are analyzed for 123 samples from 9 mostly silty sediment cores (depth: 11–20 cm) from the Shiquan Reservoir and for 250 samples from 13 mostly sandy sediment cores (depth: 9–28 cm) from the Zam Reservoir. These elemental concentrations are normalized to the upper crustal Fe abundance of 3.9% to arrive at a regional sediment geochemical background value for each element. The regional background values of most elements in the ST drainage and the YT drainage are comparable with the upper crustal abundance. However, three elements (Li, As, and Cs) in both drainage basins display significant enrichment compared to their respective upper crustal abundance. Sequential leaching of a subset of sediment samples from the ST ($n = 18$) and YT ($n = 29$) drainages reveals that chemical fractions of metals and metalloids in these two reservoirs are similar, with most of the elements dominated by the

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residual fraction with low mobility. Taken together, the ecological risks of the most studied elements in the reservoir sediments are likely low pending further aquatic bioavailability investigations, except that As, Cu, Pb, and Be deserve more attention due to their elevated levels in mobile fractions.

Keywords Geochemical background · Metals · Arsenic · Tibet · Singe Tsangpo · Yarlung Tsangpo

Introduction

Toxicity of dissolved metals and metalloids to aquatic organisms is well known (Schaller et al. 2011; Zeng et al. 2013). Fortunately, most metals and metalloids have strong affinities for solid phases and are bound to suspended particulate matters and eventually deposit in sediments, with only a small portion existing as the dissolved form in the water column (Blasco et al. 2000; Wang et al. 2015). However, in lakes or reservoirs, mobilization of these elements from the bottom sediment into the water column remains a concern (Lee et al. 2017), especially when the environmental conditions change or when the sediments are disturbed (Wang et al. 2016). Because sediment is a crucial "reservoir" of these toxic elements (Palma et al. 2015), assessment of the concentrations and mobility of such elements has been of interest (Bing et al. 2016).

To evaluate metal and metalloid pollution of sediment, a variety of methods such as geo-accumulation index, potential ecological risk index, and enrichment factor are usually adopted (Yang et al. 2014; Duodu et al. 2016; Ke et al. 2017). These approaches require establishing regional geochemical background of metals and metalloids first. Regional background levels of metals and metalloids in sediments and soils depend on local geological properties (such as mineralogical composition, grain size, organic matter), which may differ from reference levels on a global scale, such as the crustal contents (Newman and Watling 2007). Comparison with regional background values of metals and metalloids and their natural variability enables the anthropogenic impact to be definitely constrained (Xia et al. 2012; Jiang et al. 2013). Geochemical normalization is a widely used procedure to reduce the influence of variability related to mineralogical composition or grain size, allowing for establishment of regional geochemical background in sediment (Wang et al. 2015). The normalization is usually carried out using linear regression analysis accompanied with a conservative element such as Li, Fe, and Al for calculation of the contents of metals and metalloids (Aloupi and Angelidis 2001; Soto-Jimenez and Paez-Osuna 2001; Sun et al. 2018).

The Singe Tsangpo (ST) and the Yarlung Tsangpo (YT), the upper reaches of the Indus and the Brahmaputra Rivers, respectively, are the two largest rivers in Tibet. In the ST and the upper YT drainages, pronounced enrichment of arsenic in soil and sediments was observed (Li et al. 2013b). Groundwater with elevated levels of geogenic arsenic occurs frequently in the downgradient areas of the Indus and Brahmaputra rivers as well (Fendorf et al. 2010; Verma et al. 2019; Lone et al. 2020). Riverine transport of arsenic-rich sediments in Tibetan drainage basins has been recognized as the main source of arsenic anomalies in Southeast (Zhang et al. 2017) and South Asia (Edmunds et al. 2015). This raises the question whether other trace elements are also enriched in Tibet and thus may pose ecological risks. The newly constructed Shiquan dam on the ST and the Zam dam on the YT where reservoir sediments represent material from 14,870 km^2 and 157,668 km^2 of the ST and YT drainages, respectively, provide an ideal condition for investigating the regional background values of trace elements in the two drainage basins.

Therefore, this study aims to elucidate the regional background levels of metals and metalloids in sediment of the ST and the YT drainage basins. Normalization to upper crustal abundance of 3.9% Fe was utilized to determine the regional background values of As and 12 metals (Li, Be, V, Cr, Mn, Co, Ni, Cu, Zn, Cd, Cs, and Pb). The method of establishing geochemical background can be applied to similar settings in the world where dam constructions are taking place.

Materials and methods

Study area

As the upper stretch of the Indus River, the ST is the largest river in western Tibet. The total length of the

ST is 430 km with a drainage area of 27,450 km^2 (Guan et al. 1984). The headwater of the ST is located in the northern region of the Mount Kailash in the Gangdise Mountains, with an elevation of 5,164 m above sea level (asl). Hot springs are widely distributed in the upper reaches of the ST (Guan et al. 1984). The rock types in the drainage basin mainly include volcanic breccia, pyroclastic rock, sandstone, and shale of Mesozoic age. In 2007, the Shiquan Reservoir was built in the Gar County in the middle reach of the river. The Shiquan Reservoir is an annual regulating reservoir with a storage capacity of 1.85×10^8 m^3, and it receives water from a drainage basin of 14,870 km^2 in the ST (Fig. 1). The perennial average flow at the dam site is 9.36 m^3/s (Guan et al. 1984).

The YT is the largest river in the Tibetan Plateau, with a length of 2,057 km and a drainage area of 240,480 km^2. The average elevation of the YT is 4,500 m asl. The YT originates from the Gyaimane-zong Glacier on the northern slope of the Himalayas (Guan et al. 1984). The YT has significant impacts on the ecosystem of the downstream Ganges–Brahmaputra Basin where significantly high As concentrations in groundwater have been observed (Li et al. 2011) and deposited Holocene sediments have been considered as the main sources of arsenic (Zhang et al. 2017; Zhao et al. 2020).

In the YT drainage basin, precipitation is the main source of supply to the river water. Brought by the Indian summer monsoon, precipitation occurs mostly from June to September. In addition, the supply of melt water to river water is also elevated during the summer because of the higher temperature (Liu et al. 2007). The spring runoff from March to May accounted for 7–12%, the summer runoff from June to August accounted for 51–54%, the fall runoff from September to November accounted for 29–33%, and the winter runoff from December to February only accounted for 6–7% of the whole year amount (Liu et al. 2007). The YT erodes sedimentary rocks from the Paleozoic to the Eocene, as well as plutonic rocks from the Trans-Himalayan batholith (gabbros and diorites) and volcanic rocks from the Indus-Tsangpo Suture zone (Li et al. 2011).

Completed in 2014, the Zam Reservoir was the largest hydropower development project in Tibet until the end of 2017 and the first hydropower station planned for construction on the main stream of the YT. It is located in Gyaca County (perennial mean temperature 8.3 °C) in the middle reach of the YT. The largest chromite deposit in China, Luobusa chromite deposit, is located near the YT ($\sim$ 100 km upstream of the Zam Reservoir) (Yang et al. 2008). And the Tibetan Qulong copper deposit is located in the YT drainage basin in the upstream of the Zam Reservoir. The Zam Reservoir is a daily regulating reservoir with a storage capacity of 8.66×10^7 m^3, and it receives water from a drainage basin of 157,668 km^2 in the upper stretch of the YT River (Fig. 1). The perennial average flow at the dam site is 1,010 m^3/s.

Sample collection

Nine sediment cores from 11 to 20 cm depth from the Shiquan Reservoir and 13 sediment cores from 9 to 28 cm depth from the Zam Reservoir were collected during 3 sampling campaigns in August 2017, January 2018, and May 2018. The sediment cores were divided into 1-cm increments on the same day of collection and stored in sealed sterile centrifuge tubes. All the bottles and centrifuge tubes were soaked in 10% HNO$_3$ for at least 48 h and cleaned with distilled water before use. The samples were transported at room temperature in dark to the laboratory within 7 days. Sediment samples were freeze-dried, ground with an agate mortar and sieved through 200 mesh (0.075 mm) nylon sieves before chemical analysis.

Bulk sediment digestion and sequential extraction

The sediment samples (n = 373, with 123 from the Shiquan Reservoir and 250 from the Zam Reservoir) were digested for bulk chemistry analysis using nitric acid (trace metal grade) at 160 °C for 30 h in high-pressure Teflon bottles following the pressurized nitric acid digestion method (Tariq et al. 1996; Bibby and Webster-Brown 2006; Karlsson et al. 2010; Qin et al. 2010). A 0.0500 ± 0.0003 g sediment was digested, and the final digest was diluted into 100 ml of solution.

To assess the chemical fractions of the sediment, an optimized BCR (European Community Bureau of Reference) sequential extraction method was used (Sutherland and Tack 2003), with the method details presented in Zhao et al. (2020). In brief, four chemical fractions were obtained: F1: exchangeable fraction, representing surface bound elements and carbonates; F2: reducible fraction, representing elements bound to Fe and/or Mn oxides; F3: oxidizable fraction,
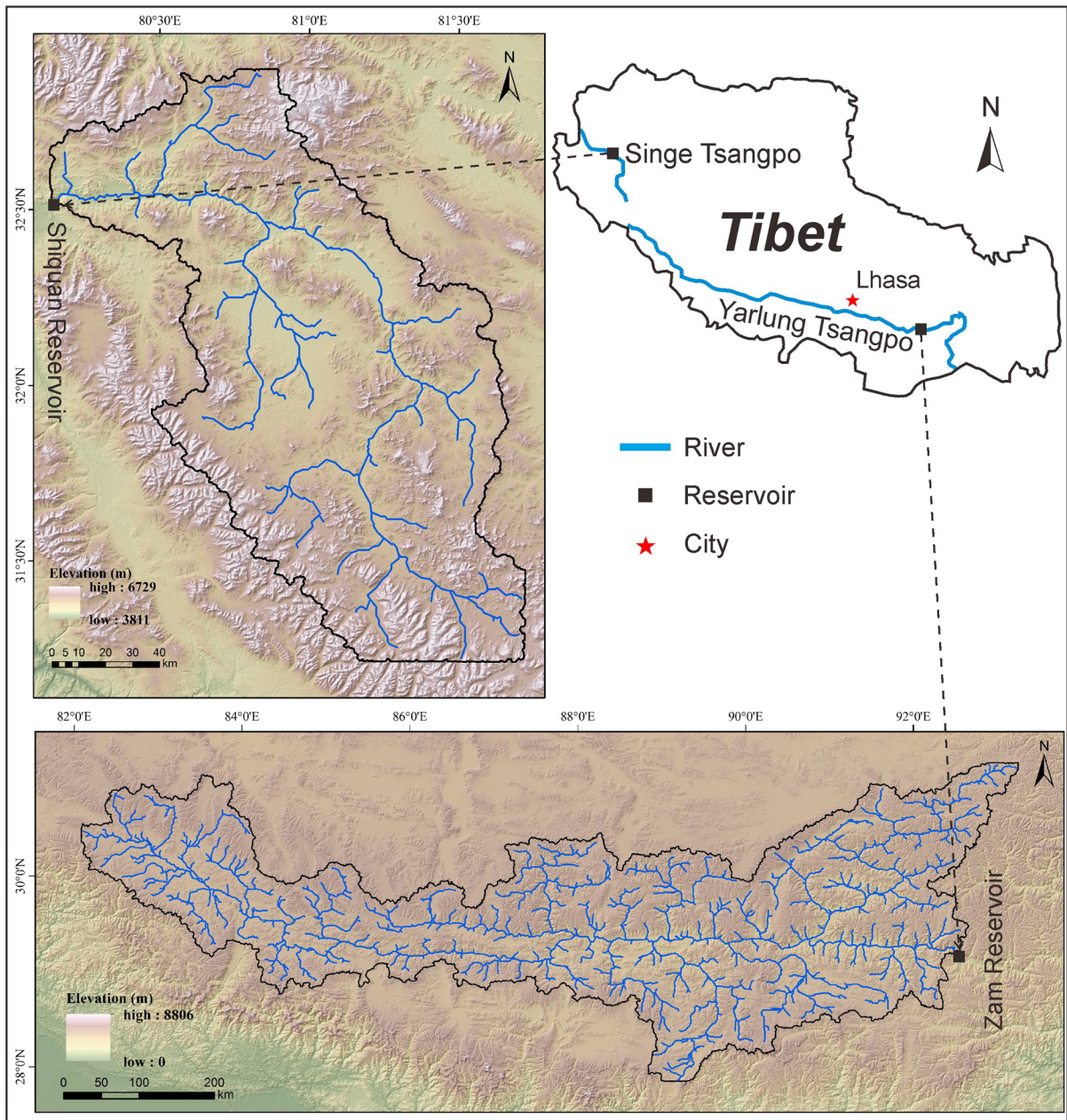
Fig. 1 Location of the Shiquan and the Zam Reservoirs. The upstream drainage basins of the Shiquan Reservoir and the Zam Reservoir cover 14,870 km^2 and 157,668 km^2, respectively

representing elements bound to organic matter and sulfides; and F4: residual fraction, representing elements associated with the crystalline structures of minerals. The residual fraction was calculated by the total element concentration determined by the nitric acid digestion minus the sum of extractable fractions

F1, F2, F3 (Yu et al. 2011; Rieuwerts et al. 2014). A certified reference material (CRM), the national soil standard GBW07430 (Pearl River delta soil), two reagent blanks, and 10% replicates of sediment samples were included in each batch of digestion or extraction.

Chemical analysis

All chemical analyses of digestion and extraction solutions were conducted at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. Dissolved concentrations of all 13 trace elements (Li, Be, V, Cr Mn, Co, Ni, Cu, Zn, As, Cd, Cs, and Pb) in the digestion solutions were determined by ICP-MS (Agilent, 7700x, USA) with detection limits lower than 0.02 µg/L. The detection contents of trace elements in blank solutions were not higher than 0.05 µg/L. The measured values of the trace elements in the external standard reference solution (1640a) were always within the range of certified values (Table S1). Dissolved Fe concentrations were measured by ICP-OES (iCAP6500, Thermo Scientific, Germany) with a detection limit of 0.01 mg/L.

The concentrations of the studied elements in the digestion and extraction blanks were always < 2% of the measured values in the sediment samples. The recovery rates of these elements in the CRM soil varied from 90 to 110% (Table S2). The relative difference between sediment replicates was < 5%.

Calculation of regional geochemical background levels

To eliminate the sediment grain size effects on element enrichment and elucidate the regional background level of metals and metalloids in the two drainage basins, geochemical normalization using the upper crust Fe abundance of 3.9% as the reference was conducted (Wang et al. 2015; Aloupi et al., 2001). The data sets consisted of 123 sediment samples in the Shiquan Reservoir and 250 sediment samples in the Zam Reservoir. Prior to normalization, a linear regression analysis between elements of interest and the chosen reference element iron was first performed to exclude sediment samples that might receive human interference, with data points falling outside of the 95% confidence interval eliminated (Soto-Jimenez and Paez-Osuna 2001; Sun et al. 2018).

Results

Bulk Concentrations of Metal(loid)s in Tibetan Reservoir Sediments

The average concentrations of metals and metalloids in sediment of the two reservoirs are reported in Table 1, with full data listed in Table S3. In particular, the bulk concentrations of Li, As, and Cs in sediments of the Shiquan Reservoir are 3.5 times, 15.7 times, and 17.1 times higher than their upper continental crust levels, respectively. The bulk concentrations of Li, Cu, As, and Cs in sediment of the Zam Reservoir are 2.2 times, 2.3 times, 7.0 times, and 7.9 times higher than their upper continental crust contents, respectively (Rudnick and Gao 2003). Moreover, the levels of Ni (3.9 times), As (4.0 times), and Cs (4.3 times) in the Shiquan Reservoir and Cu (2.9 times) in the Zam Reservoir are also significantly higher than their background values in soils in Tibet (Cheng et al. 1993). The vertical profiles of As and metals in sediment cores from the Shiquan and the Zam Reservoirs are shown in Fig. 2. In both reservoirs, bulk concentrations of all 14 elements do not show significant changes with depth.

Concentrations of metals and metalloids in fine sediments are usually higher than those in coarse sediments (Sun et al. 2018). Based on a student t test, concentrations of elements of sediments from the Shiquan Reservoir are significantly higher than those from the Zam Reservoir except for Cu ($p < 0.001$), which in part reflect the coarser sediment grain sizes of the Zam Reservoir (Fig. 3). Within the Zam Reservoir, the concentrations of all elements measured in sediments increase along the flow direction (Fig. 3), attributable to a decrease in grain size of the sediments closer to the dam due to weakened flow dynamics. The 9 sediment cores from the Shiquan Reservoir are all located at approximately 0.3 km from the dam so have similar grain sizes.

The significantly higher level of Cu in sediments of the Zam Reservoir than that those of the Shiquan Reservoir ($p < 0.001$) is believed to reflect the influence from the Qulong copper deposit located in the upstream areas of the Zam Reservoir in the YT drainage. The Cr content in sediments of the Zam Reservoir is similar to the upper continental crustal abundance, suggesting that the Cr in the YT drainage

Table 1 Concentrations of major (Fe) and trace elements in sediments from the Shiquan and the Zam Reservoirs and their calculated geochemical background values

	Li(mg/kg)	Be(mg/kg)	V(mg/kg)	Cr(mg/kg)	Mn(mg/kg)	**Fe(%)**	Co(mg/kg)
Shiquan(n=123)	84.5±12.7	2.8±0.3	162.6±14.3	163.6±24.8	950.2±166.7	4.3±0.3	23.1±2.0
Zam(n=250)	53.3±10.3	2.1±0.4	102.5±14.8	93.6±11.6	861.3±167.0	4.0±0.5	17.0±2.6
Singe-Tsangpo Background (Fe)	**99.3±15.0**	2.8±0.3	**173.4±10.3**	**193.9±29.8**	**1101.1±160.3**	3.9±0.4	**25.5±2.3**
Yarlung-Tsangpo Background (Fe)	**66.2±8.5**	**2.5±0.3**	**119.4±10.9**	**101.1±5.2**	**1100.7±153.5**	3.9±0.4	**20.5±2.3**
Upper continental crust[a]	24±5	2.1±0.9	97±11	92±17	775±77	3.9±0.4	17.3±0.6
Soil background in Tibet[b]	42.3	2.8	75.9	77.4	636	3.0	11.6

	Ni(mg/kg)	Cu(mg/kg)	Zn(mg/kg)	As(mg/kg)	Cd(mg/kg)	Cs(mg/kg)	Pb(mg/kg)
Shiquan(n=123)	126.3±22.9	41.3±4.8	115.7±5.9	75.2±15.6	0.19±0.04	83.9±14.2	32.7±5.9
Zam(n=250)	66.9±7.8	63.6±20.0	107.0±15.3	33.6±7.0	0.15±0.03	38.7±6.5	24.4±5.3
Singe-Tsangpo Background (Fe)	**149.8±23.4**	**46.7±5.3**	115.7±5.9	**81.1±7.7**	0.19±0.04	83.9±14.2	32.7±5.9
Yarlung-Tsangpo Background (Fe)	**75.6±5.8**	**79.7±11.5**	**129.1±14.2**	**43.3±6.2**	**0.20±0.03**	**46.8±5.3**	**31.5±4.7**
Upper continental crust[a]	47±11	28±4	67±6	4.8±0.5	0.09±0.01	4.9±1.5	17±0.5
Soil background in Tibet[b]	32.1	21.9	73.7	18.7	0.08	19.4	28.9

[a] Data from Rudnick and Gao (2003). [b] Data from Cheng et al. (1993), which involved a total of 205 soil sampling sites in Tibet. The bold represents the concentration obtained after normalization
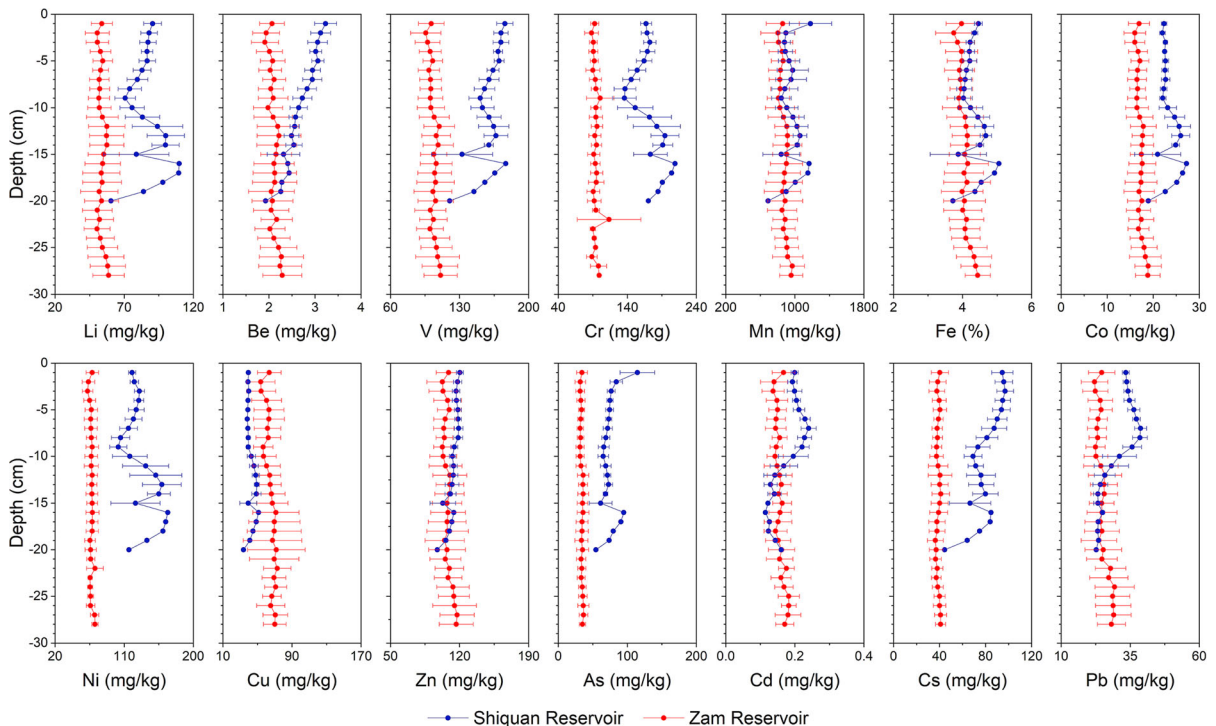
Fig. 2 Vertical distributions of metal(loid)s in 9 sediment cores with 123 samples from the Shiquan Reservoir and in 13 sediment cores with 250 samples from the Zam Reservoir
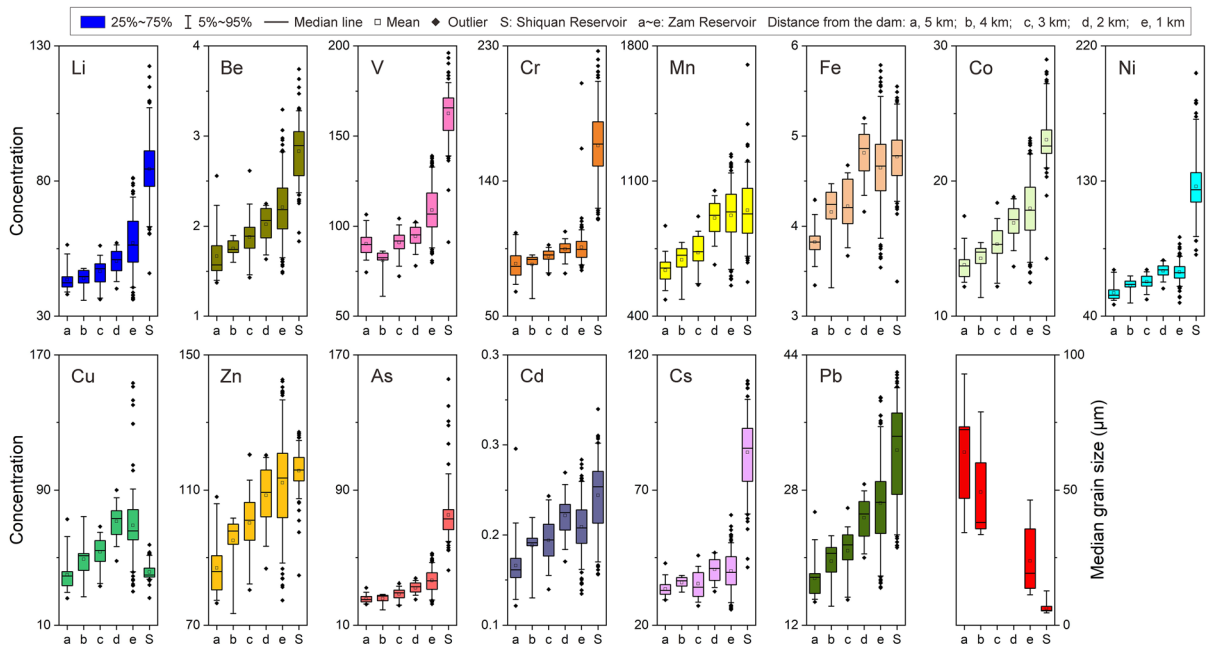
Fig. 3 Variation of Fe (%), trace elements (mg/kg), and grain size in sediments from 5 sites located 1 to 5 km upgradient from the Zam dam and from three sites located about 0.3 km upgradient of the Shiquan dam

basin is unlikely influenced by the Luobusa chromite deposit.

Background abundance of Metal(loid)s in Singe and Yarlung drainages

Geochemical normalization was carried out to eliminate the grain size effect on metals and metalloids and define their regional geochemical baselines in the ST and the YT drainage basins. Various elements have been proposed for geochemical normalization to eliminate the grain size effect on metal(loid)s, among which Li, Al, and Fe are most frequently used (Aloupi and Angelidis 2001; Wang et al. 2015; Sun et al. 2018). Because of the poor recovery of Al during acid digestion, Li and Fe are considered as alternatives in this study. All the elements (except Be, Cd, and Pb in the Shiquan Reservoir) in the two reservoirs were strongly negatively correlated with the median grain size (Mz) ($-0.89 < r < -0.48, p < 0.05$; Table 2). Moreover, the strong positive correlations between all 13 elements (except Be, Zn, Cd, and Pb in the Shiquan Reservoir) and Li or Fe ($0.44 < r < 0.95, p < 0.01$; Table 2), indicate their shared enrichment in fine grained sediments. Thus, both can be considered as the "normalizing element" for metal(loid)s (Xia et al.

2012). However, hot springs in the study area contain high levels (0.07 to 21.12 mg/L, mean: 9.99 mg/L) of Li (Meng 2020), making it a questionable choice. In contrast, the Fe contents of sediments from both reservoirs are similar to the upper continental crustal abundance (Table 1). Therefore, Fe is chosen to normalize the elements for regional geochemical background assessment.

The relationships between each element and Fe in the sediments from the Shiquan and the Zam Reservoirs are presented in Fig. 4. Most of the data points in the regression plots between the contents of the studied elements and Fe were within the 95% confidence interval, suggesting that these elements Li, V, Cr, Mn, Co, Ni, Cu, and As in the ST and the YT drainage basins are not affected by human activities (Tam and Yao 1998). There is a consensus that when the correlation between a metal(loid) and its normalizer is poor, no normalization is adopted, and the absolute contents of the metal(loid) are used (Summers et al. 1996). Based on the regression models (Table 3), the regional background of metal(loid)s in the ST and the YT drainage basins can be obtained (Table 1). Specifically, in the ST drainage basin, the regional baselines of Li, Be, V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Cs, and Pb were 99.3, 2.8, 173.4, 193.9,

1101.1, 25.5, 149.8, 46.7, 115.7, 81.1, 0.19, 83.9, and 32.7 mg/kg, respectively. In the YT drainage basin, the regional baselines of Li, Be, V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Cs, and Pb were 66.2, 2.5, 119.4, 101.1, 1100.7, 20.5, 75.6, 79.7, 129.1, 43.4, 0.20, 46.8, and 31.5 mg/kg, respectively.

Geochemical mobility of sediments in the Shiquan and Zam Reservoirs

The sequential extraction of a subset of sediment samples indicates that the chemical speciation of metals and metalloids in the sediments is similar in both reservoirs (Table 4 and Table S4). The BCR extractable fractions F1-3 are considered to be potentially mobile and bioavailable (Rieuwerts et al. 2014). Although the bulk sedimentary concentration of Cd was the lowest, Cd is primarily associated with the exchangeable fraction (63.0% in the Shiquan Reservoir and 65.7% in the Zam Reservoir), suggesting the potential for high mobility and bioavailability of Cd. Approximately 61.9% and 50.2% of the Pb exists in the reducible fraction in the Shiquan Reservoir and the Zam Reservoir, respectively, suggesting that the mobility of Pb is regulated by Fe/Mn oxides. Further, Mn is more mobile than Fe, as indicated by its higher proportions in exchangeable fraction F1, whereas non-residual Fe is found in the reducible fraction F2. A

Fig. 4 Scatter plot showing the relationships between elemental ▶ concentrations and Fe in sediments from the Shiquan Reservoir ($n = 123$) and the Zam Reservoir ($n = 250$). The dotted lines represent the 95% confidence level of the linear regression (solid lines)

high proportion of Be is associated with the reducible fraction in Shiquan Reservoir, while a high proportion of Cu is associated with the reducible in Zam Reservoir (Table 4).

The oxidizable fractions are low across the elements for both reservoirs (Table 4). Metals in oxidizable fractions usually reflect organic-rich wastewater discharge and/or inputs from aquatic organisms (Li et al. 2018). Neither is likely important in these reservoirs with little direct anthropogenic pollution. Consistent with the low oxidizable fractions, the contents of total organic carbon in sediments of the Shiquan Reservoir (0.5–1.1%) and the Zam Reservoir (0.3–0.9%) are low (Zhao et al. 2020).

Nine out of 14 elements evaluated, specifically Li, V, Cr, Fe, Co, Ni, Zn, As, and Cs, is found to reside in the residual fraction (Table 4). Elements in this fraction usually pose low ecological risk because they are bounded to the crystalline structures of minerals and therefore not bioavailable (Ma et al. 2016; Ke et al. 2017).

Table 2 Pearson correlation matrix of potential normalizers and studied elements in the Shiquan ($n = 123$) and the Zam Reservoirs ($n = 250$)

Reservoir	Normalizer	Li	Be	V	Cr	Mn	Fe	Co
Shiquan	Li	1	0.23*	0.74**	0.83**	0.60**	0.77**	0.70**
	Fe	0.77**	− 0.03	0.62**	0.70**	0.68**	1	0.79**
	Mz ($n = 17$)	− 0.81**	− 0.45	− 0.82**	− 0.49*	-0.74**	− 0.90**	-0.80**
Zam	Li	1	0.93**	0.93**	0.52**	0.88**	0.85**	0.94**
	Fe	0.85**	0.84**	0.76**	0.52**	0.93**	1	0.90**
	Mz ($n = 27$)	− 0.79**	− 0.77**	− 0.76**	− 0.68**	-0.87**	− 0.85**	-0.87**

Reservoir	Normalizer	Ni	Cu	Zn	As	Cd	Cs	Pb
Shiquan	Li	0.82**	0.61**	0.24**	0.49**	− 0.54**	0.49**	− 0.42**
	Fe	0.74**	0.75**	0.13	0.44**	− 0.58**	0.33	− 0.52**
	Mz ($n = 17$)	− 0.58*	-0.72**	− 0.61*	− 0.49*	− 0.09	− 0.48*	− 0.11
Zam	Li	0.69**	0.48**	0.92**	0.95**	0.72**	0.85**	0.88**
	Fe	0.76**	0.60**	0.92**	0.88**	0.82**	0.84**	0.89**
	Mz ($n = 27$)	− 0.84**	− 0.88**	− 0.89**	− 0.84**	− 0.78**	− 0.78**	− 0.81**

Mz: median grain size. ** Significant at the $p < 0.01$ level. * Significant at the $p < 0.05$ level
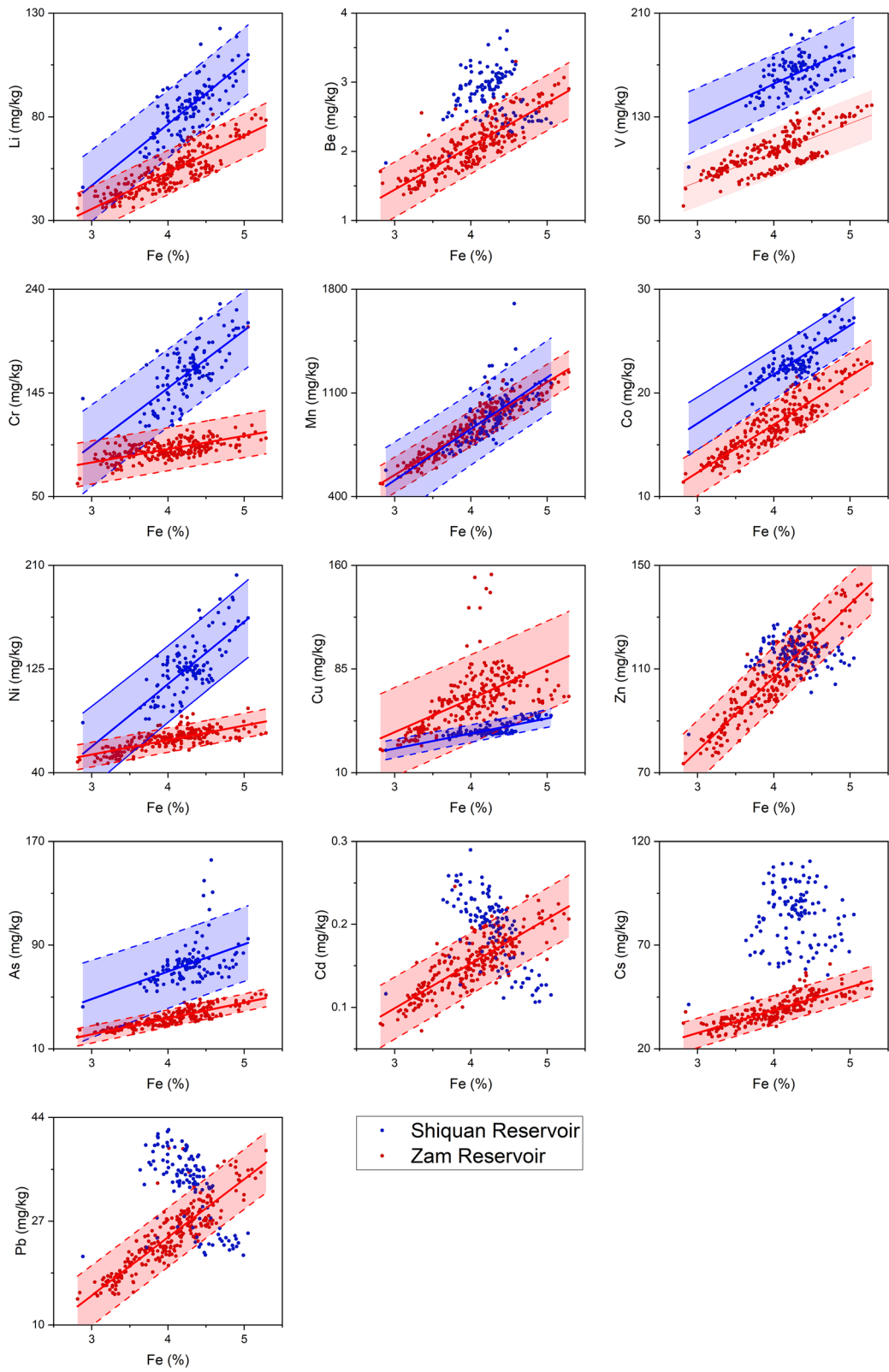
Table 3 Linear regression equations between 8 elements and Fe in sediments of the Shiquan Reservoir ($n = 123$) and between 13 elements and Fe the Zam Reservoir ($n = 250$)

Reservoir	Element (mg/kg)	Fe (%)		
		R^2	N	Regression equation
Shiquan	Li	0.68	117 (6)[a]	[Li] = 30.02[Fe]-44.75
	V	0.30	118 (5)	[V] = 20.59[Fe] + 74.55
	Cr	0.59	116 (7)	[Cr] = 59.51[Fe]-91.79
	Mn	0.61	116 (7)	[Mn] = 320.67[Fe]-438.1
	Co	0.68	116 (7)	[Co] = 4.57[Fe] + 3.53
	Ni	0.54	119 (4)	[Ni] = 46.83[Fe]-74.97
	Cu	0.61	120 (3)	[Cu] = 10.54[Fe]-3.91
	As	0.28	118 (5)	[As] = 15.47[Fe] + 6.82
Zam	Li	0.76	239 (11)	[Li] = 16.95[Fe]-15.13
	Be	0.77	241 (9)	[Be] = 0.62[Fe]-0.45
	V	0.58	245 (5)	[V] = 21.83[Fe] + 14.60
	Cr	0.40	247 (3)	[Cr] = 10.44[Fe] + 50.95
	Mn	0.89	244 (6)	[Mn] = 307.05[Fe]-373.17
	Co	0.84	238 (12)	[Co] = 4.54[Fe]-1.26
	Ni	0.66	237 (13)	[Ni] = 11.62[Fe] + 19.87
	Cu	0.55	242 (8)	[Cu] = 23.00[Fe]-30.72
	Zn	0.88	240 (10)	[Zn] = 28.33[Fe]-6.84
	As	0.81	238 (12)	[As] = 12.39[Fe]-16.21
	Cd	0.78	234(16)	[Cd] = 0.0542[Li]-0.0651
	Cs	0.76	240 (10)	[Cs] = 10.66[Fe]-4.34
	Pb	0.86	243 (7)	[Pb] = 9.32[Fe]-13.20

[a] The brackets denote the number of anomalous samples removed from the regressions

Discussion

Ecological risk assessment

Because the majority of the elements including Li, V, Cr, Co, Ni, Zn, and Cs in the reservoir sediments is found in the residual fraction, their ecological risks are considered to be relatively low. However, although most As, 75% and 78% in the Shiquan Reservoir and the Zam Reservoir, respectively, is bound to the residual fraction, the considerable quantities of As in the reducible fraction, at 22% (16.6 ± 3.4 mg/kg) and 16% (5.4 ± 1.1 mg/kg) in the Shiquan Reservoir and the Zam Reservoir, respectively, are concerning in comparison with a threshold effect concentration of 9.8 mg/kg of As in sediment (MacDonald et al. 2000). In the scenario that the reservoirs are polluted by nutrients to trigger eutrophication, reductive dissolution of Fe/Mn oxyhydroxides could release bounded As and pose ecological risks (Sohrin et al. 1997; Rahman and Hasegawa 2012).

Three other elements are also prominent in the reducible fractions, Be, Cu, and Pb. Similarly, a considerable portion of Be existed in the reducible fraction in the Shiquan Reservoir (75.0%, 2.1 ± 0.2 mg/kg) and the Zam Reservoir (36.9%, 0.8 ± 0.1 mg/kg), which is ascribed to the high adsorption capacity of Be by Fe/Mn oxyhydroxides. Copper is 38.7% and 36.3% of the reducible fraction in the Shiquan Reservoir and the Zam Reservoir, respectively. It is worth noting that the exchangeable Cu in the Zam Reservoir (21.8%) was much higher than that in the Shiquan Reservoir (6.3%). The concentration of the potential mobile Cu in the Zam Reservoir (41.2 ± 13.0 mg/kg) exceeded its threshold effect concentration of 31.6 mg/kg (MacDonald et al. 2000), and it is much higher than that in the Shiquan Reservoir (19.2 ± 2.2 mg/kg), which may resulted from the Qulong copper deposit located in the upstream of the Zam Reservoir. Because the total concentrations of Pb are not high, only 32.7 mg/kg in the Shiquan Reservoir and 24.4 mg/kg in the Zam

Table 4 Sequential extraction results of metal(loid)s in selected sediments from the Shiquan and the Zam Reservoirs

Reservoir	Fractions	Li (%)	Be (%)	V (%)	Cr (%)	Mn (%)	Fe (%)	Co (%)
Shiquan (n = 18)	F1	2.5 ± 0.4	5.4 ± 1.4	0.0 ± 0.0	0.4 ± 0.1	**47.7 ± 5.7**	1.2 ± 1.1	14.8 ± 3.4
	F2	4.3 ± 0.8	**75.0 ± 5.9**	5.3 ± 0.8	4.0 ± 0.6	14.6 ± 6.0	15.2 ± 2.6	27.9 ± 3.4
	F3	3.6 ± 0.7	8.1 ± 1.0	3.0 ± 0.3	3.4 ± 0.5	2.5 ± 0.3	0.6 ± 0.1	4.8 ± 0.5
	F4	**89.7 ± 1.7**	11.5 ± 6.0	**91.7 ± 1.0**	**92.3 ± 1.0**	35.3 ± 4.2	**83.0 ± 3.4**	**52.5 ± 4.4**
Zam (n = 29)	F1	2.7 ± 0.9	8.5 ± 1.3	0.0 ± 0.0	0.4 ± 0.2	**31.0 ± 5.1**	0.9 ± 0.4	17.8 ± 3.2
	F2	5.0 ± 0.7	**36.9 ± 7.0**	4.3 ± 0.6	3.0 ± 0.5	13.8 ± 1.8	8.3 ± 1.4	28.2 ± 4.3
	F3	7.0 ± 0.8	5.7 ± 0.8	3.8 ± 0.4	4.6 ± 0.7	2.7 ± 0.3	1.9 ± 0.2	6.0 ± 0.4
	F4	**85.3 ± 1.7**	**48.9 ± 8.1**	**91.8 ± 0.8**	**92.0 ± 1.0**	**52.4 ± 6.2**	**88.9 ± 1.7**	**47.9 ± 3.9**

Reservoir	Fractions	Ni (%)	Cu (%)	Zn (%)	As (%)	Cd (%)	Cs (%)	Pb (%)
Shiquan (n = 18)	F1	7.6 ± 1.4	6.3 ± 3.1	5.5 ± 3.1	2.0 ± 0.9	**63.0 ± 5.7**	0.8 ± 0.2	1.8 ± 0.8
	F2	17.0 ± 2.1	**38.7 ± 6.6**	17.2 ± 3.1	22.1 ± 5.4	22.7 ± 3.7	14.1 ± 1.5	**61.9 ± 3.8**
	F3	8.5 ± 1.0	1.5 ± 0.6	2.7 ± 0.4	0.7 ± 0.3	3.8 ± 0.6	23.0 ± 5.2	2.0 ± 0.2
	F4	**66.9 ± 3.8**	**53.5 ± 8.0**	**74.5 ± 3.7**	**75.2 ± 5.8**	10.4 ± 5.7	**62.1 ± 4.7**	34.3 ± 4.0
Zam (n = 29)	F1	6.9 ± 1.2	21.8 ± 5.6	6.7 ± 1.5	2.5 ± 1.4	**65.7 ± 4.3**	1.4 ± 0.6	3.5 ± 1.4
	F2	19.3 ± 1.6	**36.3 ± 5.0**	16.2 ± 2.8	16.2 ± 2.2	21.1 ± 1.9	16.7 ± 2.4	**50.2 ± 5.7**
	F3	12.6 ± 1.1	6.6 ± 3.3	6.9 ± 2.2	3.3 ± 0.4	6.9 ± 1.2	5.4 ± 1.8	6.2 ± 0.8
	F4	**61.2 ± 2.1**	35.3 ± 11.2	**70.2 ± 5.3**	**78.0 ± 3.4**	6.3 ± 5.7	**76.5 ± 3.8**	40.1 ± 7.0

F1: exchangeable fraction; F2: reducible fraction; F3: oxidizable fraction; F4: residual fraction. The bold represents the main fraction of the element

Reservoir, Pb is unlikely to pose a significant threat to aquatic biota.

Unlike other elements, the dominant phase of Cd was in the exchangeable fraction in both reservoirs, which suggests that most of Cd is exchangeable and perhaps bound to carbonates (Szolnoki and Farsang 2013). Similar patterns have been also discovered in the previous studies on lake and marine sediment (Yuan et al. 2004; Sundaray et al. 2011; Schintu et al. 2016; Guan et al. 2018). The range of pH in the sediment–water interface was 8.2–8.7 and 8.2–8.5 in the Shiquan Reservoir and the Zam Reservoir, respectively, suggesting the moderately alkaline nature (Zhao et al. 2020). Due to the similar ionic radius of Cd (97 pm) and Ca (99 pm), Cd tends to combine with carbonate minerals by replacing Ca^{2+} in crystal lattice at high pH (pH > 7) (Yuan et al. 2004; Sundaray et al. 2011). High percentage of Cd in the exchangeable fraction suggests the high mobility and bioavailability of Cd (Li et al. 2018). However, the concentrations of the potential mobile Cd in the Shiquan Reservoir (0.17 ± 0.04 mg/kg) and the Zam Reservoir (0.14 ± 0.03 mg/kg) were much lower than its threshold effect concentration of 0.99 mg/kg, implying that adverse biological effects would rarely occur (MacDonald et al. 2000).

Geothermal sources of Li, As, and Cs

Enrichment of Li, As, and Cs is observed in sediments from both reservoirs (Fig. 5). In this region, abnormally enriched Li, As, and Cs in geothermal springs have already been extensively discovered (Li et al. 2014). As the eastern part of the Mediterranean–Himalayan geothermal belt, geothermal systems are widely distributed in Tibet, among which many are discharging geothermal waters with extremely high As concentrations from 10 mg/L to 126 mg/L (Tan et al. 2018; Guo et al. 2019). Grimaud et al. (1985) discovered that Li (up to 22.2 mg/L) and Cs (up to 11.5 mg/L) are very enriched in geothermal waters of Central Tibet, and hot springs with these characteristics are very common in Tibet, especially in the ST and the YT drainages. Guo et al. (2007) reported that Li and As concentrations in Yangbajing geothermal waters in the YT drainage reached 25.0 and 5.7 mg/L, respectively. In the Kawu area in the southern YT
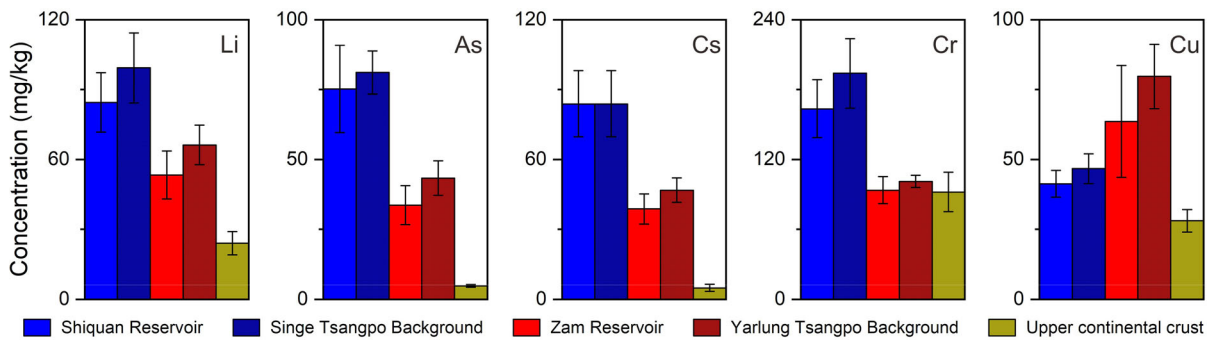
Fig. 5 Concentrations of 5 elements in reservoir sediments and their regional geochemical background established in this study (Table 1). Li, As, and Cs display significant enrichment in comparison with upper continental crustal abundance
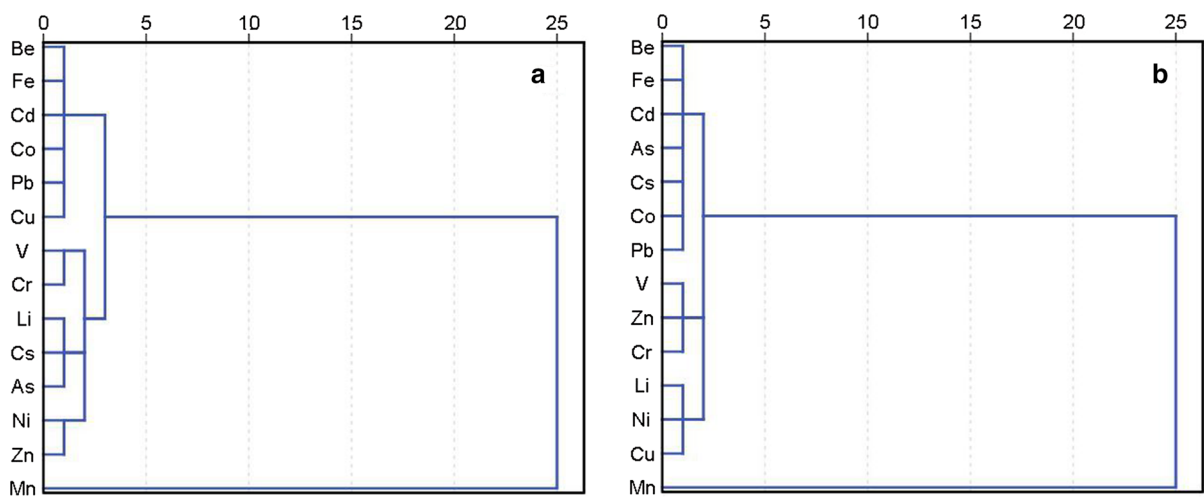
Fig. 6 Dendrogram showing clustering of metal(loid)s in sediments from the Shiquan Reservoir (**a**) and the Zam Reservoir (**b**)

drainage, Li contents in geothermal waters reached 23.3 mg/L (Tan et al. 2018).

Multiple lines of evidence show that the enrichment of Li, As, and Cs in surface waters in Tibet is closely related to the discharge of hot springs. Guo and Wang (2009) concluded that the geothermal waters were responsible for the elevated concentrations of Li in river waters in the YT drainage. The natural As source (geothermal springs) has led to a significant enrichment in As in the Duilong Qu (205 μg/L As) and the Lhasa River (26 μg/L As), which are tributaries of the YT (Li et al. 2014). Zhang et al. (2015) reported that a large amount of As-rich geothermal waters in Kawu village flowed directly into the Chongqu River, a tributary of the YT, leading to a significant rise in arsenic levels downstream. Li et al. (2013b) found that

a positive correlation existed between [As] and [Na] + [K] in Tibetan stream waters (including the YT and the ST), indicating that these surface water As enrichments were linked to the hot springs and/or salt lakes. Meng (2020) attributed the abnormal Li enrichment and Li isotopic composition of the YT water to hot springs with high Li content and low δ^7Li value, and further showed in a binary mixing model that the hot spring input contributed 60–80% of the dissolved Li in the YT waters, reflecting the significant influence of hot spring input on the YT surface waters.

The similarity, common sources and mobilization mechanisms among elements can be assessed by cluster analysis (Li et al. 2013a; Rasool and Xiao 2018). In the Shiquan Reservoir, Li, As, and Cs were clustered together into a group (Fig. 6), suggesting

these three elements may share a similar source, i.e., hot spring input. In the Zam Reservoir, As, and Cs were clustered into a same group but not for Li. This may be attributed to the strong dilution effect of the YT water on hot spring input due to the large runoff rate (Zhao et al. 2020). Moreover, significantly positive correlations existed among Li, As, and Cs in sediments from both reservoirs (Table S5), which further suggested the common geothermal source of Li, As, and Cs.

Conclusions

Concentrations of arsenic and 13 metals including Li, Be, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Cs, and Pb, and their chemical fractions were obtained from 123 sediments from the Shiquan Reservoir on the Singe Tsangpo and from 250 sediments from the Zam Reservoir on the Yarlung Tsangpo in Tibet, China. Concentrations of all elements but Cu were significantly higher in the Shiquan Reservoir than those in the Zam Reservoir due to the much finer sediment grain size in the Shiquan Reservoir. The Cu content in sediments from the Zam Reservoir was significantly higher than those from the Shiquan Reservoir, possibly due to influence by the Qulong copper deposit. Moreover, within the Zam Reservoir, the concentrations of all elements measured in sediments increased along the flow direction, attributable to a decrease in grain size of the sediments closer to the dam due to weakened flow dynamics.

The regional background values of Li, Be, V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Cs, and Pb in the ST and YT drainage basins were calculated by normalized to the upper crustal Fe abundance. Li, As, and Cs in the ST and YT drainages display an enrichment of 2.8–17.1-fold compared to their respective upper crustal abundance and are considered to be originated from the hot springs.

The chemical fractions of metals and metalloids in these two reservoirs are similar to most of the elements dominated by the residual fraction, which reflects a relatively low ecological risk in the study areas. Elevated levels of As, Cu, Pb, and Be are detected in mobile fractions and thus may present risks.

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Data availability All data included in this study are available upon request by contacting with the corresponding author.

Compliance with ethical standards

Conflicts of interest The authors have no conflicts of interest to declare that are relevant to the content of this article.

References

Aloupi, M., & Angelidis, M. O. (2001). Normalization to lithium for the assessment of metal contamination in coastal sediment cores from the Aegean Sea. *Greece. Mar. Environ. Res., 52,* 1–12. https://doi.org/10.1016/s0141-1136(00)00255-5.

Bibby, R. L., & Webster-Brown, J. G. (2006). Trace metal adsorption onto urban stream suspended particulate matter (Auckland region, New Zealand). *Applied Geochemistry, 21,* 1135–1151. https://doi.org/10.1016/j.apgeochem.2006.03.014.

Bing, H. J., Zhou, J., Wu, Y. H., Wang, X. X., Sun, H. Y., & Li, R. (2016). Current state, sources, and potential risk of heavy metals in sediments of Three Gorges Reservoir, China. *Environmental Pollution, 214,* 485–496. https://doi.org/10.1016/j.envpol.2016.04.062.

Blasco, J., Saenz, V., & Gomez-Parra, A. (2000). Heavy metal fluxes at the sediment-water interface of three coastal ecosystems from south-west of the Iberian Peninsula.

Science of the Total Environment, 247, 189–199. https://doi.org/10.1016/s0048-9697(99)00490-8.

Cheng, Y. A., & Tian, J. L. (1993). *Background values and distribution characteristics of soil elements in Tibet (in Chinese)* (p. 69). Beijing: Science.

Duodu, G. O., Goonetilleke, A., & Ayoko, G. A. (2016). Comparison of pollution indices for the assessment of heavy metal in Brisbane River sediment. *Environmental Pollution, 219,* 1077–1091. https://doi.org/10.1016/j.envpol.2016.09.008.

Edmunds, W. M., Ahmed, K. M., & Whitehead, P. G. (2015). A review of arsenic and its impacts in groundwater of the Ganges-Brahmaputra-Meghna delta, Bangladesh. *Environmental Science-Processes & Impacts, 17,* 1032–1046. https://doi.org/10.1039/c4em00673a.

Fendorf, S., Michael, H. A., & van Geen, A. (2010). Spatial and Temporal Variations of Groundwater Arsenic in South and Southeast Asia. *Science, 328,* 1123–1127. https://doi.org/10.1126/science.1172974.

Grimaud, D., Huang, S., Michard, G., & Zheng, K. (1985). Chemical study of geothermal waters of central Tibet (China). *Geothermics, 14,* 35–48. https://doi.org/10.1016/0375-6505(85)90092-6.

Guan, J. N., Wang, J., Pan, H., Yang, C., Qu, J., Lu, N., & Yuan, X. (2018). Heavy metals in Yinma River sediment in a major Phaeozems zone, Northeast China: Distribution, chemical fraction, contamination assessment and source apportionment. *Scientific Reports, 8,* 11. https://doi.org/10.1038/s41598-018-30197-z.

Guan, Z. H., Chen, C. Y., Ou, Y. X., Fan, Y. Q., Zhang, Y. S., Chen, Z. M., et al. (1984). *Tibetan rivers and lakes (in Chinese).* Beijing: Science.

Guo, Q., Wang, Y., & Liu, W. (2007). Major hydrogeochemical processes in the two reservoirs of the Yangbajing geothermal field Tibet China. *J. Volcanol. Geotherm. Res., 166,* 255–268. https://doi.org/10.1016/j.jvolgeores.2007.08.004.

Guo, Q. H., Planer-Friedrich, B., Liu, M. L., Yan, K., & Wu, G. (2019). Magmatic fluid input explaining the geochemical anomaly of very high arsenic in some southern Tibetan geothermal waters. *Chemical Geology, 513,* 32–43. https://doi.org/10.1016/j.chemgeo.2019.03.008.

Guo, Q. H., & Wang, Y. X. (2009). Trace element hydrochemistry indicating water contamination in and around the Yangbajing geothermal field, Tibet, China. *Bulletin of Environmental Contamination and Toxicology, 83,* 608–613. https://doi.org/10.1007/s00128-009-9812-7.

Jiang, J. B., Wang, J., Liu, S. Q., Lin, C. Y., He, M. C., & Liu, X. T. (2013). Background, baseline, normalization, and contamination of heavy metals in the Liao River Watershed sediments of China. *Journal of Asian Earth Sciences, 73,* 87–94. https://doi.org/10.1016/j.jseaes.2013.04.014.

Karlsson, K., Viklander, M., Scholes, L., & Revitt, M. (2010). Heavy metal concentrations and toxicity in water and sediment from stormwater ponds and sedimentation tanks. *Journal of Hazardous Materials, 178,* 612–618. https://doi.org/10.1016/j.jhazmat.2010.01.129.

Ke, X., Gui, S., Huang, H., Zhang, H., Wang, C., & Guo, W. (2017). Ecological risk assessment and source identification for heavy metals in surface sediment from the Liaohe

River protected area, China. *Chemosphere, 175,* 473–481. https://doi.org/10.1016/j.chemosphere.2017.02.029.

Lee, P. K., Kang, M. J., Yu, S., Ko, K. S., Ha, K., Shin, S. C., & Park, J. H. (2017). Enrichment and geochemical mobility of heavy metals in bottom sediment of the Hoedong reservoir, Korea and their source apportionment. *Chemosphere, 184,* 74–85. https://doi.org/10.1016/j.chemosphere.2017.05.124.

Li, C. L., Kang, S. C., Chen, P. F., Zhang, Q. G., Mi, J., Gao, S. P., & Sillanpaa, M. (2014). Geothermal spring causes arsenic contamination in river waters of the southern Tibetan Plateau, China. *Environmental Earth Sciences, 71,* 4143–4148. https://doi.org/10.1007/s12665-013-2804-2.

Li, C. L., Kang, S. C., Zhang, Q. G., Gao, S. P., & Sharma, C. M. (2011). Heavy metals in sediments of the Yarlung Tsangbo and its connection with the arsenic problem in the Ganges-Brahmaputra Basin. *Environmental Geochemistry and Health, 33,* 23–32. https://doi.org/10.1007/s10653-010-9311-0.

Li, F., Huang, J. H., Zeng, G. M., Yuan, X. Z., Li, X. D., Liang, J., et al. (2013a). Spatial risk assessment and sources identification of heavy metals in surface sediments from the Dongting Lake, Middle China. *Journal of Geochemical Exploration, 132,* 75–83. https://doi.org/10.1016/j.gexplo.2013.05.007.

Li, F., Xiao, M. S., Zhang, J. D., Liu, C. Y., Qiu, Z. Z., & Cai, Y. (2018). Spatial distribution, chemical fraction and fuzzy comprehensive risk assessment of heavy metals in surface sediments from the Honghu Lake, China. *International Journal of Environmental Research and Public Health, 15,* 17. https://doi.org/10.3390/ijerph15020207.

Li, S. H., Wang, M. G., Yang, Q., Wang, H., Zhu, J. M., Zheng, B. S., & Zheng, Y. (2013b). Enrichment of arsenic in surface water, stream sediments and soils in Tibet. *Journal of Geochemical Exploration, 135,* 104–116. https://doi.org/10.1016/j.gexplo.2012.08.020.

Liu, J., Yao, Z. J., & Chen, C. Y. (2007). Evolution trend and causation analysis of the runoff evolution in the Yarlung Zangbo River Basin. *Journal of Natural Resources, 22,* 471–477. (**(In Chinese with English abstract)**).

Lone, S. A., Jeelani, G., Mukherjee, A., & Coomar, P. (2020). Geogenic groundwater arsenic in high altitude bedrock aquifers of upper Indus river basin (UIRB). *Ladakh. Applied Geochemistry, 113,* 11. https://doi.org/10.1016/j.apgeochem.2019.104497.

Ma, X. L., Zuo, H., Tian, M. J., Zhang, L. Y., Meng, J., Zhou, X. N., et al. (2016). Assessment of heavy metals contamination in sediments from three adjacent regions of the Yellow River using metal chemical fractions and multivariate analysis techniques. *Chemosphere, 144,* 264–272. https://doi.org/10.1016/j.chemosphere.2015.08.026.

MacDonald, D. D., Ingersoll, C. G., & Berger, T. A. (2000). Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology, 39,* 20–31. https://doi.org/10.1007/s002440010075.

Meng, J.L., 2020. Lithium isotopes fraction in the Yarlung Tsangpo River: controlling factors and implications. Master. Thesis. Institute of Geochemistry, Chinese Academy of Sciences (in Chinese).

Newman, B. K., & Watling, R. J. (2007). Definition of baseline metal concentrations for assessing metal enrichment of sediment from the south-eastern Cape coastline of South Africa. *Water SA, 33,* 675–691.

Palma, P., Ledo, L., & Alvarenga, P. (2015). Assessment of trace element pollution and its environmental risk to freshwater sediments influenced by anthropogenic contributions: The case study of Alqueva reservoir (Guadiana Basin). *CATENA, 128,* 174–184. https://doi.org/10.1016/j.catena.2015.02.002.

Qin, H., Zhu, J., Li, S., & Wang, M. (2010). Determination of Total Arsenic in Environmental Samples by Hydride Generation-Atomic Fluorescence Spectrometry with PTFE Bomb. *Acta Mineralogica Sinica, 30,* 398–402. (**In Chinese with English abstract)**).

Rahman, M. A., & Hasegawa, H. (2012). Arsenic in freshwater systems: Influence of eutrophication on occurrence, distribution, speciation, and bioaccumulation. *Applied Geochemistry, 27,* 304–314. https://doi.org/10.1016/j.apgeochem.2011.09.020.

Rasool, A., & Xiao, T. (2018). *Distribution and potential ecological risk assessment of trace elements in the stream water and sediments from Lanmuchang area, southwest Guizhou.* China: Environmental science and pollution research international. https://doi.org/10.1007/s11356-018-3827-8.

Rieuwerts, J. S., Mighanetara, K., Braungardt, C. B., Rollinson, G. K., Pirrie, D., & Azizi, F. (2014). Geochemistry and mineralogy of arsenic in mine wastes and stream sediments in a historic metal mining area in the UK. *Science of the Total Environment, 472,* 226–234. https://doi.org/10.1016/j.scitotenv.2013.11.029.

Rudnick, R. L., & Gao, S. (2003). 3.01 - Composition of the Continental Crust. In H. D. Holland & K. K. Turekian (Eds.), *Treatise on Geochemistry* (pp. 1–64). Oxford: Pergamon.

Schaller, J., Brackhage, C., Mkandawire, M., & Dudel, E. G. (2011). Metal/metalloid accumulation/remobilization during aquatic litter decomposition in freshwater: A review. *Science of the Total Environment, 409,* 4891–4898. https://doi.org/10.1016/j.scitotenv.2011.08.006.

Schintu, M., Marrucci, A., Marras, B., Galgani, F., Buosi, C., Ibba, A., & Cherchi, A. (2016). Heavy metal accumulation in surface sediments at the port of Cagliari (Sardinia, western Mediterranean): Environmental assessment using sequential extractions and benthic foraminifera. *Marine Pollution Bulletin, 111,* 45–56. https://doi.org/10.1016/j.marpolbul.2016.07.029.

Sohrin, Y., Matsui, M., Kawashima, M., Hojo, M., & Hasegawa, H. (1997). Arsenic biogeochemistry affected by eutrophication in Lake Biwa, Japan. *Environmental Science & Technology, 31,* 2712–2720. https://doi.org/10.1021/es960846w.

Soto-Jimenez, M. F., & Paez-Osuna, F. (2001). Distribution and normalization of heavy metal concentrations in mangrove and lagoonal sediments from Mazatlan Harbor (SE Gulf of California). *Estuarine Coastal and Shelf Science, 53,* 259–274. https://doi.org/10.1006/ecss.2000.0814.

Summers, J. K., Wade, T. L., Engle, V. D., & Malaeb, Z. A. (1996). Normalization of metal concentrations in estuarine sediments from the Gulf of Mexico. *Estuaries, 19,* 581–594. https://doi.org/10.2307/1352519.

Sun, X. S., Fan, D. J., Liu, M., Tian, Y., Pang, Y., & Liao, H. J. (2018). Source identification, geochemical normalization and influence factors of heavy metals in Yangtze River Estuary sediment. *Environmental Pollution, 241,* 938–949. https://doi.org/10.1016/j.envpol.2018.05.050.

Sundaray, S. K., Nayak, B. B., Lin, S., & Bhatta, D. (2011). Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments-A case study: Mahanadi basin, India. *Journal of Hazardous Materials, 186,* 1837–1846. https://doi.org/10.1016/j.jhazmat.2010.12.081.

Sutherland, R. A., & Tack, F. M. G. (2003). Fractionation of Cu, Pb and Zn in certified reference soils SRM 2710 and SRM 2711 using the optimized BCR sequential extraction procedure. *Advances in Environmental Research, 8,* 37–50. https://doi.org/10.1016/s1093-0191(02)00144-2.

Szolnoki, Z., & Farsang, A. (2013). Evaluation of metal mobility and bioaccessibility in soils of urban vegetable gardens using sequential extraction. *Water Air and Soil Pollution, 224,* 16. https://doi.org/10.1007/s11270-013-1737-4.

Tam, N. F. Y., & Yao, M. W. Y. (1998). Normalisation and heavy metal contamination in mangrove sediments. *Science of the Total Environment, 216,* 33–39. https://doi.org/10.1016/s0048-9697(98)00132-6.

Tan, H. B., Su, J. B., Xu, P., Dong, T., & Elenga, H. I. (2018). Enrichment mechanism of Li, B and K in the geothermal water and associated deposits from the Kawu area of the Tibetan plateau: Constraints from geochemical experimental data. *Applied Geochemistry, 93,* 60–68. https://doi.org/10.1016/j.apgeochem.2018.04.001.

Tariq, J., Ashraf, M., Jaffar, M., & Afzal, M. (1996). Pollution status of the Indus River, Pakistan, through heavy metal and macronutrient contents of fish, sediment and water. *Water Research, 30,* 1337–1344. https://doi.org/10.1016/0043-1354(95)00300-2.

Verma, S., Mukherjee, A., Mahanta, C., Choudhury, R., Badoni, R. P., & Joshi, G. (2019). Arsenic fate in the Brahmaputra river basin aquifers: Controls of geogenic processes, provenance and water-rock interactions. *Applied Geochemistry, 107,* 171–186. https://doi.org/10.1016/j.apgeochem.2019.06.004.

Wang, C., Yao, Y., Wang, P. F., Hou, J., Qian, J., Yuan, Y., & Fan, X. L. (2016). In situ high-resolution evaluation of labile arsenic and mercury in sediment of a large shallow lake. *Science of the Total Environment, 541,* 83–91. https://doi.org/10.1016/j.scitotenv.2015.09.037.

Wang, J., Liu, G. J., Lu, L. L., Zhang, J. M., & Liu, H. Q. (2015). Geochemical normalization and assessment of heavy metals (Cu, Pb, Zn, and Ni) in sediments from the Huaihe River, Anhui, China. *CATENA, 129,* 30–38. https://doi.org/10.1016/j.catena.2015.02.008.

Xia, P., Meng, X. W., Feng, A. P., Yin, P., Zhang, J., & Wang, X. Q. (2012). Geochemical characteristics of heavy metals in coastal sediments from the northern Beibu Gulf (SW China): the background levels and recent contamination. *Environmental Earth Sciences, 66,* 1337–1344. https://doi.org/10.1007/s12665-011-1343-y.

Yang, J., Chen, L., Liu, L. Z., Shi, W. L., & Meng, X. Z. (2014). Comprehensive risk assessment of heavy metals in lake sediment from public parks in Shanghai. *Ecotoxicology and Environmental Safety, 102,* 129–135. https://doi.org/10.1016/j.ecoenv.2014.01.010.

Yang, J. S., Zhang, Z. M., Li, T. F., Li, Z. L., Ren, Y. F., Xu, X. Z., et al. (2008). Unusual minerals from harzburgite, the host rock of the Luobusa chromite deposit. *Tibet. Acta Petrologica Sinica, 24,* 1445–1452.

Yu, G. B., Liu, Y., Yu, S., Wu, S. C., Leung, A. O. W., Luo, X. S., et al. (2011). Inconsistency and comprehensiveness of risk assessments for heavy metals in urban surface sediments. *Chemosphere, 85,* 1080–1087. https://doi.org/10.1016/j.chemosphere.2011.07.039.

Yuan, C. G., Shi, J. B., He, B., Liu, J. F., Liang, L. N., & Jiang, G. B. (2004). Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. *Environment International, 30,* 769–783. https://doi.org/10.1016/j.envint.2004.01.001.

Zeng, J., Yang, L. Y., Chuai, X. M., Chen, X. F., Zhao, H. Y., & Wu, Q. L. (2013). Comparison of metal(loid) concentrations in water, sediments and fish from two large shallow lakes. *International Journal of Environmental Science and Technology, 10,* 1209–1218. https://doi.org/10.1007/s13762-013-0246-8.

Zhang, Q., Tan, H., Zhang, W., Kong, N., & Zhang, Y. (2015). Water environmental effects of Kawu geothermal water in Sajia County. *Tibet. Water Resources Protection, 31,* 45. ((**In Chinese with English abstract**)).

Zhang, Y. F., Li, S. H., Zheng, L. R., Chen, J. G., & Zheng, Y. (2017). Evaluation of arsenic sorption and mobility in stream sediment and hot spring deposit in three drainages of the Tibetan Plateau. *Applied Geochemistry, 77,* 89–101. https://doi.org/10.1016/j.apgeochem.2016.04.006.

Zhao, Z. J., Li, S. H., Xue, L. L., Liao, J., Zhao, J. J., Wu, M., et al. (2020). Effects of dam construction on arsenic mobility and transport in two large rivers in Tibet, China. *The Science of the total environment, 741,* 140406. https://doi.org/10.1016/j.scitotenv.2020.140406.