## Title

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# Temporal variations of groundwater quality in the Western Jianghan Plain, China

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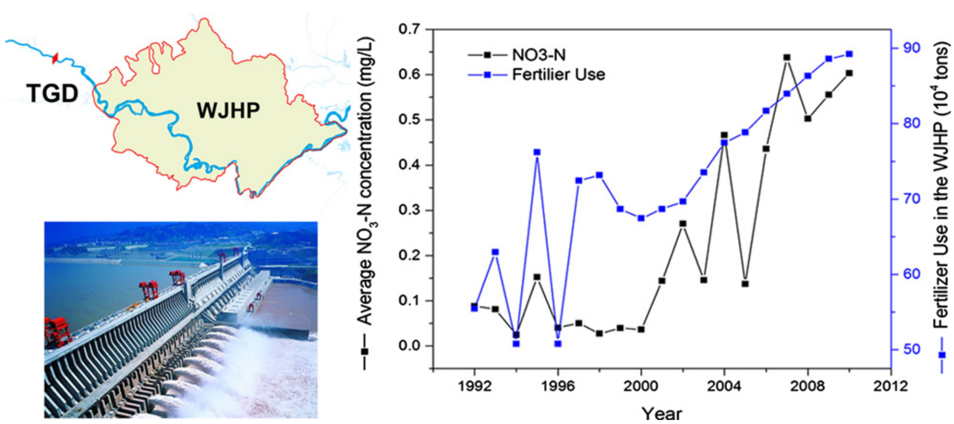
## HIGHLIGHTS

- Spatial-temporal variations of groundwater quality were characterized.
- $CO_2$ degassing caused by groundwater extraction increased the groundwater pH.
- $NO_3$-N increased coincidently with the increased use of fertilizer.
- The Three Gorges Dam contributes partly to the variations of pH, $NH_4$-N and $NO_3$-N.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The Western Jianghan Plain (WJHP) lies in the middle reaches of the Yangtze River. It has been impacted by anthropogenic activities during the past decades. The long-term variations of the WJHP's regional aquifer's hydrochemistry and groundwater quality have not been previously assessed. Sixteen physiochemical parameters at 29 monitoring wells within the Western Jianghan Plain were monitored during 1992–2010 and analyzed with multiple approaches. The confined groundwater is predominantly of the $HCO_3$-Ca-Mg type with $Cl^-$, $SO_4^{2-}$, $NH_4$-N, and $NO_3$-N showing remarkable spatial variations. Correlation analysis was used to identify the origins and contamination sources of groundwater. The seasonal Mann-Kendall test revealed that pH, $NO_3$-N, and $Cl^-$ concentrations at 27, 26 and 15 wells, respectively, exhibited significant increasing trends during 1992–2010. The increase of pH may be attributed to $CO_2$ degassing caused by extensive groundwater extraction. Regional average $NO_3$-N concentrations of groundwater increased coincidently with the increased use of fertilizer, which suggests that nitrate pollution is caused by agricultural activities. Abnormally high values of $Cl^-$ and $SO_4^{2-}$ at some wells were induced by industrial chemicals. In addition, the similarity of the temporal variations of the regional average of pH, $NH_4$-N, and $NO_3$-N concentrations in groundwater with those in the Yangtze River at the outlet of the Three Gorges Reservoir (TGR) suggests that the variations of these parameters in the WJHP is partly due to water storage by the TGR. This study presents an analysis of temporal variations of groundwater quality in the WJHP that

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reveals a relation between the creation of the TGR and downstream groundwater quality. This paper's findings provide clues for measures that could be taken to protect the groundwater quality of the WJHP's aquifer.


## 1. Introduction

Groundwater constitutes a critical water source for domestic, industrial, and agricultural activities around the world (Aeschbach-Hertig and Gleeson, 2012; Huang et al., 2013; Xiao et al., 2014). China has relied heavily on groundwater for its development. This has caused the depletion of its groundwater resources in many regions and led to groundwater pollution during the past decades (Qu and Fan, 2010; Zhang et al., 2014). The groundwater chemistry and its characteristics are influenced by many factors that include the aquifer mineralogy, geochemical processes, overlying land uses, the source of recharge, and the inputs from anthropogenic sources (Freeze and Cherry, 1979; Gurunadha Rao et al., 2013; Hem, 1986; Kurilić et al., 2015; Sahraei Parizi and Samani, 2013; Wang et al., 2016). Numerous studies have been performed regarding hydrochemical changes of groundwater in various parts of the world, which have shed light on the processes governing groundwater quality and on effective management of groundwater resources (Bozdağ, 2016; Cao et al., 2014; Ledesma-Ruiz et al., 2015; Liu et al., 2015a; Martos-Rosillo and Moral, 2015).

The Western Jianghan Plain (WJHP) is a semi-closed basin in the middle reaches of the Yangtze River. It is the major farming area of Hubei Province in central China, where groundwater is a vital source for municipal supply and other activities (Zhou et al., 2013). Previous publications concerning the groundwater quality in the Jianghan Plain have concentrated on one specific contaminant or group of contaminants, such as arsenic (Schaefer et al., 2016), dissolved organic matter (Huang et al., 2015), and antibiotics (Yao et al., 2015). The lack of a comprehensive hydrogeochemical study in the WJHP has hindered the understanding of the long-term variations of groundwater chemistry and quality in the past decades, and how it has been affected by intense agriculture, groundwater withdrawal, and dam construction (Bozdağ, 2016). The Three Gorges Dam (TGD), the world's largest hydropower project, is located upstream of the WJHP and has caused worse-than-expected deterioration of water quality since its completion in 2003 (Stone, 2011). Groundwater in aquifers adjacent to the Yangtze River are inevitably affected by the operation of the TGD due to strong stream-aquifer interactions.

This study of the temporal variations of the hydrochemistry and groundwater quality in the WJHP relied on monitoring of 16 physicochemical parameters from 1992 to 2010 at 29 confined groundwater sampling sites followed by an ensuing analysis of the data with various statistical methods. The objectives of this study are to (1) characterize the spatial and temporal variations of groundwater quality in the WJHP; (2) assess the correlations among water-quality parameters to identify the origins and contamination sources of groundwater; and (3) identify the processes causing increases in pH, $NO_3$-N, and $Cl^-$, and the potential linkage between changes in regional pH and nitrogen concentrations and the operation of the TGD. This study contributes to the understanding of groundwater quality variations driven by human activities in the WJHP, which enhances China's capacity to take timely actions and effectively protect regional groundwater resources.

## 2. The study area

The Jianghan alluvial plain in central China was formed by the Yangtze River and its largest tributary the Han River. This work's study area is the western part of the Jianghan Plain (WJHP), which encompasses a total area of about 18,660 km$^2$ and lies between 29°25′–31°15′ N latitude and 111°30′–114°05′ E longitude, ranging from 70 km to 565 km downstream from the Three Gorges Dam along the Yangtze River (Fig. 1). The Yichang and Hankou sites are two key water quality monitoring stations in the middle reaches of the Yangtze River, shown in Fig. 1. The Yangtze River has an average annual flow of 900 km$^3$, the fifth largest in the world (Loáiciga, 1997). The study area exhibits a subtropical monsoon climate, with mild temperature (average annual temperature equals 17 °C) and plentiful precipitation (average annual equals 1214 mm). The terrain is very gently sloping, with rivers and lakes interweaving with each other and supplying plentiful groundwater recharge. The aquifer system has a vadose zone, a phreatic aquifer, a confining bed, and a confined aquifer. The confined groundwater is the main focus of this study. Located mostly in the plain's Holocene series (Q4), the groundwater is slow moving given the very small regional topographic slope. The Yangtze River flows through this area, whose thalweg is lower than the upper confining for most of the reach downstream from the TGD (Fig. 2, Zhao, 2005). Thus, the confined groundwater is hydraulically connected to the Yangtze River in the WJHP. This creates an unobstructed pathway for the exchange of chemical constituents between the river and the aquifer system.

Coal mining and washing, paper making, textile and dyeing, and chemical industries are traditional competitive industries in the WJHP (Zhu and Chen, 2010). Despite the improved wastewater treatment achieved in recent years, only 30–55% of the discharged industrial sewage in the WJHP during 1990s met China's Integrated Wastewater Discharge Standards. The untreated and sub-standard industrial/domestic wastewater infiltrates into the groundwater system. Additionally, groundwater, the main source of local drinking and industrial water supply, was extracted at a rate of about $1.5 \times 10^8$ m$^3$/yr during the past decades. Several groundwater depression cones have formed in concentrated exploitation areas in Zhijiang, Jingzhou, Shashi, Jingmen, Tianmen, and Xiantao. The groundwater level contours in Jingzhou city in 2006 distinctly illustrate the two groundwater depression cones (Fig. 3). Groundwater depression cones are broader and deeper in the summer (wet) season than that in winter (dry) season given that the textile and pesticide factories in Jingzhou City exploit groundwater for cooling primarily.

## 3. Material and methods

Groundwater quality monitoring was initiated in the WJHP in 1990. Water samples were collected twice in the year, namely, in December and July which are months in the dry season and wet seasons, respectively (Deng et al., 2014). Groundwater quality data of 16 parameters at 29 confined monitoring wells during 1992–2010 were obtained from the Geological Environmental Center of Hubei Province (wells are shown in Fig. 1). These 29 groundwater quality monitoring wells had water quality data spanning at least 15 years, which is considered suitable for distinguishing long-term changes due to anthropogenic impacts from natural fluctuations on a decadal scale (Knutsson, 1994). Monthly pH values measured at the Yichang station during 1998–2010, the outlet of the Three Gorges Reservoir (TGR), were obtained from the Yangtze River Water Resources Commission. Data on the annual crop yields and fertilizer use of the 15 involved counties (see Fig. 1) from 1992 to 2010 were extracted from the Hubei Rural Statistical Yearbooks published during 1993–2011, whose total represents the annual crop yields and fertilizer use of the WJHP. Data on the total discharge and the standard discharge rate of industrial wastewater are only available for 10 counties (Dangyang, Zhijiang, Songzi, Jingzhou, Shashi, Jiangling, Gongan, Shishou, Jianli, Honghu) in the southwest of

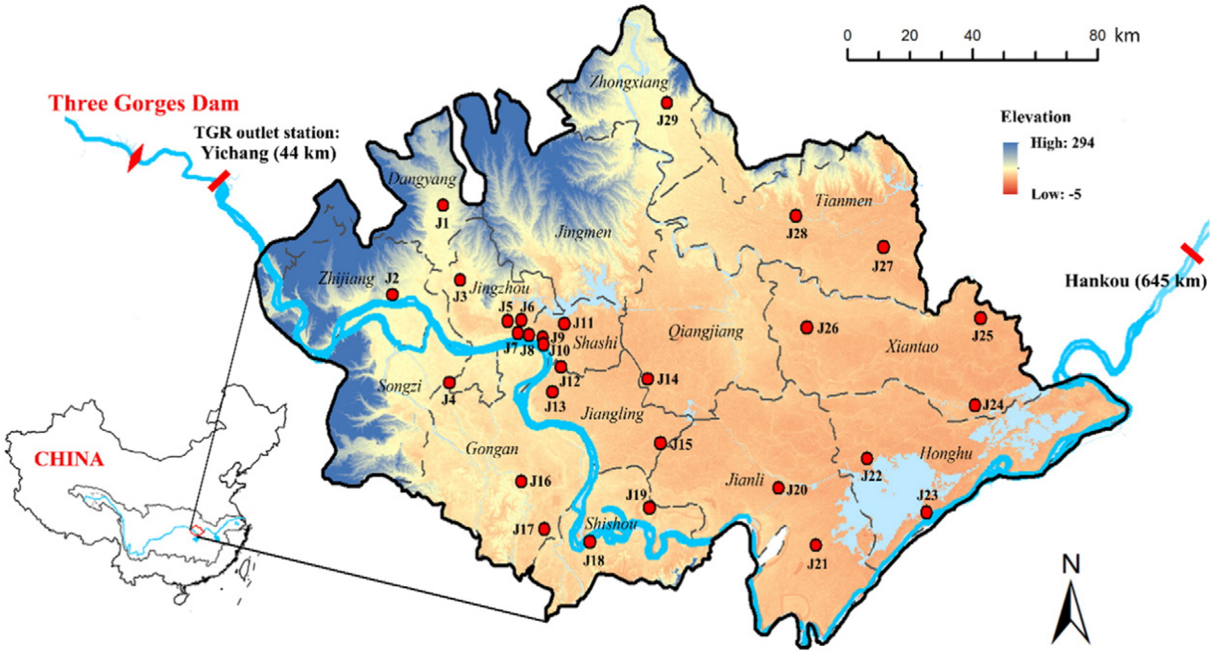


**Fig. 1.** Location of the study area, the 29 groundwater quality monitoring wells (red dots J), the Three Gorges Dam, and the Yichang and Hankou stations.

the WJHP during 1998–2010. These data were extracted from the statistical yearbook of corresponding counties published during 1999–2011. Their total values are used to represent general trends of the total discharge and the standard discharge rate of industrial wastewater in the WJHP.

Groundwater quality data were divided into three periods, namely 1992–1997, 1998–2003 and 2004–2010, for statistical analysis and preliminarily identification of the hydrochemical characteristics of the WJHP during 1992–2010. Hydrochemical facies types were illustrated by Piper diagram, which is widely used to identify dominant groundwater chemical types (Zhu et al., 2011; Chaudhuri and Ale, 2014; Dragon and Gorski, 2014). In addition, groundwater quality data of the three periods were separately analyzed using correlation analysis to identify associations among the geochemical constituents. The Spearman R correlation was applied using a pre-established significance level of 0.05. These statistical calculations were performed using SPSS 21.0. Indexes of base exchange (Schoeller, 1965), known as Chloro-Alkaline Indices, (CAI-I and CAI-II) were also calculated to determine the cation-exchange processes controlling the water chemistry. The CAI-I and CAI-II are expressed in meq/L:

$$\text{CAI-I} = \frac{\text{Cl} - (\text{Na} + \text{K})}{\text{Cl}} \tag{1}$$

$$\text{CAI-II} = \frac{\text{Cl} - (\text{Na} + \text{K})}{\text{SO}_4 + \text{HCO}_3 + \text{CO}_3 + \text{NO}_3} \tag{2}$$

The seasonal Mann-Kendall test is a commonly used non-parametric method for detecting water quality trends (Knutsson, 1994; Chen et al., 2003), because it is insensitive to seasonality, outliers, missing data, and non-normality of the time series (Sarkkola et al., 2009). This study applied the seasonal Mann-Kendall test separately to each sequence data of 16 groundwater quality parameters of the 29 monitoring wells to determine their variation tendencies from 1992 to 2010. This test process was completed based on a Kendall.exe program, developed by Hirsch and Slack (1984) of the U.S. Geological Survey (http://pubs.usgs.gov/sir/2005/5275/downloads/). The Pettitt test is employed to identify changes in the mean, which is commonly applied to detect a single change-point in series with continuous data (Pettitt, 1979; Tomozeiu et al., 2000). The Pettitt tests are herein applied to detect change-points in the average pH values during 1992–2010.

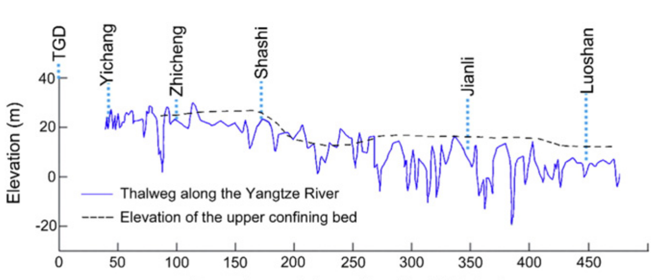


**Fig. 2.** Elevation of the thalweg of the Yangtze River and the upper confining bed within the WJHP.

## 4. Results and discussion

### 4.1. Hydrochemical characteristics

Basic statistics of groundwater quality parameters in the three periods 1992–1997, 1998–2003, and 2004–2010 are summarized in Table 1. Overall, the groundwater of the study area is neutral to slightly alkaline with a pH ranging from 6.44 to 8.90, while the average pH value in the three periods gradually increased from 7.34 to 7.48, and to 7.85. The total dissolved solids (TDS) value varied from 287.86 to 1380 mg/L, which increased along the groundwater flow direction from northwest to the southeast. The TDS values of 25 groundwater monitoring wells are below 1000 mg/L during 1992–2010, and only wells J18, J21, J23, and J25 occasionally exhibited higher TDS values.

The major ion composition plot on the Piper diagram (Fig. 4) shows that $Ca^{2+}$ (45%–75%) and $Mg^{2+}$ (25%–55%) are the dominant cations, and $HCO_3^-$ (>75%) is the dominant anion in groundwater, and the major hydro-geochemical facies is $HCO_3$-Ca-Mg clustering at the left corner of the diamond on the plot. Thus, major ion chemistry of

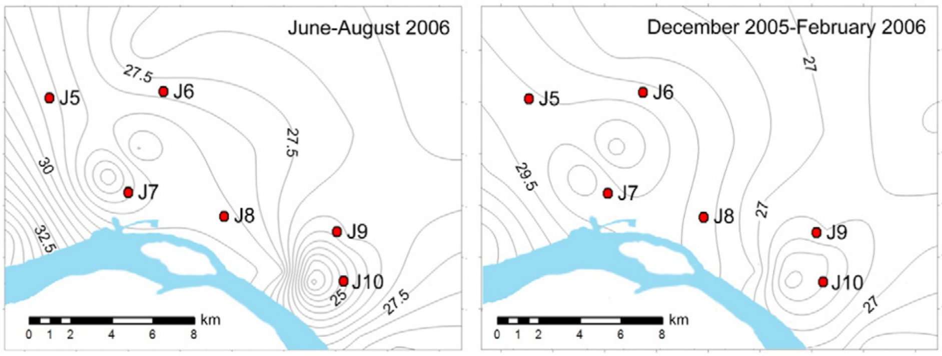


**Fig. 3.** Two groundwater depression cones in Jingzhou City (groundwater-level contour lines in meters, drawn with 0.5 m vertical interval).

confined groundwater in the WJHP is dominated by carbonate rock weathering, i.e., calcite and dolomite are responsible for water chemistry (Dalai et al., 2002). Besides, the study area is humid with abundant rainfall and active groundwater circulation and exchange, which also makes the chemical type mostly bicarbonate water (Zhou et al., 2013). Several groundwater wells exhibited higher $Cl^-$ proportions during 2004–2010 than in earlier times (Fig. 4), which is revealed by the increased average concentration of $Cl^-$ from 9.64 to 16.83 mg/L. Conversely, there was a steady decline in the maximum and average concentrations of $HCO_3^-$. The large coefficient of variation of $Cl^-$ (124–136.79) and $SO_4^{2-}$ (163.31–203.44) exceeds those of pH, TDS, and other major ions (4.46–88.13). This reflects their significant spatial variation, which is thought to be caused by water imports to the aquifer system by anthropogenic activities.

$NH_4$-N and $NO_3$-N exhibited discontinuous patterns in space and time. The maximum concentration of $NH_4$-N in groundwater significantly lowered during the 3 periods, owning to the improvement of wastewater treatment infrastructures. Although the mean concentration of $NH_4$-N decreased during the three periods, it was in excess of the Class V (0.5 mg/L) category of the Quality Standard for Groundwater of China (GB/T 14848-93). Besides, an increasing trend was found in the maximum and average concentrations of $NO_3$-N even though this parameter fell within the Class III (20 mg/L) category during 2003–2010. $Fe^{2+}$ and $Fe^{3+}$ concentrations also show obvious spatial variation, some concentrations were about zero but some wells reached 24 and 21.6 mg/L, respectively. The mean average of $Fe^{2+}$ is higher than that of $Fe^{3+}$, which indicates relatively strong reducing environments. Fe is obtained from weathering of minerals. Under reducing conditions the ferric oxides and oxy-hydroxides such as hematite ($Fe_2O_3$) or goethite (FeOOH) could leach out as dissolved Fe. The mean concentrations of manganese (Mn) in the three periods were all above the limit of Class III (≤0.1 mg/L) of the Quality Standard for Groundwater of China. The high Mn concentrations in the WJHP are related to lithology, since they are quite often released from minerals weathering (Hem, 1986). The oxygen demand (OD) during 1992–2010 remained relatively stable, with the mean value of 2.12, 1.84, and 1.95 mg/L in the three periods, respectively. $CO_2$ dissolved in groundwater displayed decreasing mean concentration and increasing coefficient of variation during the 3 monitoring periods.

### *4.2. Evolution of the correlation among parameters*

The relations between physicochemical parameters of groundwater samples could reveal the origin of solutes and the processes that generated the observed water composition (Sahraei Parizi and Samani, 2013; Varol and Davraz, 2014). Pearson's correlation coefficients between all parameters averaged over the three periods 1992–1997, 1998–2003, and 2004–2010 were separately calculated, and only significant correlations ($p > 0.05$) are portrayed in Fig. 5. Green lines and red lines denote positive and negative correlations, respectively, in Fig. 5. The color tone (say, light green, dark green), the width, and the length of the lines denote the magnitude of the absolute correlation coefficient in Fig. 5, that is, the line corresponding to the largest absolute correlation coefficient is shown with the darkest tone, has the largest width and the shortest length. There are 8 parameters, $Ca^{2+}$, $Mg^{2+}$, $K^+$, $HCO_3^-$, OD, $Fe^{2+}$, $CO_2$, and TDS exhibiting significant pairwise positive correlations and thus forming a relatively stable cluster. Almost all the correlation coefficients ($r$) between the 8 parameters are higher than 0.5, except K-$Ca^{2+}$ ($r =$

**Table 1**
Statistical summary of physicochemical parameters in groundwater.

| Year | 1992–1997 | | | | 1998–2003 | | | | 2004–2010 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Min | Max | Ave. | C.V. | Min | Max | Ave. | C.V. | Min | Max | Ave. | C.V. |
| pH | 6.70 | 8.90 | 7.34 | 4.46 | 6.44 | 8.43 | 7.48 | 5.22 | 6.90 | 8.65 | 7.82 | 4.91 |
| TDS | 290.30 | 1380.99 | 672.38 | 27.59 | 287.86 | 1210.20 | 664.71 | 28.57 | 388.70 | 1306.04 | 674.68 | 26.05 |
| $Ca^{2+}$ | 18.14 | 174.79 | 101.22 | 33.08 | 31.33 | 181.39 | 99.58 | 33.77 | 32.16 | 221.79 | 101.00 | 33.24 |
| $Mg^{2+}$ | 7.00 | 52.50 | 24.51 | 36.85 | 7.50 | 55.50 | 24.77 | 39.04 | 11.00 | 70.00 | 25.92 | 39.56 |
| $Na^+$ | 7.00 | 46.40 | 20.49 | 47.40 | 6.47 | 45.30 | 21.41 | 44.46 | 5.26 | 56.95 | 21.22 | 48.17 |
| $K^+$ | 0.50 | 6.90 | 1.64 | 60.08 | 0.44 | 8.69 | 1.75 | 66.57 | 0.28 | 12.77 | 1.51 | 88.13 |
| $HCO_3^-$ | 182.50 | 925.00 | 469.31 | 30.27 | 170.01 | 880.04 | 460.48 | 31.96 | 222.50 | 800.00 | 446.62 | 28.33 |
| $Cl^-$ | 0.00 | 68.80 | 9.64 | 130.00 | 1.25 | 78.75 | 11.66 | 124.00 | 1.25 | 162.50 | 16.83 | 136.79 |
| $SO_4^{2-}$ | 0.00 | 180.00 | 8.34 | 174.75 | 0.20 | 58.00 | 6.47 | 163.31 | 0.20 | 160.00 | 13.61 | 203.44 |
| $NH_4$-N | 0.00 | 232.95 | 3.08 | 748.47 | 0.00 | 38.83 | 1.65 | 261.26 | 0.00 | 20.19 | 1.43 | 243.83 |
| $NO_3$-N | 0.00 | 4.18 | 0.07 | 424.27 | 0.00 | 6.78 | 0.11 | 476.70 | 0.00 | 10.17 | 0.45 | 284.04 |
| $Fe^{2+}$ | 0.00 | 24.00 | 2.27 | 121.11 | 0.00 | 16.00 | 2.43 | 103.64 | 0.00 | 21.00 | 2.42 | 124.51 |
| $Fe^{3+}$ | 0.00 | 3.50 | 0.38 | 167.25 | 0.00 | 18.50 | 0.42 | 371.04 | 0.00 | 21.60 | 0.48 | 323.25 |
| Mn | 0.01 | 0.50 | 0.12 | 76.35 | 0.01 | 1.25 | 0.16 | 103.65 | 0.01 | 1.07 | 0.16 | 99.14 |
| OD | 0.20 | 12.20 | 2.12 | 63.66 | 0.04 | 6.19 | 1.84 | 60.12 | 0.34 | 9.75 | 1.95 | 57.78 |
| $CO_2$ | 0.00 | 114.90 | 24.48 | 77.59 | 0.00 | 146.86 | 16.02 | 106.82 | 0.00 | 104.61 | 15.09 | 129.84 |

Concentrations in mg/L C.V.: coefficient of variation; OD: oxygen demand.

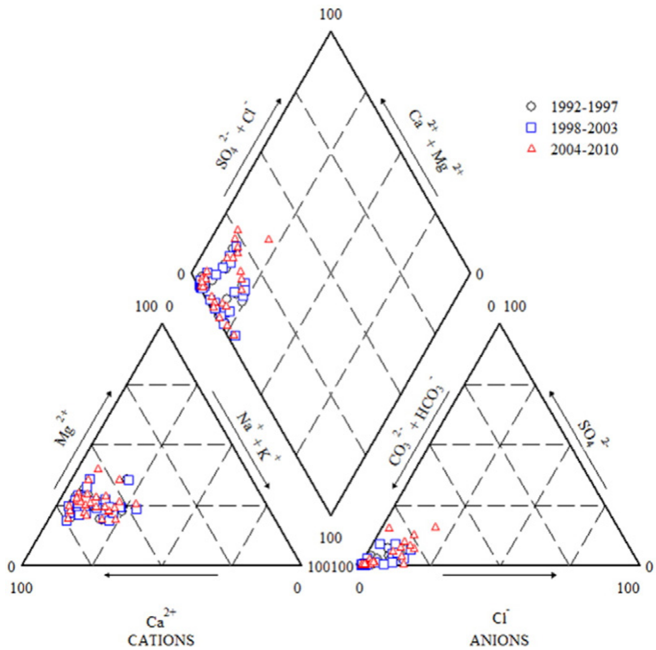


**Fig. 4.** Piper diagram of major ions in groundwater of the three periods.

0.394) and K-$Fe^{2+}$ ($r = 0.385$) in the period 2004–2010, with the correlations between $Ca^{2+}$, $Mg^{2+}$, $HCO_3^-$, $CO_2$, and TDS being higher ($r > 0.8$ in 1992–1997). The dissolution of Ca–Mg carbonatite, i.e. calcite, dolomite, and limestone, generates most of the TDS, and the dissolved $CO_2$ is intimately bound in the complex carbonate equilibria. Fig. 5 shows that the correlations decreased in periods 1998–2003, 2004–2010 as seen by the loosened correlation clusters.

The possible sources of $Na^+$ and $K^+$ in natural waters are atmospheric precipitation, evaporite dissolution and the weathering of Na-bearing silicate minerals (Xiao et al., 2014). In this study the Chloro-Alkaline indices (CAI-I and CAI-II) at most wells were found to be negative, only well J8 during 1992–1997 and J9-J10 during the last two periods exhibited positive values. The negative correlation between $Na^+$ and $Ca^{2+}$ and the negative Chloro-Alkaline indices indicate ion exchange occurring between $Ca^{2+}$ and $Mg^{2+}$ in groundwater with $Na^+$ and $K^+$ in the aquifer material (Ishaku et al., 2011). $Fe^{2+}$ is significantly correlated with most other parameters, while Mn is relatively independent only showing significant correlations with $K^+$ in 1992–1997 and with $Na^+$ and $NO_3$-N in 2004–2010. Both iron and manganese are derived from natural water-rock processes rather than from land use activities, and the content of iron in rocks of the WJHP is hundreds of times that of manganese (Zeng, 1994). pH maintained negative correlations with $Ca^{2+}$ and $CO_2$ and a positive correlation with $Na^+$. Notably, it can be seen in Fig. 5 that the relations of pH-$Ca^{2+}$ and pH-$CO_2$ become closer, with their absolute correlation coefficient increasing from 0.568 and 0.652 in 1992–1997 to 0.844 and 0.899 in 2004–2010, respectively. $Cl^-$ and $SO_4^{2-}$ are exclusively correlated element in the first two periods. Thereafter, $NO_3$-N begins to establish positive relationship with them. The significant correlations between $NH_4$-N and $K^+$ and between $NH_4$-N and OD indicate that the source of $NH_4$-N is mainly from fertilizer use and industrial/domestic sewage, and is produced in situ via the anaerobic degradation of organic matter (Costa et al., 2016; Lewandowski et al., 2015; Umezawa et al., 2009). Furthermore, the high concentration of $Fe^{2+}$, representing a strong reducing conditions, prevents the oxidation of ammonium to nitrate (Miao et al., 2013). Generally, $NO_3^-$ could enter the subsurface system through several pathways: the nitrogen oxides in precipitation, leaching from nitrous fertilizers, recharge via river water contaminated with $NO_3^-$, bacterial conversion from $NH_4^+$ via nitrification under oxidizing conditions, and especially in city areas, through industrial spillage and gasworks sites (Umezawa et al., 2009). Only in 1998–2003, $NO_3$-N and $NH_4$-N show significant correlation ($r = 0.689$) indicating a transformation process between them. In 2004–2010, $NO_3$-N had high correlation coefficient with Cl ($r = 0.702$) and $SO_4^{2-}$ ($r = 0.665$), and it can be inferred that they all originate from agricultural fertilizer.

### 4.3. Parameters with significant changes

The 16 parameters of each well during 1992–2010 were separately tested using the seasonal Mann-Kendall test, and the number of wells showing significant increasing (+) and decreasing (−) trends ($p < 0.1$) are portrayed in Fig. 6. More than half of the wells exhibited significant increasing trend of $Cl^-$ (15), pH (27), and $NO_3$-N (26); meanwhile, the concentration of $HCO_3^-$ and $CO_2$ at 16 and 15 wells respectively exhibit significant decreasing trend.

#### 4.3.1. pH and $CO_2$

The pH of groundwater is a key groundwater quality characteristic because it largely controls many of the chemical reactions involving groundwater and it also strongly influences the presence or absence of iron, manganese and nitrogen (Sullivan and Krieger, 2001). It is evident that the pH of groundwater in the WJHP experienced a significant increasing trend during 1992–2010 (Table 1 and Fig. 6). The variation of

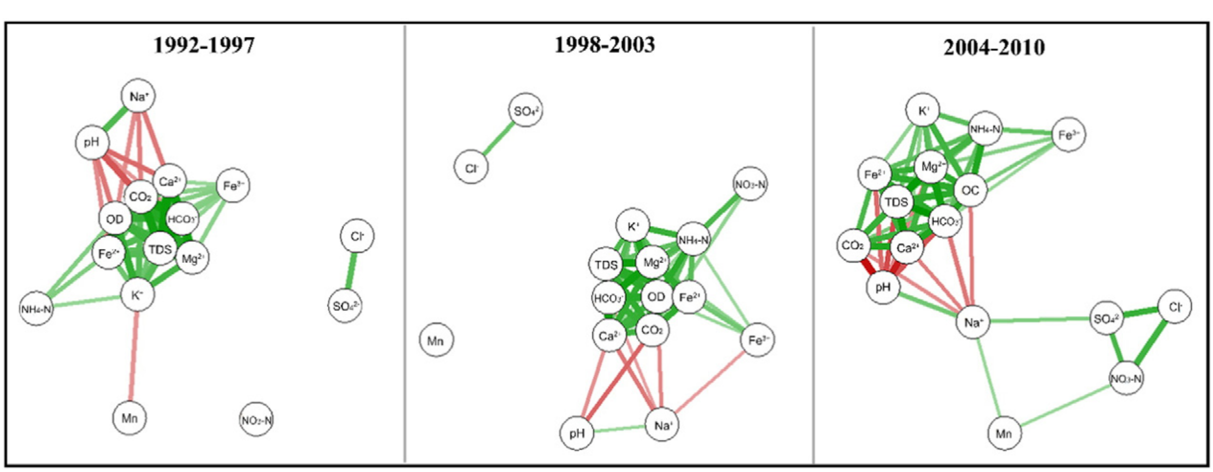


**Fig. 5.** Correlation evolution of the physicochemical parameters. Green lines and red lines denote positive and negative correlations, respectively. The line with the darkest tone, the largest width and the shortest length represents the largest absolute correlation coefficient.

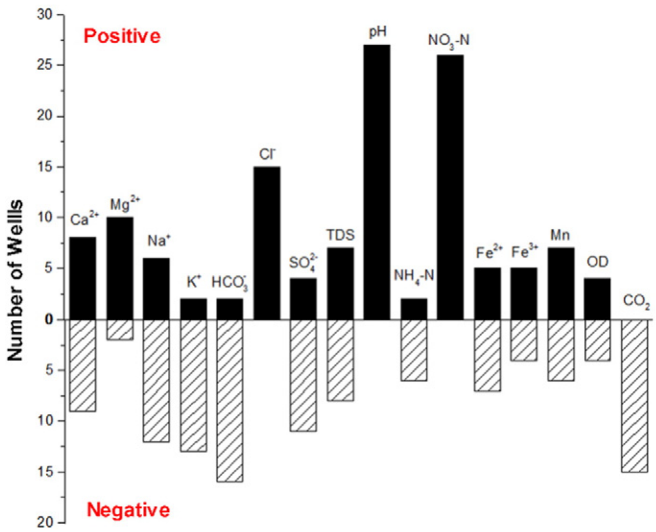


**Fig. 6.** Number of wells showing significant increasing (+) and decreasing (−) trends during 1992–2010.

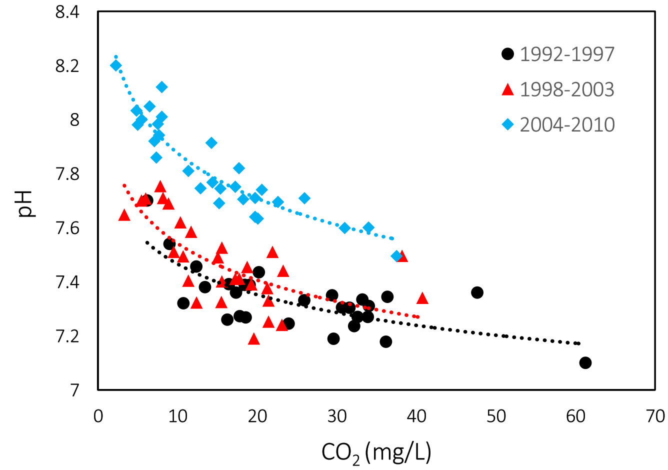


**Fig. 7.** The geochemical relation between the pH and $CO_2$ dissolved in groundwater.

groundwater pH reflects the nature of the recharge water, catchment geology, and its transformational history.

Generally, carbon dioxide ($CO_2$) enters the water through equilibrium with the atmosphere and biological degradation of organic carbon, and the reaction of dissolved $CO_2$ with water is one of the most important in establishing pH in natural groundwater systems (Kresic, 2006; Trautz et al., 2013). Groundwater pH in the study area is positively correlated with $Na^+$ and negatively correlated with $CO_2$ during 1992–2010 (Fig. 5). It is possible that the following reaction occurs:

$$Na_2Al_2Si_6O_{16} + 2H_2O + CO_2 \rightarrow Na_2CO_3 + H_2Al_2Si_2O_8 + H_2O + 4SiO_2 \quad (3)$$

This reaction consumes $CO_2$ and increases the concentration of $Na^+$ and $HCO_3^-$, thus causing the increase of the groundwater pH (Liu et al., 2015b). In addition, the $CO_2$ dissolves in water to form carbonic acid also induces a negative correlation with pH.

The $CO_2$ concentration at about half of the monitoring wells decreased significantly during 1992–2010, which are distributed over the entire study area, mainly located in the west Zhijiang and Jingzhou (J2-J8, J9), the south Gongan, Shishou and Jianli (J16-J18, J21), and the east Tianmen and Xiantao (J26-J28) (Fig. 1). Groundwater has been an important water source of local drinking water and industrial water in the WJHP, and the confined aquifer is the major withdrawal layer providing about 90% of the groundwater extraction (Zhao, 2005). Groundwater extraction has increased during the period, and some groundwater depression cones have persisted in concentrated production and residential areas (Geological environment monitoring report of the Jingsha Region, Hubei Province (2010)). Groundwater $CO_2$ partial pressures are typically ~10–100 times higher than atmospheric, which means that groundwater extraction would inevitably cause $CO_2$ degassing and thus the increase of the groundwater's pH (Macpherson, 2009).

The geochemical relation between the average pH and the concentration of dissolved $CO_2$ in groundwater of the 29 monitoring wells during the three periods are depicted in Fig. 7. The pH value during 2004–2010 (blue line) is evidently higher than those during the first two periods. At $CO_2$ concentrations of 10, 20, and 30 mg/L, to be specific, the pH values during 2004–2010 are 0.34, 0.303, and 0.29 pH units, respectively, higher than those during 1998–2003, and are 0.41, 0.36, and 0.33 pH units, respectively, higher than those during 1992–1997. This confirms that some other exogenous factors exerted extensive influence on the regional groundwater pH, especially during the period of 2004–2010.

### 4.3.2. $NO_3$-N

Nitrogen, particularly in the form of nitrate, is the most common contaminant in aquifer systems overlying agricultural areas. The $NO_3$-N concentrations at 26 monitoring wells significantly increased during the monitoring period even though they remained within the Class III of the Quality Standard for Groundwater of China by the end of the monitoring period. Fig. 8 depicts the trends of the annual average $NO_3$-N concentration, annual crop yields, and fertilizer use during 1992–2010. The total amount of fertilizer applied in the WJHP exhibited an upward trend as a whole even though the regional annual crop yields showed distinct decrease from 1997 to 2003, which indicates the low fertilizer efficiency during that period. It has been demonstrated that the primary source of dissolved inorganic nitrogen in the Yangtze River Basin was mainly due to agricultural practices, and the riverine nutrient loads were likely to be heavily altered by chemical fertilizer use (Dai et al., 2011; Ding et al., 2010). Excess fertilizers in solution may reach underlying aquifers where groundwater tends to move very slowly, thus contaminants would take years to appear in wells. Therefore, the large and increasing amount of fertilizer use after 1996 caused the continuous and rapid rise of the average $NO_3$-N concentration and its standard deviation in the WJHP after 2000, indicating the rise of N pollution with high spatial variability.

### 4.3.3. $Cl^-$ and $SO_4^{2-}$

Solute salts $Cl^-$, $SO_4^{2-}$, $NH_4^+$, and $NO_3^-$ in groundwater generally originate from landfill leachate, domestic waste-water, agricultural chemicals, industrial chemicals, and recharge waters (McArthur et al., 2012). The high coefficient of variation of the four elements indicates that groundwater at the 29 monitoring wells were influenced by the above pathways with various degrees of intensity (Table 1). Both $Cl^-$ and $SO_4^{2-}$ concentrations at 23 (~80%) of monitoring wells always satisfied the Class I (50 mg/L) of the Quality Standard for Groundwater of China during 1992–2010, with higher concentration occurring at limited and similar locations. Specifically, $Cl^-$ concentration at monitoring wells J6, J8-J10, J23 and J25, as well as $SO_4^{2-}$ at wells J6, J8, J9, J23, J25, and J29 exceeded 50 mg/L at least once during the period. The highest $Cl^-$ concentration of 162.5 mg/L at well J25 and $SO_4^{2-}$ concentration of 160 mg/L at well J23 meet the Class III (250 mg/L) of the Quality Standard for Groundwater of China. Monitoring wells J6, J8-J10 are located near two cotton mills and a pesticide factory, J23 is near a chemical fertilizer plant, and J25 and J29 are located near a water supply plant. The organic chloride discharged from fabric chloride bleaching and pesticide production as well as inorganic chloride from the fertilizer production

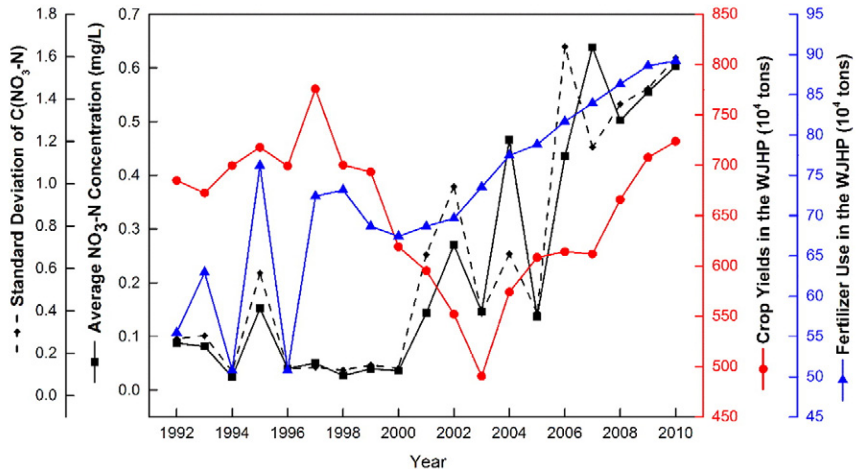


**Fig. 8.** Comparison of the rise in average $NO_3$-N concentrations, annual crop yields, and fertilizer use in the WJHP.

and the water sterilization strongly influenced the $Cl^-$ concentration in groundwater in the vicinity of above plants.

Fig. 9 depicts the trends of the annual average $Cl^-$ and $SO_4^{2-}$ concentrations in the WJHP during 1992–2010, the total discharge and the standard discharge rate of industrial wastewater in the southwest of the WJHP during 1998–2010. The total discharge of industrial wastewater decreased significantly at first and kept at about 70–90 million tons after 2004. Meanwhile the standard discharge rate of industrial wastewater increased significantly from ~33% in 1998 to ~96% in 2010 owing to the functioning of expanded industrial wastewater treatment facilities, which reduced the discharge of $Cl^-$ and $SO_4^{2-}$ to groundwater during this period. However, the average $Cl^-$ and $SO_4^{2-}$ concentrations showed significant increasing trends during 2004–2010, whereas their correlation with $NO_3$-N increased (Fig. 5). It can be inferred that the increased regional average $Cl^-$ and $SO_4^{2-}$ concentrations are mainly induced by the increased fertilizer use, and the industrial wastewater are responsible for abnormal high $Cl^-$ and $SO_4^{2-}$ concentrations at some wells near factories due to pipe leakage, landfill leachate, and underground discharges.

The constant significant correlation between $Cl^-$ and $SO_4^{2-}$ indicates their identical origins (Fig. 5), yet, $SO_4^{2-}$ concentration increased significantly at only 4 wells and decreased at 11 wells. Sulfate reduction is common in natural groundwater systems, being the second most reducing condition in natural groundwater systems occurring after iron reduction (Miao et al., 2012). Sulfate reduction involves the consumption of a substantial amount of hydrogen ions and the production of $HS^-$ at near neutral pH. The general form of the reaction is as follows:

$$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O \quad (4)$$

Consequently, part of the $SO_4^{2-}$ discharged from anthropogenic activities to the groundwater system is eliminated by the sulfate reduction to some extent.

### 4.4. The role of the TGD operation

The variations of the Yangtze River quality would inevitably influence the riparian groundwater owning to their close aquifer-stream hydraulic interaction in the WJHP. Previous studies have reported that the presence of dams could have considerable impacts on water quality characteristics (Kurunc et al., 2006; Macleod and Whitfield, 1996). Zhao et al. (2013) found that Three Gorges Reservoir (TGR) outlet water (Yichang) contained higher pH and lower $NH_3$-N levels than the TGR inlet water.

The higher pH at the outlet may be due to the decreased water self-purification capacity and prolonged hydraulic residence time, resulting from a reduced rate in river flow, and nutrient release from decaying plants in water level fluctuations zone due to seasonal dam regulations

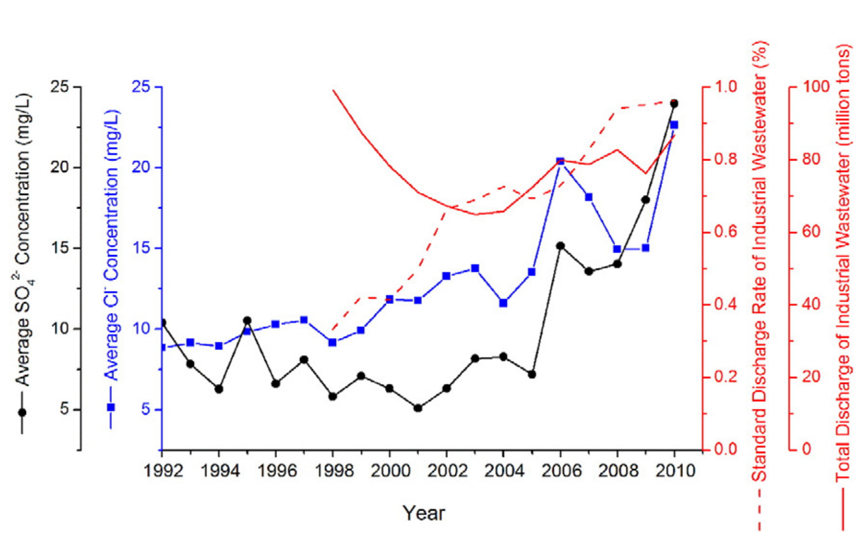


**Fig. 9.** Trends of the average $Cl^-$ and $SO_4^{2-}$ concentrations in the WJHP during 1992–2010, the total discharge and the standard discharge rate of industrial wastewater in the southwest WJHP during 1998–2010.

(Gaudet and Muthuri, 1981; Wei et al., 2009; Zhao et al., 2013). In general, the annual average pH at the TGR outlet, ranging from 7.88 to 8.19, is higher than the average groundwater pH in the WJHP, which exhibited an obvious upward trend with fluctuations during 1998–2010 (Fig. 10). The change point analysis on the average pH values of the 29 wells demonstrated that the groundwater pH experienced an abrupt change at about 2003, which increased ~0.43 pH units as a whole (red line in Fig. 10). The year 2003 coincided with the start of operation of the Three Gorges Dam (TGD). The similar trend pattern between the water pH at the TGR outlet and groundwater pH in the WJHP suggests that the rise of groundwater pH levels in the WJHP is partly contributed by the impoundment of the TGD.

Sun et al. (2013) illustrated the monthly monitoring concentrations of $NH_4^+$ and $NO_3^-$ at the Yichang and Hankou monitoring stations on the Yangtze River during 1990–2010 (see locations in Fig. 1), which confirmed that the impoundment of the TGD reduced the annual peaks of the $NH_4^+$ concentration from about 0.3–0.8 mg/L during 1990–2003 to ~0.10–0.15 mg/L during 2004–2010 at the Yichang station. These impacts decayed from the Yichang station to the Hankou station. While concentrations of $NO_3^-$ at the Yichang Station shows no perceptible correlation with the operation of the TGD, it rose from ~0.5 to ~1.5 mg/L during 1996–2003 and then remained at a relative high level (~1.0–2.0 mg/L) after 2003 (Sun et al., 2013). Decreased concentrations of $NH_3$-N and $NH_4^+$ at the outlet of the TGR are possibly due to a reduction by sediment associative processes after impoundment (Wang et al., 2010). Meanwhile, the TGD-induced longer retention would increase nitrification of $NH_4^+$. It can be inferred that the operation of the TGD played a role in deceasing $NH_4$-N concentrations and increasing $NO_3$-N concentrations in confined groundwater of the WJHP via reducing concentrations of $NH_3$-N and $NH_4^+$ in recharging waters to the regional aquifer, albeit the degree of influence may be small.

## 5. Conclusion

Groundwater in the Western Jianghan Plain is slightly alkaline with a relatively wide range of TDS from 288 to 1380 mg/L. It is generally characterized as $HCO_3$-Ca-Mg dominated by carbonate rock weathering. The high spatial variation of $Cl^-$, $SO_4^{2-}$, $NH_4$-N, and $NO_3$-N indicate anthropogenic impacts. High content of Fe and Mn are attributed to geological factors which cause their release from mineral weathering.

The pH values, $NO_3$-N and $Cl^-$ concentrations at 27, 26 and 15 wells, respectively, exhibited significant increasing trends during 1992–2010, and the concentration of $HCO_3^-$ and $CO_2$ of 16 and 15 wells exhibit respectively significant decreasing trends. The significant negative correlation between pH and $CO_2$ revealed that the increase of pH may be attributed to the $CO_2$ degassing caused by extensive groundwater extraction. Regional average $NO_3$-N concentrations of groundwater increased coincidently with the increased use of fertilizer. Abnormally high values of $Cl^-$ and $SO_4^{2-}$ at some wells were induced by industrial chemicals.

In addition, the temporal variations of regional pH value, $NH_4$-N and $NO_3$-N concentrations in groundwater are almost identical to their changes in the Yangtze River at the outlet of the Three Gorges Reservoir. It can be inferred that the variations of these parameters in the WJHP can be partly contributed by the impoundment of the TGD, which constitutes a worthy topic for future research.

Overall, water quality of the confined aquifer in the Western Jianghan Plain remained in relatively good condition during the study period. However, the pH value and $NO_3$-N concentration exhibited rising trends indicating that groundwater quality could decline significantly in the future. This implies that more effective pollution mitigation strategies, particularly increasing the efficiency of fertilizer use in agriculture and nutrient management must be taken into account to protect the groundwater quality of the Western Jianghan Plain.

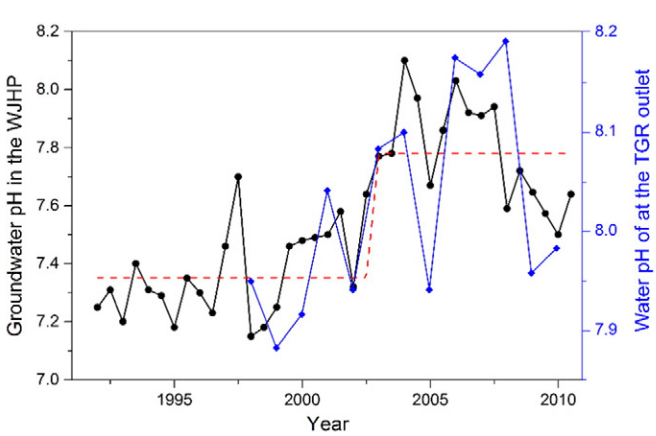


**Fig. 10.** Average groundwater pH of the 29 monitoring wells during 1992–2010 and annual average pH at the TGR outlet (Yichang Station) during 1998–2010.

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