Water quality variation and its conditioning factors in the Three Gorges Reservoir, China

Xiaoxiao Wang, Haijian Bing, Yanhong Wu, Jun Zhou, He Zhu, Yong Wu and Hongyang Sun

ABSTRACT

The variation of water quality has been an issue of concern since the impoundment of the Three Gorges Reservoir (TGR). In this study, water samples from the TGR were collected in July and November 2015 and in May and July 2016 to reveal the variations of water quality and its key conditioning factors. The results showed that the concentrations of major ions, nutrients and heavy metals in the TGR’s water body exhibited heterogeneous variations. Especially, the hotspot for major ions and heavy metals emerged at Chongqing downtown, and a decreasing trend from Chongqing toward the TGR dam was spatially observed. The heterogeneous variation of hydrochemistry in the TGR revealed the integrated influences of natural processes and human activities. Especially, the intense rainfall in the spring and early summer of 2016 promoted the transport of pollutants to the TGR, and further magnified the influence of large cities on the spatial variations of the hydrochemistry in the TGR. This study will give more insights into the change of water quality in large reservoirs in the context of the intense rainfall and the human activities.

Key words | heavy metals, major ions, rainfall, Three Gorges Reservoir, water quality

HIGHLIGHTS

- The spatial and seasonal variations of water quality indexes in the TGR were revealed.
- The heterogeneous variations of the major ions and heavy metals revealed the integrated influences of natural processes and human activities.
- The intensified rainfall promoted the pollutants transport and magnified large cities’ effects on the variations of the hydrochemistry in the TGR.
INTRODUCTION

Dam construction is a global issue that contributes to the loss of river connectivity. So far, more than 63% of rivers in the world have lost the capacity to flow freely, which has altered the hydrological processes, transport of sediment and pollutants, and the water quality in reservoirs (Chen & Chau 2019; Grill et al. 2019). At least 3,665 reservoirs (≥1 km²) have been built in China during the past 15 years and about one-third of the newly impounded area is located in the upper Yangtze River (Zhu et al. 2020). The impoundment of the Three Gorges Reservoir (TGR) decreases flow velocity and leads to a lake-oriented alteration of hydrological environment, which has potential effects on the geochemical cycles of key elements and the water quality in the TGR (Bao et al. 2015). The TGR is also a vital drinking water source for approximately 1.45 million people in Chongqing and Hubei provinces. Therefore, the water quality has consequently become an issue of wide concern in the TGR, and it is necessary to comprehensively understand the dynamic variations of potential pollutants in the TGR water column.

Many researchers have observed contaminants entering the TGR by runoff and wet/dry deposition from the catchment (Shen et al. 2015; Zhang et al. 2016a, 2016b; Li et al. 2018; Zhao et al. 2019; Gao et al. 2020). Especially in recent decades, the discharge of industrial and domestic sewage and the application of fertilizers, pesticides, and herbicides in the farming system have altered the water quality of the TGR (Gao et al. 2016). The issue of heavy metal contamination in the water and sediment of the TGR has been focused on due to its toxicity, bioaccumulation, and non-degradability (Han et al. 2015; Bing et al. 2016; Gao et al. 2016; Xiong et al. 2020). Major ions are also a potential threat for the water quality in the TGR (Zhao et al. 2013; Tang et al. 2015; Wang et al. 2020a). For example, nitrate and phosphate are the most concerning indices in water due to their contribution to water eutrophication, and there are many reports revealing their seasonal and spatial distributions in the TGR (Shen & Liu 2009; Huang et al. 2014; Tang et al. 2020). The migration and
distribution of these elements in the water and sediment may threaten the water quality and ecological service of the TGR (Han et al. 2015; Bing et al. 2016; Zhu et al. 2019). However, a whole reservoir scale understanding of the key mechanisms underlying the spatial and seasonal variations of major ions and heavy metals in the water of the TGR is still lacking.

Since the operation of the TGR, human activities and land use changes have been considered as major reasons for the accumulations or variations of heavy metals and nutrients in the TGR water (Zhang et al. 2019a). Apart from human activities, rainfall event is another important factor affecting the water quality (Wang et al. 2018; Tiyasha et al. 2020) which lacks comprehensive exploration in the TGR. Since 1900, at least 26 El Niño events have been observed. Especially in 2015 and 2016, El Niño caused more precipitation in China (China Meteorological Administration), and the intensified rainfall led to flooding in the Yangtze River (Zhang et al. 2016a, 2016b). The discharge of the Yangtze River increased by 11.3 billion m$^3$ at Yichang station in May 2016 compared with that in 2015 (Changjiang Water Resources Commission of the Ministry of Water Resources (CWRC)). As a result, the pollutants may enter the water bodies through the surface runoff (Qiu et al. 2018), and lead to the variations in hydrochemistry of the TGR. Especially in urban areas, the road dust acts as a key sink of various pollutants, which will migrate through surface runoff and potentially alter the hydrochemistry of the receiving water (Zhang et al. 2019a, 2019b; Zhang et al. 2020). However, since the full operation of the TGR in 2010, the integrated influence of human activities and rainfall events on the water quality has not been comprehensively explored.

In this study, 14 sites covering the entire TGR were selected to collect water samples for the determination of water physiochemical properties, major ions, and heavy metals. Since some knowledge is lacking in the variations of hydrochemical characteristics and the influence of rainfall events on the water quality in the TGR, the main objectives of this study are to: 1) illustrate the spatial and seasonal variations of hydrochemical characteristics in the TGR; 2) reveal the factors controlling the hydrochemical variations; and 3) clarify the effects of anthropogenic versus rainfall events on the water quality of the TGR.

**MATERIALS AND METHODS**

**Study area**

The TGR (29°16′–31°25′N, 106°20′–111°50′E) is located between Jiangjin District, Chongqing, and Zigui County, Hubei Province (Figure 1). With a mean water depth of approximately 70 m, the TGR has a volume of 39.3 km$^3$ and a total surface area of 1,045 km$^2$. The annual average water discharge recorded by the hydrologic station of Cuntan was 34.5 billion m$^3$ during 1950–2010 (CWRC). The TGR region is subject to a subtropical monsoon climate with a humidity of 60–80%. The mean annual precipitation is approximately 1,000 to 1,500 mm, and the annual mean temperature varies from 16.7 to 18.7 °C with an extreme maximum temperature exceeding 41 °C. More details of the study area are presented by Bao et al. (2015).

**Sample collection**

In order to cover most of the counties in the TGR, surface water samples (0.5 m below water surface, ca. 5 m to the river bank) for spatial analysis were collected from May 4 to May 12, 2016 at 14 sections within the entire TGR (Figure 1, Table S1 in Supplementary Materials). Sampling sections were selected with 20–100 km intervals, most of which were located several kilometers upstream of the cities in order to avoid the direct influence of cities on the hydrochemical parameters. The surface water samples for seasonal analysis were collected in the dry season (November 11–12, 2015), flood season (July 12–13, 2015 and July 8–10, 2016), and the transition period from the dry season to the flood season (May 10–11, 2016) at the inflow control section (S6) of the TGR (Figure 1). The bottom water samples were also collected following the flow direction at the center of the river with depth of 30 m in November 2015 at S6 (S6-1, S6-2, S6-3, S6-4, S6-5) to reveal the vertical variation of hydrochemical parameters. Both the surface and the bottom water were collected by a Niskin sampler three times at each section and mixed as one sample. A portion of the mixed water was immediately filtered through a pre-combusted (450 °C for 6 h) and pre-weighted 0.45 μm Whatman GF/F glass fiber filter. All the water samples were stored...
in clean polyethylene bottles (pre-marinated with 1:10 HCl for 24 h and washed by deionized water) at 4 °C before laboratory analysis.

**Sample analysis and data collection**

The filters were dried at 105 °C to a constant weight for the determination of suspended solids (SS), which was calculated by the difference in weight between pre- and post-filtration. An EXO2 multi-parameter water quality monitor (YSI Co., Ohio, USA) was used for the in-situ measurements of water temperature (T_w), specific conductivity (Spc), total dissolved solids (TDS), dissolved oxygen (DO), pH, oxidation-reduction potential (ORP), turbidity (Turb) and chlorophyll (Chl), and the detection limits are 0.01 °C, 1 μS/cm, 0.01 g/L, 0.01 mg/L, 0.01, 0.1 mV, 0.01 NTU, and 0.01 μg/L, respectively.

The concentrations of fluorine (F⁻), chloride (Cl⁻), nitrate (NO₃⁻), sulfate (SO₄²⁻), sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), and magnesium (Mg²⁺) ions in the filtrates were determined by ICS-90 ion chromatography (Dionex Co., Sunnyvale, USA), with the detection limit of 0.001 mg/L. The analytical precision for Ca²⁺, Mg²⁺, SO₄²⁻, Cl⁻, NO₃⁻ is <1% relative standard deviation (RSD), for Na⁺, K⁺ is <2% RSD, and for F⁻ is <5% RSD. Bicarbonate (HCO₃⁻) analysis was carried out via acid titration, and phosphate (PO₄³⁻-P) was measured using the molybdenum blue colorimetric method with a Shimadzu UV-2600 spectrophotometer at 700 nm. Dissolved heavy metals, copper (Cu), cadmium (Cd), lead (Pb), zinc (Zn), chromium (Cr), and nickel (Ni) in the filtrates were detected by a Nexion500 ICP-MS (PerkinElmer Co., Fremont, USA), and the results of certified samples and cross-checking agree within ±5%. The oxygen and hydrogen isotopes (δD, δ¹⁸O) for water samples collected in November 2015 were analyzed using an ISOPrime-100 connected to a Vario ISOTOPE Cube elements analyzer (Elementar Co., German), and the data were calibrated against the standards of V-SMOW. The standard deviation of all repeated measurements of the standards and samples is ±0.4‰.

The continuously monitored data for discharge at Cuntan, representing the inflow of the TGR, were manually collected from the Yangtze River hydrological network.
RESULTS

Water physicochemical characteristics

The water physicochemical parameters of the TGR are shown in Table S2. The mean concentrations of SS, Spc, TDS, DO, pH, ORP, Turb, and Chl during our study were 0.046 ± 0.038 g/L, 349 ± 51 μS/cm, 227 ± 33 mg/L, 7.53 ± 0.37 mg/L, 7.68 ± 0.15, 170 ± 35 mV, 48.9 ± 55.8 NTU, 0.358 ± 0.322 μg/L, respectively. The spatial variation of the water physicochemical parameters in May 2016 is illustrated in Figure S1. The SS and Turb showed a decreasing trend towards the dam, indicating a marked deposition of suspended particles along the TGR. Spc and TDS presented similar variations with marked low levels at Chongqing downtown (S2, S3), where the confluence of the Yangtze River and Jialing River is located (Figure 1). Furthermore, the levels of Spc and TDS were slightly higher downstream of the inflow control section (S6) and showed minor fluctuations longitudinally along the TGR. The variation of DO was inconsistent with pH, which showed a high level at S7. The ORP reached a lower value in the midstream of the TGR (S5–S9), while Chl presented a high value in the midstream of the TGR. Vertical variations of water physicochemical characteristics at S6 implied pH, Turb, and DO were higher in the bottom water than in the surface water, and there was no marked difference among the other parameters (Figure S2).

Variations of the water physicochemical characteristics in different seasons are presented in Figure S3. Two groups of these parameters were classified according to the seasonal variations (Table S3). In the first group, the highest values of Tw, pH, Turb, and Chl appeared in July 2016, however, the DO and ORP showed an opposite trend with the higher values in November 2016. The second group included Spc and TDS with the higher values in May 2016. The first group indicates more sediment loads, higher water temperature, and the growth of algae in the summer periods, while the low temperature, less suspended particles, and weak microbial activities decreased the consumption of dissolved oxygen and facilitated the aerobic conditions of the water in the winter. Moreover, the second group implies the piston effect of the runoff driven by concentrated rainfall, which flushed out the contaminants that accumulated in the dry season and increased the dissolved solids in the TGR water.

Major ions

The concentrations of major ions in the TGR water are summarized in Table 1. The cations were in the order of Ca²⁺ > Na⁺ > Mg²⁺ > K⁺, and the anions were HCO₃⁻ > SO₄²⁻ > Cl⁻. A Piper diagram illustrates the hydrochemistry type of the TGR water was HCO₃-Ca, Mg (Figure S4). The concentrations of Ca²⁺, Mg²⁺, HCO₃⁻, SO₄²⁻, and K⁺ increased slightly compared with previous studies in the TGR and the Yangtze River, while the concentrations of Cl⁻ and Na⁺ were comparable to those in the previous studies (Table 1). Variations of major ions in different seasons are illustrated in Figure 2. It is remarkable that the variations of major ions are heterogeneous. The concentrations of Cl⁻ and Na⁺ were higher in July 2016, and the concentrations of SO₄²⁻, K⁺, Ca²⁺, and Mg²⁺ displayed the higher levels in May 2016. The spatial distributions of the ions showed that the peak values of Cl⁻, SO₄²⁻, Na⁺, K⁺, Mg²⁺, and Ca²⁺ appeared at Yubei (S3) (Figure 3). The vertical variation of the major ions at S6 was heterogeneous, and there was no marked difference in the parameters between the bottom water and the surface water (Figure S5).

The concentration of PO₄³⁻-P in the TGR water was in the range of 0.020–0.147 mg/L, with mean concentration of 0.102 ± 0.023 mg/L. The concentration of NO₃-N in the TGR water varied between 0.551 and 2.37 mg/L, with a mean concentration of 1.88 ± 0.386 mg/L. The concentrations of PO₄³⁻-P and NO₃-N were both above the guideline values for level IV, suggested by Surface Water Quality Guideline of China (Table 1). Annually, the concentrations of PO₄³⁻-P and NO₃-N in the TGR water increased after the impoundment of the TGR (Table 1). Seasonally, the
concentrations of \( \text{PO}_4^{3-} \)-P and \( \text{NO}_3^- \)-N presented the highest levels in July 2016 (Figure 2). Spatially, the concentrations of \( \text{PO}_4^{3-} \)-P and \( \text{NO}_3^- \)-N showed relatively high values from Chongqing downtown (S2) to Fengdu (S7) (Figure 3), which might refer to the distribution of nutrients loss through the surface runoff.

Table 1  | Concentration of major ions and nutrients in the TGR water (units: mg/L)

|          | Mean | SD  | Min. | Max. | China\(^{a,b}\) (Level IV for P, N) | WHO\(^{c}\) | US\(^{d}\) | TGR (2006–2009)\(^{e}\) | Yangtze River (2007–2008)\(^{f}\) |
|----------|------|-----|------|------|----------------------------------|-----------|----------|-----------------|-------------------------------|
| \( \text{Cl}^- \) | 14.1 | 3.56 | 11.2 | 22.9 | 250                               | –         | 250      | 16.6            | 12.2                          |
| \( \text{SO}_4^{2-} \) | 46.8 | 3.98 | 39.9 | 57.9 | 250                               | –         | –        | 33.6            | 32.4                          |
| \( \text{HCO}_3^- \) | 148  | 11.6 | 123  | 168  | –                                 | –         | –        | 129             | 123                           |
| \( \text{Na}^+ \) | 12.4 | 2.61 | 10.4 | 20.3 | –                                 | 50        | –        | 12.8            | 8.8                           |
| \( \text{K}^+ \) | 2.83 | 0.74 | 2.29 | 4.91 | –                                 | –         | –        | 1.79            | 2.1                           |
| \( \text{Mg}^{2+} \) | 12.0 | 0.797| 9.92 | 13.3 | –                                 | –         | –        | 9.41            | 9.7                           |
| \( \text{Ca}^{2+} \) | 50.6 | 3.62 | 43.0 | 55.5 | –                                 | –         | –        | 40.9            | 39.3                          |
| \( \text{PO}_4^{3-} \)-P | 0.102 | 0.023 | 0.020 | 0.147 | 0.10–0.20                           | –         | –        | 0.01–0.08 | –                            |
| \( \text{NO}_3^- \)-N | 1.88 | 0.386 | 0.551 | 2.37 | 2                                  | –         | –        | 1.40            | –                            |

\(^{a}\)Environmental Protection Administration of China (2002).

\(^{b}\)Ministry of Health (2007).

\(^{c}\)WHO (2006).

\(^{d}\)US Environmental Protection Agency (2004).

\(^{e}\)Müller et al. (2008); Wu et al. (2012).

\(^{f}\)Xia et al. (2008).

Figure 2  | Variation of major ions in the TGR water in the flood season (a, d), dry season (b), and the transition period from the dry season to the flood season (c).
Dissolved heavy metals

The concentrations of dissolved heavy metals for water samples are summarized in Table 2. The concentrations of heavy metals were below the values recommended for drinking water by the Environmental Protection Administration of China, the World Health Organization, and the US Environmental Protection Agency. The dissolved Cu, Cd, and Pb in the TGR water were generally lower than those in the Yangtze River and the world rivers, indicating that the TGR was less polluted by heavy metals.

After the impoundment of the TGR, the concentration of heavy metals (except for Cr and Ni) showed a lower level compared with that in 2006 (Table 2). The variation

Table 2 | Concentration of dissolved heavy metals in the TGR water (units: µg/L)

| Mean  | SD   | Min. | Max. | Drinking water guidelines |
|-------|------|------|------|---------------------------|
|       |      | 10   |      | China (level I)           | WHO                   | US         | TGR (2006)° | World riversf | Yangtze Riverg |
| Cu    | 1.343| 1.979| 10   | 2,000 | 1,300                  | 1.80                  | 1.47       | 8.40         |
| Cd    | 0.024| 0.045| 1    | 3     | 5                      | 0.03                  | 0.08       | 0.28         |
| Pb    | 0.022| 0.053| 10   | –     | –                      | 0.12                  | 0.08       | 6.40         |
| Zn    | 1.089| 1.564| 50   | –     | –                      | 1.58                  | 0.60       | 18.75        |
| Cr    | 0.856| 0.155| 10   | 50    | 100                    | 0.69                  | 0.70       | 8.90         |
| Ni    | 2.683| 3.144| 20   | –     | –                      | 0.37                  | 0.80       | 3.69         |

*Environmental Protection Administration of China (2002).
Ministry of Health (2007).
WHO (2006).
US Environmental Protection Agency (2004).
*Müller et al. (2008).
†Gaillardet et al. (2003).
‡Wang et al. (2011).
of heavy metals in different seasons is presented in Figure 4. The concentrations of Cu, Cr, and Ni were higher in May 2016, and the peak level of Cd appeared in July 2015. Additionally, the concentrations of Pb and Zn were marked in November 2015.

The spatial variations of the heavy metals illustrated the peak levels at Chongqing (S3) and Wanzhou (S9) (Figure 5), where the chemistry industry plays an important role in the national production. Specifically, the hot spots for Cu, Cd, and Ni appeared only at Chongqing, and the peak level for

![Figure 4](image-url) Variation of heavy metals in the TGR water in flood season (a), dry season (b), and the transition period from the dry season to the flood season (c). (Data in July 2016 are absent.)

![Figure 5](image-url) Spatial distribution of dissolved heavy metals in the TGR water in May 2016.
Cr was only marked at Wanzhou, however, Zn showed higher levels both at Chongqing and Wanzhou. Furthermore, Pb presented a declining trend from the upstream TGR to the dam. The vertical variation of the heavy metals at S6 also indicated the heavy metals were well distributed in the water column of the TGR (Figure S6).

**Precipitation, discharge, and D-O isotopes**

The precipitation and the inflow discharge of the TGR during El Niño in 2015 and 2016 are shown in Figure 6. In comparison with the mean precipitation during 1981–2010, the precipitation presented a higher level from December 2015 to June 2016. Affected by the intense rainfall, the inflow discharge of the TGR increased earlier in 2016 than in 2015. The mean values of δD and δ¹⁸O in the TGR water were −75.3‰ and −10.8‰, respectively. The values of δD and δ¹⁸O in 2015 and 2016 were more negative than the mean value for 2003–2012 (Figure 7). In addition, the narrow ranges of the δD and δ¹⁸O values during 2015–2016 implied the homogeneity of the TGR water.

![Figure 6](image1.png)

Figure 6 | Monthly precipitation (a) and the inflow discharge of the TGR (b) during 2015–2016. The average precipitation during 1981–2010 is given for contrast, and some data for the discharge are absent.

![Figure 7](image2.png)

Figure 7 | Annual variations of D-O isotopes in the TGR water. Data were collected from Ding et al. (2013), Deng et al. (2016), Chen et al. (2018), and Jiang et al. (2018).
DISCUSSION

Factors driving the hydrochemistry variation in the TGR

Bed rock weathering is a main source for ions in river waters, and many previous studies have pointed out that the hydrochemical characteristic of the Yangtze River was controlled by the bedrock weathering (Zhang et al. 2016a, 2016b; Li et al. 2018). The carbonate area contributes about 24% of the total area in the Yangtze River basin, especially in the catchment of the Wujiang River (a tributary of the Yangtze River), about 70% of which is covered by carbonate rocks (Zhang et al. 2017; 2016a, 2016b). The weathering of the carbonate rocks contributed nearly 92% of the ions in the water of the Yangtze River, which featured high concentrations of Ca²⁺, Mg²⁺, and HCO₃⁻ (Zhang et al. 2016a, 2016b; Wang et al. 2020a). Therefore, the geology background and the natural weathering dominate the hydrochemistry type of the TGR water (Figure S3).

The water flow velocity slowed down to 0.09–2.43 m/s after the impoundment of the TGR, which has caused stratification in the water column within the confluence area of the tributaries (Jiang et al. 2018). However, in the downstream of the TGR, stratification was found neither in flood seasons nor in dry seasons (Wu et al. 2012; Wang et al. 2020b). Moreover, the stratification in the mainstream of the TGR did not occur during our study (Figures S2, S5, and S6), and the minor difference in the hydrochemical parameters between the surface and the bottom water at S6 might result from the mixture of the waters from the Yangtze River and the Wujiang River (Figure 1).

The slowed down water flow prolonged the retention time of the water and further stimulated the flocculation and deposition of sediment particles associated with absorbed elements in the TGR (Tang et al. 2018). A decreasing trend in the concentration of heavy metals from upstream to downstream of the TGR was revealed by Gao et al. (2016), which was associated with the self-purification due to the increase in the possibility of atoms absorbed on suspended solids. In our study, the factor analysis showed the close relationship between the suspended sediment and the hydrochemistry parameters in the TGR (Table S4). The first two groups contributed about 60% of the spatial variation of the hydrochemistry parameters, indicating the influence of the transport and deposition of suspended sediment on the water quality. A decreasing trend (with fluctuations) in the concentrations of SS and heavy metals (Cu, Cd, and Pb) downstream of Chongqing downtown (S3) was found in our study (Figures S1 and S). This trend indicated the self-purification of the TGR water with the absorption of heavy metals on fine particles. Previous studies have pointed out the accumulation of heavy metals in the bed sediments of the TGR, especially in the fine sediment particles downstream the inflow control section (S6) (Bing et al. 2016, 2019). This study provided a reference for the occurrence of absorption and deposition of heavy metals associated with the fine sediment particles in the TGR.

Different sources and transport processes influence the seasonal variations of pollutants in the TGR. Non-point source pollution (NPS) has become an important factor leading to the water deterioration in the TGR (Wu et al. 2012; Shen et al. 2013), and nearly 60–80% of the pollutants came from the NPS sources (Wang et al. 2020b). Land use types, especially farmland and urban land, possibly create more NPS pollution, which contributed to the water quality deterioration in the TGR (Zhang et al. 2019a). Especially, the phosphorus and nitrogen is always transported by the surface runoff in dissolved or particulate forms (Li et al. 2015). The amount of fertilizers used in the TGR area was growing rapidly to meet the requirements of agricultural activities (Gao et al. 2016). In 2016, 83,000 tons of nitrogen fertilizer and 28,000 tons of phosphorus fertilizer were used in the TGR area, among which, 9% nitrogen and 5.7% phosphorus were lost though surface runoff. It was reported that the area from Jiangjin (S1) to Fengdu (S7) was a major area for the losses of sediment, phosphorus, and nitrogen (Wu et al. 2012). Therefore, the phosphorus and nitrogen from the NPS contributed to the high concentrations of PO₄³⁻-P and NO₃⁻-N in the section from Jiangjin (S1) to Fengdu (S7) (Figure 3).

The Cu, Cr, and Ni were also mainly from the NPS pollution in the catchment of the TGR (Zhu et al. 2019). The accumulated Cu, Cr, and Ni in the catchment of the TGR in dry seasons could be washed into the TGR by surface runoff, which resulted in an increase in the concentrations of Cu, Cr, and Ni in the TGR water (Figure 4). Cd showed a high background level in the sediments and soils of the
TGR area (Bing et al. 2016), and Cd was transported in the particulate form in the surface runoff and then released into the TGR water in a specific condition. Based on the Pb isotope composition, the ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{206}\text{Pb}$ indicated a low natural contribution, and the sources of Pb and Zn in the TGR area were mainly related to anthropogenic emissions, such as industrial discharge, domestic sewage, mining and smelting, and shipping industry (Bing et al. 2019). Especially in the dry seasons, the influence of the anthropogenic emissions on the variations of Pb and Zn might be marked due to the weak dilution effect. Therefore, the high levels of Pb and Zn in the winter highlighted the contribution of the anthropogenic emissions to the change of Pb and Zn in the TGR water.

The built-up land is a main source area for domestic and factory sewage (Zhang et al. 2019a; Zhang et al. 2020). According to the Environmental and Ecological Monitoring Bulletins of the Three Gorges Project (EEMB), the discharge of domestic and industrial sewage from Chongqing downtown is 0.660 billion tons and 0.029 billion tons, accounting for nearly 54 and 21% of the total domestic and industrial sewage in the TGR area, respectively. The hotspots of heavy metals (Cu, Cd, Zn, and Ni) and major ions (SO$_4^{2-}$, Na$^+$, K$^+$, etc.) were marked downstream of Chongqing downtown (S3) (Figures 3 and 5), which indicated the influence of large cities on the variation in hydrochemistry of the TGR. Therefore, the large cities may play a key role in the spatial variations of major ions and heavy metals in the TGR area, especially under the influence of intense rainfall.

**Rainfall’s effect on hydrochemistry of the TGR**

The extreme El Niño during 2015–2016 started in the spring of 2015, then reached its peak in the winter of 2015, and ultimately weakened in the spring and early summer of 2016 (Guo et al. 2016). It was evidently proved that the precipitation within the region of the Yangtze River increased during the extreme El Niño, especially in the decaying period of the El Niño (Yuan et al. 2016). The seasonal variation of the precipitation in the TGR catchment also illustrated the intense rainfall in the spring and early summer of 2016 (Figure 6(a)). Specifically, in comparison with the average precipitation during 1981–2010, the precipitation began to increase in December 2015 and the most intensified rainfall appeared in June 2016. Furthermore, the response of the inflow discharge of the TGR to the increased rainfall is visible in Figure 6(b).

The stable isotopic compositions of H$_2$O provide useful information for identifying the sources of water and studying the hydrological processes according to the distinct isotopic signatures of various waters (Zhao et al. 2015). The linear regressions of $\delta$D and $\delta^{18}$O in the TGR water ($\delta$D = 7.19*$\delta^{18}$O + 0.42 and $\delta$D = 7.67*$\delta^{18}$O + 0.12 in the wet and dry seasons, respectively), were illustrated by Jiang et al. (2018). The parameters of the linear regressions were similar to those of Meteoric Water Line of the Yangtze River Basin (Zhou et al. 2017), which indicated the TGR water was mainly from the precipitation. With more moisture transported to southwest China from the Indian Ocean and the west Pacific Ocean, the values for $\delta$D and $\delta^{18}$O in the rainwater of southwest China became more negative (Wen & Wang 2016). In our study, the values of $\delta$D and $\delta^{18}$O in the TGR water were more negative compared with the mean values for 2003–2012, especially after the intense rainfall in 2016 (Figure 7). This indicated that the increased rainfall in the decaying period of the El Niño affected the D-O isotope composition of the TGR water and might have been a matter of significance to the variation of water quality in the TGR.

In order to reveal the influence of the intense rainfall on the hydrochemistry of the TGR in the spring and early summer of 2016, we compared the hydrochemistry in different seasons. After the continuous increase in the precipitation and discharge (Figure 6(a) and 6(b)), the Spc and TDS reached their highest values in May 2016, and the pH presented the lowest values in comparison with those in the other seasons (Figure S3). The high levels of Spc and TDS in May 2016 revealed the increase in the dissolved organic and inorganic materials in the TGR water, most of which might be carried by the surface runoff in the catchment of the TGR. The increased rainfall also caused the flushing and dissolving of acid matters, which contributed to an increase in the concentrations of SO$_4^{2-}$, NO$_3^-$, HCO$_3^-$ and the low value of pH in May 2016 (Figure 2). Associated with the increase in acid anions, Ca$^{2+}$, Mg$^{2+}$, and K$^+$ also showed higher levels in May 2016. Previous studies have revealed that the natural processes (weathering and erosion) and the industrial activities were the main sources of Cu, Cr,
and Ni, especially the fine particles are main carriers for Cu, Cr, and Ni in the TGR (Gao et al. 2016; Wang et al. 2017). The high concentrations of Cu, Cr, and Ni were highlighted in May 2016, when more fine particles and sewage were transported into the TGR during the intense rainfall period (Figure 4). As discussed in the section ‘Factors driving the hydrochemistry variation in the TGR’, the source of Cd, Pb, and Zn in the TGR area was mainly related to the anthropogenic emission, therefore, the concentrations of Cd, Pb, and Zn in the TGR water were diluted by the increased discharge in May 2016.

The spatial variation of the hydrochemistry could also provide a reference for the influence of the increased rainfall. The large cities are hotspots for the emission of industry and domestic sewage, and the dust in the built-up area plays a key role in the export of pollutants. During the intense rainfall periods, the sewage and dust will be washed out of the cities by surface runoff and affect the hydrochemistry of the receiving water (Zhang et al. 2019b; Zhang et al. 2020). The higher levels of the major ions and heavy metals at Chongqing downtown (S3) and Wanzhou (S9) were marked in May 2016 (Figures 3 and 5), which indicated that the surface runoff promoted the export of pollutants from the large cities. The spatial variation of heavy metals in the upstream of the TGR in April and August 2015 were studied by Zhao et al. (2017), when the precipitation was comparable to the mean values of 1981–2010. However, no remarkable high level for heavy metals at Chongqing downtown was shown in their study, which provided a contrasting reference for the influence of the intense rainfall on the hydrochemistry of the TGR. Consequently, the intense rainfall in the spring and early summer of 2016 promoted the transport of pollutants and magnified the influence of cities on the hydrochemistry of the TGR.

CONCLUSION

The heterogeneous spatial and seasonal variations of the major ions and heavy metals were found during 2015–2016, which revealed the integrated influences of natural processes and human activities on the hydrochemistry of the TGR. The influence of the intense rainfall on the TGR water was identified by the negative hydrogen and oxygen isotopes, which promoted the transport of pollutants by the surface runoff and further magnified the influence of cities on the spatial variation of water quality. Even though affected by the intense rainfall event in the spring and early summer of 2016, the water in the TGR still presented good quality according to the water quality guidelines of China and the World Health Organization. Our study gave more insights into the change of water quality in large reservoirs both in the context of intensified rainfall and human activities. However, our study was only a short-term investigation of the hydrochemistry, and long-term monitoring and assessment with more hydrochemistry indexes is expected in the future to acquire a full understanding of the change in water quality in the TGR.

ACKNOWLEDGEMENTS

This work was supported by the Start-up funds for doctoral research of China West Normal University (412654), Youth Innovation Promotion Association of the Chinese Academy of Sciences (2017424), the Science and Technology Service Network Initiative of Chinese Academy of Sciences (KFJ-EW-STS-008), and the CAS ‘Light of West China’ Program.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Bao, Y., Gao, P. & He, X. 2015 The water-level fluctuation zone of Three Gorges Reservoir-A unique geomorphological unit. Earth-Science Reviews 150, 14–24.
Bing, H., Zhou, J., Wu, Y., Wang, X., Sun, H. & Li, R. 2016 Current state, sources, and potential risk of heavy metals in sediments of Three Gorges Reservoir, China. Environmental Pollution 214, 485–496.
Bing, H., Wu, Y., Zhou, J., Sun, H., Wang, X. & Zhu, H. 2019 Spatial variation of heavy metal contamination in the riparian sediments after two-year flow regulation in the Three Gorges Reservoir, China. Science of the Total Environment 649, 1004–1016.
Chen, X. & Chau, K. 2019 Uncertainty analysis on hybrid double feedforward neural network model for sediment load estimation with LUBE method. *Water Resources Management* 33, 3563–3577.

Chen, Z., Song, X. & Zhang, Y. 2018 Impact of mainstream backwater on the water environment of the tributaries of the Three Gorges Reservoir at low water level. *Environmental Science* 59, 4946–4955. (in Chinese).

Deng, K., Yang, S., Lian, E., Li, C., Yang, C. & Wei, H. 2016 Three gorges Dam alters the changjiang (Yangtze) river water cycle in the dry seasons: evidence from H-O isotopes. *Science of the Total Environment* 562, 89–97.

Ding, T., Gao, J. & Shi, G. 2013 Spacial and temporal variations of H and O isotope compositions of the Yangtze River water and their environmental implications. *Acta Geologica Sinica* 87, 661–676. (in Chinese).

Environmental Protection Administration of China. 2002 *Environmental Quality Standards for Surface Water.* GB3838-2002. State Environmental Protection Administration, PR China.

Gaillardet, J., Viers, J. & Dupré, B. 2003 Trace elements in river waters. *Treatise on Geochemistry* 5, 225–272.

Gao, Q., Li, Y., Cheng, Q., Yu, M., Hu, B., Wang, Z. & Yu, Z. 2016 Analysis and assessment of the nutrients, biochemical indexes and heavy metals in the Three Gorges Reservoir, China, from 2008 to 2013. *Water Research* 92, 262–274.

Gao, Y., Zhou, F., Ciais, P., Miao, C., Yang, T., Jia, Y., Zhou, X., Klaus, B., Yang, T. & Yu, G. 2020 Human activities aggravate nitrogen-deposition pollution to inland water over China. *National Science Review* 7, 430–440.

Grill, G., Lehner, B., Thieme, M., Geenen, B., Antonelli, F., Babu, S., Borrelli, P., Cheng, L., Crochetteri, H., Ehalt Macedo, H., Filgueiras, R., Goichot, M., Higgins, J., Hogan, Z., Lip, B., McClain, M. E., Meng, J., Mulligan, M., Nilsson, C., Olden, J. D., Opperman, J. P., Petry, P., Reidy Liermann, C., Saenz, L., Salinas-Rodriguez, S., Schelle, P., Schmitt, R. J. P., Snider, J., Tan, F., Tockner, J., Valdujo, P. H., van Soesbergen, A. & Zarfl, C. 2019 Mapping the world’s free-flowing rivers. *Nature* 569, 215–221.

Guo, D., Wang, L., Li, Z., Su, Y., Qin, H. & Huang, Y. 2016 Comparison between anomalies of summer rainfall in the China in decaying years during super El Niño events of 2015/2016 and 1997/1998. *Trans. Atmos. Sci.* 39 (6), 835–844. (in Chinese).

Han, L., Gao, B., Zhou, H., Xu, D., Wei, X. & Gao, L. 2015 The spatial distribution, accumulation and potential source of seldom monitored trace elements in sediments of Three Gorges Reservoir, China. *Scientific Reports* 5, 16170.

Huang, Y. L., Zhang, P., Liu, D. F., Yang, Z. J. & Ji, D. B. 2014 Nutrient spatial pattern of the upstream, mainstream and tributaries of the Three Gorges Reservoir in China. *Environmental Monitoring and Assessment* 186, 6833–6847.

Jiang, R., Bao, Y., Shui, Y., Wang, Y., Hu, M., Cheng, Y., Cai, A., Du, P. & Ye, Z. 2018 Spatio-temporal variations of the stable H-O isotopes and characterization of mixing processes between the mainstream and tributary of the Three Gorges Reservoir. *Water* 10, 563.

Li, K., Zhu, C., Wu, L. & Huang, L. 2013 Problems caused by the Three Gorges Dam construction in the Yangtze River basin: a review. *Environmental Reviews* 21, 127–135.

Li, Z., Ma, J., Guo, J., Paerl, H. W., Brookes, J. D., Xiao, Y., Fang, F., Ouyang, W. & Lu, L. 2018 Water quality trends in the Three Gorges Reservoir region before and after impoundment (1992–2016). *Ecohydrology & Hydrobiology* 205, 1–11.

Ministry of Health. 2007 *Standards for Drinking Water Quality* (GB5749-2006). Minist. Heal., PR China.

Müller, B., Berg, M., Yao, Z. P., Zhang, X. F., Wang, D. & Pfuffer, A. 2008 How polluted is the Yangtze river? water quality downstream from the Three Gorges Dam. *Science of the Total Environment* 402, 232–247.

Qiu, J., Shen, Z., Wei, G., Wang, G., Xie, H. & Lv, G. 2018 A systematic assessment of watershed-scale nonpoint source pollution during rainfall-runoff events in the Miyun Reservoir watershed. *Environmental Science & Pollution Research* 25 (7), 6514–6531.

Shen, Z. L. & Liu, Q. 2009 Nutrients in the changjiang river. *Environmental Monitoring and Assessment* 153, 27–44.

Shen, Z. Y., Chen, L., Hong, Q., Qiu, J. L., Xie, H. & Liu, R. M. 2013 Assessment of nitrogen and phosphorus loads and causal factors from different land use and soil types in the Three Gorges Reservoir area. *Science of the Total Environment* 454, 383–392.

Tang, J., Wang, T., Zhu, B., Zhao, P., Xiao, Y. & Wang, R. 2015 Tempo-spatial analysis of water quality in tributary bays of the Three Gorges Reservoir region (China). *Environmental Science and Pollution Research* 22, 16709–16720.

Tang, X., Wu, M. & Li, R. 2018 Distribution, sedimentation, and bioavailability of particulate phosphorus in the mainstream of the Three Gorges Reservoir. *Water Research* 140, 44–55.

Tang, X., Li, R., Han, D. & Scholz, M. 2020 Response of eutrophication development to variations in nutrients and hydrological regime: a case study in the Changjiang River (Yangtze) Basin. *Water* 12 (6), 1634.

Tiyasha, T., Tung, T. M. & Yaseen, Z. M. 2020 A survey on river water quality modelling using artificial intelligence models: 2000–2020. *Journal of Hydrology* 585, 124670.

US Environmental Protection Agency. 2004 *Risk Assessment Guidance for Superfund.* Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment) final (EPA/540/R/99/005), Washington DC, USA.

Wang, L., Wang, Y., Xu, C., An, Z. & Wang, S. 2011 Analysis and evaluation of the source of heavy metals in water of the River Changjiang. *Environmental Monitoring and Assessment* 173, 301–313.

Wang, X., Bing, H., Wu, Y., Zhou, J. & Sun, H. 2017 Distribution and potential eco-risk of chromium and nickel in sediments after impoundment of Three Gorges Reservoir, China.
Monsoon and Yangtze River summer flooding. Geophysical Research Letters 43, 11375–11382.
Zhang, J., Li, S., Dong, R., Jiang, C. & Ni, M. 2019a Influences of land use metrics at multi-spatial scales on seasonal water quality: a case study of river systems in the Three Gorges Reservoir Area, China. Journal of Cleaner Production 206, 76–85.
Zhang, J., Wang, X., Zhu, Y., Huang, Z., Yu, Z., Bai, Y., Fan, G., Wang, P., Chen, H., Su, Y., Trujillo-González, J. M., Hu, B. X., Krebs, P. & Hua, P. 2019b The influence of heavy metals in road dust on the surface runoff quality: kinetic, isotherm, and sequential extraction investigations. Ecotoxicology and Environmental Safety 176, 270–278.
Zhang, T., Xiao, Y., Liang, D., Tang, H., Yuan, S. & Luan, B. 2020 Rainfall runoff and dissolved pollutant transport processes over idealized urban catchments. Frontiers in Earth Science 8, 305.
Zhao, P., Tang, X., Tang, J. & Wang, C. 2015 Assessing water quality of Three Gorges Reservoir, China, over a five-year period from 2006 to 2011. Water Resources Management 27, 4545–4558.
Zhao, Y., Zheng, B., Wang, L., Qin, Y., Li, H. & Cao, W. 2015 Characterization of mixing processes in the confluence zone between the Three Gorges Reservoir mainstream and the Daning River using stable isotope analysis. Environmental Science & Technology 50, 9907–9914.
Zhao, X., Li, T., Zhang, T., Luo, W. J. & Li, J. 2017 Distribution and health risk assessment of dissolved heavy metals in the Three Gorges Reservoir, China (section in the main urban area of Chongqing). Environmental Science & Pollution Research 24 (5), 2697–2710.
Zhao, Y., Zheng, B., Jia, H. & Chen, Z. 2019 Determination sources of nitrates into the Three Gorges Reservoir using nitrogen and oxygen isotopes. Science of the Total Environment 687, 128–136.
Zhou, Y., Wu, H., He, B., Li, J., Duan, W. & Wang, J. 2017 Study on spatial and temporal variations of δ18O and δD in Yangtze River water and its factors. Resources and Environment in the Yangtze Basin 26, 678–686. (in Chinese).
Zhu, H., Bing, H., Wu, Y., Zhou, J., Sun, H., Wang, J. & Wang, X. 2019 The spatial and vertical distribution of heavy metal contamination in sediments of the Three Gorges Reservoir determined by anti-seasonal flow regulation. Science of the Total Environment 664, 79–88.
Zhu, J., Song, C., Wang, J. & Ke, L. 2020 China’s inland water dynamics: the significance of water body types. Proceedings of the National Academy of Sciences 117, 13876–13878.