Agriculture, Ecosystems and Environment 294 (2020) 106857

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

journal homepage: www.elsevier.com/locate/agee

Damming effects on river sulfur cycle in karst area: A case study of the Wujiang cascade reservoirs

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ARTICLE INFO

Keywords:
Sulfur cycle
Sulfur isotope
Wujiang river
Cascade dams
Cumulative effects

ABSTRACT

Damming effects on sulfur (S) cycling remains unclear at basin scales due to the lack of basic data prior to dam construction. To explore the influence of damming on the riverine S cycle, we investigated the spatiotemporal variations of water chemistry, sulfate (SO_4^{2-}) concentration, and $\delta^{34}S\text{-}SO_4^{2-}$ in January 2017 and July 2017 in the impounded Wujiang River, and the measured results in this study were compared with the data in 2002 when no dams were built in the middle and lower reaches. Results showed that SO_4^{2-} was the second dominant anion and accounted for up to 30% of the total anions, and sulfuric acid played a vital role in carbonate weathering. Sulfate reducing process and organic S oxidation were markedly enhanced by seasonal thermal stratification induced by damming, particularly in summer. The seasonal differences of SO_4^{2-} concentration and $\delta^{34}S\text{-}SO_4^{2-}$ in this study were not readily discernable compared to those in 2002, when the average SO_4^{2-} concentration and $\delta^{34}S\text{-}SO_4^{2-}$ in winter were 31.0% and 63.3% greater than that in summer respectively. The $\delta^{34}S\text{-}SO_4^{2-}$ from upstream WJD reservoir to downstream YP reservoir in 2002 increased by 17.2% in summer; however, in this study, it drastically increased by 76.7%. The reduced seasonal variations and increased spatial differences of SO_4^{2-} concentration and $\delta^{34}S\text{-}SO_4^{2-}$ reflected the damming effect of cascade dams on S cycling in river waters. Interestingly, SO_4^{2-} concentration gradually decreased while the $\delta^{34}S\text{-}SO_4^{2-}$ value became positive from upstream to downstream reservoir, but both their variations inside reservoirs were homogenized to narrow ranges, which could be derived from the cumulative effects of cascade dams. After damming, the increased hydraulic retention time and water depth caused significant seasonal thermal stratification in reservoirs, which enhanced the S biogeochemical process, and this damming effect was accumulated through bottom released water. Therefore, SO_4^{2-} concentration together with $\delta^{34}S\text{-}SO_4^{2-}$ could be useful indicators in assessing the damming effects of cascade dams in the river-reservoir systems.

1. Introduction

Large amounts of dams have been built worldwide in the past century to meet the need for electricity and irrigation (Biemans et al., 2011; Zarfl et al., 2015; Poff and Schmidt, 2016; Zhou et al., 2016), with ~ 58,000 high-dam > 15 m already in place and another 3700 in planning in developing countries (Poff and Schmidt, 2016; Winemiller et al., 2016). Forty-six percent of the high-dams are located within China with the largest number of reservoirs in the world (Han et al., 2010). The buildup of reservoirs has greatly changed the original hydrodynamic condition and water quality of the rivers in these regions (Ledec and Quintero, 2003; Liu et al., 2009). Water quality of reservoirs is closely related to soil properties and plant growth of farmland (Bandara et al., 2011; Zhang et al., 2012). Any changes of the water quality in reservoir may break the acid-base balance/ion balance in soil dependent on reservoir irrigation, thus affecting crop growth (Tan et al., 2007). On the other hand, agricultural activities and soil property can in turn affect the water quality of reservoirs to a certain extent (Islam et al., 2000). The chemical fertilizer loss in the agricultural soil could eventually enter the environment through runoff, leaching, and volatilization, probably causing an increasing of nutrient concentrations in the reservoir (Liu et al., 2014). Besides, the nutrients accumulated in the bank cultivated land could be greater than those contained within the river estuary sediment as well as in the reservoir bay sediment, and the loosely exchangeable nutrients in cultivated land could easily lead to the development of algal blooms in the reservoirs

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https://doi.org/10.1016/j.agee.2020.106857
Received 9 July 2019; Received in revised form 17 January 2020; Accepted 4 February 2020

(Tang et al., 2012). Therefore, the properties of surrounding soil are closely related to the geochemical cycling of nutrient elements in reservoirs, and human activities play an important role in the interaction between farmland soil and nutrient elements cycling in reservoir.

A critical issue associated with dam presence is the disturbance to the migration, circulation, and transformation of terrestrial nutrients to ocean (Ledec and Quintero, 2003; Liu, 2007; Liu et al., 2009; Bauer et al., 2013; Beusen et al., 2016). Damming increases the hydraulic retention time (HRT) by means of decreasing flow velocity and turbidity, and in turn alters the biogeochemical cycle of vital elements like carbon (C), nitrogen (N), phosphorus and sulfur (S) (Lewicka-Szczebak et al., 2008; Maavara et al., 2015; Van Cappellen and Maavara, 2016; Maavara et al., 2017; Yang et al., 2018a, b). In addition, damming could also influence element biogeochemical cycles by means of affecting the composition as well as the structure of the neighboring biological community (Wang et al., 2018), particularly in warm seasons (von Schiller et al., 2016; Han et al., 2018). At present, most studies concerning dam interception of elements focused on C and N (Wang et al., 2015; Zuijdgeest and Wehrli, 2017; Kumar et al., 2019). The status quo thus leads to an incomplete understanding of the nutrient cycle due to the lack of attention to other important elements such as S.

S is a vital element controlling biological activities through redox process and hence intimately linked with the cycling of C, N, and iron (Turchyn and Schrag, 2006; Megonigal et al., 2014; Li et al., 2015; Burke et al., 2018). For example, the presence of sulfate could result in the oxidation of organic C through sulfate-reducing bacteria (Canfield and Robert, 1991), whereas the presence of hydrogen sulfide (H_2S) in the overlying water could inhibit the denitrification of nitrous oxide (N_2O) (Senga et al., 2001, 2002, 2006). Moreover, S is a redox-sensitive element, whose biogeochemical processes vary greatly with soil flooding conditions (Liu et al., 2017a). Under alternate wetting and drying conditions, the sulfate reducing process not only affects the value of soil pH, but also produces H_2S, which has a certain toxicity and affects the growth of crops (Grzybkowska et al., 2017; Fryer, 2018). It is reported that the water level fluctuation zone of the Three Gorges Reservoir is a redox rotation area and the accumulation of elemental S appeared both in sulfate reduction and sulfide re-oxidation. Moreover, the methylmercury content in soil is positively correlated with elemental S content during the flooding period and the methylmercury during the flooding period may be fixed by pyrite (Liu et al., 2017a). Therefore, the S cycle in reservoir is important for farmland soils that rely on reservoir irrigation.

Under the influence of complicated biogeochemical processes in aquatic systems, the form of S species could be converted between organic S (e.g., carbon-bonded S and ester sulfate) and inorganic S (e.g., SO_4^{2-}, sulfite (SO_3^{2-}), sulfide, sulfur dioxide (SO_2), and H_2S) (Reddy and Delaune, 2008; Cao et al., 2018). Sulfate is the dominant S-containing species in aerobic water systems; the reduction of sulfate to sulfide by dissimilatory sulfate-reducing microbes in hypoxic settings produces the largest fractionation in $\delta^{34}S$ (Zerkle et al., 2010). The large variation of $\delta^{34}S$-SO_4^{2-} in nature coupled with the small S isotope fractionation occurring in dissolution of sulfate minerals, oxidation of sulfides in sedimentary and crystalline rocks, as well as precipitation of sulfate minerals makes it possible to be good environmental tracer (Hong et al., 1994; Yuan and Mayer, 2012). Thus, $\delta^{34}S$-SO_4^{2-} are widely used in tracing sulfate sources and exploring S biogeochemical processes in rivers, groundwater, and watersheds (Li et al., 2011a, b; Yuan and Mayer, 2012; Li et al., 2015; Cao et al., 2018).

Most studies focused on the use of C/N isotope to study C/N biogeochemical cycle and H–O isotopes to investigate water cycle in cascade reservoirs on basin scales (Jossette et al., 1999; Yu et al., 2008; Wang et al., 2011; Wei et al., 2011; Zhang et al., 2018). For instance, Wang et al. (2019a) found cumulative effects of cascade dams (a jagged increase) by the H–O isotopes of water, and the HRT was the key influencing factor. Shi et al. (2017) and Zhou et al. (2016) clarified that C/N emissions from the river were increased by dam construction, and cascade reservoirs acted as multi-filters in regulating nutrients mobilization and export to coast. The latest research showed the reservoir N_2O flux had a significant negative logarithmic relationship with the hydraulic load (the ratio of the mean water depth to the residence time), suggesting its control on the N_2O emission (Liang et al., 2019). In contrast, there are relatively few studies which use S isotope to study the S cycle inside the reservoir. Lewicka-Szczebak et al. (2008) found the differences in S biogeochemistry during different seasons in a single reservoir and Li et al. (2009) explored the spatial changes of $\delta^{34}S$-SO_4^{2-} in series of cascade reservoirs in upper reaches of one season, which might lack of consideration of the whole basin and couldn't be conducive to the evaluating the environmental effects of reservoir. Although there were investigations on S cycle in cascade reservoirs of Wujiang River (Li et al., 2009), and Jialing River (Li et al., 2011b; Yang et al., 2018b), which mainly focused on the characteristics of S biogeochemical process in reservoirs after damming, but to date no comparison has been conducted with corresponding data before damming in this river system. Thus, it appears that the understanding of damming effects on S cycle in cascade dams remains unclear, and more attention should be paid to this concern on S cycle on the basin scale.

To explore the damming effects on the S cycle, this study investigated the spatiotemporal variations of water chemical parameters, SO_4^{2-} concentration and its S isotopic composition. The measured SO_4^{2-} concentration together with $\delta^{34}S$-SO_4^{2-} in surface water samples were compared with those from the corresponding sites sampled in 2002 when the GPT reservoir, SL reservoir and the YP reservoir in the middle and lower reaches of the Wujiang River had not yet been constructed. The objectives of this study were (1) to explore the spatiotemporal changes of water chemistry in reservoirs and its linkages with SO_4^{2-} concentration and $\delta^{34}S$-SO_4^{2-} variations; (2) to identify spatiotemporal variations of SO_4^{2-} concentration and its S isotopic composition before and after dam construction; (3) to assess the cumulative effects of cascade reservoirs and its influencing factors; (4) to discuss the relationship between nutrients cycling and agroecosystem under dam construction. Findings from current research might help us better understand the spatiotemporal changes in S cycles within reservoirs and the damming effects on S cycle of cascade dams, and provide a reference for better reservoir management.

2. Materials and methods

2.1. Study area

The Wujiang River Basin (WRB), a typical karst area and the largest river system in Guizhou, is located in the east region of the Yunnan-Guizhou Plateau and the southern margin of the Sichuan Basin (N25°56′ ~ 30°01′, E105°09′ ~ 109°26′). The upper reaches of the Wujiang River are located in the eastern margin of the Yunnan-Guizhou Plateau where the bedrock is dominated by Permian and Triassic carbonate rocks (grey, dolomitic) and coal-bearing rock; in contrast, the downstream belongs to the eastern slope of the Yunnan-Guizhou Plateau and the southeastern Sichuan Mountains where carbonate rocks compose of the main rock formation, followed by shale and siltstone. The study area has a characteristic subtropical humid monsoon climate; the average annual temperature is 12.3 °C, with extreme temperatures of 35.4 °C in summer and −10.1 °C in winter. The wet season of the watershed is from May to October every year, accounting for 80 % of the total annual rainfall. The main stream of the Wujiang River has the total length of 1037 km, the drainage area of 87,920 km^2, and the total drop of 2124 m. Superior geographical conditions make WRB having very good hydropower development conditions. Since 1979, eleven reservoirs have been built on the main stream of the Wujiang River. Besides bringing economic benefits, the development of cascade reservoirs in WRB may also influence the biodiversity and promote eutrophication. There have been several reports about the retention effects of cascade reservoirs on nutrient elements in the WRB in recent

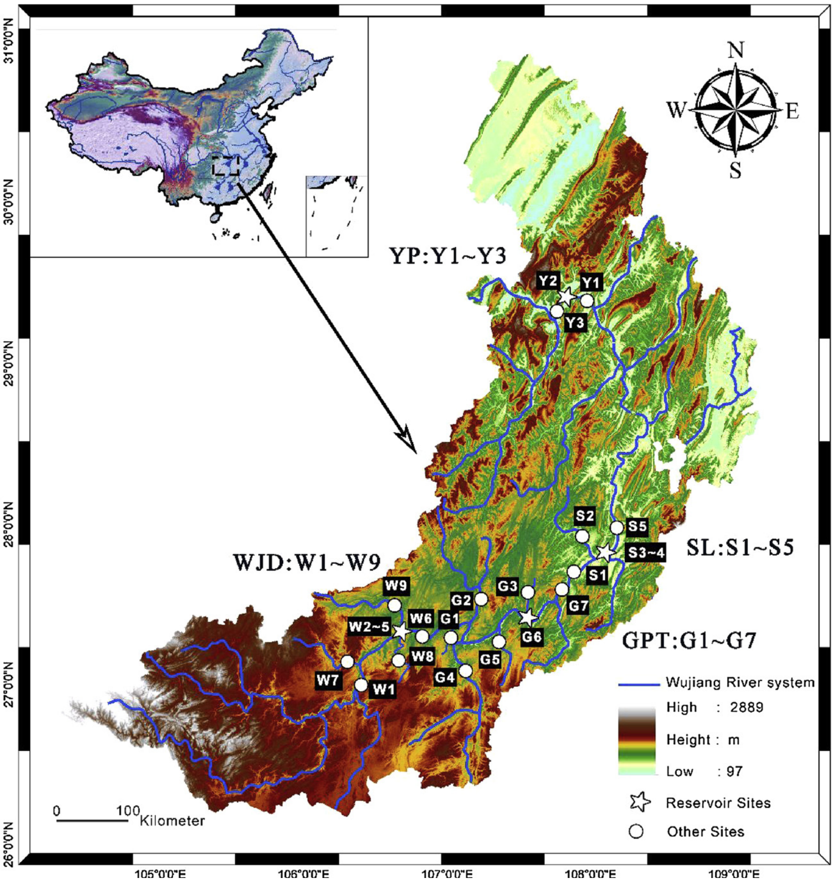

Fig. 1. Map showing sampling locations and numbers. WJD, Wujiangdu reservoir; GPT, Goupitan reservoir; SL, Silin reservoir; YP, Yinpan reservoir.

Table 1
The basic characteristics of the studied reservoirs.

Reservoir	WJD	GPT	SL	YP
Height of dam (m)	168	233	117	80
Average annual runoff ($\times 10^8$ $m^3 \cdot s^{-1}$)	483	716	844	1380
Catchment area (km^2)	27790	43250	48558	74910
Normal water level (m)	760	630	440	215
Total reservoir capacity ($\times 10^8$ m^3)	21.4	55.64	12.05	3.2
Regulated storage capacity ($\times 10^8$ m^3)	9.28	31.54	3.17	0.37
Hydraulic retention time (d)	49.3	89.8	19.4	2
Surface area (km^2)	47.8	57.6	38.4	11.24
Regulation performance	Season	Year	Week	Day
Age (yrs., to 2019)	40	8	11	8
Distance from the mouth (km)	594	455	366	93

years (Yang et al., 2018a; Zhou et al., 2018). However, very few studies focused on the change of nutritive materials cycling before and after damming in the WRB. In this study, four reservoirs were selected, from the upper to the lower reaches, they are Wujiangdu (WJD), Goupitan (GPT), Silin (SL), and Yinpan (YP) reservoirs (Fig.1). The specific characteristics of the four reservoirs are shown in Table 1.

2.2. Sampling and analysis

Water samples, including the inflow water (surface water), outflow water (surface water), water column, and the tributaries, were collected in January 2017 (dry period) and July 2017 (wet season) from the four studied reservoirs using Niskin Water Sampler (General Oceanics, USA). The detailed information about the sample points are shown in Table 2. Water temperature (T), pH, and dissolved oxygen (DO) were measured in-situ with a calibrated automated multi-parameter profiler (model: YSI EXO-1). The bicarbonate (HCO_3–) was calculated from alkalinity, which was determined by titrating with a concentration of 0.02 $mol \cdot L^{-1}$ hydrochloric acid within 8 h after sampling. The collected samples were filtered with a 0.45 μm microporous nitrocellulose membrane (Millipore, USA) in the lab. The filtered samples for $\delta^{34}S\text{-}SO_4^{2-}$ measurements were acidified to pH < 2 with appropriate amount of concentrated HCl, and the acidified water were boiled on an electric furnace to prevent the influence of $BaCO_3$ on oxygen isotope before SO_4^{2-} was finally precipitated as $BaSO_4$. The anions (SO_4^{2-}, NO_3– and Cl–) were analyzed by ion chromatography ICS-90 (Dionex, USA) and the cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}) by inductively coupled plasma-optical emission spectrometry (ICP-OES). The $\delta^{34}S\text{-}SO_4^{2-}$ was measured using isotope ratio mass spectrometer IRMS (Delta C Finningan Mat) at the State Key Laboratory of the Institute of Geochemistry, Chinese Academy of Sciences. Notation is expressed in terms of δ (‰) relative to the Vienna Canyon Diablo Troilite (V-CDT) standards for S. The precision of the $\delta^{34}S\text{-}SO_4^{2-}$ analysis was estimated to be better than ± 0.2‰, based on repeated analyses of internal laboratory standards and international standard (NBS127), respectively.

3. Results and discussion

3.1. Contribution of SO_4^{2-} to water chemistry

In WRB, total cationic charge ($TZ^+ = Na^+ + K^+ + 2Ca^{2+} + 2Mg^{2+}$) ranged from 3.93 $meq \cdot L^{-1}$ to 5.28 $meq \cdot L^{-1}$ with an average of 4.63 $meq \cdot L^{-1}$ in January, and from 2.93 $meq \cdot L^{-1}$ to 4.99 $meq \cdot L^{-1}$ with an average of 4.45 $meq \cdot L^{-1}$ in July, which was similar to the previous study in WRB (2.1 ~ 6.3 $meq \cdot L^{-1}$) (Han and Liu, 2004). However, it was several times greater than the world rivers' average value of 1.25 $meq \cdot L^{-1}$ (Meybeck, 1981). Ca^{2+} was the dominant cation with

Table 2
The detailed information about the sample points of four studied reservoirs.

Reservoir	Inflow water	Profile water (depth, m)			Outflow water	Tributaries
			January	July		
WJD	W1	W2	0, 5,15	0, 5,15	W6	W7-W9
		W3	0,5,15,45	0,5,15,45		
		W4	0,5,15,30,60	0,5,15,30,60		
		W5	0,5,15,30,45,60	0,5,15,30,45,60		
GPT	G#-W6	G6	0-130	0-175	G7	G1-G5
SL	S1-G7	S3	0,10,20,30,60	0,5,10,15,30,45,60	S5	S2
		S4	0,10,20,30,60	0,5,10,15,30,45,60		
YP	Y1	Y2	0,10,20,40	0,5,10,20,30,40	Y3	——

The inflow water in GPT wasn't collected, thus G#-W6 was used to represent for the inflow water which ranges from the outflow water of WJD to the reservoir entrance of GPT.

proportions ranging between 52.1% and 74.0%, followed by the Mg^{2+} which ranged from 15.3%–30.8%, and the $[Na^+ + K^+]$ accounted for 6.6%–20.0% of the total cations. HCO_3^- was the dominant anion with proportions from 47.0%–66.0 %, followed by SO_4^{2-} which ranged from 25.6%–40.5% in January and 26.3%–44.6% in July, and the $[NO_3^- + Cl]^-$ accounted for nearly 10.0% of the total cations (Table S1 in the supplementary material). In the Wujiang River, Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-} dominated the water chemistry, which was similar rivers in other karst regions of China, such as Jialing River, Minjiang, and upper Xijiang (Qin et al., 2006; Xu and Liu, 2007; Yoon et al., 2008; Li et al., 2011b; Liu et al., 2017b).

While lithology and water chemistry indicated that carbonate weathering through carbonic acid played a dominant role in controlling the solute compositions. The poor correlation between $[Ca^{2+} + Mg^{2+}]$ and $[HCO_3^-]$ (Fig. 2a) whilst 1:1 correlation between $[Ca^{2+} + Mg^{2+}]$ and $[HCO_3–^-SO_4^{2-}]$ (Fig. 2b) indicated that additional SO_4^{2-} was required to achieve the ionic balance, implying that sulfuric acid played an important role in carbonate weathering in WRB.

3.2. Spatiotemporal variations of SO_4^{2-}, $\delta^{34}S$-SO_4^{2-} and DO

The thermal stratification of water bodies, which directly affected the water quality, was one of the most important characteristics separating lakes and reservoirs from rivers (Liu et al., 2009). Obvious seasonal thermal stratification was observed in WJD, GPT and SL reservoirs in summer, but weak thermal stratification in winter, while the degree of stratification varied with reservoir depth (Fig.3). Several factors, such as the depth of the reservoir, the condition of local weather, and the surface water temperature, may led to the thermal stratification (Monismith et al., 1990). The warm water in the surface was unable to move through the cold, dense water of the hypolimnion. As a result of incomplete mixing in the water column and low light conditions for the photosynthesis at the hypolimnion, the oxygen was depleted and the bottom water can become hypoxic (Elçi, 2008). The DO stratification can influence SO_4^{2-} concentration and its' isotopic composition in water column, due to different processes of S cycling occurred under different redox conditions.

In WJD reservoir, the SO_4^{2-} concentration of W5 in winter was significantly higher than that in summer (Fig. 4), due to the afflux of tributary W8 whose SO_4^{2-} concentrations was two-fold higher than the W5 and greatly increased the SO_4^{2-} concentration of W5. The decreasing $\delta^{34}S$-SO_4^{2-} with increasing SO_4^{2-} concentration in the top 5 m of W5 in summer was possibly caused by the organic S oxidation, because the sulfate formed in organic S oxidation inherited the isotopic signature of organic S which is depleted in ^{34}S (Li et al., 2009). The simultaneous decrease of SO_4^{2-} concentration and $\delta^{34}S$-SO_4^{2-} in the top 5 m of W4 in summer was caused by the coupling processes of organic S oxidation and S assimilation. In general, ^{34}S was enriched in the residual sulfate because the ^{34}S was discriminated by aquatic organisms in the assimilation process of S (Rudd et al., 1990; Szpak et al., 2019). However, in the bottom 30 m of W4 and W5 in summer, the $\delta^{34}S$-SO_4^{2-} became positive while the DO decreased, which implied the enhanced sulfate reducing process occurring at the sediment-water interface of the reservoir, resulting in ^{34}S enrichment in the residual water. In the GPT reservoir, the relatively high $\delta^{34}S$-SO_4^{2-} but low SO_4^{2-} concentrations with drastically reduced DO in the top 5 m indicated the enhanced S assimilation, while in water below 5 m, the variations of $\delta^{34}S$-SO_4^{2-} and SO_4^{2-} concentration were similar to those in the WJD reservoir, which were controlled by the oxidation of organic S and sulfate reducing process. In the surface 5 m of the SL reservoir, the SO_4^{2-} concentration increased while $\delta^{34}S$-SO_4^{2-} value decreased with increasing depth, which suggested that the organic S oxidation might be the main controlling process. However, in the deep water, there was no obvious variation in both SO_4^{2-}concentration and $\delta^{34}S$-SO_4^{2-}, which

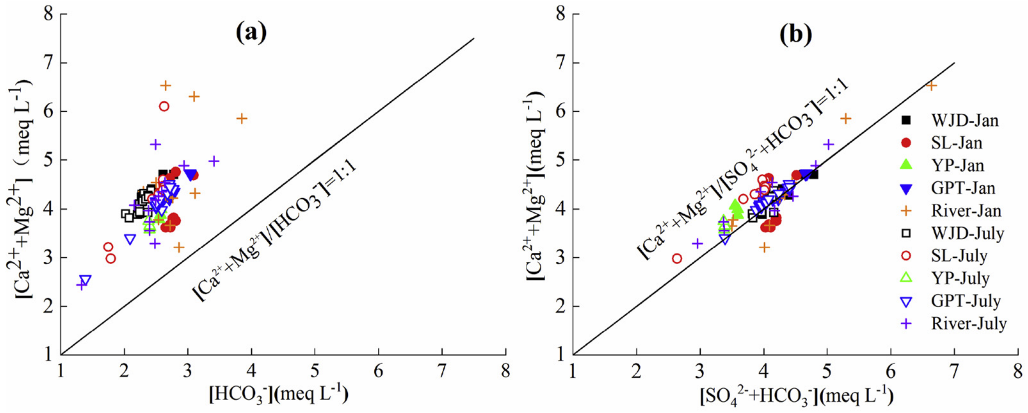

Fig. 2. Relationship between equivalent concentration ratios of $[Ca^{2+}] + [Mg^{2+}]$ and $[HCO_3^-]$, of $[Ca^{2+}] + [Mg^{2+}]$ and $[SO_4^{2-}] + [HCO_3^-]$ in the study area.

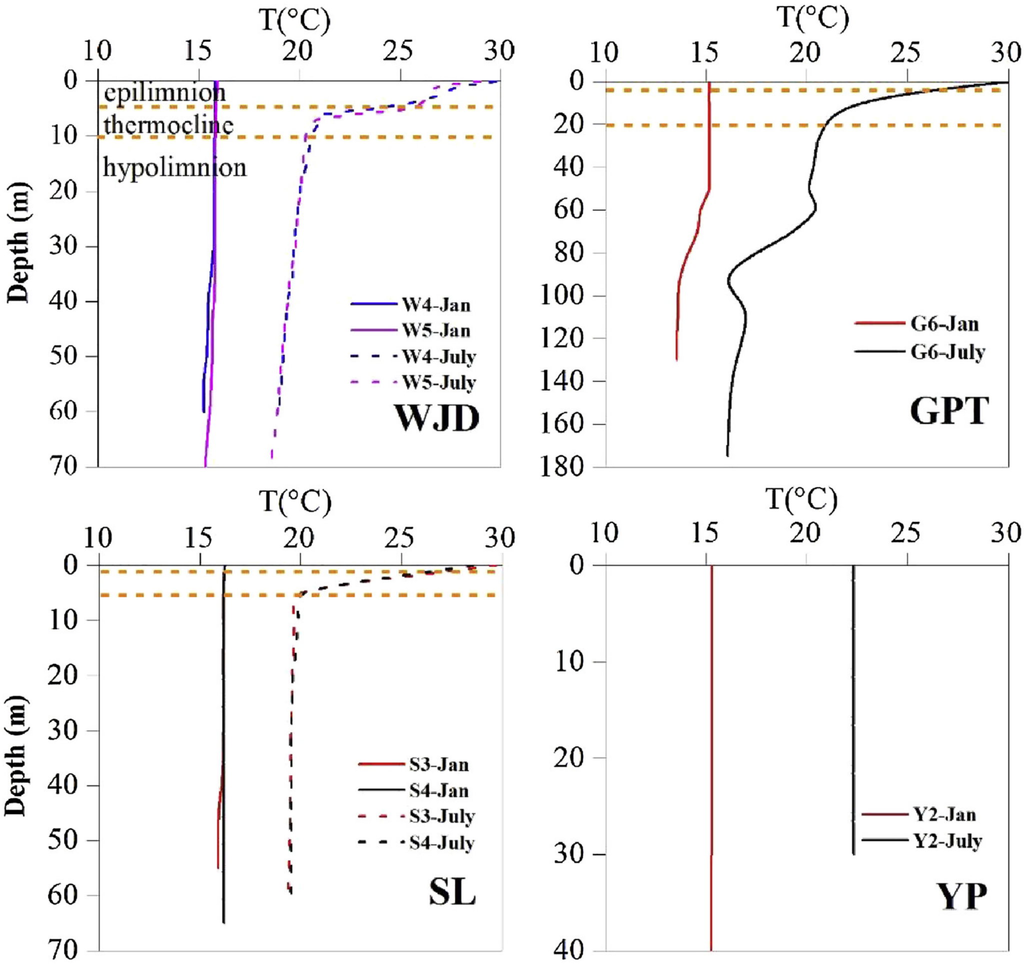

Fig. 3. Variation of temperature (T) in water columns of sites W4, W5, G6, S3, S4 and YP2. See Fig. 1 for site names and abbreviations of the reservoirs.

may be a result of short HRT in the SL Reservoir.

Thus, the SO_4^{2-} concentration increased while the $\delta^{34}S$-SO_4^{2-} value decreased in the surface water was possibly due to the oxidation of S-containing organic matter in high DO environments. The increased $\delta^{34}S$-SO_4^{2-} may be caused by sulfate reduction which was facilitated by thermal stratification of water bodies in the bottom hypoxic environment. It is the variations of DO in the water column caused by seasonal thermal stratification that has important effects on the S biogeochemical cycle in the reservoir (Winton et al., 2019). Damming increased river water HRT and mean depth, and would gradually transform the river from the original system to the plankton-based autotrophic system (Topping et al., 2000; Winton et al., 2019). The different levels of seasonal stratification occurred within the reservoirs because of the different basic characteristics of reservoirs (Table 1). This also might be the possible reason why the S assimilation occurred in surface water of WJD and GPT reservoir. WJD and GPT reservoirs have the physicochemical characteristics of lakes such as long HRT, large storage capacity and obvious spatial heterogeneity. Due to the relatively short HRT, SL and YP reservoirs are more similar to lake-to-river transition system in water chemistry (Klaver et al., 2007). Therefore, the damming effects are responsible for differences in S biogeochemical process in the water column indicated by SO_4^{2-} concentration and S isotopic composition.

3.3. Damming effects on SO_4^{2-} concentration and $\delta^{34}S$-SO_4^{2-} in the Wujiang River-reservoir system

There was a slight seasonal difference in the SO_4^{2-} concentration of the surface water in the four reservoirs (Fig. 5). Specifically, the average value of surface water SO_4^{2-} concentrations in the four reservoirs in winter was 0.72 mmol·L^{-1}, which was a little bit higher than that in summer of 0.70 mmol·L^{-1}, and at each sampling sites, the winter value was higher than that in summer. However, due to several influencing factors, the change of $\delta^{34}S$-SO_4^{2-} was relatively complicated. The $\delta^{34}S$-SO_4^{2-} in four reservoirs and their tributaries ranged from -4.4‰ to 8.1‰ and -6.6‰ to 8.4‰ during winter and summer respectively, the results indicated the main sources of sulfate in WRB were atmospheric deposition, oxidation of sulfide, evaporite dissolution, coal containing organic S and pyrite (Fig.S1 in the supplementary material), which were similar to previous results in Jiang et al. (2006, 2007) and Li et al. (2009). In addition, the SO_4^{2-} concentration and $\delta^{34}S$-SO_4^{2-} in different reservoirs were mainly controlled by the released water from upper reservoir, and they could be affected by S biogeochemical processes inside reservoirs as well as the tributaries with different sources of sulfate. However, the S biogeochemical process inside the reservoir is particularly essential for understanding the damming effect on SO_4^{2-} concentration and $\delta^{34}S$-SO_4^{2-}.

The data from 2002 (before damming) were referred to the sampling figure and data table in Jiang et al. (2006) and Jiang et al. (2007), and according to the locations of the sampling sites in 2002 and 2017, the sampling sites were renumbered to facilitate comparative analysis (Table S2 of the supplementary material). In 2002, there were significant seasonal differences at the same sampling site between winter and summer both in SO_4^{2-} concentration and $\delta^{34}S$-SO_4^{2-} in the surface water. The average SO_4^{2-} concentration and $\delta^{34}S$-SO_4^{2-} in winter were 31.0% and 63.3% higher than that in summer respectively. In addition,

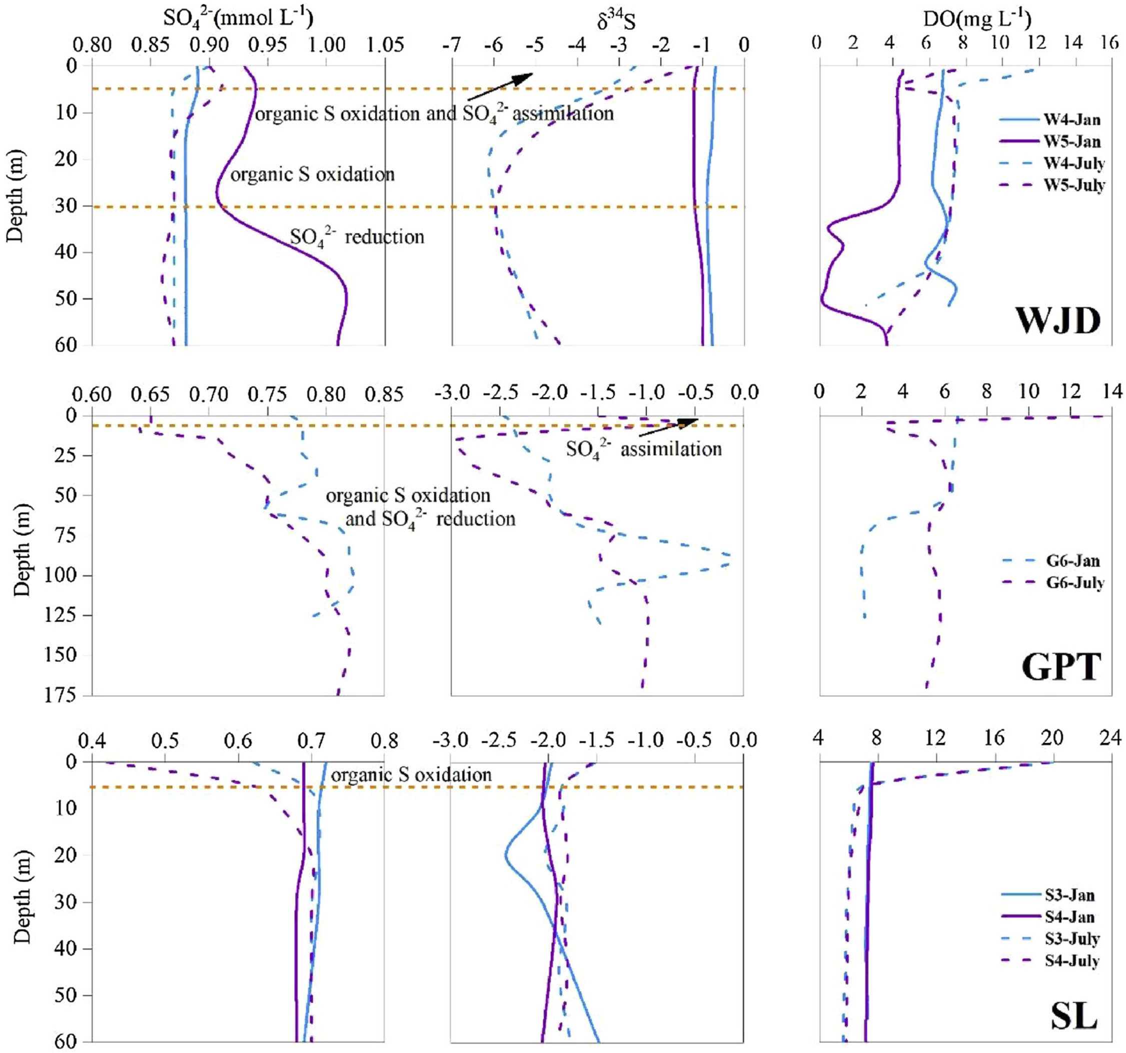

Fig. 4. Variation of dissolved oxygen (DO), SO_4^{2-} and $\delta^{34}S$-SO_4^{2-} in water columns of sites W4, W5, G6, S3 and S4. See Fig.1 for site names and abbreviations of the reservoirs.

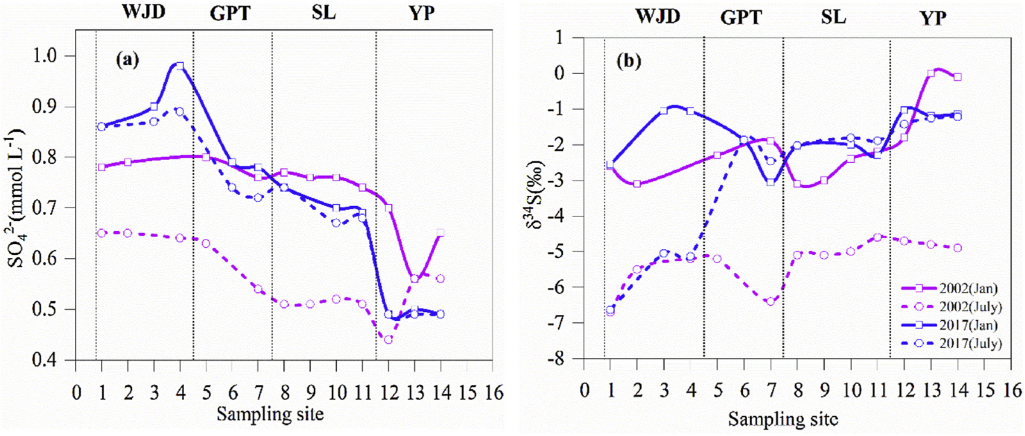

Fig. 5. Comparison of SO_4^{2-} and $\delta^{34}S$-SO_4^{2-} in surface water between 2017 and 2002 in the study area.

the differences between winter and summer were essentially constant along the river direction both in SO_4^{2-} concentration and $\delta^{34}S$-SO_4^{2-}, except the sampling sites 12, 13 and 14 which might be influenced by anthropogenic inputs (Fig.5). Therefore, in 2002 reported by Jiang et al. (2006, 2007), the spatiotemporal changes of SO_4^{2-} concentration and $\delta^{34}S$-SO_4^{2-} could imply the different sources of sulfate in winter and summer in WRB as well as the anthropogenic influence in the downstream area to a certain extent (Jiang et al., 2006, 2007; Li et al., 2009).

Comparing the data of the present study with those in 2002, it could be found that the seasonal difference in SO_4^{2-} concentration between winter and summer was not significant in this study (Fig.5). It was large increase of the SO_4^{2-} concentration in summer of 2017 that narrowed the gap between winter and summer compared with summer of 2002. As for the $\delta^{34}S\text{-}SO_4^{2-}$, the initial values of the WJD reservoir both in winter and summer were almost the same in 2017 and 2002. Before the dams were constructed, the average value of $\delta^{34}S\text{-}SO_4^{2-}$ at the sampling sites located in WJD, GPT, SL and YP reservoirs were -2.9‰, -2.1‰, -2.7‰ and -0.6‰ in winter; -5.8‰, -5.8‰, -5.0‰, and -4.8‰ in summer respectively, and the difference between winter and summer was almost unchanged along the river direction. However, after the cascade dams were built, the respective average value of $\delta^{34}S\text{-}SO_4^{2-}$ in GPT, SL and YP reservoirs of 2017 were -2.5‰, -2.1‰, and -1.1‰ in winter, and -2.2‰, -1.9‰, and -1.3‰ in summer. The average value of changes in $\delta^{34}S\text{-}SO_4^{2-}$ between winter and summer in 2017 was drastically decreased and nearly negligible compared to that in 2002. Overall, the seasonal difference of SO_4^{2-} concentration and its isotopic value between winter and summer of the sampling sites located in these three reservoirs were significantly reduced, reflecting that there was a significant damming effect on the SO_4^{2-} concentration and $\delta^{34}S\text{-}SO_4^{2-}$ of river water.

With regards to the spatial variations, the average SO_4^{2-} concentration decreased by 0.15 mmol·L^{-1} and 0.13 mmol·L^{-1} in winter and summer, respectively, from the sampling sites located in WJD reservoir to those located in YP reservoir in 2002; while in this study the SO_4^{2-} concentration decreased by 0.41 mmol·L^{-1} and 0.38 mmol·L^{-1} severally. Correspondingly, $\delta^{34}S\text{-}SO_4^{2-}$ from sampling sites located in upstream WJD reservoir to those located in downstream YP reservoir increased by 17.2% in summer in 2002, but in the present study it increased by 76.7%. It was clear that there were significant spatial differences in SO_4^{2-} concentration and $\delta^{34}S\text{-}SO_4^{2-}$ between reservoirs in downstream and upstream in 2017, especially in summer, and the differences were more evident than the results of 2002. Thus, the construction of cascade dams also greatly changed the spatial distribution of SO_4^{2-} concentration and $\delta^{34}S\text{-}SO_4^{2-}$ value in surface river water, and finally increased the spatial differences between upstream and downstream reservoirs.

The water depth and HRT of the reservoir increased after damming, compared with the original river state (Liu, 2007; Van Cappellen and Maavara, 2016). The increased water depth and HRT made it easier to form seasonal thermal stratification inside deeper reservoirs such as WJD and GPT. Besides, the surface oxygen rich environment and the bottom hypoxic environment caused by seasonal thermal stratification in summer were the important factors affecting the organic S oxidation and assimilation of S in surface water, as well as the bottom sulfate reducing process (Zerkle et al., 2010; Londe et al., 2016). Therefore, damming could greatly modify the SO_4^{2-} concentration and $\delta^{34}S\text{-}SO_4^{2-}$ by enhancing the biogeochemical processes associated with the S cycle.

3.4. *Cumulative effects of cascade reservoirs on SO_4^{2-} and $\delta^{34}S\text{-}SO_4^{2-}$ in the Wujiang River*

Overall, there were significant regional differences not only in SO_4^{2-} concentration but also in $\delta^{34}S\text{-}SO_4^{2-}$ of all water samples inside reservoirs: the concentration of SO_4^{2-} presented a significant downward trend while $\delta^{34}S\text{-}SO_4^{2-}$ showed an opposite upward trend from WJD reservoir in upper reaches to GPT, SL and YP reservoirs in the middle and lower reaches of Wujiang River, particularly in summer (Fig.6). From upstream reservoirs to downstream reservoirs of the Wujiang River, the SO_4^{2-} concentration ranged from 0.83 to 1.01 mmol·L^{-1} for WJD reservoir, 0.64 to 0.82 mmol·L^{-1} for GPT reservoir, 0.42 to 0.72 mmol·L^{-1} for SL reservoir and 0.49 to 0.51 mmol·L^{-1} for YP reservoir, respectively, and their $\delta^{34}S\text{-}SO_4^{2-}$ values ranged from -6.3‰ to -0.7‰, -3.0‰ to -0.1‰, -2.4‰ to -1.5 and -1.4‰ to -1.1‰, respectively. It can be noted that the concentration of SO_4^{2-} gradually decreased and the range became narrower along the flow direction. Meanwhile, the $\delta^{34}S\text{-}SO_4^{2-}$ gradually became positive and the range was also narrower. However, the longitudinal variations of SO_4^{2-} concentration and $\delta^{34}S\text{-}SO_4^{2-}$ were not significant along the flow direction before damming (Fig. 5). Thus, in the present study, the concentration and S isotopic composition of sulfate in one reservoir will be affected by the upper reservoir through the discharge of water, which subsequently could result in the significant cumulative effects on S cycle by dam construction.

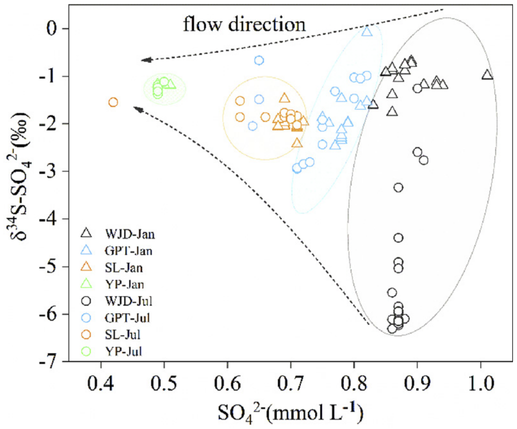

Fig. 6. $\delta^{34}S\text{-}SO_4^{2-}$ vs. SO_4^{2-} diagram for samples collected in WJD, GPT, SL and YP reservoir.

Seasonal thermal stratification existed in reservoirs such as WJD where lake characteristics were prominent. On the one hand, such stratification favored the growth of phytoplankton in the surface water, leading to the water SO_4^{2-} more enriched in ^{34}S due to the assimilation of aquatic organisms in summer; on the other hand, the bottom water was in hypoxic environments, where the sulfate reduction by sulfate-reducing bacteria made water $\delta^{34}S\text{-}SO_4^{2-}$ more positive, and this was the dominant process in the S biogeochemical cycle. The most important factor for causing the cumulative effects is that the reservoirs adopted the mode of the bottom drainage (Westhorpe et al., 2015; Grzybkowska et al., 2017; Wang et al., 2019b), namely from upstream to downstream, the inflow water of the reservoir was more and more enriched in ^{34}S, and thus the SO_4^{2-} concentration and $\delta^{34}S\text{-}SO_4^{2-}$ of each reservoir would be affected by the upper reservoir through water released which makes the SO_4^{2-} concentration decrease and conversely the $\delta^{34}S\text{-}SO_4^{2-}$ increase from upstream to downstream. The similar cumulative effects were also reported in Jialing River (Yang et al., 2018b).

In consideration of the narrowing ranges both in SO_4^{2-} concentration and its isotopic value in reservoirs from upstream to the downstream Wujiang River, it is the different basic characteristics of the reservoir that counts. As mentioned before, basic characteristics have great impacts on the water chemistry inside the reservoir, which, in turn, affects the degree of thermal stratification in the reservoir and regulates the intensity of biogeochemical processes inside the reservoir, particularly in summer (Park et al., 2018; Wang et al., 2019b). The HRT and mean depth of SL and YP reservoirs were significantly lower than in WJD and GPT reservoirs, inducing significant seasonal thermal stratification occurring in the WJD and GPT reservoirs while inapparent stratification in SL and YP reservoirs, S oxidation and sulfate reducing process associated with redox conditions are more intense in reservoirs with obvious thermal stratification, thereby the ranges of SO_4^{2-} concentration and isotopic value inside the downstream SL and YP reservoir are narrowed than WJD and GPT reservoir. Pearson correlation analysis showed the $\delta^{34}S\text{-}SO_4^{2-}$ had no correlation with other chemical parameters like pH, DO, T and TDS in both summer and winter. However, there was a strong negative correlation between the $\delta^{34}S\text{-}SO_4^{2-}$ and SO_4^{2-} concentration in summer (Table 3). When sulfate is concerned, it had strong correlations with pH, DO, TDS ($p < 0.05$) both in summer and in winter. It can be seen from the correlation analysis

Table 3
Correlation analysis between water chemical parameters, SO_4^{2-}, and $\delta^{34}S$ in January and July.

	Temp	pH	DO	TDS	SO_4^{2-}	$\delta^{34}S$
Winter(n = 46)						
Temp	1					
pH	0.170	1				
DO	0.335*	0.778**	1			
TDS	−0.265	−0.776**	−0.801**	1		
SO_4^{2-}	−0.077	−0.819**	−0.468**	0.804**	1	
$\delta^{34}S$	−0.166	−0.539**	−0.209	0.101	0.346*	1
Summer(n = 52)						
Temp	1					
pH	0.797**	1				
ODO	0.703**	0.932**	1			
TDS	−0.474**	−0.420**	−0.378**	1		
SO_4^{2-}	−0.169	−0.296*	−0.286*	0.499**	1	
$\delta^{34}S$	0.062	0.174	0.002	−0.197	−0.654**	1

**. Significantly correlated at the 0.01 level (both sides).
*. Significantly correlated at the 0.05 level (both sides).
The 46 samples in winter and 52 sample in summer were for sampling sites in reservoir, not including the inflow water, outflow water and tributaries.

that the change of SO_4^{2-} concentration between different reservoirs might have a great relationship with the internal environment of the reservoir compared to $\delta^{34}S\text{-}SO_4^{2-}$, and it was greatly affected by the internal biogeochemical process of the reservoir; while the $\delta^{34}S\text{-}SO_4^{2-}$ of the reservoir was more likely to be influenced by sulfate reducing process in which the sulfate was transformed into sulfide and made the residual water enriched in ^{34}S, particularly in summer when the water was obviously stratified (Zerkle et al., 2010).

Interestingly, both HRT and mean water depth were positively correlated with the $\Delta\delta^{34}S\text{-}SO_4^{2-}$ (the difference of $\delta^{34}S$ between the outflow water and the inflow water of the reservoir) in summer (Fig. 7). The possible reason is that water in reservoirs with shallow depth and short HRT were less stratified, causing the S isotopic composition well homogenized; while water in reservoirs with deep depth and long HRT formed obvious thermal stratification, and the bottom hypoxic environment led to the enhancement of the sulfate reduction process, which made larger transformation of S isotopic values in deeper reservoir (Klaver et al., 2007). Therefore, the cumulative effects on S cycle inside the reservoirs were mainly regulated by the change of HRT and mean water depth, and finally change the S isotopic composition in the WRB to some extent by means of changing the degree of seasonal thermal stratification. Although the sulfate sources and tributaries import can affect the SO_4^{2-} concentration and $\delta^{34}S\text{-}SO_4^{2-}$ in the basin, after the construction of cascade dams, the variations in the water physicochemical characteristics of the reservoir cause significant changes in the S biogeochemical process, which then have a vital impact on SO_4^{2-} concentration and $\delta^{34}S\text{-}SO_4^{2-}$ in the basin (Fig. 8).

3.5. Interactions between nutrients cycling and agroecosystem under dam construction

The agricultural ecological environment in karst areas is fragile due to sparse vegetation, slow soil formation, and serious soil erosion. Nutrient loss from soils is a serious environmental problem for agroecosystem (Wang et al., 2019c). Because of the improvement in agricultural yields by irrigation, there is a growing need to expand the irrigated land size (Abrahao et al., 2011), for which the dam construction provides irrigation water. Upon dam construction, part of the agricultural fields were submerged and the changes in physicochemical conditions would affect the nutrients (C/N/P/S) cycling inside the reservoir. Meanwhile, reservoir water quality for irrigation will exert great influences on soil properties and crop growth, and water leaching from agricultural soils may in turn affect the natural regimes of water systems. Therefore, under the influence of agricultural activities and damming, the nutrient cycling in the river basin can more likely lead to the deterioration of ecological environment.

With dam construction, the gradual release of N, P and other nutrients from the submerged agricultural lands will potentially deteriorate water quality and threaten water supply safety (Tang et al., 2012). Nutrients, mainly N and P resulting from agricultural practices like liming and fertilization, contained in flooded soils (and vegetation) may lead to an increase in the biological productivity and cause algae blooms in the reservoir. Meanwhile, the evolution of flooded soils may have consequences on the ecological dynamics of reservoirs, resulting in a pulse in greenhouse gas (GHG) emissions in the deep water of the reservoir after impoundment (Barros et al., 2011; Prairie et al., 2018). On the other hand, the enhanced degradation of OC will control the redox process at the bottom of the reservoir and accelerate the biogeochemical cycle of C/N/P/S within the reservoir.

Water quality in the reservoir for irrigation has great influences on the agroecosystem. For example, long-term use of Beni Haroun dam (in Algeria) had resulted in the enrichment of OC in the soils, and increases in pH, EC, Cd and Pb (Bouaroudj et al., 2019). In addition, high nutrient loading and related algal growth and cyanobacteria blooms in the Hartbeespoort Dam (in South Africa), have posed a severe threat to animal and human health, as well as the crop production (Du Preez et al., 2018). Besides, the low adsorption capacities of agricultural soils made them prone to nutrients leaching promoted by percolated rainwater (Eriksen and Thorup-Kristensen, 2002). The nutrients in the soil originated from fertilizers entered the adjacent reservoir via the surface

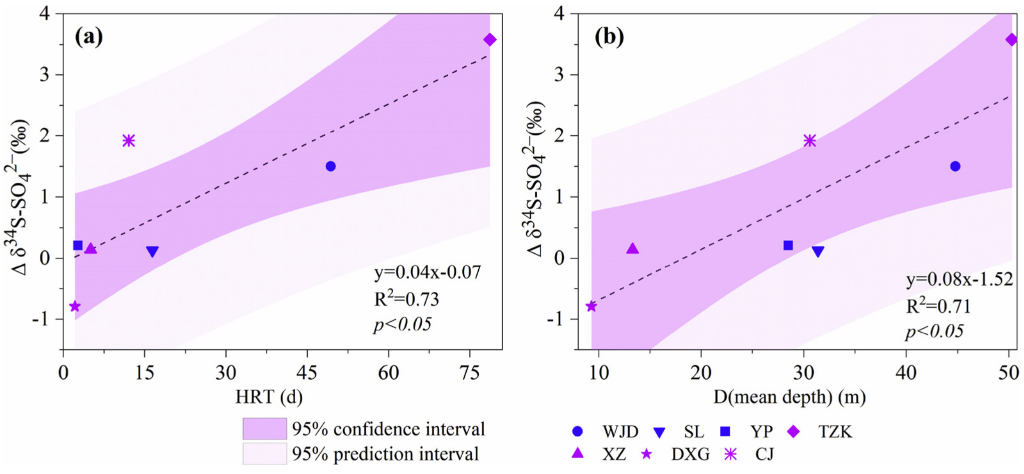

Fig. 7. Relationship between $\Delta\delta^{34}S\text{-}SO_4^{2-}$ and HRT (or mean depth), respectively.

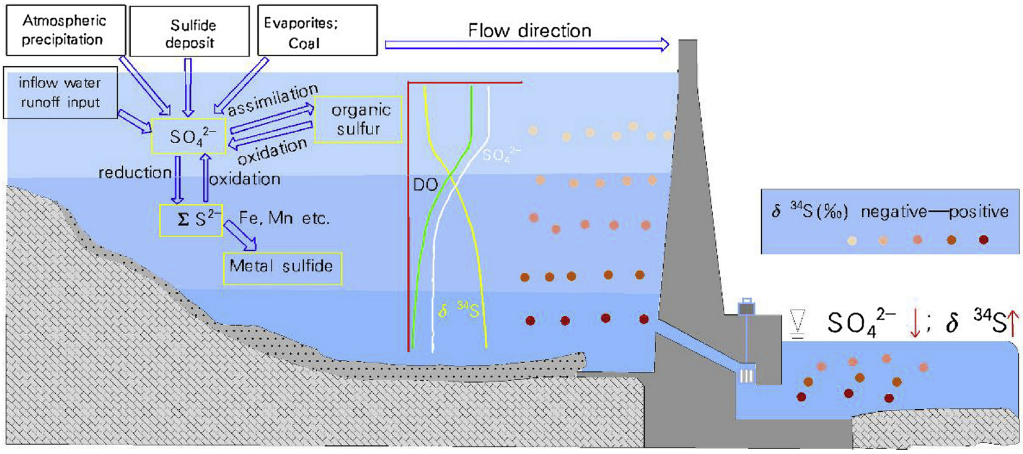

Fig. 8. Sulfur cycle influenced by dam in the Wujiang River Basin.

runoff, which substantially affected the nutrients cycling in the reservoir catchment (Joukainen and Yli-Halla, 2003). In the Lerma Basin of Spain, Merchán et al. (2014) found the irrigated agriculture had affected the quality of water bodies receiving irrigation return flows as indicated by high concentrations of nitrate that was resulted from applied fertilizers. Neissi et al. (2019) demonstrated that intensive use of fertilizers in the upstream of the Zard River in Iran deteriorated the downstream water quality in the reservoir. Therefore, agroecosystem is closely related to nutrient cycling in river basin, and dam construction further enhances the interaction between them.

This study demonstrated that sulfuric acid could play an important role in carbonate weathering in WRB, and damming has increased HRT and water depth of river water. Therefore, the biogenic elements resulting from chemical erosion and farmland soil erosion entered the river and reservoirs through surface runoff (Joukainen and Yli-Halla, 2003), which might affect the C/N//P/S biogeochemical cycles as well as the aquatic ecosystem at local scales (Maavara et al., 2015; Akbarzadeh et al., 2019). At present, the relationships between nutrients cycles and the agricultural environment in the reservoir are mostly focused on organic carbon burial and the release of greenhouse gases (e.g., N_2O and CH_4; Barros et al., 2011; Prairie et al., 2018; Felix-Faure et al., 2019a, 2019b). As such, systematic study of sulfur and its biogeochemical cycling in crop land associated with dam construction may provide a comprehensive view for better agricultural management in karst areas.

4. Conclusions

The present study investigated damming effect on S cycling in Wujiang River by examining the spatiotemporal variations of SO_4^{2-} concentration and $\delta^{34}S\text{-}SO_4^{2-}$ over a 15-year period before and after dam construction. In this study, the sulfate was found to be the second dominant anions and the sulfuric acid played an important role in carbonate weathering. Longer HRT and deeper depth caused by damming enhanced thermal stratification, which greatly influenced SO_4^{2-} concentration and $\delta^{34}S\text{-}SO_4^{2-}$ in water column, particularly in summer. After damming, the spatial variations of SO_4^{2-} concentration and $\delta^{34}S\text{-}SO_4^{2-}$ were induced to increase, while the seasonal differences of them were seemly decreased. Besides, the cumulative effects of cascade dams made the SO_4^{2-} concentration gradually declined and the range of variation gradually narrowed, while $\delta^{34}S\text{-}SO_4^{2-}$ gradually became positive and the scope of change also narrowed from upstream to downstream reservoirs. The HRT and mean depth of the reservoir are the main controlling factors influencing the cumulative effects of the reservoir.

These results suggested that dam construction in the WRB had influenced biogeochemical cycle of S in the river system due to altering the original hydrodynamic condition and water chemistry, comparing to the data before river damming. Specifically, the increase of HRT and water depth resulted in more obvious thermal stratification of water body in summer, and finally enhanced the organic S oxidation in surface water and the sulfate reduction in bottom water, which drastically modified the S biogeochemical cycle. Moreover, the SO_4^{2-} concentration and $\delta^{34}S\text{-}SO_4^{2-}$ in one reservoir were affected by the upper reservoir through the bottom released water, which resulted in the cumulative effects. Therefore, the use of SO_4^{2-} concentration and $\delta^{34}S\text{-}SO_4^{2-}$ associated with S biogeochemical cycle are of great significance in assessing the damming effects of cascade dams.

Our results can be further enhanced by additional study that investigate other S-containing compounds such as thiosulfate, sulfite, and sulfide. For future work, microbial analysis is needed to better understand the S biogeochemical cycle in reservoirs.

Declaration of Competing Interest

Mengdi Yang, Xiao-Dong Li, Jun Huang, Shiyuan Ding, Gaoyang Cui, Cong-Qiang Liu, Qinkai Lia, Hong Lv, Yuanbi Yi declare that they have no conflicts of interest or financial conflicts to disclose.

Acknowledgments

We are grateful to Jun Zhang, Siqi Li, Jie Shi for their help in the field work and teacher Ning An for the test work in the lab. Thanks to professor Henry Teng and Tiejun Wang for their help in the revision. This study was financially supported by the National Key Research and Development Program of China (2016YFA0601000) and the National Natural Science Foundation of China (U1612442).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.agee.2020.106857.

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