



## Effects of dam construction on arsenic mobility and transport in two large rivers in Tibet, China



Zhenjie Zhao<sup>a,b</sup>, Shehong Li<sup>a,\*</sup>, Lili Xue<sup>a,b</sup>, Jie Liao<sup>a,b</sup>, Jingjing Zhao<sup>a,b</sup>, Mei Wu<sup>a,b</sup>, Mingguo Wang<sup>c</sup>, Jing Sun<sup>a</sup>, Yan Zheng<sup>d</sup>, Qiang Yang<sup>e,\*</sup>

<sup>a</sup> The State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, China

<sup>c</sup> Center for Hydrogeology and Environmental Geology Survey, China Geological Survey, Baoding 071051, China

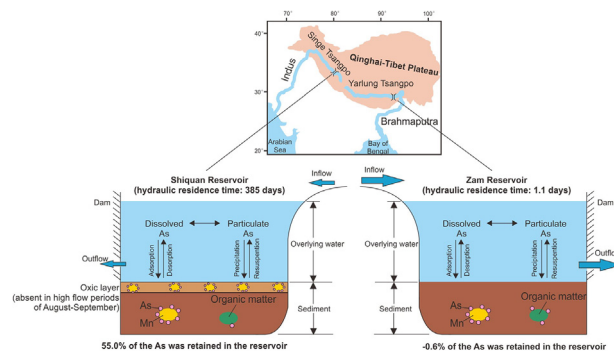
<sup>d</sup> School of Environmental Science and Engineering, South University of Science and Technology of China, Shenzhen 518055, China

<sup>e</sup> Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964, USA

### HIGHLIGHTS

- High levels of As were present in water and sediments of the two reservoirs.
- Manganese oxides are the main carrier of As in sediments of the two reservoirs.
- Water residence time is a vital factor affecting As retention in the reservoirs.
- The Shiquan Reservoir can effectively retain As and reduce As transport downstream.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Construction of dams on the Singe Tsangpo (ST) and the Yarlung Tsangpo (YT) Rivers, the upper stretch of the Indus and the Brahmaputra Rivers, respectively, are expected to affect material transport. To evaluate the effects of dam construction on arsenic (As) mobility and transport in the ST River and the YT River in Tibet and the downstream river basins, water column and sediment core samples in the Shiquan Reservoir of the ST River and in the Zam Reservoir of the YT River were obtained in August 2017, and January and May 2018, and additionally, at the inflows and outfalls of the reservoirs. The seasonal variation of dissolved As contents in the inflow water of the Zam Reservoir and the Shiquan Reservoir was regulated by the mixing between the low-As river runoff and the high-As hot spring input. Water residence time (WRT) is a key variable regulating the variation of dissolved As contents in reservoirs and outflow waters with time. The absence of the oxic layer at the sediment-water interface reduced the accumulation of As in surface sediments under high-flow conditions. Arsenic mobility in sediment of the two reservoirs was mainly controlled by Mn oxides and organic matter. Reservoirs with long water residence time are more favorable for As retention. Sedimentation was the main mechanism of As retention. The Shiquan Reservoir with a longer WRT of 385 days can effectively retain 55% of the total arsenic load from upstream, while the Zam Reservoir has no effective retention of arsenic due to the very short WRT of 1.1 days. These have important implications on the geochemical and ecological environments of the downstream river basins.

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\* Corresponding authors.

E-mail addresses: [lishenhong@vip.gyig.ac.cn](mailto:lishenhong@vip.gyig.ac.cn) (S. Li), [sunjing@mail.gyig.ac.cn](mailto:sunjing@mail.gyig.ac.cn) (J. Sun), [qyang@ldeo.columbia.edu](mailto:qyang@ldeo.columbia.edu) (Q. Yang).

## 1. Introduction

To utilize river water resources, reservoirs of different sizes have been built on at least 70% of the world's rivers (Chen et al., 2019). More than 45,000 dams of >15 m high have been built worldwide until 2005 (Nilsson et al., 2005). Dam construction can change the hydrological conditions of rivers, and thereby alter the migration and transport patterns of elements (Syvitski et al., 2005; Zhang et al., 2019). Moreover, the sediments in the reservoirs may undergo physical and geochemical processes that could affect the fate of elements (Grygar et al., 2018) and thus the downstream geochemical environment and ecosystem.

Arsenic (As) enriched groundwater is widespread in the major Himalayan river basins including Indus and Brahmaputra (Mukherjee et al., 2019). It has been reported that 82% of groundwater samples had As concentrations above the World Health Organization (WHO) drinking water guideline of 10 µg/L in bedrock aquifers of the upper Indus river basin (Lone et al., 2020). As enriched groundwater (up to 420 µg/L As) was observed in the eastern part of the upper Brahmaputra river basin (Verma et al., 2019). Furthermore, Li et al. (2013) reported As enrichment anomaly in the Singe Tsangpo (ST) River (upstream of the Indus River) drainage and the Yarlung Tsangpo (YT) River (upstream of the Brahmaputra River) drainage. Average concentrations of As in stream waters, sediments and soils were as high as  $58 \pm 70$  µg/L,  $42 \pm 40$  mg/kg, and  $44 \pm 27$  mg/kg, respectively, for the ST River

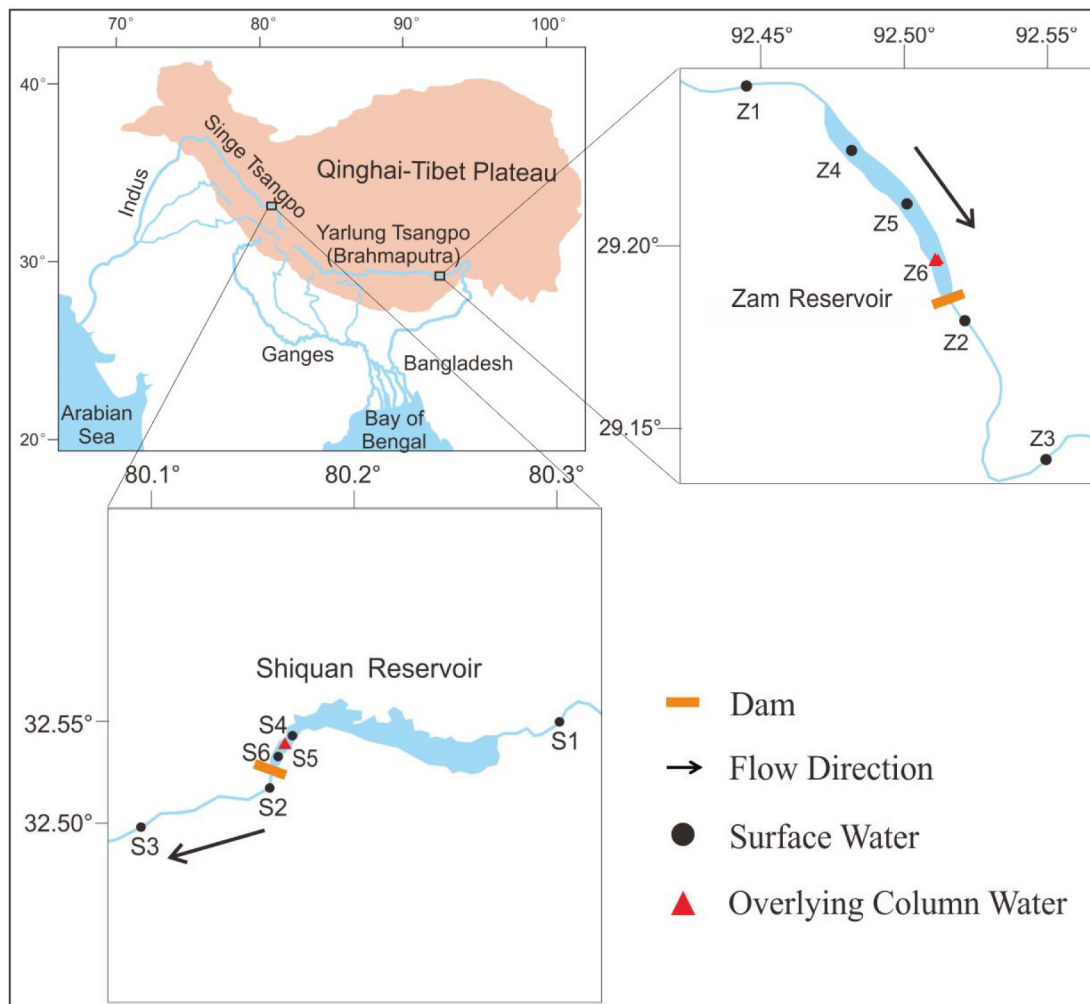
drainage and were  $11 \pm 17$  µg/L,  $28 \pm 11$  mg/kg, and  $30 \pm 34$  mg/kg, respectively, for the YT River drainage.

In 2007 and 2014, the Shiquan Reservoir dam and the Zam Reservoir dam were built respectively on the ST River (the upper Indus) and the YT River (the upper Brahmaputra). It is unknown that after the interception of dam, whether and how the amount of As transported to downstream areas would change. It is also unknown how As mobility and migration within the reservoirs would change after dam construction. To assess the risks on public health and the ecosystem from As exposure in the adjacent areas and downstream river basins, it is essential to quantify the effects of dam construction on arsenic mobility and transport. The main objectives of this study therefore were to: (1) investigate the spatiotemporal variations of As in water and sediment of the Shiquan Reservoir and the Zam Reservoir; (2) elucidate the migration mechanisms of As; and (3) reveal the impact of dam interception on As transport in plateau rivers.

## 2. Materials and methods

### 2.1. Study area

The ST River is the upper stream of the Indus River which is one of the largest rivers in South Asia (Zhang et al., 2015). It originates from the northern region of Mount Kailash, the main peak of the Gangdise Mountain. The river head is 5164 m above sea level. The total length



**Fig. 1.** The sampling location map of the Shiquan Reservoir and the Zam Reservoir, Tibet. S1 and Z1 were the inflow water sample collection sites, S2 and Z2 were the outflow water sample collection sites, and S3 and Z3 were the downstream water sample collection sites. Surface water samples from the reservoirs were collected at the sites of S4, S5, S6, Z4, Z5, and Z6, and water columns and sediment cores were collected at the sites of S5 and Z6.

of ST River is 430 km with a basin area of 27,450 km<sup>2</sup>. The ST River basin is located in the arid region of Tibet. Hot springs are widely distributed in the upper reaches of the ST River, which can replenish the river runoff in addition to precipitation and groundwater (Guan et al., 1984). The Shiquan Reservoir is located in the Gar County, with a perennial mean temperature of 0.2 °C. With a max depth of 23 m, the Shiquan Reservoir is located in the middle reach of the ST River. The capacity of the Shiquan Reservoir is 1.85 × 10<sup>8</sup> m<sup>3</sup>.

The YT River is the upper reach of the Brahmaputra River. It is the largest river in Tibet and also the highest river in the world. It originates from the Gyaimanezong Glacier at an elevation of 5200 m above sea level in the northern Himalayas (Zhang et al., 2015). The YT River runs from west to east across southern Tibet with a total length of 2057 km and a basin area of 240,480 km<sup>2</sup> in China, and it has many large tributaries. The average elevation of the river basin is ~4500 m. The river has a strong erosion on Paleozoic to Eocene sedimentary rocks together with volcanic and plutonic rocks of the Indus-Tsangpo Suture (Li et al., 2011). In the YT River basin, precipitation is the main source of supply to river water. Brought by the Indian summer monsoon, the precipitation occurs mostly from June to September in the YT River basin (Bai et al., 2014). As a result, the runoff from June to August accounted for 51–54% of the whole year, and the runoff from December to February only accounted for 6–7% of the whole year (Liu et al., 2007). The Zam Reservoir is located in the Gyaca County with a perennial mean temperature of 8.3 °C. It is a canyon reservoir in the middle reach of the YT River with a max depth of 50 m. The capacity of the Zam Reservoir is 8.7 × 10<sup>7</sup> m<sup>3</sup>.

## 2.2. Sampling

Surface water samples, water column samples from different depth, and sediment core samples were collected from the Shiquan Reservoir and the Zam Reservoir in August 2017, January 2018 and May 2018, which represented the high flow period, low flow period, and medium flow period, respectively. Surface water samples were collected from the inflows, outflows and reservoirs, while water column samples and sediment cores were only collected from the reservoirs (Fig. 1). Water temperature (T), dissolved oxygen (DO), pH and electrical conductivity (EC) were measured *in situ* using a multiparameter water quality analyzer (Multi 3430, WTW; Table 1).

Surface water samples were collected using a water sampler with a 5 L capacity at ~20 cm beneath the surface. Water column samples were collected at different depths using a stratified water sampler. Water samples were filtered immediately after collection through 0.45 µm cellulose acetate filtration membranes using a diaphragm

vacuum pump to obtain the suspended particulates and dissolved fractions. The membranes were dried in a vacuum freeze dryer to a constant weight. The concentration of suspended particulates was calculated by dividing the weight difference between the membrane with and without particles by the volume of the filtered water (Yang et al., 2016). For each site, both filtered and unfiltered waters were stored in 60 mL polypropylene plastic bottles. Unfiltered water and one bottle of filtered water were acidified to pH 2 with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) for total phosphorous (TP) and dissolved phosphorous (DP) analysis. One bottle of filtered water was acidified to 2% nitric acid (HNO<sub>3</sub>) for cation and arsenic analysis. Another bottle of filtered water was used for anion analysis. Sediment cores were collected using a 100 cm long gravity corer with 6 cm internal diameter at the same sites as the stratified water column. The cores were sliced into 1 cm sections in the field and stored in sealed sterile centrifuge tubes. All the containers including bottles and centrifuge tubes were acid-washed. Samples were transported to the laboratory in 7 days at room temperature in dark. Water samples were kept at 4 °C until analysis. Sediment samples were dried in a vacuum freeze dryer before particle size analysis. A fraction of the dried sediments was ground in an agate mortar and then sieved through a 200-mesh nylon sieve (74 µm) for chemical analysis of fine sediments.

## 2.3. Analytical procedures

### 2.3.1. Water

Dissolved As concentrations in the water samples were determined by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent, 7700X, USA). Major cations were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES, iCAP6500, Thermo Scientific, Germany). Anions were determined using ion chromatography (IC, DIONEX ICS-90). The contents of TP and DP were analyzed using the molybdenum blue method (Murphy and Riley, 1962).

### 2.3.2. Sediment and suspended particulates

For sediment particle size analysis, ~0.3 g unground sediment sample was treated with 10% H<sub>2</sub>O<sub>2</sub> and 10% HCl to eliminate organic matter and carbonates, and a dispersant solution ((Na<sub>2</sub>PO<sub>3</sub>)<sub>6</sub>) was added to disperse sediment samples. The particle size was determined using a laser grain size meter (Mastersizer 2000 Ltd., UK) (clay: <4 µm; silt: 4–64 µm; sand: >64 µm) (Wu et al., 2016; Sun et al., 2018). Total organic carbon (TOC) and total sulfur (TS) in the sediments were measured using an element analyzer (Vario MACRO cube) (Chang et al., 2019). Total As, Fe and Mn were analyzed by ICP-MS after digesting filter membranes with adherent particles or 50 mg ground sediment samples in a 30 mL Teflon tube with nitric acid (Tariq et al., 1996; Bibby and

**Table 1**  
Field parameters and As concentrations in surface waters from the Shiquan Reservoir of the Singe Tsangpo.

Sampling time	Position	Temperature (°C)	pH	DO (mg/L)	EC (µs/cm)	Total P (mg/L)	Dissolved P (mg/L)	Total As (µg/L)	Dissolved As (µg/L)	Particulate As (µg/L)	Particulates (mg/L)
August 2017 (high flow)	Inflow	16.9	8.46	5.60	358	–	0.06	90.0	67.9	22.0	258.0
	Reservoir (n = 3)	18.9 ± 0.2	8.45 ± 0.02	5.15 ± 0.09	298 ± 14	–	0.04 ± 0.00	62.6 ± 0	58.3 ± 0.7	4.0 ± 0.5	34.1 ± 5.8
	Outflow	15.6	8.43	5.69	290	–	0.04	68.6	63.1	5.4	49.3
	Downstream	15.8	8.44	5.88	309	–	0.04	68.3	63.7	4.6	41.3
January 2018 (low flow)	Inflow	0.5	8.56	9.17	380	0.24	0.12	42.6	41.6	1.0	12.1
	Reservoir (n = 2)	0.0 ± 0.0	8.61 ± 0.01	8.45 ± 0.05	367 ± 2	0.30 ± 0.00	0.12 ± 0.01	52.3 ± 0.1	51.4 ± 0.0	1.0 ± 0.0	4.9 ± 0.0
	Outflow	2.6	8.65	8.33	359	0.20	0.08	52.0	51.0	1.0	6.1
	Downstream	4.8	8.68	9.06	350	0.21	0.09	52.1	51.2	0.9	5.8
May 2018 (medium flow)	Inflow	11.5	8.63	7.02	332	0.12	0.03	76.7	68.7	8.0	52.3
	Reservoir (n = 3)	7.4 ± 0.5	8.65 ± 0.03	7.27 ± 0.01	367 ± 6	0.03 ± 0.00	0.02 ± 0.00	37.5 ± 0.1	36.7 ± 0.1	0.8 ± 0.0	3.2 ± 0.0
	Outflow	6.9	8.64	7.25	363	0.03	0.02	37.7	36.1	1.7	11.0
	Downstream	9.5	8.72	7.32	363	0.03	0.02	37.6	36.7	0.9	5.1

Webster-Brown, 2006; Qin et al., 2010). Accuracy of the digestion method was verified based on method blanks, duplicates and standard reference materials (GBW07302 and GBW07430). The recoveries of total As, Fe and Mn were 97.1–103.3%, 95.9–105.7%, and 97.1–101.9%, respectively. The difference between duplicates was <6% for As and Fe and <3% for Mn.

To investigate sediment As speciation, three major As fractions (F1–3) were extracted using a modified BCR (European Community Bureau of Reference) sequential extraction protocol (Sutherland and Tack, 2003; Mossop and Davidson, 2003; Yu et al., 2011; Rieuwerts et al., 2014). Briefly, step 1 aims to extract exchangeable As (F1) which is mainly bound to carbonates and weakly adsorbed onto particle surface. 0.5 g ground sediment and 20 mL of 0.11 M acetic acid were combined in a 50 mL polypropylene centrifuge tube. The tube was shaken for 16 h at the room temperature. After centrifugation at 4000 rpm for 20 min, the supernatant was obtained. Step 2 aims to extract reducible As (F2) which is fixed in Fe/Mn oxyhydroxides/oxides. 20 mL of 0.5 M hydroxylammonium chloride was added to step 1 residue, before adjusting pH to 2 with nitric acid. The mixture was then shaken and centrifuged following the same procedure as step 1 before the supernatant was obtained for analysis. Step 3 aims to extract oxidizable As (F3) which is bound to organic matter and sulfides. 10 mL hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30% w/w in H<sub>2</sub>O, with pH adjusted to 2–3 using nitric acid) was added to the residual solid from step 2 for extraction at 85±2 °C till the volume of the solution reduced to nearly 1 mL. This H<sub>2</sub>O<sub>2</sub> extraction was repeated once, then 25 mL of 1.0 M ammonium acetate (pH adjusted to 2 with nitric acid) was added before following the same shaking and centrifuge procedures as in step 1. For each step, the supernatant was filtered through 0.45 µm filter membrane and analyzed for As, Fe and Mn by ICP-MS. The residue of each step was washed with 20 mL Milli-Q water, abandoning the supernatant after centrifuge at 4000 rpm for 20 min. The residual As (F4), which is considered to be recalcitrant, was calculated as the difference in concentration between the total As derived from digestion and the sum of the three As extractions.

## 2.4. Data analysis

### 2.4.1. Statistical analysis

Pearson correlation analysis was performed to reveal the relationship of As with other elements. Partial correlation analysis was used to analyze the primary factor controlling As mobility in sediments. Since the content of As, Fe, Mn and TOC in sediments from the Zam Reservoir is greatly affected by the particle size, the particle size is taken as the control variable. SPSS 21.0 was used for statistical analyses.

### 2.4.2. As retention by reservoirs

A rough estimation of As retention ( $As_{ret}$  in t As yr<sup>-1</sup>) by the two reservoirs was derived by the difference between As input ( $As_{in}$ ) and As output ( $As_{out}$ ) in forms of total As, dissolved As, or particulate As:

$$As_{ret} = As_{in} - As_{out} = (C_{in} * Q_{in}) - (C_{out} * Q_{out}) \quad (1)$$

where  $C_{in}$  and  $C_{out}$  are the observed As concentrations (µg/L) in a certain form (total As, dissolved As, or particulate As) in the inflow water (S1, Z1) and outflow water (S2, Z2), respectively, during a hydrological period.  $Q_{in}$  and  $Q_{out}$  are the flow rates of the inflow and outflow, respectively, during a hydrological period. Arsenic retention ratio ( $As_{ratio}$ , %) was calculated as:

$$As_{ratio} = As_{ret} / As_{in} * 100\% \quad (2)$$

Considering the small size of the two reservoirs, As input from the atmospheric deposition and groundwater discharge were omitted from the As budget, which made As retention slightly underestimated. The As budget was calculated for each hydrological period and then summed as the annual As retention.

### 2.4.3. As storage in the reservoir sediment

As storage in the reservoir sediment was calculated following Wu et al. (2016):

$$Q = \sum_{i=1}^n S_i * C_i * 10^{-9} \quad (3)$$

where Q is the As storage (tons),  $S_i$  is the deposited sediment load (kg) at a given 1-cm depth in the lacustrine zone,  $C_i$  is the As concentration (mg/kg) at a given 1-cm depth in the sediment, and n is the total depth of the sediment in cm.

## 3. Results

### 3.1. Spatiotemporal profiles of surface water physicochemical parameters

The seasonal variations of surface water quality parameters (T, pH, DO and EC) were basically the same in the two reservoirs (Tables 1 and 2). Surface water in the two reservoirs was slightly alkaline (pH 8.43–8.72 and 8.24–8.54 for the Shiquan Reservoir and the Zam Reservoir, respectively), with slightly lower pHs in August than in January or May. The DO content in surface water of the two reservoirs was high (DO 5.15–9.17 mg/L and 7.05–10.14 mg/L for the Shiquan Reservoir and the Zam Reservoir, respectively), and the highest values were observed in January. The EC values of surface water in the Shiquan Reservoir (290–367 µS/cm) were significantly higher than those in the Zam Reservoir (222–306 µS/cm). The maximum EC values of surface water in both reservoirs were also observed in January.

Seasonal variations in As content in surface water existed in both reservoirs (Tables 1 and 2). For the Shiquan Reservoir, the total and dissolved As concentrations (42.6 and 41.6 µg/L, respectively) in the inflow water in January 2018 were much lower than those in August 2017 (90.0 and 67.9 µg/L, respectively) or May 2018 (76.7 and 68.7 µg/L, respectively). While the total and dissolved As in surface water from the reservoir and the outflow water decreased following the order: August 2017 > January 2018 > May 2018. In the Zam Reservoir, the highest values of total As in surface water (70.1–72.1 µg/L) were observed in August 2017, followed by in May 2018 (11.5–11.9 µg/L) and January 2018 (9.1–9.9 µg/L). Whereas, the dissolved As in August 2017 was only 3.0–3.3 µg/L, lower than that in January 2018 (8.1–8.4 µg/L) or May 2018 (10.5–10.8 µg/L). Different from the Shiquan Reservoir, the As content in surface water of the Zam Reservoir showed no significant difference among inflow, reservoir and outflow waters.

### 3.2. Vertical profiles of physicochemical parameters of water column

A slight chemical stratification was observed during the high flow period in the Shiquan Reservoir (Fig. 2). There was a mild temperature stratification leading to the formation of the epilimnion (0–4 m) and the hypolimnion (4–21 m). The concentration of dissolved oxygen (DO) gradually decreased from 5.4 mg/L between 0 and 4 m to 4.5 mg/L close to the sediment-water interface (SWI). Similar to the profile of DO, the pH value peaked (8.5) in the epilimnion and decreased to minimum (8.2) near the SWI. The dissolved As concentration was slightly lower (56.4 µg/L) in the epilimnion zone and higher (62.6 µg/L) in the hypolimnion zone. This vertical profile was not observed during low and medium flow periods in January and May sampling. Whereas in the Zam Reservoir, no obvious chemical stratification was found and the dissolved As concentration showed little variation in vertical distribution in overlying water during any hydrological period.

### 3.3. Vertical profiles of sediment

In the Shiquan Reservoir, the depth of the deposited sediment in the high, low and medium flow periods was 11 cm, 15 cm and 14 cm,



**Table 2**  
Field parameters and As concentrations in surface waters from the Zam Reservoir of the Yarlung Tsangpo.

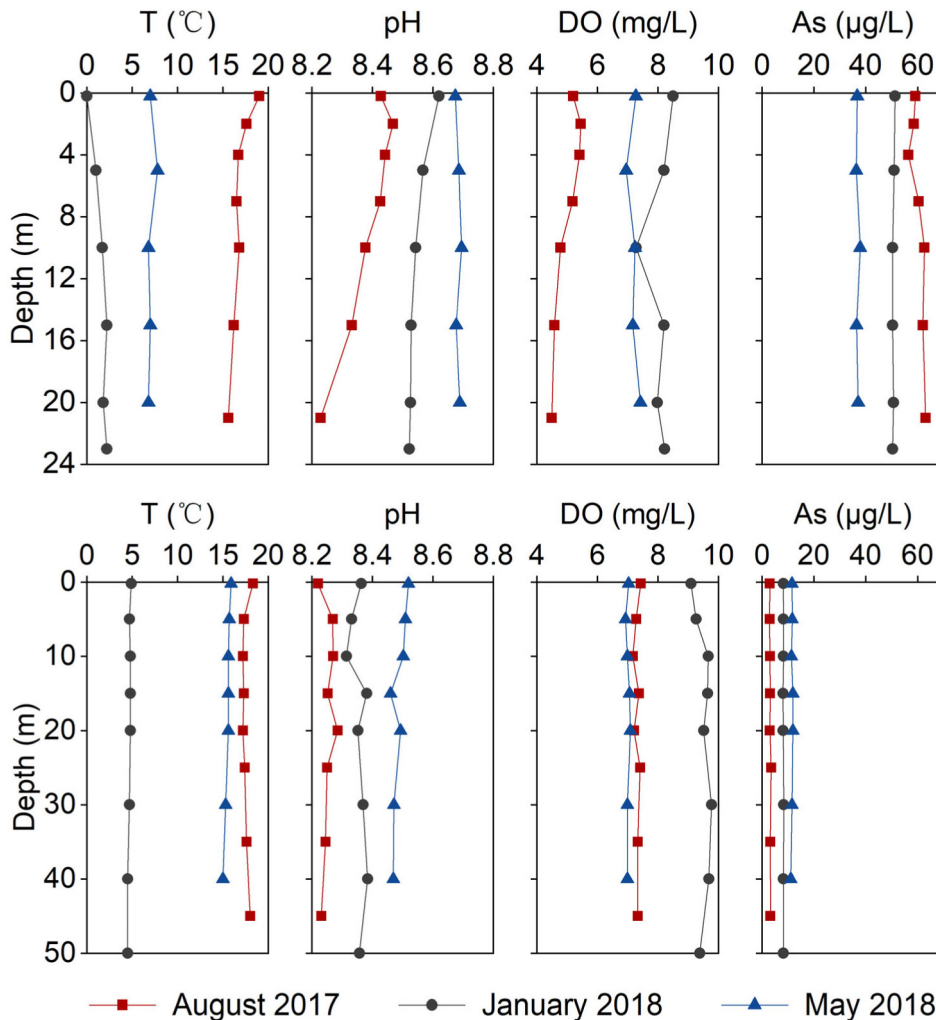
Sampling time	Position	Temperature (°C)	pH	DO (mg/L)	EC (µs/cm)	Total P (mg/L)	Dissolved P (mg/L)	Total As (µg/L)	Dissolved As (µg/L)	Particulate As (µg/L)	Particulates (mg/L)
August 2017 (high flow)	Inflow	18.2	8.24	7.42	222	0.68	0.23	70.1	3.3	66.8	1810
	Reservoir (n = 3)	17.1 ± 0.8	8.28 ± 0.05	7.05 ± 0.43	228 ± 11	0.55 ± 0.01	0.29 ± 0.07	71.1 ± 4.7	3.0 ± 0.0	65.6 ± 8.0	1722 ± 161
	Outflow	18.3	8.32	7.81	223	0.77	0.27	70.8	3.3	67.5	2095
January 2018 (low flow)	Downstream	18.8	8.30	7.43	285	0.76	0.26	72.1	3.3	68.8	2088
	Inflow	3.4	8.38	10.14	296	0.3	0.08	9.9	8.4	1.5	24.5
	Reservoir (n = 3)	4.2 ± 0.7	8.37 ± 0.04	9.71 ± 0.36	294 ± 2	0.21 ± 0.02	0.08 ± 0.01	9.5 ± 0.3	8.4 ± 0.1	1.1 ± 0.1	14.0 ± 3.5
May 2018 (medium flow)	Downstream	4.1	8.41	9.63	293	0.23	0.11	9.1	8.2	1.0	11.1
	Inflow	15.2	8.44	9.5	306	0.18	0.09	9.2	8.1	1.1	12.0
	Reservoir (n = 3)	15.8 ± 0.2	8.53 ± 0.02	7.1 ± 0.14	284 ± 3	0.03 ± 0.00	0.02 ± 0.00	11.9 ± 0.4	10.7 ± 0.6	1.1 ± 0.3	10.0 ± 2.4
May 2018 (medium flow)	Outflow	16.0	8.54	7.56	287	0.03	0.02	11.7	10.8	0.9	9.0
	Downstream	16.1	8.40	7.70	286	0.03	0.02	11.5	10.5	1.0	7.6

respectively. In the Zam Reservoir, the depth of the deposited sediment was 25 cm throughout the three sampling campaigns.

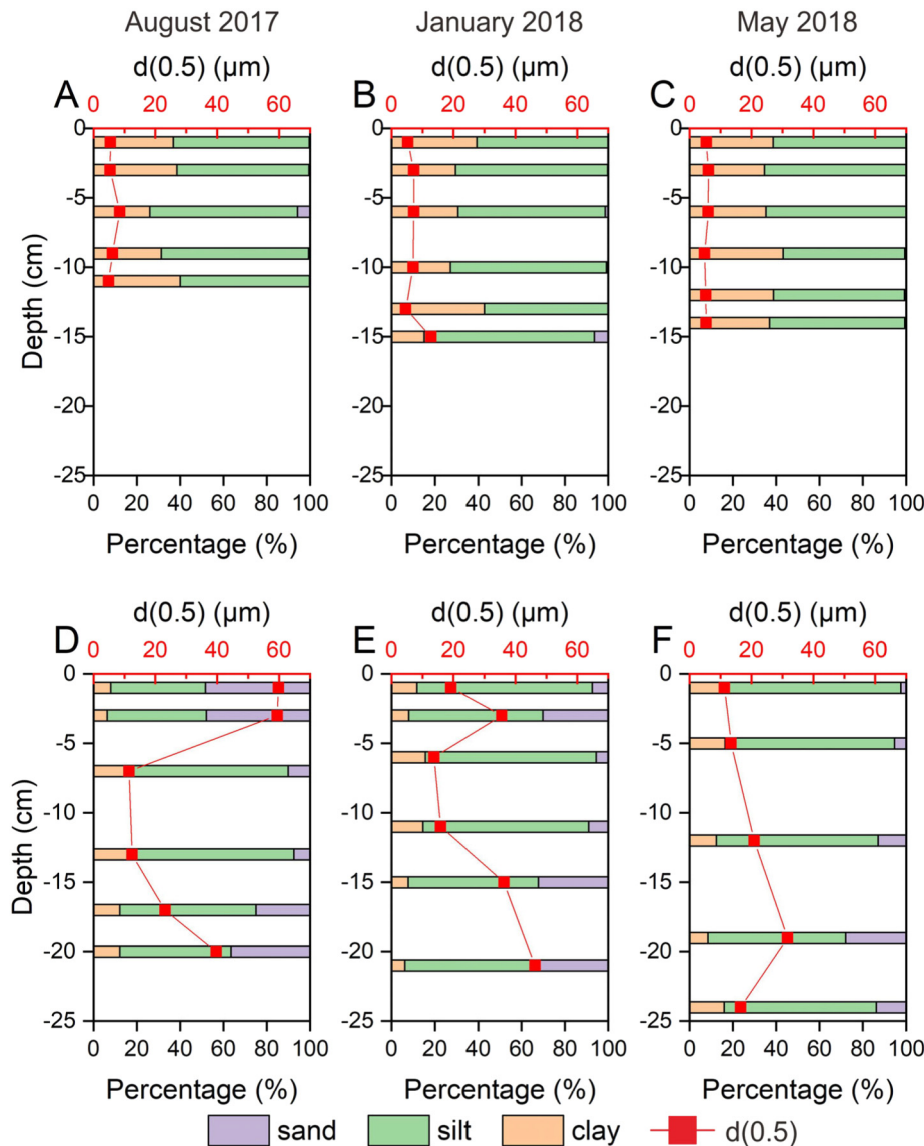
3.3.1. Sediment grain size

The grain size of sediment from the Shiquan Reservoir was finer than that from the Zam Reservoir (Fig. 3), which might be due that the lower

flow rate and longer residence time in the Shiquan reservoir allow finer sediments to settle down. In the Shiquan Reservoir, the sediment was mostly composed of silt and clay, with an average of the median particle sizes from various depths and during the three sampling events of 6.4 µm. The sediment in the Zam Reservoir was consisted mainly of silt (44–81%), with an average of the median particle sizes from various



**Fig. 2.** Depth profiles of water temperature (T), pH, dissolved oxygen (DO), and dissolved arsenic (As) in the water column of the Shiquan Reservoir (top) and the Zam Reservoir (bottom) for the three sampling events.



**Fig. 3.** Median grain sizes ( $d(0.5)$ ) and texture analysis results of the sediments cored in August 2017 (A, D), January 2018 (B, E) and May 2018 (C, F) from the Shiquan Reservoir (top) and the Zam Reservoir (bottom). (sand:  $> 64 \mu\text{m}$ ; silt:  $4\text{--}64 \mu\text{m}$ ; clay:  $< 4 \mu\text{m}$ ).

depths and during the three sampling events of  $27.5 \mu\text{m}$ . In August 2017, the median particle size of the top 5 cm sediment from the Zam Reservoir even reached  $60 \mu\text{m}$ .

### 3.3.2. Total as in sediment

Arsenic concentrations in sediments from the Shiquan Reservoir were higher than those from the Zam Reservoir (Fig. 4). In the Shiquan Reservoir, As concentrations in sediments ranged from  $42.4$  to  $130.7 \text{ mg/kg}$  with an average of  $73.7 \text{ mg/kg}$ . In the Zam Reservoir, As concentrations in sediments ranged from  $22.6$  to  $48.2 \text{ mg/kg}$  with an average of  $34.3 \text{ mg/kg}$ . There were obvious surficial enrichments of As and manganese (Mn) in January 2018 and May 2018 in the Shiquan Reservoir. The minimum As concentration was observed in 2 cm deep in August 2017 and January 2018 in the Zam Reservoir.

Strong positive correlations were observed between As and Mn in the Shiquan Reservoir sediment (Fig. S1 and S2). The positive relationship between As and Fe was weak. There was no significant correlation between As and TOC. Negative correlations were observed between As and S when the surficial sediments from January 2018 and May 2018 were removed. In contrast, in the Zam Reservoir sediments, As had strong positive correlations with Fe, Mn and TOC (Fig. S1). However,

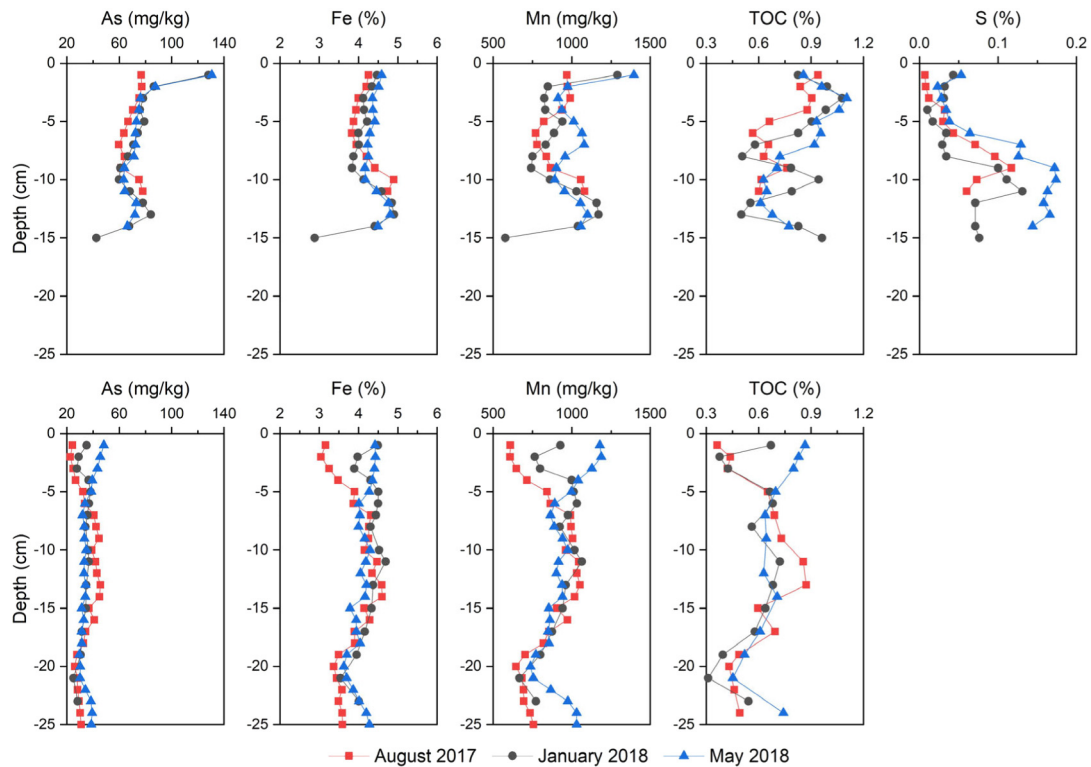
partial correlation analysis with particle size as the control variable showed that As was not correlated with Fe (Table S3).

### 3.3.3. Chemical forms of as in sediment

In both reservoirs, As was mainly present in the recalcitrant residual fraction (Fig. 5). Residual As after the sequential extraction accounted for  $59.9\text{--}73.7\%$  of the total As in the Shiquan Reservoir and  $77.6\text{--}85.7\%$  of the total As in the Zam Reservoir. Extractable As mainly existed in reducible fraction in both reservoirs. Similar with As, the residual fraction of Fe was the most dominant fraction followed by the reducible fraction in both reservoirs, while the proportions of the exchangeable fraction and the oxidizable fraction were quite small. Different from As and Fe, the proportions of exchangeable Mn were much higher in both reservoirs, ranged from  $35.4\%$  to  $60.6\%$  in the Shiquan Reservoir and from  $28.1\%$  to  $41.4\%$  in the Zam Reservoir.

### 3.4. Retention and storage of as

In the ST River, As transport was dominated by dissolved As with  $2.9 \text{ t}$  particulate As and  $15.8 \text{ t}$  dissolved As transported from the upper ST River annually (Table S4). In the YT River, As transport was



**Fig. 4.** Vertical distributions of total arsenic (As), iron (Fe), manganese (Mn), total organic carbon (TOC) and sulfur (S) in sediments from the Shiquan Reservoir (top) and the Zam Reservoir (bottom) for three sampling events. The sulfur content in the sediments of the Zam Reservoir was all below the detection limit of 0.01%.

dominated by particulate As with 1209.9 t particulate As and 170.8 t dissolved As transported from the upper YT River at an annual scale. The annual retained As in the lacustrine zone was 10.3 t (55.0% of the total As input) in the Shiquan Reservoir and  $-8.7$  t ( $-0.6\%$  of the total As input) in the Zam Reservoir, respectively (Table 3). As much as 7.7 t dissolved As, or 49.0% of the dissolved As input, was retained in the Shiquan Reservoir on an annual scale. The annual particulate As retention was 2.5 t, or 87.2% of the particulate As input in the Shiquan Reservoir.

Total As storages in the sediment of the Shiquan Reservoir and the Zam Reservoir were 94.9 t and 14.6 t, respectively.

## 4. Discussion

### 4.1. Arsenic cycling in the water of the two reservoirs

The relatively high pH values in surface water from the Shiquan Reservoir and the Zam Reservoir are a result of evaporation in arid climates, while lower pH values in August 2017 seem to be a result of dilution driven by inflow of atmospheric precipitation and glacier melting water through the ST River and the YT River (Guan et al., 1984; Brandenberger et al., 2004). The high DO content in surface water from the Shiquan Reservoir and the Zam Reservoir reflects the strong reoxygenation capacity of the water body and a good water quality (Zhu, 2005). The higher DO concentration in surface water in January 2018 in the two reservoirs might be a result of the increased atmospheric pressure over the water surface caused by the low temperature (Feng, 2015).

Dissolved As concentrations in surface water from the Shiquan Reservoir (36.1–68.7  $\mu\text{g/L}$ ) were well above the WHO drinking water guideline value of 10  $\mu\text{g/L}$  and also much higher than those in the Zam Reservoir (3.0–10.7  $\mu\text{g/L}$ ). The difference of dissolved As concentrations between the two reservoirs and the seasonal variation of dissolved As contents in the inflow water of the two reservoirs are regulated by the

mixing between the low-As river runoff and the high-As hot spring and groundwater input. Li et al. (2013) found that high-As hot springs and shallow groundwater might contribute to the enrichment of As in surface water in the ST River and the YT River. Guan et al. (1984) also indicated that several hot springs distributed on both sides of the upper inflow river of the Shiquan Reservoir, which could supply the river runoff. The lower dissolved As level in the Zam Reservoir compared to that in the Shiquan Reservoir is probably mainly due to the lower mixing ratio of high-As hot spring and groundwater because the annual average flow rate of the inflow river was 8  $\text{m}^3/\text{s}$  for the Shiquan Reservoir and 936  $\text{m}^3/\text{s}$  for the Zam Reservoir. For the Zam Reservoir, the mixing effect was particularly lower in August due to the much higher runoff and thus resulted lower dissolved As. Moreover, the seasonal variation of dissolved As in surface water was consistent with that of EC in the Zam Reservoir. In contrast, for the Shiquan Reservoir, seasonal distribution of dissolved As and EC in the inflow water showed an opposite trend, with the highest EC and lowest dissolved As in January 2018 although the discharge of inflow river in August 2017 (17.7  $\text{m}^3/\text{s}$ ) was much higher than that in May 2018 (6.6  $\text{m}^3/\text{s}$ ) and January 2018 (5.9  $\text{m}^3/\text{s}$ ). More hot spring water with high As contents might discharge to the ST River in warmer months (communications with the Shiquan River Hydropower Station), causing elevated As concentrations in the inflow water observed in August 2017 and May 2018. A groundwater flow modeling study in the northern central Tibet Plateau also showed that with increased air temperature, more groundwater typically with high As flowed in the active layer (the supra-permafrost zone) and discharged to rivers (Ge et al., 2011).

Water residence time is a key variable regulating the variation of dissolved As contents in reservoirs and outflow waters with time. In the Shiquan Reservoir, the response of dissolved As concentration in the outflow river to that in the inflow river lags behind due to the long residence time (385.1 days). The content of dissolved As in the outflow water is consistent with that in the reservoir. In August 2017, high dissolved As concentrations existed in the inflow water (67.9  $\mu\text{g/L}$ ) and

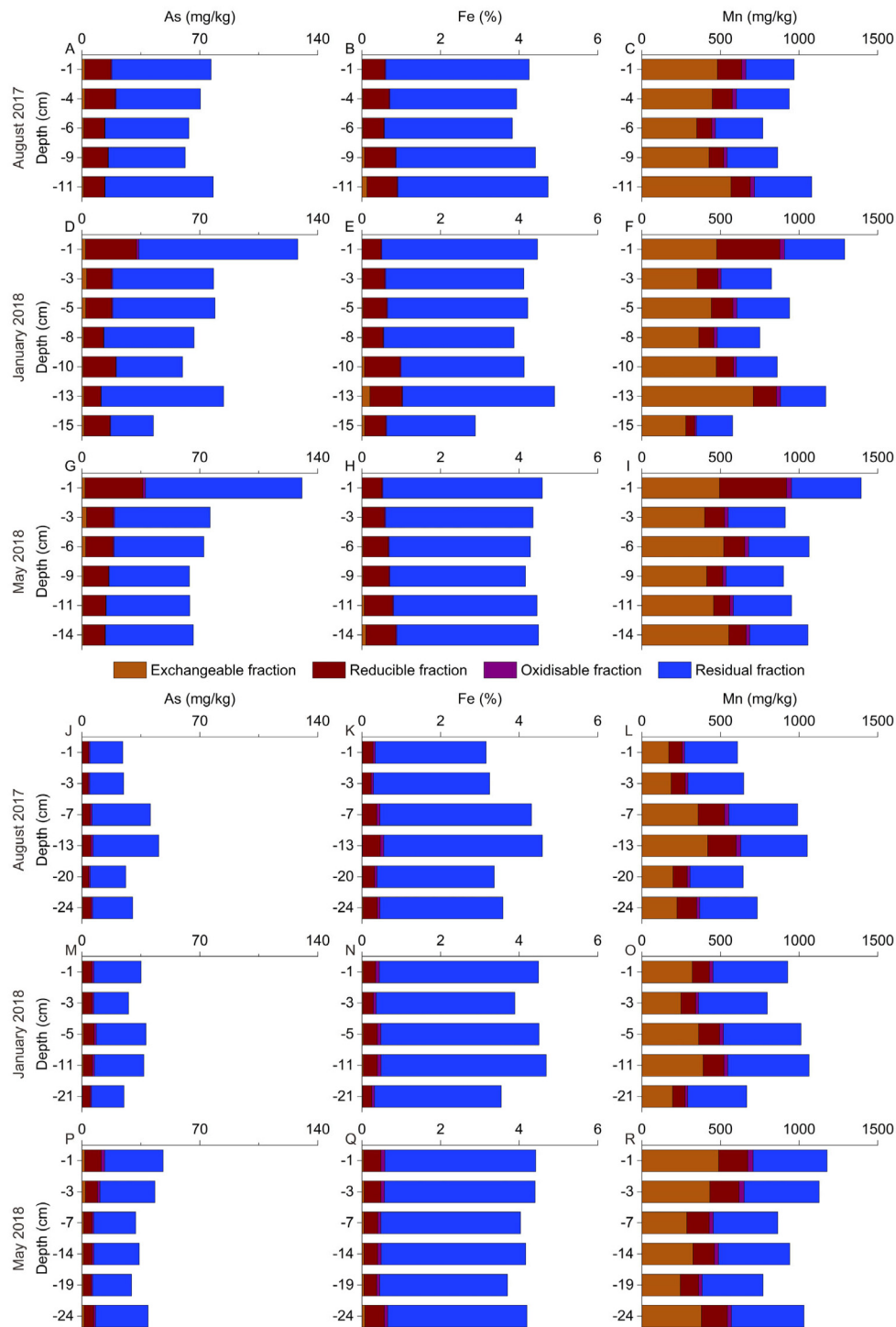


Fig. 5. Depth profiles of chemical fractions of As, Fe and Mn in the sediments from the Shiquan Reservoir (A-I) and the Zam Reservoir (J-R) for three sampling events.

reservoir (58.3  $\mu\text{g/L}$ ). In January 2018, the low As content in the inflow river (41.6  $\mu\text{g/L}$ ) led to a slight decrease in the dissolved As content in the reservoir (51.4  $\mu\text{g/L}$ ). Affected by low As contents in the inflow river, the content of dissolved As in the reservoir decreased continuously. By May 2018, the dissolved As concentration in the reservoir had dropped to 36.7  $\mu\text{g/L}$ . Meanwhile, high As inflow water (68.7  $\mu\text{g/L}$ ) caused by the high As hot spring supply continuously input into the reservoir from this period on. Consequently, the dissolved As concentration in the reservoir might be considerably high in August

2018. In the Zam Reservoir, dissolved As concentrations in the outflow water and the reservoir were consistent with that in the inflow water in each sampling period due to the short residence time (1.1 days).

#### 4.2. Controls on arsenic distribution in sediment profiles

##### 4.2.1. The Shiquan reservoir

The absence of the surficial oxic layer in the sediment can reduce the accumulation of As in surface sediments. In the Shiquan Reservoir, the



**Table 3**  
Water residence times, flow rates and arsenic retention in the Shiquan Reservoir and the Zam Reservoir (2017–2018).

Reservoir	Period <sup>a</sup>	WRT <sup>b</sup> (days)	Discharge (m <sup>3</sup> /s)		Retention (tons)			Retention ratio (%)		
			Inflow	Outflow	Total As	Dissolved As	Particulate As	Total As	Dissolved As	Particulate As
Shiquan	High flow period	385.1	17.65	6.25	6.0	4.2	1.8	73.0	67.1	91.3
	Low flow period		5.85	5.93	−0.6	−0.6	0	−22.7	−24.1	−1.2
	Medium flow period		6.57	5.09	4.9	4.2	0.7	61.9	59.3	83.5
	Annual		8.18	5.56	10.3	7.7	2.5	55.0	49.0	87.2
Zam	High flow period	1.1	2300	2300	−12.5	0	−12.5	−1.0	0	−1.0
	Low flow period		309	309	2.2	0.6	1.6	7.1	2.4	33.3
	Medium flow period		618	618	1.6	−1.6	3.2	1.7	−1.9	30.8
	Annual		935.5	935.5	−8.7	−1.0	−7.7	−0.6	−0.6	−0.6

<sup>a</sup> Based on monthly discharges, for the Shiquan Reservoir the high flow period was August to September 2017, the medium flow period was October to November 2017 and April to July 2018, the low flow period was December 2017 to March 2018; for the Zam Reservoir the high flow period was August to September 2017 and July 2018, the medium flow period was October to December 2017 and May to June 2018, the low flow period was January to April 2018.

<sup>b</sup> WRT is the water residence time, which is equal to the reservoir storage capacity divided by the average daily outflow.

top sediment in August 2017 had much lower As and Mn contents compared with January 2018 and May 2018 (Fig. 4). Because the grain size of top sediments was similar, the significant enrichment of As and Mn in the surficial sediment in January 2018 and May 2018 was not controlled by particle size. The presence of surficial oxic layer can trap As and Mn through sorption and/or oxidative precipitation at the SWI (Kneebone et al., 2002; Nikolaidis et al., 2004). However, As did not accumulate in the surface sediment in August 2017. On the one hand, relatively low DO concentrations in bottom water and extensive remineralization of organic carbon in August 2017 might cause migration of the redox boundary to the SWI (Kneebone et al., 2002). Moreover, strong hydraulic disturbance in August 2017 might re-suspend surface sediments and destroy the surficial oxic layer. On the other hand, in August 2017, reducing conditions near the SWI drove the dissolution of As-bearing Fe/Mn oxyhydroxides and released As to water (Keimowitz et al., 2005; Couture et al., 2010).

The mobility of As in sediment was mainly controlled by Mn oxides. In the Shiquan Reservoir, significant positive correlations existed between As and Mn ( $r = 0.75, p < 0.01$ ) and between reducible As and reducible Mn ( $r = 0.91, p < 0.01$ ), while no correlations were observed between As and Fe ( $r = 0.46, p > 0.05$ ) or between reducible As and reducible Fe ( $r = -0.37, p > 0.05$ ). This suggests that an intense coupled recycling of As and Mn existed in sediments of the Shiquan Reservoir. An earlier study demonstrated that Mn oxides were superior to Fe oxides in trapping As (Gao et al., 2017). Moreover, the reduction of Fe (III) (hydr)oxides occurs more slowly and at lower redox potentials than Mn(IV) oxides (Kneebone et al., 2002; Brandenberger et al., 2004). When the redox potential decreases, Mn(IV) oxides are more easily to be reduced to soluble Mn(II) and release As (Gao et al., 2017). Therefore, Mn(IV) oxides had the stronger ability to control As mobility and As is mainly host by Mn oxides in sediments of the Shiquan Reservoir (Deng et al., 2014).

Degradation of organic matter affects the chemical fraction of As. Although no significant correlations existed between As and TOC in any hydrological period of the Shiquan Reservoir (Fig. S1), the TOC contents in sediments were significantly positively correlated with the proportions of exchangeable As, the proportion of reducible As and the proportion of oxidizable As (Fig. S3). These evidences suggest that the proportion of potentially-mobile As (exchangeable As, reducible As and oxidizable As) decreased with the decomposition of organic matter during mineralization.

Negative correlations between the total As and S (Fig. S1) illustrates the As-bearing sulfide minerals are not the main source of As in sediments. The limited formation of As-sulfide minerals in the Shiquan Reservoir might be a result of the high redox conditions and the high Fe/S ratios (molar ratio: 13.7–347.3) (Keimowitz et al., 2005; Toevs et al., 2006).

#### 4.2.2. The Zam reservoir

In the Zam Reservoir, As concentrations in sediments were greatly affected by sediment grain size. A significant negative correlation ( $r = -0.88, p < 0.001$ ) existed between As and the median grain size of sediments in the Zam Reservoir (Fig. S4). Fine particles are more conducive to the accumulation of As because of their large surface area and high As adsorption capacity (Wu et al., 2016). The lowest As concentrations in the top several centimeters of the sediment column in August was attributed to the flushing of sediments caused by the fast flow velocity during this period, resulting in fine-grained sediments being suspended and discharged from the reservoir (Chatterjee et al., 2007; Reza et al., 2010).

The mobility of As in sediments was mainly controlled by Mn oxides and organic matter. In the Zam Reservoir, As was significantly positively correlated with Fe, Mn and TOC in sediments (Fig. S1), which was also observed in the sediments of Brahmaputra, the downstream of the Zam Reservoir (Reza et al., 2010). However, As was not correlated with Fe ( $r = 0.30, p = 0.26$ ) after the particle size was set as the control variable (Table S3). Under oxic conditions, As is captured by sediment mainly through adsorption on and co-precipitation with Mn (hydr)oxides (Pierce and Moore, 1982; Aurillo et al., 1994; Dixit and Hering, 2003). Under anoxic and high Fe/S ratio conditions, As could be released following the reductive dissolution of Mn (hydr)oxides (Xie et al., 2018). In addition, organic matter, especially biofilms, has a strong adsorption capacity for As (Weiske et al., 2013).

#### 4.3. Arsenic retention in the two reservoirs

The Shiquan Reservoir has a strong retention effect on As. The hydrologic data used in the mass balance calculation of the two reservoirs are from local hydrologic stations in 2012. The annual discharge of outflow ( $5.6 \text{ m}^3 \text{ s}^{-1}$ ) was lower than inflow ( $8.18 \text{ m}^3 \text{ s}^{-1}$ ), indicating that the Shiquan Reservoir was in a storage state in 2012 and that 31.5% of the inflow water was retained for the whole year. The estimated annual retention percentages of total As, dissolved As and particulate As were 55.0%, 49.0% and 87.2%, respectively, which were significantly higher than the retention percentage of water. The Shiquan Reservoir Dam was put into operation in 2007. Assuming that the retention flux for the total As was always 8.6 t per year, then by 2018, a total of 94.3 t As was retained, which is comparable with the calculated total As storage of 94.9 t. Therefore, the Shiquan Reservoir is a net As sink. The significantly higher retention ratios of particulate As than dissolved As suggests that sedimentation was the main mechanism of As retention in the Shiquan Reservoir. Dissolved As was retained in the Shiquan Reservoir mainly through the following two ways: (1) dissolved As was absorbed or diffused into sediments; and (2) adsorbed on suspended particulates. Because of the long water residence time of the Shiquan

Reservoir (385.1 days), suspended particulates with adsorbed As can be fully deposited in the lacustrine zone.

The retention for As in the Zam Reservoir was weak. The annual retention percentages of the Zam Reservoir for total As, dissolved As and particulate As were all  $-0.6\%$ . This is owing to the insufficient deposition of suspended particulates in the Zam Reservoir due to the short water residence time (1.1 days) and very high flow rates. Compared with the large input flux of the total As (1380.8 t) in the Zam Reservoir, the storage of total As in the sediment was negligible (only 14.6 t), which also supported the weak retention of As in the Zam Reservoir.

#### 4.4. Implications on the downstream environments

The operation of river-dammed reservoirs can significantly influence the ecological health of their downstream catchments. For the Shiquan Reservoir, its operation can effectively retain 55% of the total arsenic load from upstream and therefore reduce the transport of arsenic downstream to the Indus River Basin. In the long run, it could play a positive role in alleviating arsenic enrichment in sediments, surface water and groundwater in the Indus River Basin. In contrast, the Zam Reservoir has no effective retention of arsenic due to the very short residence time and accordingly it is not likely to have a significant implication on the ecological environment of the downstream basin (Brahmaputra River Basin).

## 5. Conclusions

The seasonal variation of dissolved As contents in the inflow water of the Zam Reservoir and the Shiquan Reservoir was regulated by the mixing between the low-As river runoff and the high-As hot spring input. Besides the As content in the inflow water, reservoir water residence time is a key variable regulating the variation of dissolved As contents in reservoirs and outflow waters with time. The absence of surficial oxic layer can reduce the accumulation of As in surface sediments. Arsenic mobility in sediment of the two reservoirs was mainly controlled by Mn oxides and organic matter. Arsenic in sediments of the two reservoirs mainly existed in the reducible fraction among the extractable fractions. Reservoirs with long water residence times are more favorable for As retention. Sedimentation was the main mechanism of As retention in the two reservoirs. While the Zam Reservoir has no effective retention of arsenic, the Shiquan Reservoir retained more than half of the total arsenic load and could have positive implications on the ecological environment of downstream river basins.

### CRedit authorship contribution statement

**Zhenjie Zhao:**Resources, Formal analysis, Writing - original draft, Writing - review & editing.**Shehong Li:**Conceptualization, Formal analysis, Writing - original draft, Writing - review & editing.**Lili Xue:**Resources.**Jie Liao:**Resources, Formal analysis.**Jingjing Zhao:**Resources.**Mei Wu:**Formal analysis.**Mingguo Wang:**Resources.**Jing Sun:**Writing - original draft, Writing - review & editing.**Yan Zheng:**Writing - original draft.**Qiang Yang:**Conceptualization, Formal analysis, Writing - original draft, Writing - review & editing.

### Declaration of competing interest

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

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### Appendix A. Supplementary data

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