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Research article

Variability in water chemistry of the Three Gorges Reservoir, China

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ABSTRACT

The environmental influence of the Three Gorges Reservoir (TGR) on the Changjiang River has been widely studied since the Three Gorges Dam (TGD) began operation in 2003. However, the changes in water chemistry in the reservoir in response to damming effect variations are poorly documented in the area of this large reservoir. The results suggest that in comparison to the water chemistry before the TGR operation, the inflow concentrations of Mg^{2+}, K^+, Na^+ and Cl^- increased in the TGR, and the abundance of Ca^{2+} and HCO_3^- decreased in the inflow in the period after the TGR filling as a result of climate change and human activities in the Changjiang River basin. The ionic composition in the TGR is primarily controlled by contributions from the upstream region of the Changjiang River but was modified by the interaction between water and rocks within the TGR. The concentrations of most major ions as well as the equivalent ratios of the major ions increased in the TGR after the operation of TGD. This change yielded a 6% increase in the major ion loading downstream of the TGD. The Three Gorges area strongly contributes to the increase in ion loading in the TGR due to enhanced water and rock interactions in comparison with the period before TGD operation.

1. Introduction

Rivers are the direct connection between land and ocean, and constitute an essential exogenous part of the global marine biogeochemical cycle (Milliman and Meade, 1983; Meybeck, 2003; Beusen et al., 2009). The construction of dams in large rivers basin has deeply changed riverine material delivered to the ocean (Milliman and Meade, 1983; Kelly, 2001; Maavara et al., 2014; Ran et al., 2016). For the changes in river chemistry induced by the large reservoir, it has attracted the worldwide attention (Margolis et al., 2001; Brink et al., 2007; Guo et al., 2015). The delivery of major elements in a heavily regulated river system is normally altered by the interaction between the inflowing water chemistry and biogeochemical processes occurring within man-made lakes. Water regulation by dams can thus influence the chemistry of river water in the reservoir area and downstream areas (Chetelat et al., 2008; Ran et al., 2010, 2018a; Barros et al., 2011; Wang et al., 2018, 2019). Although major ions have been studied for years to reveal the impact of riverine interaction, limnologic processes and human alteration on river chemistry, the determination of the variation in water chemistry by the in-reservoir process, like man-made lakes worldwide, is fairly rare.

As the largest river in China, the Changjiang River (Yangtze River) has great impacts on the ecosystem in the Yellow and East China Seas (Dai et al., 2011; Liu et al., 2016; Ran et al., 2018b). Therefore, the operation of the TGD has led to global interest due to its potentially great influence on hydrologic and biogeochemical processes in riverine and coastal marine environments. The interaction between the water and rocks may be altered within the TGR region due to water level regulations and reservoir capability. Additionally, large-scale eutrophication and other ecological issues have also been triggered by the establishment of this large reservoir (Zeng et al., 2006; Ran et al., 2010, 2018a). These variations might thus impact the river water chemistry in the middle and lower Changjiang River.

In recently decades, the major elements abundances and loadings in the Changjiang River basin have been changing due to the variations in chemical weathering and human activities. There was a sharp increase in concentrations of Cl^-, SO_4^{2-}, NO_3^-, Na^+ and K^+ after the TGD impoundment to the 135 m water level stage compared to the long-term data before the TGD operation (Chen et al., 2002; Duan et al., 2007; Chetelat et al., 2008; Ding et al., 2014). Meanwhile, a decreasing trend in the riverine dissolved silicate (DSi) flux was observed in recent few decades in the Changjiang River basin (Dai et al., 2011; Ma et al., 2018), which

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could have a drastically impact on the biodiversity of primary production in the Changjiang estuary under the background of increasing nitrogen and phosphorus fluxes (Liu et al., 2013; Zhou et al., 2017; Xiao et al., 2018). These variation of major ion may be attributed to the enhanced intensity of human activities (e.g., riverine damming, unban input and changes in land use) in the Changjiang River basin.

However, the current data were mostly collected downstream of the TGD (Chetelat et al., 2008; Dai et al., 2011; Wang et al., 2018). The impacts of TGD operation on the water chemistry in the TGR (~156 m water level filling stage)are still poorly documented. Therefore, it is critical to investigate the changes in the water chemistry in the TGR after the TGD operation to figure out the impacts on variation in water chemistry of the increasing damming process in this large river system and the potential effects on estuarine ecosystem. In this study, we analyze the variations in the major ions in the water samples collected from the inflow and outflow of the TGR during the full year from 2006-2007. The major aim of this study is to identify the variability of these major ions in the water across the TGR and assess the chemical reactions within this large man-made lake that have altered the composition of the water as a result of the TGD impoundment.

2. Sample collection and methods

2.1. Study site

This study focuses on the TGR (Figure 1), a large and well-known man-made lake in the Changjiang River and has a total volume of nearly 39 km^3 and a surface water area of 1100 km^2 (Wu et al., 2003). The types of bedrock in the Changjiang River basin are complicated, and the dominant rock type in the TGR region is carbonate rock. The TGR was first filled to the 135 m water level in 2003 (above the water level of the East China Sea, hereinafter), and the water storage in the reservoir then reached the level of 156 m in November 2006.

Between the inflow and outflow points, there are approximately 30 tributaries in the Three Gorges area, which contribute approximately 5% of the water that discharges to the TGR according to long-term observation (Huang et al., 2006). The specific sampling locations are shown in Figure 1. Based on the precipitation and runoff patterns in the catchment, the hydrologic year of the Changjiang River is usually divided into two seasons: a flood season (May to October) and a dry season (November to April).

2.2. Sample collection

Sampling expeditions on the 1st and 16th of each month were carried out in the main channel of the TGR at Fuling (the reservoir inflow, located at the city of Chongqing) in the upper section of the TGR and at the TGD (Hubei Province) in the lower section of the TGR from June 2006 to May 2007. Samples were immediately filtered in a clean plastic tent with precleaned and preweighed 0.45 μm polyethersulfone membranes. The filtrates were collected for the measurements of major ions and dissolved inorganic nutrients (e.g. nitrate and silicate).

Before measurements, all of the water samples were kept in a cool environment at 4 °C away from light. Concentrations of HCO_3^- were determined by alkalinity titration in the field. Major ions were measured by a Dionex ICS3000 system (Dionex Corporation, USA) with an analytical precision less than 1% (Ran et al., 2010). The cationic and anionic charge balance (<10%) is added proof of the precision of the data. Concentrations of dissolved SiO_2 (DSi) and NO_3 were analyzed by a Bran-Luebbe AAIII Autoanalyzer (SEAL Analytical, USA) with a precision of 1–5% (Liu et al., 2003; Ran et al., 2013). The concentration unit used in this manuscript is mg/L. The concentration represents the atomic form for most ions, while the data reported for HCO_3^-, SO_4^{2-}, DSi and NO_3 represent the whole oxyanion group. Total dissolved solids are the sum of all measurements.

All analyses were carried out in the College of Environment Science and Technology at Ocean University of China. The daily discharge data were acquired from the Ministry of Water Resources, the People's Republic of China. Figure 2 shows the temporal variations in river discharge at the Qingxichang and Yichang hydrological stations (upper stream of the Changjiang River) in 2007. There was a clear trend in the monthly variation in freshwater discharge, and the annual discharge mainly fluctuated around approximately 258 km^3/a and 268 km^3/a over the sampling year at the inflow and outflow stations, respectively, in the TGR. The major ions from 1958–1990 (Changjiang River Water Resource Committee, 1955–1999) were used for comparison.

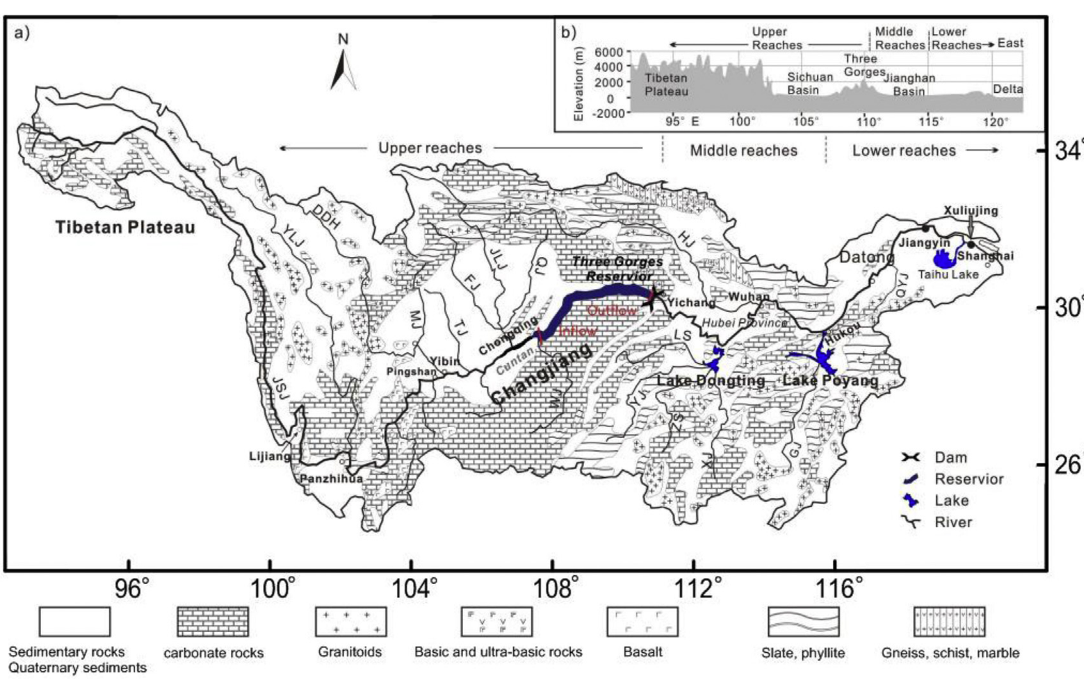

Figure 1. Sampling stations in the Three Gorges Reservoir.

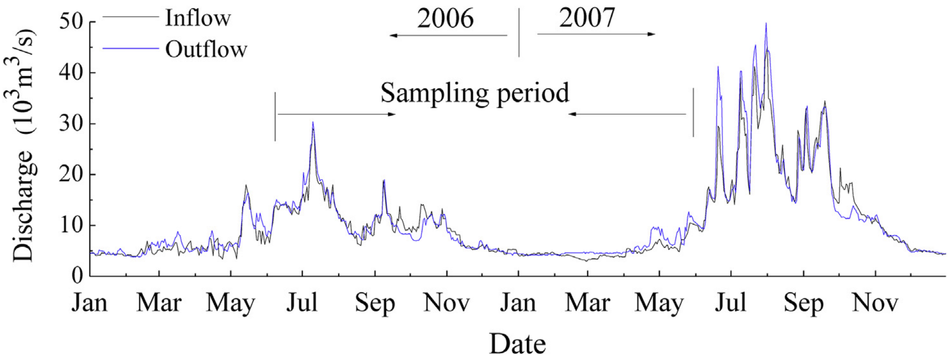

Figure 2. Daily discharges at the inflow and outflow of the Three Gorges Reservoir.

2.3. Flux calculations

We employed Load Estimator (LOADEST) (Runkel et al., 2004) to estimate the major element loads from 2006-2007 using the measurement data at the inflow and outflow sites via the adjusted maximum likelihood estimator was used with the uncertainty at the 95% confidence level.

2.4. Mass balance

The major ion retention by the reservoir is calculated using a mass balance approach as follows:

$$(1 + q)\ F_{IN}\text{-}F_{OUT}\text{-}F_{R} = 0 \quad (1)$$

Where, F_{IN} represents the total inputs at Fuling, F_{OUT} is the outflow through the dam, and F_{R} represents the reservoir retention (Positive value is removal by reservoir, and the negative value is addition). q is the yearly (outflow-inflow)/inflow ratio of water through the TGR, which is used to quantify the contribution of tributaries to the transport of major ions from 2006-2007 for which no measurements were available; for the full year of 2006–2007, $q = 0.04$. This estimation approach is based on the water balance in the reservoir. We consider it is reasonable because major ion fluxes and water discharge at the inflow of the TGR are correlated strongly and the contribution of major ions loadings from the tributaries is fairly close to their share of the water discharge to the TGR (Ran et al., 2017).

3. Results

3.1. Water discharge in the TGR

During the sampling period, the water discharge at the inflow ranged from 2900 m^3/s to 29000 m^3/s, with an average of 8180 m^3/s. The outflow discharge varied between 4030 m^3/s and 30400 m^3/s and averaged 8500 m^3/s. The monthly inflow and outflow from the TGR were fairly consistent over time. The annual discharges were approximately 258 km^3/a at the inflow and 268 km^3/a at the outflow. The tributaries in the TGR watershed thus contribute approximately 4% of the outflow water without considering the contribution of other factors. The annual discharge roughly represents the hydrological regime of a dry year in the Changjiang River.

The water discharge was high in the rainy season and low in the nonflood season during the sampling period (Figure 2). Overall, the discharge trends were similar between the inflow and outflow. However, the TGR could alter the monthly outflow discharge through the regulation of the reservoir capabilities, e.g., September and October 2006 (increase in the reservoir capability) and March 2007 (decrease in the reservoir capability) (Figure 2).

3.2. Monthly variations in major ion concentrations in the TGR

HCO_3^- and Ca^{2+} were the dominant ions in the TGR, and the sequence of ion concentrations was present in the proportions $HCO_3^- > SO_4^{2-} > Ca^{2+} > Cl^- > Na^+ > Mg^{2+} > DSi > NO_3 > K^+ > F^-$. For the dominant cation and anion, the HCO_3^- concentration ranged from 53.0 to 112 mg/L with averages of 93.5 mg/L at the inflow and 99.3 mg/L at the outflow (Table 1); Ca^{2+} yielded concentrations from 20.8 to 38.0 mg/, with averages of 28.2 mg/L at the inflow and 31.3 mg/L at the outflow. Despite obvious seasonal variations in river discharge (Figure 2), the ions showed only slight seasonal variability in concentrations within the sampling period. Generally, HCO_3^- and Ca^{2+} were higher in the flood season and lower in the nonrainy period, while other ions were lower in the flood season and higher in the dry season (Figure 3). The concentrations of Na^+, K^+, Mg^{2+} and Ca^{2+} in the flood season (June to September) from 2006-2007 were overall higher than those in October to May of the following year ($p < 0.01$). The major ions, including Ca^{2+} and HCO_3^-, were slightly more concentrated at the outflow than at the inflow, while the concentration of other ions decreased slightly across the reservoir (Table 1). Thus, the equivalent ratios changed slightly between the inflow and outflow (Table 2).

3.3. Mass balance of major ions in the TGR

The annual fluxes of all the major ions that were measured at the inflow and the outflow were approximately 4380×10^4 t/a and 4640×10^4

Table 1. Chemical composition of major ions in Three Gorges Reservoir (mg/l).

		Strontium	Sodium	Potassium	Magnesium	Calcium	Fluoride	Chloride	Sulfate	Bicarbonate	Silicate[5)]	Nitrate[6)]
Inflow[1)]	Mean	0.23	13.2	2.01	9.84	28.2	0.20	14.5	32.8	93.5	6.61	5.90
	±1 SD	0.04	3.24	0.20	1.16	3.37	0.07	4.80	5.70	12.6	1.20	0.77
Outflow[2)]	Mean	0.24	12.1	1.93	9.52	31.3	0.21	14.1	33.4	99.3	6.44	5.94
	±1 SD	0.04	1.68	0.24	1.13	2.52	0.06	2.50	5.16	5.53	1.05	1.70
Cuntan[3)]			8.6[4)]		8.6	37.2		7.1	23.8	136		
Yichang[3)]			7.8[4)]		7.8	39.2		7.2	16.5	146	6.78	

[1)] Fuling; [2)] Guizhou (hereinafter); [3)] Chen et al. (2002); [4)] the sum of Na + K; [5)] SO_2; [6)] NO_3.

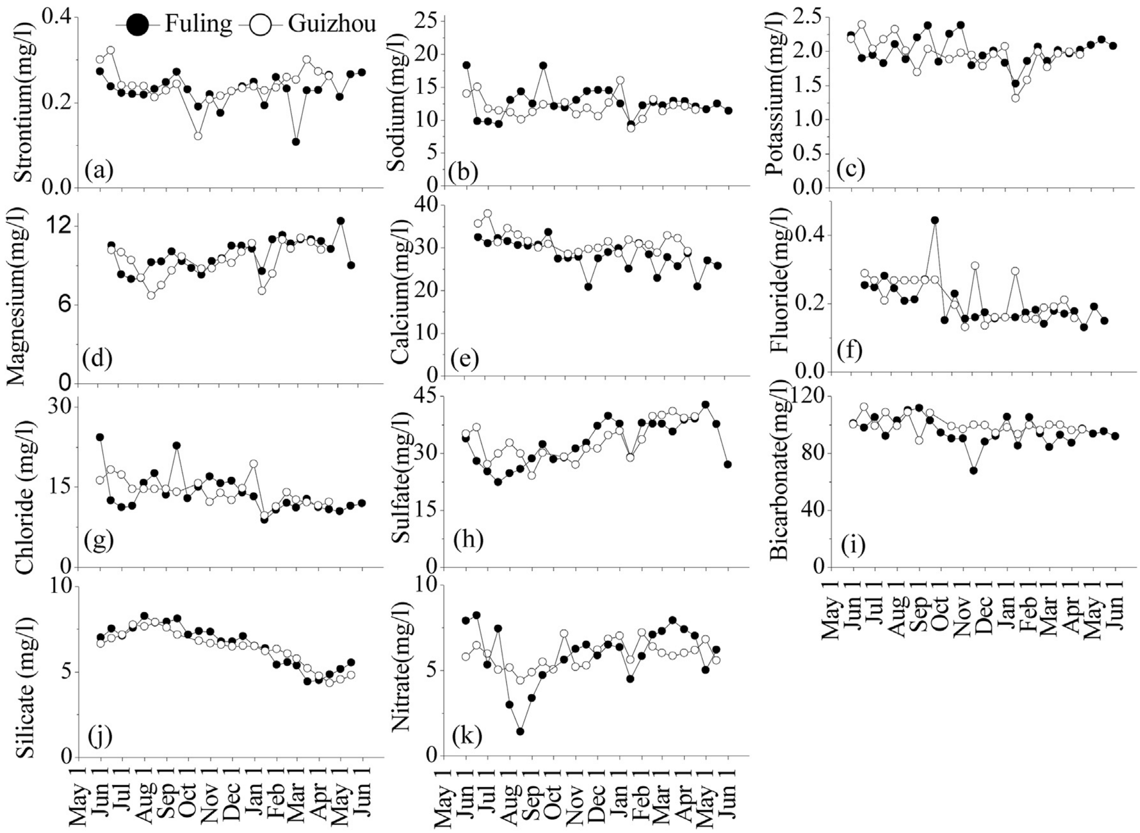

Figure 3. Variation of major ions in the Three Gorges Reservoir (the enhancing of reservoir capability from 135 m to 156 m above the sea level was operated in October and November).

t/a, respectively, in 2006–2007 (Table 3), suggesting that approximately 260×10^4 t/a was yielded in the Three Gorges area with a chemical weathering rate of 260 t/km^2/a. The fluxes of major ions increased significantly across the TGR, accounting for 6% of the inflow flux to the TGR (Table 3), which exceeded that of the discharge should be attributed to the tributaries in this area.

Fluxes of HCO_3^- and Ca^{2+} were significantly enhanced across the TGR ($p < 0.05$), while fluxes of Na^+, Mg^{2+}, K^+ and Cl^- decreased slightly (Table 3). A 6% reduction in the DSi flux out of the TGD from 2006-2007 (a whole hydrological year) was also observed on the basis of the mass balance approach. However, the NO_3 loading increased approximately 1% at the outflow in comparison with the loading at the inflow.

3.4. Changes in the TGR water chemistry with the dam operation

In comparison with the water chemistry before the TGR operation, the concentrations of Na + K, Mg^{2+} and Cl^- increased by approximately 54%, 14% and 104%, respectively, at the inflow. Ca^{2+} and HCO_3^- decreased by approximately 24% and 31%, respectively, at the inflow after the filling of the TGR. Similar to the variation in the inflow, the abundances of Na + K, Mg^{2+} and Cl^- were enhanced by 57%, 22% and 102%, respectively, at the outflow, and Ca^{2+} and HCO_3^- were decreased by approximately 20% and 32%, respectively, at the outflow after impoundment of the TGR (Table 1).

Table 2. Equivalent ratios of major ions in the Three Gorges Reservoir (molar ratios, dimensionless).

	Na/(Na + Ca)	Cl/(Cl + HCO_3)	(Ca + Mg)/(Na + K)	(Na + K)/TZ^+	(Na + K)/Ca	HCO_3/Na	Ca/Na	Mg/Na	Cl/Na
Inflow	0.29	0.19	3.57	0.22	0.44	2.67	2.46	1.43	0.71
Outflow	0.25	0.18	4.10	0.20	0.37	3.10	2.97	1.51	0.75

Table 3. Fluxes of major ions in Three Gorges Reservoir estimated by the LOADEST[1)] (10^4 t/a).

		Strontium	Sodium	Potassium	Magnesium	Calcium	Fluoride	Chloride	Sulfate	Bicarbonate[3)]	Silicate[4)]	Nitrate[5)]
Inflow	Mean	5.18	284	45.0	206	647	4.90	331	670	2110	159	192
	±1 SD[2)]	0.29	14.6	1.1	3.8	18.8	0.29	24.1	16.6	81.0	5.4	5.9
Outflow	Mean	5.24	270	44.3	202	724	5.17	329	694	2290	155	202
	±1 SD	0.28	11.3	1.9	9.6	13.6	0.36	16.6	32.4	39.0	6.0	20.0

[1)] The method used in the software is adjusted maximum likelihood estimation (AMLE); [2)] the relative standard deviation; [3)] HCO_3; [4)] SO_2; [5)] NO_3.

4. Discussion

4.1. Water discharge in the mainstream of the lower Changjiang River

The TGD impounds the upstream water during the dry season to a high water level and releases the reservoir water to a low level before the onset of the flood season. Therefore, more water supplies come from the TGR to the mid-lower Changjiang River from March to April, and less water is discharged from the TGR from September to October due to the extension of water storage in dry season (Figure 2). The regional atmospheric precipitation accounts for only a minor share of the variation in the water discharge from the TGR (Ran et al., 2013). Therefore, the water regulation by the TGD, especially the enhanced reservoir capacity from 135 m to 156 m in 2006, plays a considerable role in the seasonal variation in water discharge in the lower Changjiang mainstream.

The amount of discharge during the sampling period from 2006-2007 (Figure 2) is fairly close to the amount of runoff in 2006. However, the Changjiang River runoff reached its lowest level over the last 50 years in 2006 (Dai et al., 2008), accounting for only 65% of the multiyear average discharge due to extreme drought at the Yichang gauging station (Changjiang Water Resources Commission, 2007). As a result, the river discharge in the flood season was 20–30% less than that in a normal year. Despite the great variation in the annual discharge of the Changjiang River in 2006, the discharge in the dry season was fairly close to that in a normal year and almost remained the same. The TGD alters the seasonal distributions of water discharge out of this large dam by regulating the peak flow. There was, however, no evident trend for the variation in freshwater discharge, and the decennial discharge mainly fluctuated around approximately 900 km^3/a over the past 60 years (Dai et al., 2011) at the Datong station in the Changjiang River.

4.2. Mechanisms controlling the water chemistry of the TGR

The observed values of the major ion concentrations are two or more times higher than the world average values except for the concentration of DSi, which is slightly lower than the global average value (Dürr et al., 2011). The natural composition of reservoir waters was essentially controlled by the breakdown of rock matrices in the catchments. The equivalent ratios of Na/(Na + Ca) and Cl/(Cl + HCO_3) were less than 0.5 (molar ratio, unitless, Figure 4), which indicates that the river water chemistry was dominated by rock weathering (Gibbs, 1970; Wang, 2005; Ran et al., 2010). The equivalent ratio of (Ca + Mg)/(Na + K) was greater than 1, revealing that the river water chemistry was controlled by carbonates and silicates (Singh and Hasnain, 2002). A high ratio of (Ca + Mg)/(Na + K) (3.6–4.1) and the relatively high contribution of (Ca + Mg) to the total cation concentration indicated that the contribution of silicates was only of minor importance, whereas the contribution of carbonates was significant at all stations (Singh et al., 2005).

The relative importance of each chemical weathering process varied with the weathering materials and the conditions of the weathering environment. Among the two sites in the TGR, the strongest carbonate weathering was observed (Figure 5). In contrast, the upstream area before the TGR showed the highest intensity of silicate weathering (Table 2). Evaporate minerals contributed to more than 70% of the Na + K and Cl in the water but provided only a minor Ca contribution in the Changjiang basin (Wang, 2005). Thus, the equivalent ratios of (Na + K)/Ca and Cl/(Cl + HCO_3) reflected the intensity of the dissolution effects on the evaporate minerals, suggesting that the TGR region had a lower intensity of evaporate weathering than that in its upstream basin. The weak linear relationship of HCO_3^- between the inflow and outflow in the TGR (Figure 6) may suggest the influence of carbonate rocks on the HCO_3^- abundance in this area (addition in loading; Table 3).

In comparison with the water chemistry before the operation of the TGR, the inflow concentrations of Na + K, Mg^{2+} and Cl^- increased in the TGR. In contrast, the abundance of Ca^{2+} and HCO_3^- decreased at the inflow after the filling of the TGR (Table 1). The river water is normal in saturation or supersaturation with respect to calcite and dolomite (Chen et al., 2002), and the precipitation of calcium with carbonate and sulfate may be responsible for lowering the Ca^{2+}. Furthermore, the equivalent ratios suggest that the contribution of silicate weathering was enhanced slightly in recent decades, while the carbonate weathering was weakened (Table 1). Climate change and acid deposition in the upper Changjiang River may also result in changes in chemical weathering. In recent decades, the temperature has been increasing in comparison with that in the 1990s (Van Vliet et al., 2011), which could enhance the chemical weathering in the upper channel of the Changjiang River (Chetelat et al., 2008).

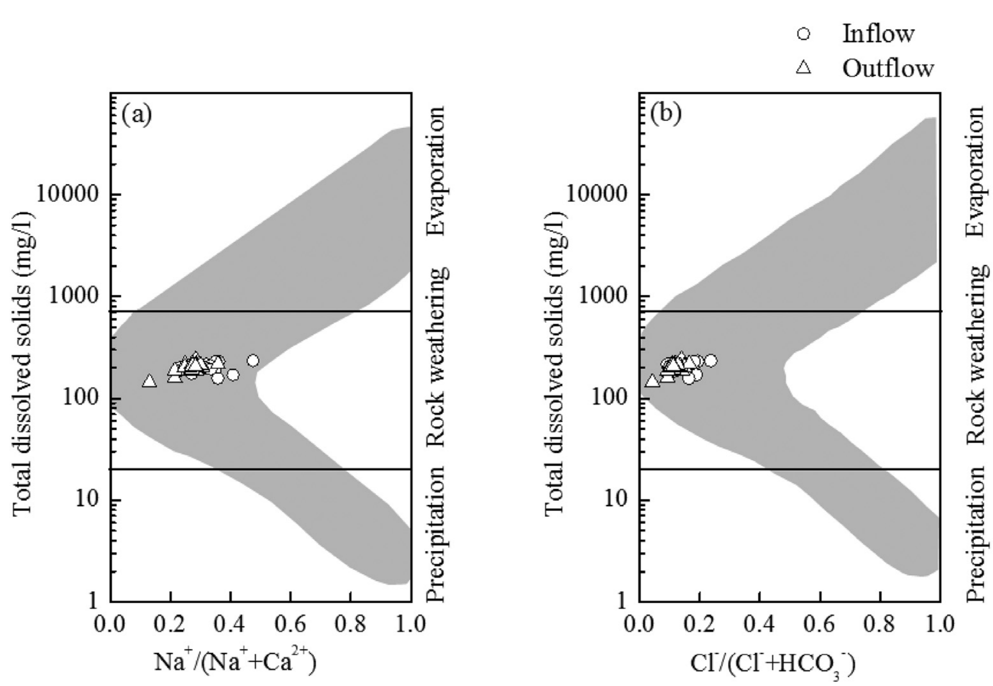

Figure 4. Relationship between total dissolved solids and ion ratios at Cuntan and Yichang in the Changjiang River.

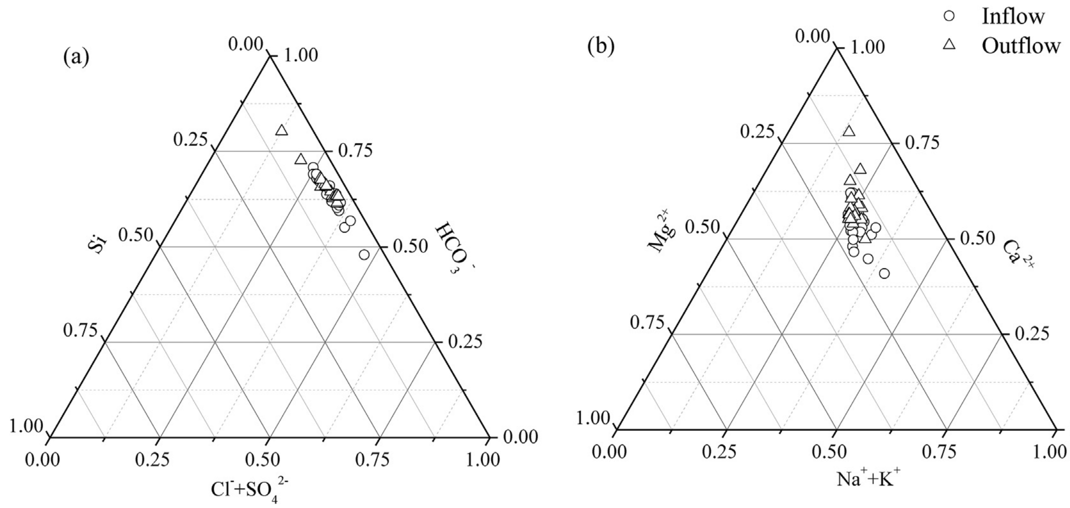

Figure 5. Ternary plots showing in the relative of major inorganic ions at Cuntan and Yichang in the Changjiang River.

Furthermore, the current ionic concentrations commonly varied over two to three times those in the period from 1962-1990 (Chen et al., 2002). The seasonal variation in major elements also decreased at the inflow of the TGR in comparison with the seasonal variation from 1962-1990 observed at the Cuntan station, possibly implying the influence of damming in the upper river basin. Due to the control of water discharge in the upper Changjiang River, the runoff fluctuations also decreased, which could also affect the abundance of major ions. This trend, which was also observed in the Datong reach the downstream of Changjiang River (Chen et al., 2002; Wang et al., 2018), could expand in recent decades due to increased reservoir construction.

4.3. Impacts of water regulation by the TGD on river water chemistry

4.3.1. Major ion abundance and composition

Similar to the water in the mainstream Changjiang River (Wang et al., 2018), the carbonate system in the TGR is dominated by HCO_3^-. Moreover, the variation in the HCO_3^- concentration in natural water is primarily governed by the alkalinity equilibrium because the pH values typically range from 7.6-8.3 (Ran et al., 2008). The input of anthropogenic strong acid into the river could cause a decrease in HCO_3^- in the water (Scofield et al., 2016). In the Three Gorges area, the increasing coal usage could contribute more acid deposition than in the past few decades (Chen et al., 2002), which would decrease the abundance of HCO_3^-. Similarly, the increasing SO_4^{2-} in the water of the TGR could support the influence of acid deposition due to coal consumption (Chen et al., 2002; Wang et al., 2018). This trend would result in a decline in Ca^{2+} via the precipitation of gypsum. Moreover, the enhanced photosynthesis within the TGR due to algal blooms in the adjacent bays (Ye et al., 2006; Ran et al., 2010) could also decrease the amount of HCO_3^- in the water. Accordingly, the decline in the HCO_3^- concentration in the lower mainstream of the Changjiang River (Wang et al., 2018) suggests a change in the HCO_3^- concentration in the TGR. Dams appear to have a variable impact on the abundance of HCO_3^- (Jacinthe et al., 2012). For example, the dams in the Wujiang River have caused an increase in HCO_3^- in the river water (Wang et al., 2011, 2013). After the TGD operation began, HCO_3^- in the lower mainstream of the Changjiang River generally decreased (Wang et al., 2018), which can be supported by the change in HCO_3^-abundance through the reservoir.

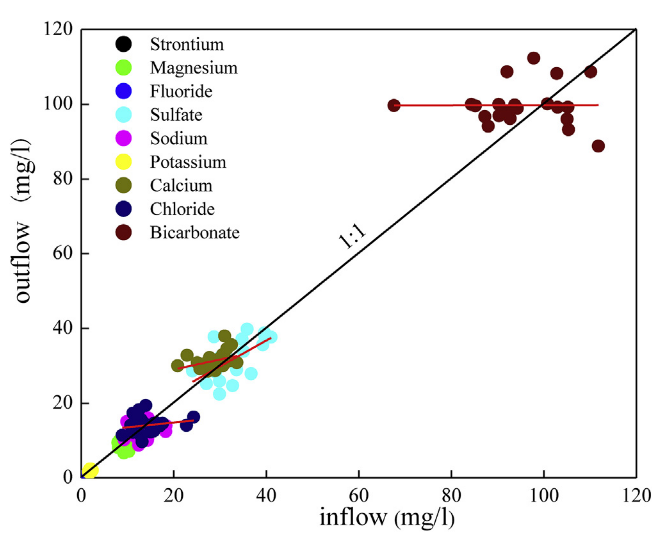

Figure 6. Ions relationship at inflow and outflow in the Three Gorges Reservoir.

In contrast to HCO_3^- in the TGR, there were overall increases in Mg^{2+}, Na^++K^+, SO_4^{2-}, and Cl^-. This result is similar to the results that occurred after the initial impoundment of the TGD (Chetelat et al., 2008), when the concentrations of Na + K, Cl^- and SO_4^{2-} increased. The long-term variability in major ions is mainly controlled by chemical weathering in the Changjiang River (Chen et al., 2002). The enhanced ion loading in the TGR suggests that the ion ratios indicative of rock weathering intensity increased after the TGD operation compared to those before the TGD operation. The contribution of carbonate weathering may become stronger at the outflow than at the inflow result from the total weathering production and the dominant rock type in the TGR. Moreover, anthropogenic acid rain could enhance chemical weathering in the Changjiang drainage basin (Guo et al., 2014). Consequently, the concentrations of Mg^{2+} and Na + K could be enhanced with increasing chemical weathering by acid precipitation. Again, the extreme drought and the decline in HCO_3^- may respond to the decline in Ca^{2+}.

Several other factors, e.g., water supply shortages and enhanced evaporation in the TGR (Chen et al., 2001), might result in water with greater ion concentration flowing into the mid-lower reaches. Correspondingly, the concentrations of major ions (i.e., Ca^{2+}, Mg^{2+}, Na^+ and K^+) could also increase after the impoundment of the TGD.

Meanwhile, variations in the DSi concentration were observed in the TGR ($p < 0.01$). The average DSi concentration in the outflow decreased by approximately 3% compared with the average inflow value (Table 1). This result suggests a slight effect of reservoir retention on the DSi concentration in the TGR. The annual retention of DSi in the TGR from 2006-2007 is similar to that in the reported data (in 2007 (Ran et al., 2013);). However, the obvious decreases in DSi concentrations (Table 1) and fluxes (Table 3) after the TGD impoundment are very minor, suggesting a slight increase in DSi fixation by diatoms in the large reservoir (Ran et al., 2013). Similar to DSi, the changes in the NO_3 concentrations were fairly small between the inflow and the outflow (Table 1), indicating that the reservoir had a minor influence on NO_3.

Based on the observations (C_{Datong}) in Datong station from 2010-2011 (Wang et al., 2018), a comparison of ion concentrations was made between TGR channel and downstream of the Changjiang River (Datong) (Figure 7), monthly variation of all C_{Datong}-C_{TGD} were opposite to that of water discharge in Yichang, which indicates that water flow is the main factor controlled the export of major ion in the Changjiang River. Transportation process from TGR to mid-low stream has obvious dilution effect on DSi, Na^+ and Mg^{2+}. On the contrary, Ca^{2+}, K^+ and HCO^{3-} are added during the transport. Therefore, compare to the upstream, the carbonate weathering could have larger contribution to major ions in water body of the downstream of TGR. Decreased export of DSi from the Changjiang River in recent years may be the combined effects of dam retention and relatively low proportion of silicate weathering in downstream of TGD in the Changjiang River.

4.3.2. Major ion loadings

The Changjiang River transported approximately 154 $\times 10^6$ t/a of total dissolved solids to the sea based on the data from 1962-1990 (Chen et al., 2002), with a specific chemical weathering rate of 86 t/km^2/a. The loading of major dissolved elements at the outflow of the TGR (2006–2007) accounts for only 30% of the average flux of total dissolved solids in the Changjiang River (1962–1990), which is comparable to the discharge at the Yichang hydrological station between the studied period and 1962–1990. Ion loading is largely governed by chemical weathering in water (Brink et al., 2007) and discharge (Hartmann and Moosdorf, 2011).

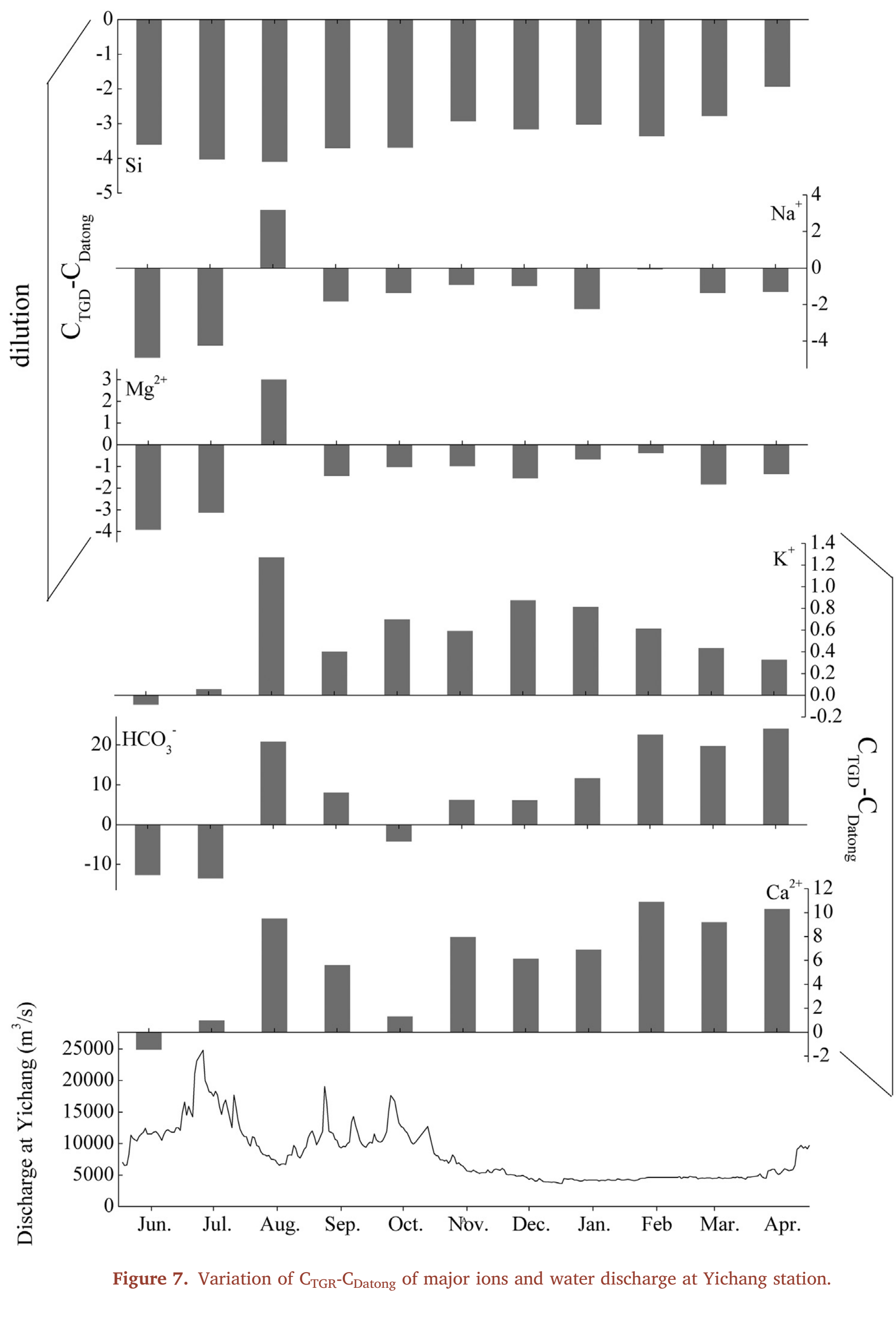

Figure 7. Variation of C_{TGR}-C_{Datong} of major ions and water discharge at Yichang station.

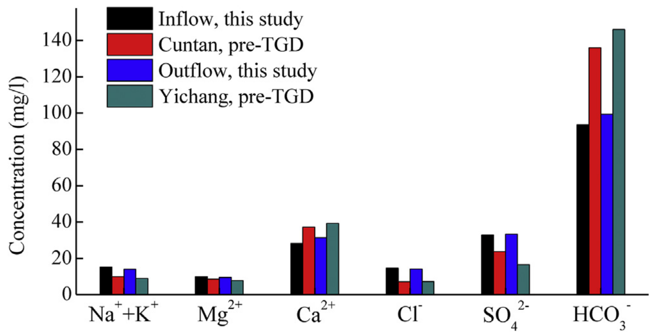

Figure 8. Comparison of major ions at inflow and outflow of the Three Gorges Reservoir (post-TGD) and at Cuntan (close to inflow) and Yichang (close to outflow) in the Changjiang River (pre-TGD (Changjiang River Water Resource Committee, 1955–1999)).

Therefore, the low discharge during the extreme drought hydrological regime from 2006-2007 decreased the contribution of riverine fluxes of total dissolved solids to the river mouth. The reduction in DSi flux out of the TGD in recent years is the result of the damming retention effect (Ran et al., 2013). However, other processes, i.e., the interaction between water and rocks, might yield ion loadings in the TGR, counteracting the ion loadings due to the retention of DSi by the TGD. Carbonate is the dominant rock type in the Three Gorges area (Figure 1). The addition of carbonate weathering could be responsible for the increase in the loading of total dissolved solids in the TGR. As a result, the total ion loadings at the outflow slightly increased, which would increase the riverine loadings in the Changjiang River. As a direct instance, the specific flux in the region of the TGR was 3 times higher than that at the Datong station in the Changjiang River (1962–1990 (Chen et al., 2002);), suggesting the large inputs from chemical weathering from the TGR. The mass balance approach (Table 3) also suggests a change in complicated hydrological and biogeochemical processes in the reservoir system. The increased flux of HCO_3^- and Ca^{2+} represented approximately 37% and 20%, respectively, of the total dissolved solid loadings that were added in the TGR. No additions of Cl^- and SO_4^{2-} were found (Figure 8), suggesting minor anthropogenic sources in the Three Gorges area. However, the concentrations of Cl^- and SO_4^{2-} increased significantly in recent decades (Figure 8 (Chen et al., 2002; Ran et al., 2010);) as a result of acid deposition in the upper Changjiang River. These anthropogenic loads could be higher than natural loads Cl^- and SO_4^{2-} relative to natural loads, implying the high sensitivity of river chemistry to human activities.

Due to the impoundment of the TGD, the water level in the Three Gorges area increased by approximately 100 m compared to the level before the TGR filling, which could have changed the interaction between water and rocks in this area. We believe that the ion loading variations could be the result of the impoundment effect. In 2010, the water level reached 175 m, which may have strengthened the interaction between water and rocks resulted in slightly increased discharge of total dissolved solids compared to that observed in this study due to the increased contact area between water and rocks resulting from the enhanced water level. Similarly, Wang et al. (2018) observed enhanced fluxes in the lower part of the Changjiang River. The chemical variation in the TGR may thus play an important role in controlling the ion loadings of the Changjiang River. This process likely occurred because nutrient loads have increased due to the alteration of the water-rock interactions. We observed an increasing trend of NO_3 loading in the TGR (Table 3), which may have caused a shift in nutrient stoichiometry and enhanced eutrophication in the river and estuary (Ran et al., 2018a). Further investigations should thus be carried out to explore the evolution of the water quality and ecosystems in this large river system that is subject to rapid climate change and anthropogenic disturbances.

5. Conclusions

We reported the limnologic water chemistry variations that were related to the damming of the TGR from 2006-2007. The dominant ions in the TGR are Ca^{2+} and HCO_3^-; The ionic composition of the TGR is primarily controlled by the contributions from the upstream of the Changjiang River, but annual observations suggest that the TGD operation impacts on the water chemistry in the TGR reaches and downstream in the Changjiang River. The concentrations of most major ions increased through the TGR after the operation of the TGD began. This change yielded a 6% increase in major ion loading downstream of the TGD. The DSi loading in the TGR from 2006-2007 declined slightly due to reservoir retention.

Although the concentrations of Cl^-, Mg^{2+}, K^+, Na^+ and DSi changed slightly across the reservoir, changes in weathering processes and human activities in the Three Gorges area contributed to the increase in ion concentrations to some extent in the TGR region. Compared to the water chemistry before the TGR operation, the inflow concentrations of Mg^{2+}, K^+, Na^+ and Cl^- increased in the TGR. However, the abundance of Ca^{2+} and HCO_3^- decreased at the inflow after the TGR filling. The change in chemical weathering processes and human activities in the upper Changjiang River before reaching the Three Gorges area could result in greater contributions to the ion loading than the alteration by the TGR in the Changjiang River. This study provides recognition of the mechanisms controlling ion loading in man-made lakes, highlighting the influence of large reservoirs on riverine material loadings.

Declarations

Author contribution statement

H. Wang: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

M. Li: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

C. Sun: Analyzed and interpreted the data; Wrote the paper.

W. Wu: Performed the experiments.

X. Ran: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

J. Zang: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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