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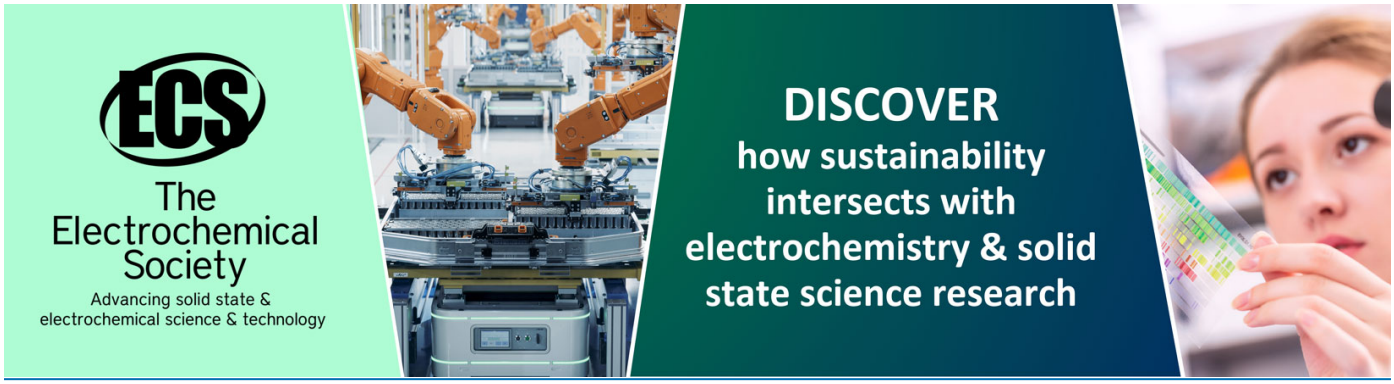

Analysis on the spatiotemporal characteristics of water quality and trophic states in Tiegang Reservoir: A public drinking water supply reservoir in South China

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Abstract: Shenzhen is the most densely populated city in China and with a severe shortage of water. The per capita water resource is less than 200 m^3, which is approximately 1/12 of the national average level. In 2016, nearly 90% of Shenzhen's drinking water needed to be imported from the Pearl River. After arrived at Shenzhen, overseas water was firstly stockpiled in local reservoirs and then was supplied to nearby water works. Tiegang Reservoir is the largest drinking water supply reservoir and its water quality has played an important role to the city's drinking water security. A fifteen-month's field observation was conducted from April 2013 to June 2014 in Tiegang Reservoir, in order to analyze the temporal and spatial distribution of water quality factors and seasonal variation of trophic states. One-way ANOVA showed that significant difference was found in water quality factors on month ($p<0.005$). The spatial heterogeneity of water quality was obvious ($p<0.05$). The distribution pattern of WT, TOC, Silicate, NO_3^--N, TN and Fe was pre-rainy period > latter rainy period > high temperature and rain free period > temperature jump period > winter drought period, while SD showed the contrary. Two-way ANOVA showed that months rather than locations were the key influencing factors of water quality factors succession. Tiegang reservoir was seriously polluted by TN, as a result WQI were at IV~V level. If TN was not taken into account, WQI were atI~III level. TLI (Σ) were about 35~60, suggesting Tiegang reservoir was in mesotrophic and light-eutrophic trophic states. The WQI and TLI (Σ) in sampling sites 9 and 10 were poorer than that of other sites. The 14 water quality factors were divided into 5 groups by factor analysis (FA). The total interpretation rate was 73.54%. F1 represents the climatic change represented by water temperature. F2 and F4 represent the concentration of nutrients. F3 and F5 represent the sensory indexes of water body, such as turbidity, transparency. The FA results indicated that water quality potential risk factors was total nitrogen (TN), and potential risk factors also include chlorophyll-a and nitrate nitrogen (NO_3^--N).

1. Introduction

Shenzhen is the most densely populated city in mainland China and with a severe shortage of water. While bringing vitality to the economic development, the influx of a large immigrant population also placed unprecedented pressure on the water supply and seriously polluted the water environment [1-3].

Although Shenzhen is located in the subtropical region, no large rivers or lakes exist in the territory. Thus, rich rainfall cannot be effectively gathered, resulting in scarce water resources [4, 5]. The per capita water resource is less than 200 m^3, which is approximately 1/12 of the national average level. In 2015, nearly 90% of the city's drinking water needed to be imported from the Pearl River. Shenzhen water supply system is mainly composed of overseas water diversion engineering and local reservoirs. There are nearly 168 reservoirs in Shenzhen. The total catchment area is 611 km^2 and total capacity is 778 million m^3. After arrived at Shenzhen, overseas water was firstly stockpiled in local reservoirs and then was supplied to nearby water works. Therefore, water quality of those reservoirs has played an important role to the city's drinking water security. And how to ensure the safety of drinking water and to meet the people's increasing requirement for the quality of drinking water became important topics in the construction of ecological civilization in Shenzhen.

It is widely accepted that characterizing the spatiotemporal trends of water quality parameters and identifying correlated variables with water quality are indispensable for the management and protection of water resources [6-8]. In order to analyze the temporal and spatial distribution of water quality factors and seasonal variation of trophic states, a fifteen-month's field observation was conducted from April 2013 to June 2014 in Tiegang Reservoir. Monitoring factors include WT, SD, pH, DO, COD, TOC, TN, NH_4^+-N, NO_3^--N, TP, Fe, silicate, turbidity, chlorophyll, and so on. Through the stratified monitoring of 10 sampling points, the evolution path of water environment in Tiegang reservoir was studied. Our research can provide basic data for the protection of the ecological safety of water environment and safeguard the safety of drinking water in Shenzhen. Our research can also provide scientific basis for the management of water quality department.

2. Another section of your paper

2.1. A subsection

There were a total of 10 sampling sites (Figure 1): the No. 1 site is near the inlet of Xili Reservoir, No. 2 site is near the intake point of the water plant, No. 3 and No. 4 sites are in the running water area in the middle east reservoir (where water flow velocity is fast), No. 5 and No. 6 sites are in the dead water area (where water flow velocity is slow), No. 7 site is near the water intake point of Shiyan Reservoir, No. 8 site is in the running water area in the western reservoir, No. 9 site is near the Jiuwei River, and No. 10 site is near the Liaokeng River. For each sampling site, the samples were collected within 3 layers from top to bottom. The surface layer is the water layer approximately 10 cm below the surface, the transparent layer is the water layer corresponding to the depth of the transparency measurement, and the bottom layer is the water layer approximately 10 cm above the sediment.

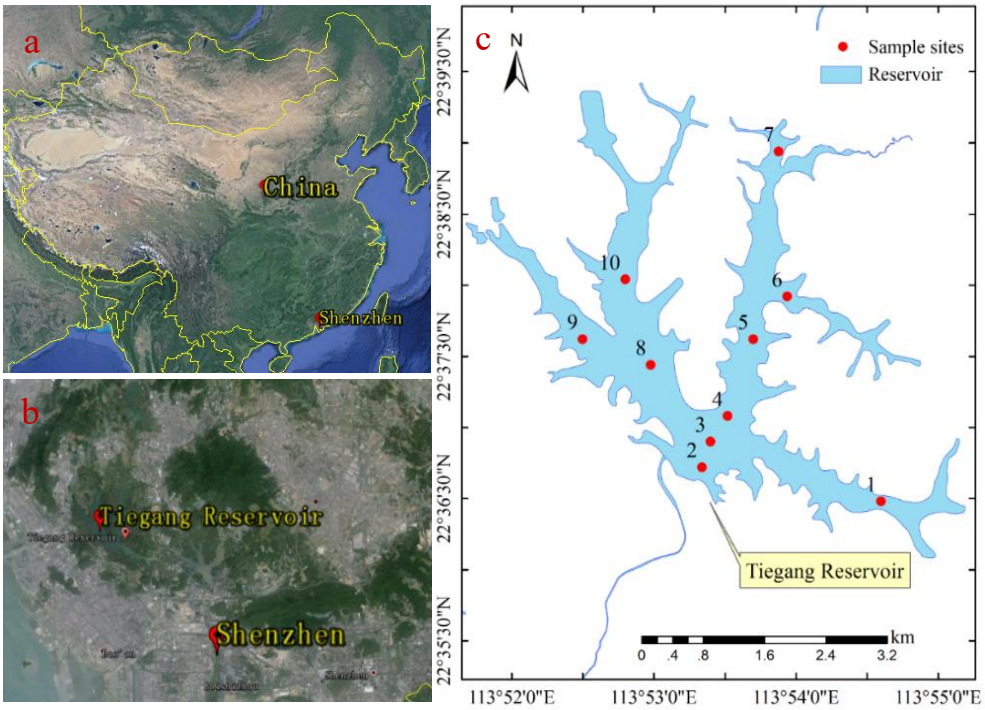


Fig.1 Sampling sites at Tiegang Reservoir

2.2. Sampling and analysis

The samples were collected using a ZPY-1 water collector and stored separately. The water samples were transferred to the laboratory within 2 hours after collected and kept at 4°C. The chemiluminescence detection of the permanganate index (COD_{Mn}) and determination of ρ(Chla), total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), ammonia nitrogen (NH_4^+-N,), nitrate nitrogen (NO_3^--N), iron (Fe) and silicate were carried out within two days. Chlorophyll-a was measured by using a modulated fluorometer (WALZ Phyto-PAM, Germany) that was periodically calibrated by acetone extraction spectrophotometry. The depth of the water, WT, pH, DO and turbidity were measured in-site using a multi-parameter water quality analyzer (YSI 6600V2, USA). The transparency (SD) was measured in-site using a secchi disk. COD was measured by the acidic potassium permanganate method; TP was determined by ammonium molybdate spectrophotometry; silicate was determined by silicon molybdenum blue spectrophotometry; TN, NH_4^+-N and NO_3^--N were analyzed by a flow analyzer (AMS-Alliance-Futura, French); and TOC was determined using a TOC analyzer (GE-Siever 5310C).

2.3. Climate period

According to the weather characteristics, sampling time was divided into five periods. Pre-rainy period was from April to June 2013 and 2014. Latter rainy period was from July to September 2013. High temperature and rain free period was from October to November 2013. Winter drought period was from December 2013 to February 2014. Temperature jump period was March 2013.

2.4. Method of Water quality evaluation

On the basis of "surface water environmental quality standard" (GB3838-2002) and the "surface water environmental quality assessment methods", WT, pH, DO, COD, TN, NH_4^+-N, NO_3^--N, TP were used for water quality evaluation. Water quality was measured by water quality index (WQI). Single factor evaluation method was used. The final water quality was determined by the highest category in the participating index. Water quality was divided into 6 levels, including I, II, III, IV, V, VI (see Table 2).

2.5. Method of Synthetic evaluation of nutritional status

Chl-a, TN, TP, SD, and COD were used for quantitative evaluation of trophic level for eutrophication, as measured by **trophic level index** (TLI).

Trophic level index TLI (Σ) was calculated according to the equations and the parameters given below:

$$TLI(\sum) = \sum_{j=1}^{m} W_j \cdot TLI(j) \quad (1)$$

where W_j is correlative weighted score for trophic level index of j; TLI (j) is the trophic level index of j; j present Chla, TP, TN, SD, or COD_{Mn};

$$W_j = \frac{r_{ij}^2}{\sum_{j=1}^{m} r_{ij}^2} \quad (2)$$

where r_{ij} is relative coefficient between Chl-a and other parameters j; r_{ij}, r_{ij}^2, and W_j is the value for parameters with Chl-a of lakes in China was shown in Table 1.

Table 1 r_{ij}, r_{ij}^2 and W_j value for parameters with Chla of lakes in China

	Chl-a	TP	TN	SD	COD_{Mn}
r_{ij}	1	0.84	0.82	-0.83	0.83
r_{ij}^2	1	0.7056	0.6724	0.6889	0.6889

According to the assessed standard values of the trophic state for Chl a, TP, TN, SD and COD_M in different lake regions, the single trophic state index was calculated according to the equations given below.

The single trophic state index was calculated as follow equations:

TLI (Chl a) = 10 [2.5 + 1.086 ln (Chl a)] (3)

TLI (TP) = 10 [9.436 + 1.624 ln (TP)] (4)

TLI (TN) = 10 [5.453 + 1.694 ln (TN)] (5)

TLI (SD) = 10 [5.118 – 1.94 ln (SD)] (6)

TLI (COD_{Mn}) = 10 [0.109 + 2.66 ln (COD_{Mn})] (7)

Table 2 Lake trophic state for corresponding designated uses of water body

WQI	Trophic state	TLI (Σ)	Designated uses
I	Oligotrophic	0-30	National natural protection region and rural distributed life drinking water source, etc.
II	Mesotrophic	30-50	The first-grade protection zone of centralized drinking water source, rare aquatic habitats, fish and prawn production field, etc.
III	Light-eutrophic	50-60	The second-grade protection zone of centralized drinking water source; fish and prawn wintering grounds, migration channel, aquaculture etc.
IV	Mid-eutrophic	60-70	Industrial water and human indirect contact recreation water
V	High-eutrophic	70-80	Agricultural irrigation water and general landscape water
VI	Hypereutrophic	>80	Loss of water ecological functions; with poor function except regulating local climate

2.6. Statistical analysis

Pearson correlation analysis, one-way ANOVA, two-way ANOVA and factor analysis were performed on SPSS20. The distribution chart of trophic level was generated on ArcMap10.2 by the Kriging interpolation method based on the mean of the TLI (Σ) of several months at each sampling site in the corresponding climatic period. Other graphics were prepared using Origin9.0.

3. Results and Discussion

3.1. Spatiotemporal characteristics Physical chemical factors

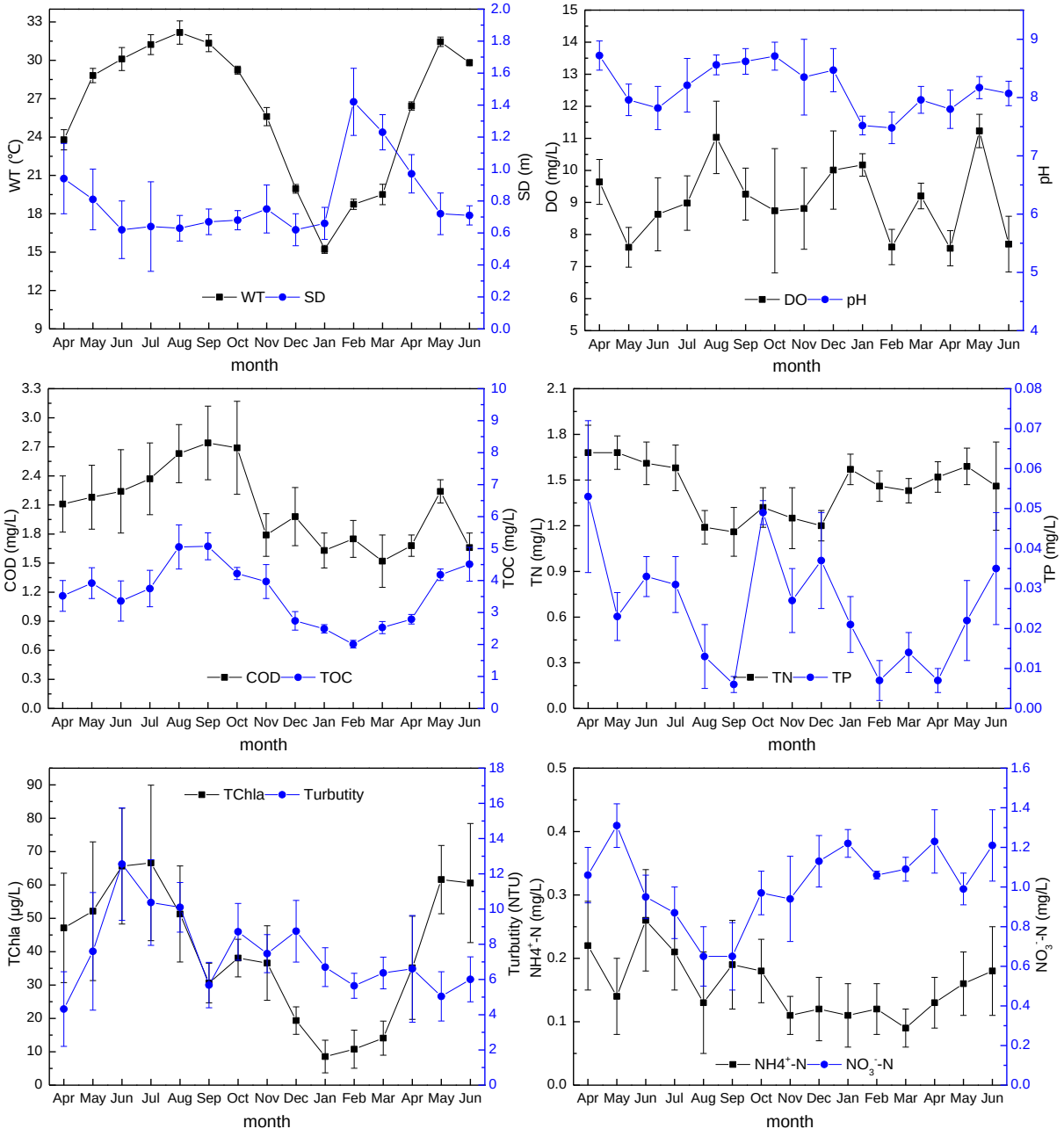
Figure 2 shows the seasonal variations of the water quality factors. WT in Tiegang Reservoir was 14.52-32.17℃. The average WT of surface layer, transparent layer and bottom layer were 25.97, 25.74, 23.20℃. WT was highest during July to September, and declined rapidly since November. WT reached the lowest in January and then raised sharply in March. WT was the driving factor of the growth of plankton. Sustained high temperatures may cause algal blooms, which threaten drinking water safety. SD in Tiegang Reservoir was 0.62~1.55 m. The SD was low in most of the year except in winter. When entering the flood season in April, the sediment brought by surface runoff was the main reason for the decrease of SD. COD and TOC were 1.52~2.81 mg/L and 2.01~5.15 mg/L respectively which showed that organic pollution was not serious in Tiegang Reservoir. DO and pH were 7.65~11.23 mg/L and 7.48~8.72 mg/L respectively. In the year 2014 pH was slightly lower than in 2013. The change of DO was not obvious between the months. The high DO illustrated a good state water quality and ecological system. Tiegang Reservoir was seriously polluted by nitrogen. TN was 1.21-1.73 mg/L, which was the main pollutant. NO_3^--N was 0.65-1.34 mg/L and NH_4^+-N was 0.09-0.26 mg/L. Nitrogen mainly came from the surrounding runoff pollution, such as Jiuwei River and Liaokeng River. Besides, agricultural non-point source pollution and domestic pollution was also an important reason. The concentration of TP was low, and the seasonal variation was not obvious. The concentration of Fe in was 0.05-0.14 mg/L and was slightly increased in 2014. The concentration of silicate was 4.48-11.69 mg/L, showing the characteristics of lower in flood season than in dry season. The successions of chlorophyll-a and turbidity were similar and the mainly pattern was Pre-rainy period > Latter rainy period > High temperature and rain free period > Temperature jump period > Winter drought period.

One-way ANOVA showed that significant differences were found in the physical and chemical factors such as WT, SD, COD, TOC, silicate, NO_3^--N, TN and Fe on month ($p<0.005$).The distribution pattern of WT, TOC, Silicate, NO_3^--N, TN and Fe was pre-rainy period > latter rainy period > high temperature and rain free period > temperature jump period > winter drought period, while SD Show the contrary. Seasonal variation of DO, pH, NH_4^+-N and TP were not obvious.

The spatial differences of DO, SD, COD, TOC, TN, NH_4^+-N and Fe were significant at different sampling points($p<0.01$). Concentration of COD, TOC, TN, NH_4^+-N and Fe raised gradually from east to west, while DO and SD reduced gradually in the same direction. The water quality of the Southeast part of Tiegang Reservoir near the No.1 sampling sites was better than other area. The water quality around the No.9 and No.10 sampling sites was the worst. The spatial difference of WT, pH, Silicate, TP, and NO_3^--N were not significant.TN was the primary pollutant in Tiegang Reservoir. The average concentration of TN was 1.48 mg·L^{-1}. The highest TN concentration was 2.34 mg L^{-1}, which appeared on the surface layer of the No. 9 sampling site on June 17, 2013. The lowest TN concentration was 1.08 mg L^{-1}, which appeared on the bottom layer of the No. 2 sampling site on February 22, 2014. According to the evaluation results of surface water environment evaluation method, TN of all sampling points in the monitoring period were no better than grade VI. Tiegang Reservoir was a nitrogen polluted water body. Other pollutants concentration was low. DO, COD and TP have reached the surface water environmental quality standard class II ~ III.

Two-way ANOVA shows that there was a statistically significant interaction between the effects of location and month on the surface water temperature of Tiegang Reservoir. The variation of environmental factors can be explained by the interaction effect between month and sampling point (R^2, 21.3 % - 71.5 %). Month was the most important factor affecting environmental factors, which

had significantly effects on WT, SD, COD, TOC, Silicate, NH_4^+-N, NO_3^--N and Fe($p<0.01$). Month also has a certain correlation with TN ($p=0.065$), but had little effect on pH, DO, TP. Sampling points had a significant effect on SD ($p<0.01$), which had little effect on other environmental factors ($p>0.3$). The interaction between the month and the sampling point had a slight effect on Fe and SD, but had little effect on other environmental factors ($p>0.8$).On the whole, the main influencing factors of the environmental factors were month, which showed that the temporal heterogeneity of environmental factors was higher than that of spatial heterogeneity.



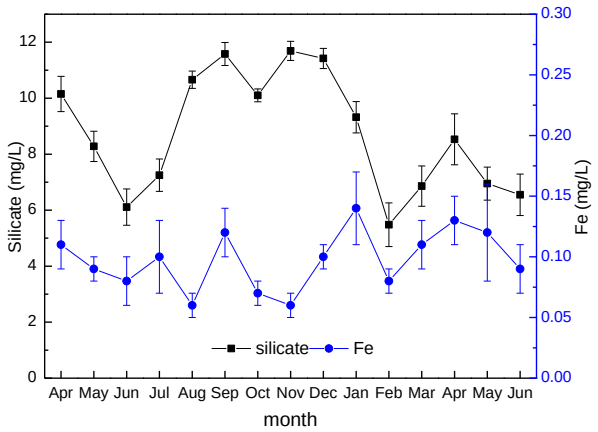


Fig.2 Seasonal variation of water quality factors at Tiegang Reservoir

3.2. Water quality evaluation

Tiegang reservoir was seriously polluted by total nitrogen. In April, May, June, July in the year 2013 and March, April, May, June in the year 2014, average TN concentration was 1.5~2.0mg/L, and WQI was at V level. In other months average TN concentration was 1.0~1.5mg/L, and WQI was at IV level.

Considering that TN concentration was too high, the results of single factor water quality assessment was only the reflection of total nitrogen. Besides, TN was listed as the reference index by "surface water environmental quality assessment method". So the water quality was reevaluated using pH, DO, NH_4^+-N, TP and permanganate index (Figure 3). The result of figure 3 showed that the water quality of Tiegang reservoir was good, and the WQI were mainly atIIIlevel in surface layer and transparent layer. TP or NH_4^+-N was the decisive factor of water quality. When the water depth was more than 5 meters, DO decreased significantly in the bottom layer, resulting in WQI at IV~VI levels. The spatial heterogeneity of water quality was obvious. Water quality in sampling sites 1 and 2 were pretty good. Especially from November 2013 to February 2014, the WQI was atIIlevel. Water quality in sampling sites 9 and 10 were poor. In rainy seasons the WQI was at III~IV level.

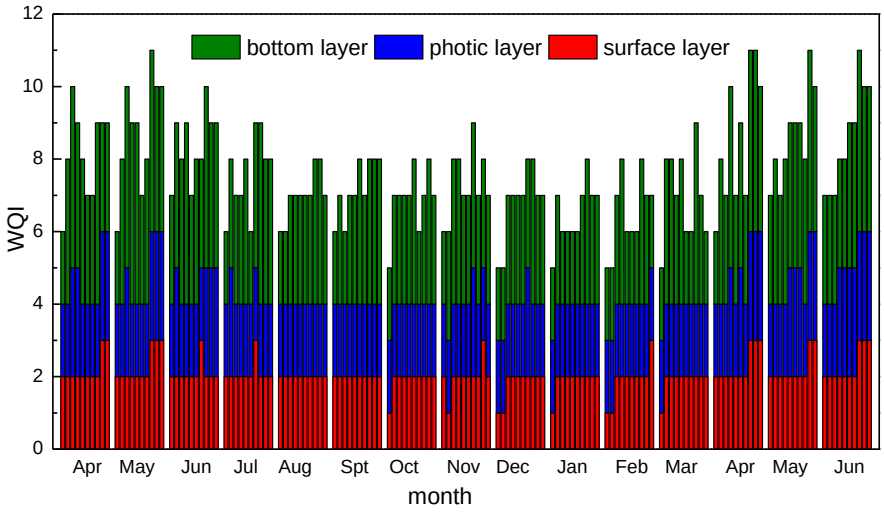


Fig.3 Spatial-temporal characteristic of water quality at Tiegang Reservoir

There are 10 columns every month and each column from left to right represents sampling sites 1 to 10.

3.3. Synthetic evaluation of nutritional status

The single factor evaluation method used in water quality evaluation chose the worst water quality to calculate the WQI. Its quantization ability was relatively poor and the water quality difference was not obvious. Therefore, comprehensive assessment of water quality was carried out using comprehensive

nutrition status evaluation method (Figure 4). Evaluation indicators include five water indexes including chlorophyll-a, TP, TN, SD and COD. The distribution chart of trophic level was generated by the Kriging interpolation method based on the mean of the TLI (Σ) of several months at each sampling site in the corresponding climatic period (Figure 5).

Figure 4 and Figure 5 clearly show the temporal and spatial succession of the trophic state of Tiegang reservoir. The succession pattern of TLI (Σ) was pre-rainy period > latter rainy period > high temperature and rain free period > temperature jump period > winter drought period. In rainy season in 2013, the TLI (Σ) of sampling sites 7, 8, 9, 10 were more than 50, indicating that there was a slight eutrophication in these area. In January and February, TLI (Σ) were about 35~45, suggesting water quality was very good. Compared with the same period in 2013, the comprehensive nutritional status of the 2014 in flood season decreased slightly, indicating that the water pollution of Tiegang reservoir had been effectively controlled. There was a risk of algae blooming at northwest part of Tiegang reservoir in rainy season especially in pre-rainy period. The reservoir authorities should pay great attention to the algal growth in this region during rainy season. Once the concentration of total Chlorophyll-a is over 80 μg/L, or if there are small algal blooms on the water surface, immediate measures should be taken to prevent algal blooms.

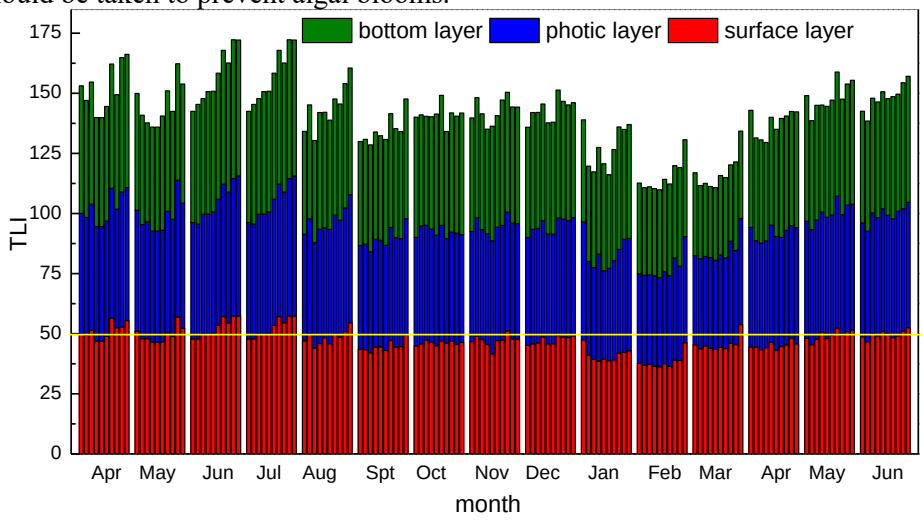
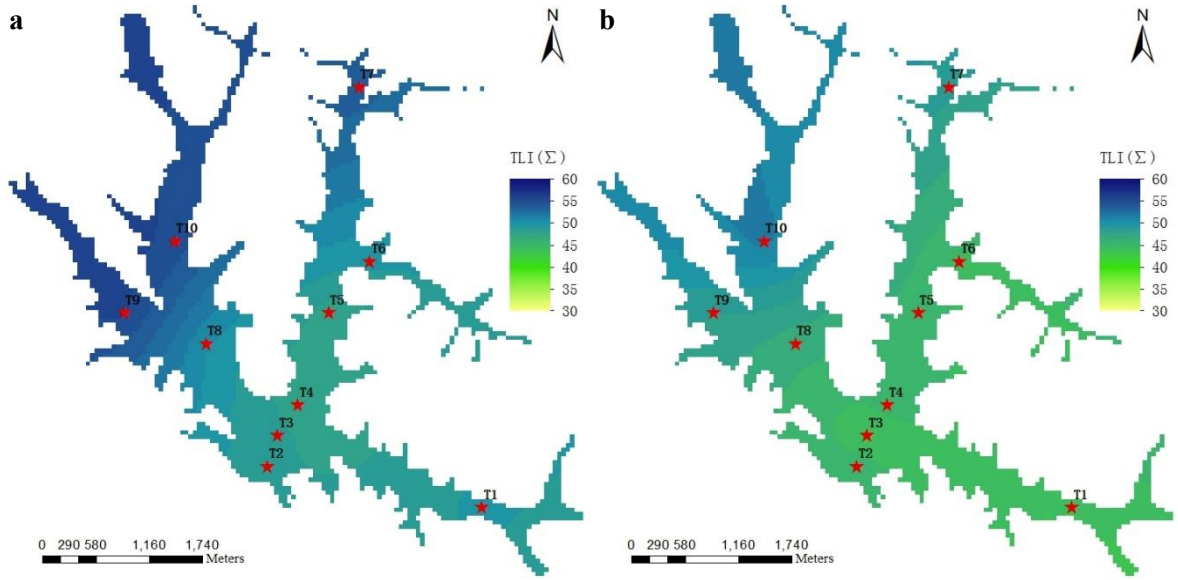


Fig.4 Spatial-temporal characteristic of Trophic States at Tiegang Reservoir



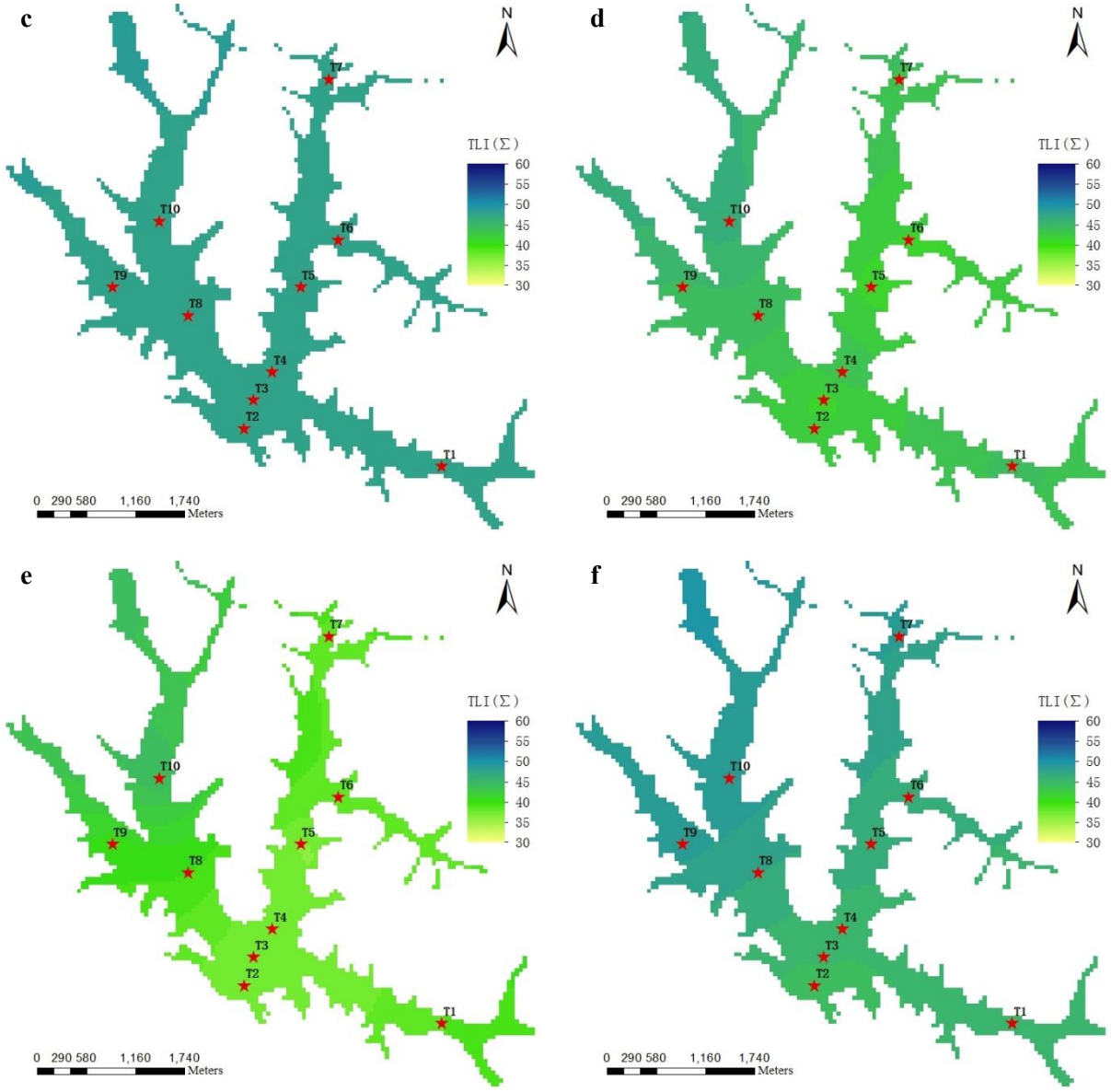


Fig.5 Spatial-temporal distribution chart of Trophic States at Tiegang Reservoir; a. Pre-rainy period in 2013; b. Latter rainy period in 2013; b. Latter rainy period in 2013; c. High temperature and rain free period in 2013; d. Winter drought period in 2013; e. Temperature jump period in 2014; f. Pre-rainy period in2014.

3.4. Pearson correlation between water quality factors

Table 3 shows the result of the pearson correlation between water quality factors. Water temperature was positively related to multiple water quality factors. The main correlated factors in descending order of the absolute value of the correlation coefficient were TOC > total chlorophyll-a (TChla) > COD > NO_3^--N > Fe > pH, in which the NO_3^--N and Fe were negatively correlated. There are two reasons for WT positively related to the TOC (0.839). On the one hand, in the beginning of summer, the surface runoff brought the non-point source pollutants into the reservoir, rising the organic matter concentration in the water. On the other hand, when the temperature raised, algae blooms leading to the rising of TOC. WT was positively related to TChla (0.590), indicating that temperature was the primary driving factor for algal growth. TN was positively related to NO_3^--N (0.672), because NO_3^--N

was the main component of TN. SD was negatively correlated with Silicate, TOC, COD, TChla. Chlorophyll-a is a measure of algal biomass. Chlorophyll-a was highly positively correlated with water temperature, but not significantly correlated with nitrogen and phosphorus. This indicated that the meteorological factors represented by water temperature were the primary driving factor of algal succession in Tiegang reservoir.

Table 3 Pearson correlation coefficient ts between water quality factors

	WT	pH	DO	SD	TD	COD	TOC	Silicate	NH_4^+-N	NO_3^--N	Fe	TN	TP	TChla
WT	1.000													
pH	**0.320**													
DO	0.039	**0.303**												
SD	-0.312	**-0.314**	**-0.363**											
TD	0.016	-0.103	-0.070	-0.188										
COD	**0.483**	**0.384**	0.280	**-0.316**	0.024									
TOC	**0.839**	**0.499**	0.239	**-0.450**	0.022	**0.546**								
Silicate	-0.012	**0.577**	**0.309**	**-0.496**	-0.124	0.249	0.280							
NH_4^+-N	0.153	0.092	-0.012	-0.045	-0.040	0.196	0.093	-0.075						
NO_3^--N	**-0.421**	**-0.416**	-0.417	0.185	-0.085	**-0.434**	**-0.578**	-0.237	-0.230					
Fe	**-0.333**	**-0.374**	0.091	-0.061	-0.118	-0.215	-0.294	-0.095	-0.056	0.272				
TN	-0.104	**-0.332**	-0.243	0.117	-0.100	-0.190	-0.291	**-0.366**	0.298	**0.672**	0.171			
TP	0.028	**0.363**	0.035	-0.233	0.065	0.106	-0.125	0.222	0.129	0.122	**-0.303**	0.177		
TChla	**0.590**	0.169	0.034	**-0.315**	0.084	0.259	**0.521**	-0.083	**0.389**	-0.154	-0.249	0.213	0.206	1.000

3.5. Factor analysis of water quality factors

Factor analysis can convert a large number of water quality factors that may be related to each other to a small number of synthetic indicators that are not related to each other. In Environmental Science, factor analysis is often used to identify key pollutants. In order to further understand the water quality of Teigang reservoir, factor analysis was used to identify potential pollutant factors. KMO and Bartley sphere tests were performed before factor analysis. When the KMO test coefficient >0.5 and $p<0.05$, it indicated that the data is taken from a normal distribution. Thus the correlation between variables was recognized, and that the original data is suitable for principal component analysis. KMO and Bartley Sphere Tests results showed that KMO test coefficient is 0.625, $p<0.01$, so it is suitable to use factor analysis to identify the main pollutants in Teigang reservoir.

Factor analysis (Table 4) showed that the 14 water quality factors can be divided into 5 categories. The total contribution rate of the five factors was 73.54%. F1 accounted for 22.10% of the total contribution rate, which was positively correlated with WT (0.863), TChla (0.798), and TOC (0.798). F2 accounted for 15.82% of the total contribution rate, which was strongly correlated with total nitrogen (0.898) and nitrate nitrogen (0.726). F3 accounted for 14.35% of the total contribution rate, which was positively correlated with SD (-0.775) and DO (0.686). F4 accounted for 12.93% of the total contribution rate, which was positively correlated with TP (0.783). F5 accounted for 8.34% of the total contribution rate, which was positively correlated with TD (-0.886). F1 represents the climatic change represented by water temperature. F2 and F4 represent the concentration of nutrients in water. F3 and F5 represent the sensory indexes of water body, such as turbidity, transparency.

Table 4 Matrix of rotated factor loadings

Water quality factors	Component				
	F1	F2	F3	F4	F5
WT	**0.863**	-0.188	-0.020	0.069	-0.083
TChla	**0.798**	0.297	0.012	0.108	-0.106
TOC	**0.777**	-0.334	0.250	0.184	-0.068
COD	0.571	-0.252	0.286	0.135	0.078
NH_4^+-N	0.508	0.336	-0.034	0.004	0.353
TN	0.050	**0.898**	-0.169	-0.054	0.118
NO_3^--N	-0.481	**0.726**	-0.177	0.012	-0.079
SD	-0.315	-0.083	**-0.775**	-0.142	0.331
DO	0.103	-0.247	**0.686**	-0.081	0.156
Silicate	-0.104	-0.275	**0.656**	0.480	0.119
TP	0.057	0.350	0.144	**0.783**	-0.088
Fe	-0.304	0.295	0.405	**-0.665**	0.092
pH	0.261	-0.340	0.342	**0.653**	0.211
TD	0.067	-0.034	-0.035	-0.003	**-0.886**
Eigenvalue	4.221	2.079	1.546	1.296	1.152
Cumulative %	22.099	37.923	52.273	65.203	73.540

Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization.

4. Conclusion

The results of this study indicated that Tiegang reservoir was seriously polluted by nitrogen. Other water quality factor including WT, SD, pH, DO, COD, TOC, TP, Fe, silicate, turbidity, chlorophyll-a were pretty good. One-way ANOVA showed that significant difference was found in water quality factors on month ($p<0.005$). The spatial heterogeneity of water quality was obvious ($p<0.05$).Two-way ANOVA showed that months rather than locations were the key influencing factors of water quality factors succession. TLI (Σ) were about 35~60, suggesting Tiegang reservoir was in mesotrophic and light-eutrophic trophic states. The 14 water quality factors were divided into five groups by factor analysis. The total interpretation rate was about 73.54%. F1 represents the climatic change represented by water temperature. F2 and F4 represent the concentration of nutrients. F3 and F5 represent the sensory indexes of water body, such as turbidity, transparency.

Acknowledgements

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