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Long-term variations of water quality in a reservoir in China

Y. Y. Chen, C. Zhang, X. P. Gao and L. Y. Wang

ABSTRACT

To study the spatial and temporal trends of water quality in the Yuqiao Reservoir (Ji County, Tianjin) in China, water quality data for ten physical and chemical parameters from three monitoring stations (S1, S2 and S3) was collected from 1989 to 2007 and from an other three stations (S4, S5 and S6) during the period of 1999–2007. A one-way ANOVA was employed to evaluate the spatial variation of water quality for each station. The results showed that there were statistically significant spatial differences for most water quality parameters except temperature and dissolved oxygen in the entire reservoir, and the concentrations of most parameters were higher in the uppermost part of the reservoir. The temporal trend study was conducted using the Seasonal–Kendall's test. The results revealed improving trends of water quality from 1989 to 2007, including a reduction of total phosphorous, temperature and biochemical oxygen demand and an increase of dissolved oxygen. High N:P ratios, ranging from 52.61 to 78.75, indicated that the reservoir was a phosphorous-limited environment. This study suggests long-term spatial and temporal variations of water quality in the Yuqiao Reservoir, which could be informative for water quality managers and scientists.
Key words | long-term trends, N:P ratio, spatial variation, water quality, Yuqiao Reservoir

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INTRODUCTION

The pollution of surface water with toxic chemicals and excess nutrients is of great environmental concern worldwide. The concentrations of toxic chemicals and bioavailable nutrients in excess seriously degrade aquatic ecosystems and impair the use of water for drinking, industry, agriculture, recreation and other purposes. Therefore, an estimation of the quality of surface waters is necessary for human and ecological use. A monitoring program is important for providing a representative and reliable estimation of spatial and temporal variations in water quality.

In previous research, identifying spatial variation and conducting temporal trend analysis of surface water based on long-term measured data have been a major focus. Water bodies studied in previous works include the Keonggi Bay in Korea (Park & Park 2000), the Han River basin in South Korea (Chang 2008), the Fuji River Basin in Japan (Shrestha & Kazama 2007), the Ebro River in Spain (Bouza-Deaño *et al.* 2008), the lower St. Johns River in the USA (Ouyang *et al.* 2006), and the Eymir Lake in Ankara (Yenilmez *et al.* 2011).

In this study, a long-term water quality program was undertaken from 1989 to 2007 in a reservoir in China. A rich historical dataset allows us to track spatial and temporal trends in water quality for the Yuqiao Reservoir. Although there have been many studies that have investigated the water quality problems of the Yuqiao Reservoir, Liu *et al.* (2008) used a 2-D coupled model to simulate the characteristics of hydrodynamic field and mass transport processes in the Yuqiao Reservoir. Chen *et al.* (2005) examined the seasonal variation of nitrogen concentration in the surface water of the Yuqiao Reservoir basin. Zhang *et al.* (2011) studied the impact on water quality of excessive growth of *Potamogeton crispus* for the Yuqiao Reservoir. However, there is no study focusing on long-term systematic trend analysis for the Yuqiao Reservoir.

The objectives of this study are the following: (1) to identify long-term spatial variations in water quality; (2) to analyse long-term temporal trends in water quality; and (3) to determine the key factors regulating the reservoir's productivity. The results reveal water quality changes in the Yuqiao Reservoir over a long period, which will

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hopefully help scientists gain a broader perspective on the processes evolving in a reservoir.

MATERIALS AND METHODS

Study area

The Yuqiao Reservoir (40°02′ N and 117°34′ E, Figure 1) is located in the Zhou River in Tianjin City in China. The reservoir was formed in 1965 to meet water needs mainly for hydropower and irrigation. It has been the only source for water supply in Tianjin City (population more than 10 million) since 1983. The principle tributaries draining into the reservoir are the Lin, Sha and Li Rivers. The reservoir has a watershed area of 2,060 km^2, a storage capacity of 15.59×10^8 m^3 and a surface area of 86.8 km^2 at an elevation of 19.97 m, according to the 1985 national elevation standard (China). The maximum depth is 12.16 m, the average depth is 4.74 m, and the annual precipitation of the watershed during the study period is 750 mm, with a 5.06×10^8 m^3 annual average inflow.

Monitoring stations and sampling

Six monitoring sites are located in the Yuqiao Reservoir (Figure 1). Stations S1, S2 and S3 have been used to collect water quality parameters for 19 years (1989–2007), which typifies the water in the uppermost part of the reservoir (near the contributing rivers), inside the reservoir and the water output from the reservoir, respectively. Because the reservoir is so broad, stations S4 through S6 were additionally investigated from 1999 to 2007 for the purpose of detailed spatial analysis.

Water samples were taken once a month from 1989 to 1998 and twice a month from 1999 to 2007. Ten physicochemical parameters obtained from each station were used for analysis. The samples were collected only on the surface. We sampled, preserved and analysed all parameters

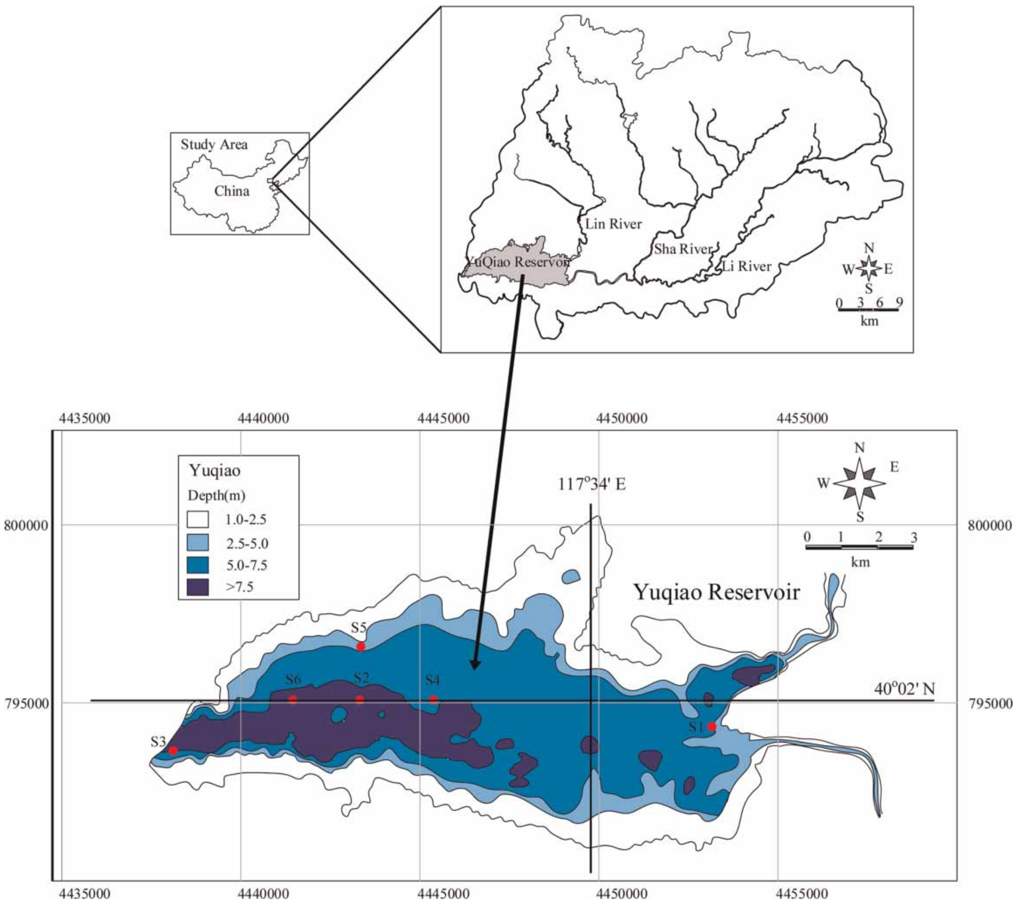

Figure 1 | The Yuqiao Reservoir watershed and the monitoring stations (Station S1–Station S6).

according to the *Standard Method for Water and Wastewater of China* (Standard Methods 2002). The water quality parameters, their abbreviations, units and methods of analysis are summarised in Table 1.

Statistical analysis

One-way ANOVA was used to test the spatial variation. If there were significant differences between stations regarding parameters, the Tukey's honestly significant difference (HSD) test was chosen as the *post-hoc* test for pairwise comparisons to determine which two stations had statistically significant differences. This analysis was performed using SPSS17 for windows. The Seasonal–Kendall's test (SK) was used to evaluate temporal trends of water quality parameters. This test has been widely used in identifying water quality in previous study (e.g., Lettenmaier *et al.* 1991; Zipper *et al.* 2002; Boeder & Chang 2008). This analysis was performed using the Computer Program for the Kendall Family of Trend Tests (Helsel *et al.* 2005). For the one-way ANOVA and the SK test, the data were $\log_{10}(x+1)$ transformed to reduce skewness. The results were reported at a p-value of 0.05 (significant difference, $p < 0.05$).

RESULTS

Spatial variation of water quality

Statistically significant characteristics of the samples were calculated for 1989–2007 (Table 2). The results of the one-way ANOVA showed that there were statistically significant differences for most water quality parameters between stations except Temp (mean = 13.97 °C, $p = 0.056$) and DO (mean = 10.09 mg/l, $p = 0.863$).

The pH varied between 7.94 (Station S1) and 8.39 (Station S2), and a pH of 8.23 was the average for the entire watershed. The Tukey's HSD test indicated that the pH for Station S1 was significantly lower than that of Station S2 ($p = 0.000$) and Station S3 ($p = 0.000$).

The spatial variations of NH_4-N, NO_3-N and NO_2-N were consistent for the entire reservoir. DIN is the sum of three forms of nitrogen. The DIN concentration varied from 1.21 mg/l (Station S3) to 5.22 mg/l (Station S1), with an average of 2.58 mg/l in this watershed. The range for the TN concentration was from 1.60 mg/l (Station S3) to 6.05 mg/l (Station S1), and the average for the entire watershed was 3.11 mg/l. The TP range was 0.05 mg/l (Station S2) – 0.25 mg/l (Station S1). DIN, TN and TP showed similar spatial patterns, and their concentrations were all high at Station S1, which was significantly different from that of Station S2 (DIN, $p = 0.000$; TN, $p = 0.000$; TP, $p = 0.000$) and Station S3 (DIN, $p = 0.000$; TN, $p = 0.000$; TP, $p = 0.000$).

The concentration of COD varied between 3.03 (Station S1) and 4.00 mg/l (Station S3), with an average of 3.64 mg/l. The BOD varied from 1.88 (Station S3) to 2.61 mg/l (Station S1), with an average of 2.22 mg/l. The BOD and COD did not show a similar spatial pattern, and the concentration of BOD in the upper part was significantly higher than in the middle and lower parts ($p = 0.000$), while the COD was converse.

Due to the broadness of the reservoir, data collected from Stations S4 through S6 were used to make a detailed

Table 1 | Physicochemical parameters determined and analytical techniques used in the study

Parameters	Abbreviations	Units	Analytical methods
Water temperature	Temp	°C	Thermometer
pH	pH	pH unit	Glass electrode method
Ammonia nitrogen	NH_4-N	mg/l	Nessler's reagent colorimetric method
Nitrate nitrogen	NO_3-N	mg/l	Spectrophotometric method with phenol disulfonic acid
Nitrite nitrogen	NO_2-N	mg/l	Spectrophotometric method
Dissolved inorganic nitrogen[a]	DIN	mg/l	–
Total nitrogen	TN	mg/l	Alkaline potassium persulfate digestion-UV spectrophotometric method
Total phosphorous	TP	mg/l	Ammonium molybdate spectrophotometric method
Chemical oxygen demand	COD	mg/l	Acidic potassium permanganate method
Biochemical oxygen demand	BOD	mg/l	Dilution and seeding method
Dissolved oxygen	DO	mg/l	Iodometric method

[a]DIN is the sum of ammonia nitrogen, nitrate nitrogen and nitrite nitrogen.

Table 2 | Descriptive statistics of water quality parameters at different Yuqiao Reservoir stations

Water quality parameters		S1	S2	S3	S4	S5	S6
Temp (°C)	Mean ± SD	13.55 ± 9.13	14.09 ± 9.74	14.28 ± 9.48	13.93 ± 9.75	14.08 ± 9.80	14.00 ± 9.72
	N	228	228	228	216	216	216
	Ranges	0.74–28.74	0.00[a]–29.5[b]	1.00–29.50[b]	0.00[a]–29.50[b]	0.05–29.50[b]	0.01–29.50[b]
pH	Mean ± SD	7.94 ± 0.42	8.39 ± 0.44	8.36 ± 0.40	8.44 ± 0.48	8.44 ± 0.49	8.38 ± 0.52
	N	303	302	300	216	216	216
	Ranges	6.67[a]–9.01	7.09–9.39	7.20–9.30	7.36–9.72[b]	7.47–9.55	7.10–9.45
NH_4-N (mg/l)	Mean ± SD	1.20 ± 1.67	0.16 ± 0.10	0.17 ± 0.11	0.18 ± 0.06	0.18 ± 0.06	0.17 ± 0.06
	N	336	326	329	216	216	216
	Ranges	0.03–8.11[b]	0.01[a]–0.65	0.02–0.78	0.06–0.37	0.05–0.33	0.04–0.36
NO_3-N (mg/l)	Mean ± SD	3.89 ± 2.28	1.11 ± 0.66	1.01 ± 0.63	1.09 ± 0.62	0.76 ± 0.53	0.78 ± 0.54
	N	335	327	327	216	216	216
	Ranges	0.20–15.20[b]	0.02–3.29	0.01[a]–2.91	0.07–2.63	0.08–2.11	0.06–2.16
NO_2-N (mg/l)	Mean ± SD	0.14 ± 0.19	0.03 ± 0.03	0.03 ± 0.03	0.03 ± 0.02	0.03 ± 0.02	0.03 ± 0.02
	N	335	325	327	216	216	216
	Ranges	0.010–2.100[b]	0.003[a]–0.280	0.005–0.280	0.010–0.110	0.010–0.110	0.008–0.110
DIN (mg/l)	Mean ± SD	5.22 ± 3.29	1.31 ± 0.67	1.21 ± 0.64	1.30 ± 0.23	0.97 ± 0.27	0.98 ± 0.28
	N	335	325	325	216	216	216
	Ranges	0.68–21.23[b]	0.07–3.70	0.04[a]–3.06	0.15–1.53	0.19–1.33	0.12–1.38
TN (mg/l)	Mean ± SD	6.05 ± 3.67	1.70 ± 0.59	1.60 ± 0.56	1.68 ± 0.56	1.45 ± 0.51	1.36 ± 0.46
	N	332	328	323	216	216	216
	Ranges	1.14–24.02[b]	0.52–4.00	0.57–3.52	0.47–3.15	0.52–2.71	0.39[a]–2.66
TP (mg/l)	Mean ± SD	0.25 ± 0.53	0.05 ± 0.03	0.06 ± 0.28	0.04 ± 0.02	0.04 ± 0.02	0.04 ± 0.02
	N	327	323	327	216	216	216
	Ranges	0.001[a]–5.690[b]	0.003–0.170	0.004–4.000	0.004–0.140	0.001[a]–0.170	0.005–0.110
COD (mg/l)	Mean ± SD	3.03 ± 0.96	3.91 ± 1.14	4.00 ± 0.98	4.20 ± 0.96	4.41 ± 1.08	4.26 ± 1.01
	N	334	328	328	216	216	216
	Ranges	0.81–7.34	0.30[a]–10.25[b]	1.95–8.80	2.47–7.50	2.21–9.00	2.39–8.10
BOD (mg/l)	Mean ± SD	2.61 ± 1.28	2.17 ± 1.37	1.88 ± 0.96	2.10 ± 0.95	1.91 ± 0.76	1.67 ± 0.59
	N	330	326	322	216	214	216
	Ranges	0.46–7.25	0.40–8.40[b]	0.07[a]–6.70	0.55–5.86	0.77–5.90	0.26–3.40
DO (mg/l)	Mean ± SD	10.09 ± 3.16	10.25 ± 2.82	9.92 ± 2.79	10.22 ± 2.24	10.36 ± 2.43	9.81 ± 2.07
	N	323	324	329	216	216	216
	Ranges	0.89–25.95[b]	0.73[a]–19.40	1.05–19.35	6.08–18.31	5.73–20.93	6.10–17.17

Mean: arithmetic mean; SD: standard deviation; *N*: number of data; range: interval in which data varies.

[a]Minimum value.

[b]Maximum value.

There are very few missing water quality data during the study period except water temperature and pH (less than 4% of total). Mean values amongst Stations S1, S2 and S3 were used to calculate the covariance matrix of the water quality parameters. The pH had negative covariance with most parameters except Temp and COD. Temp and COD were the same as pH, while BOD and DO were converse.

spatial analysis of the water quality condition for the inner part of the reservoir after 1999. The one-way ANOVA results showed that there were no significant differences between the stations (Station S2, Station S4 – Station S6) for most parameters except NO_3-N ($p = 0.044$) and TN ($p = 0.032$) in the inner part of the reservoir. The concentrations of NO_3-N and TN in the east part of inner watershed were significantly higher than the other regions, which were consistent with the spatial pattern for the entire reservoir.

Long-term temporal trends of water quality

The SK's test was applied to study the trends of water quality parameters for 1989–2007. The results of the trend study are presented in Table 3. Decreasing trends were detected for most parameters. The most significant was TP, and a negative trend was found at all the stations. The next was Temp, which showed a decreasing trend at Stations S1 and S3. The BOD exhibited a decreasing trend at one station (Station S2). As for the detected positive trends, only the DO conditions showed an upward trend (water quality improvement) at Station S1. For parameters such as DIN, TN, pH and COD, no significant trends were detected by the test in any of the stations. The results showed a slight improvement of water quality in the reservoir.

Table 3 | The overall water quality trends during the monitoring period for three stations in the Yuqiao Reservoir

Water quality variables	S1	S2	S3
Temp	↓	↔	↓
pH	↔	↔	↔
DIN	↔	↔	↔
TN	↔	↔	↔
TP	↓	↓	↓
COD	↔	↔	↔
BOD	↔	↓	↔
DO	↑	↔	↔

'↓' downward (95% confidence), '↔' no significant changes, '↑' upward (95% confidence).

Nutrient limitation trends

The N:P ratio is often used to predict the limiting nutrients for phytoplankton production. We used TN and TP for the N:P ratio computation in this study. In Stations S1, S2 and S3, the average of mass ratios of TN:TP were 78.75 ± 187.97, 59.81 ± 76.09 and 52.61 ± 38.77, respectively. Approximately 98% of the TN:TP ratios for all stations were greater than the N-limitation boundary (16N:1P) (Redfield 1934) (Figure 2), indicating the potential of a P limitation for phytoplankton growth. The decreasing trends in TP indicated that phosphorous would be the limiting nutrient for phytoplankton production in the future.

DISCUSSION

The result showed high TN (3.11 mg/l) and TP (0.12 mg/l) in the reservoir, with values far above the China GB recommended limits for drinking water of TN < 1.0 mg/l and TP < 0.05 mg/l (Surface Water Environmental Quality

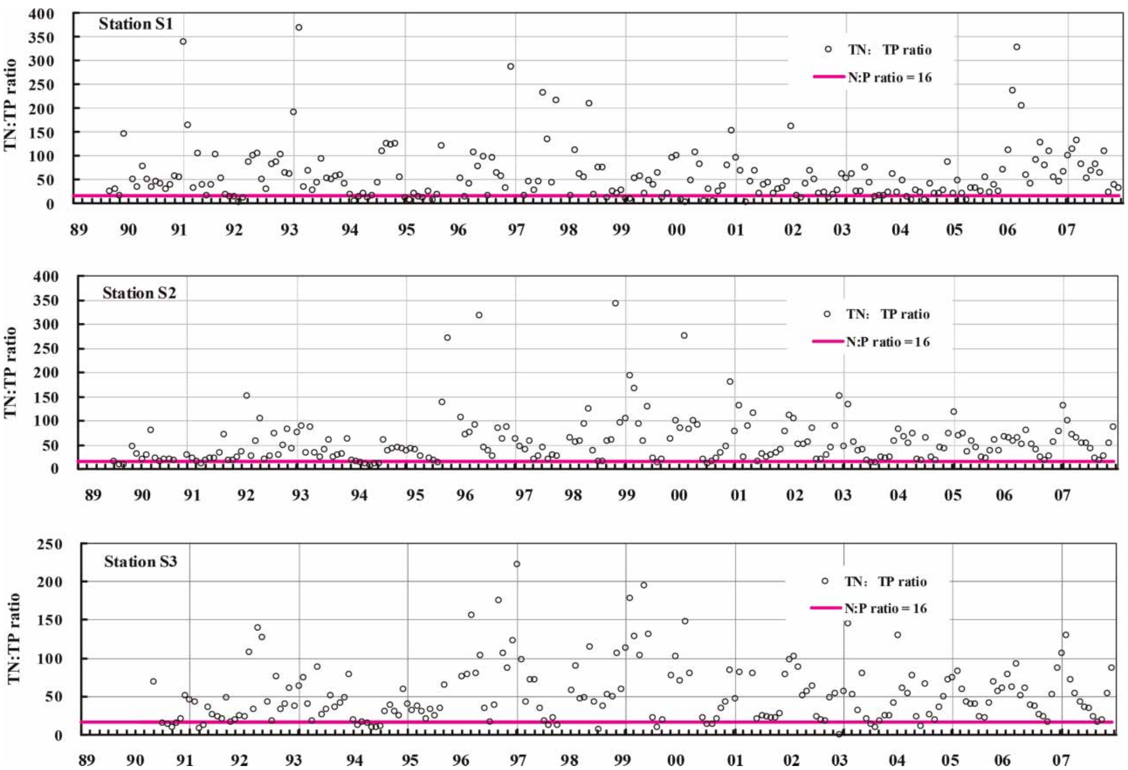

Figure 2 | The TN:TP mass ratios for the monitoring periods 1989–2007 based on monthly averaged values by sites in the reservoir. In the figure, a value of 16 for the ratio of TN:TP indicates the P limitation and N limitation boundaries of Redfield (Redfield 1934).

Standard, Ministry of Environmental Protection of People's Republic of China 2002, see the Appendix, Table A1).

For spatial variations, most parameters were highly variable between the monitoring stations. The concentrations of TN and TP were highest in the uppermost part of the reservoir (Station S1) and were significantly different from those of Stations S2 and S3. It was concluded that the reservoir received significant quantities of nitrogenous and phosphoric constituents from tributary inflow and surrounding agriculture and urban land uses. Some nutrients were absorbed by aquatic plants and deposited in sediments in the reservoir, which is why the concentrations of nutrients in the upper part were higher than in the middle and lower parts.

The concentrations of COD and BOD did not show a similar spatial pattern; the concentration of BOD was significantly higher in the upper part, and the COD was converse. Two possible factors may contribute to the spatial pattern of BOD and COD: the spatial variation of oxygen and aquatic plant growth. There was no statistically significant difference for DO ($p = 0.863$) between stations, and the oxygen level was sufficient throughout the entire watershed, so the spatial pattern of BOD and COD may not be from the spatial variation of oxygen. The second possible factor was aquatic plant growth. The above nutrient analysis indicated that the concentrations of nutrients were higher in the upper part of the reservoir. The water depth in this region was lower than that in the lower part. These factors all suggest that the upper region of the reservoir was more favourable for plant growth, which is probably why the concentration of BOD was higher in the region. More plants would mean more COD was absorbed, so the concentration of COD was lower in this region.

As for the temporal trend, with the rapid urbanisation and development of the region's economy, the concentration of TP was decreasing in the whole basin for the reduction of the point source pollution, and the nitrogen loadings into the reservoir from the watershed were steady during the monitoring period for reservoir restoration activities, including management in the agricultural parts of the drainage area.

The concentrations of COD and BOD remained at low levels during the monitoring period, and no significant trends were detected in the reservoir except at Station S2, which had a significantly decreased BOD parameter. It was concluded that there was no significant pollution from industrial wastes.

The changes in Temp (decreasing) and DO (increasing) during the monitoring period were observed, and the trend of DO indicated water quality improvement in the watershed in recent years. The most likely cause of these changes was reservoir restoration activities, including riparian vegetation and the reduction of inorganic pollution in the upper reaches.

CONCLUSIONS

The nutrient concentration levels in the reservoir were high, and the results appeared to be associated with the high nitrogenous and phosphoric constituents input from the watershed, thus becoming a potential threat for the trophic state in the reservoir.

There were statistically significant differences for most water quality parameters in the reservoir except Temp and DO using the ANOVA method. The highest concentrations (e.g., DIN, TN, TP and BOD) were mostly found in the uppermost part of the reservoir (Station S1). Therefore, it is imperative to find the best control for agricultural and urban land uses and human activities in the uppermost part of the watershed to further reduce nutrient loadings to the reservoir.

No significant long-term temporal trends were found by using the SK test in DIN, TN and COD, but the Temp and TP concentrations decreased for the majority of the monitoring stations. DO showed increasing trends at Station S1, which demonstrated increased water quality in the upstream reaches.

Phosphorous was identified as a primary controlling factor for phytoplankton growth in the reservoir according to the high N:P ratios (52.61–78.75) at all stations from 1989 to 2007. The decreasing trend in TP indicated that phosphorous would be the limiting nutrient for phytoplankton production in the future, and the variation of phosphorous concentration in the reservoir in the future should be a concern of reservoir managers.

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APPENDIX A

See Table A1 for the parameters of the Surface Water Environmental Quality Standard in China.

Table A1 | Standard limit values of basic parameters for surface water in China

Parameters	Classification I	Classification II	Classification III	Classification IV	Classification V
Temp	Range of water temperature change caused by artificial factors: average maximum temperature rise each week $\leq$1: average maximum temperature drop each week $\leq$ 2				
pH	6–9				
DO $\geq$	Saturation factor 90% (or 7.5)	6	5	3	2
COD $\leq$	2	4	6	10	15
BOD $\leq$	3	3	4	6	10
NH_4-N $\leq$	0.15	0.5	1.0	1.5	2.0
TN $\leq$	0.2	0.5	1.0	1.5	2.0
TP $\leq$	0.02 (Lakes 0.01)	0.1 (Lakes 0.025)	0.2 (Lakes 0.05)	0.3 (Lakes 0.1)	0.4 (Lakes 0.2)

According to the surface water environmental functions and protected objects, five classes of standards are defined as follows:
I: applies to headwaters and national nature reserves;
II: applies to Grade-I protective zones of surface water resource areas of drinking water, habitats for rare aquatic species and spawning and feeding grounds;
III: applies to Grade-II protective zones of surface water resource areas of drinking water, wintering grounds and migration channels of fish and shrimp as well as aquaculture grounds and swimming areas;
IV: applies to ordinary industrial water areas and recreation areas without direct contact from humans;
V: applies to agricultural water areas and ordinary scenery water areas.