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Water quality assessment and source identification of water pollution in the Banchengzi reservoir, Beijing, China

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ABSTRACT

Water quality in the Banchengzi reservoir in Beijing has been deteriorating year by year, and it was embodied by increasing concentrations of COD and stable but high levels of total nitrogen. In order to identify the causes and to formulate a strategy for pollution prevention and control, we examined the temporal and spatial variations of water pollution and carried out source identification studies. Routine monthly monitoring data for seven water quality and six hydro-meteorological variables of the Banchengzi reservoir from 2007 to 2012 were analyzed by statistical techniques, including correlation analysis and principle component analysis. In addition, water samples at six different sites in the reservoir were collected and analyzed to investigate the spatial variation of water quality and to further identify the water pollution sources by UV–vis spectroscopy, three-dimensional excitation-emission matrix spectroscopy, and nitrogen stable isotope (δ^{15}N) analysis. The results revealed that dissolved organic matter and nitrogen were the main pollutants and were principally derived from anthropogenic point source pollution in the upper areas, which included domestic sewage and livestock farming. We speculated that the biodegradable organic pollutants from sewage were degraded to form soluble microbial products (SMP) by aerobic microorganisms and that nitrogen pollutants were mostly transformed to nitrate by nitrification. These SMP, nitrate, and other refractory pollutants were carried by the upper stream flowing into the Banchengzi reservoir, where it accumulated. Effective control of point source pollution and upper river ecological restoration should be done to improve the water quality and protect the reservoir.

Keywords: Water quality; Source identification; Statistics analysis; Dissolved organic matter (DOM); Nitrogen

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1. Introduction

In the last few decades, surface water has undergone large changes in chemical and biological composition as a result of growing human interference [1], which has caused or is about to cause a variety of problems, including eutrophication, destruction of biodiversity, degradation of ecosystem, and potentially even threatening human health [2]. Appropriate management and engineering measures can be an effective way to control the deterioration of water quality and to improve the surface water environment [3,4].

The quality of surface water is influenced by a multivariate and complex combination of both natural and anthropogenic factors. Therefore, a fundamental understanding of the spatial and temporal variation in the water characteristics and an identification of the source of water pollution are necessary to provide more precise and detailed information of the environmental conditions and to help researchers establish priorities for sustainable water management [5,6].

Since water quality assessment and source identification of water pollution relate to many different water quality and hydro-meteorological variables; multivariate statistical techniques, such as cluster analysis (CA), principal component analysis (PCA), correlation analysis, and more, are valuable tools for improving our understanding of complex databases and identifying possible factors that are responsible for variations in water quality [7–10].

In addition, some instrumental analysis methods have proven to be useful in assessing pollution sources and water quality, including UV–vis spectroscopy, three-dimensional excitation-emission matrix (EEM) spectroscopy, and nitrogen stable isotope (δ^{15}N) analysis. Optical properties of dissolved organic matter (DOM), such as absorbance and fluorescence spectra, are particularly useful and can be determined by relatively simple, rapid, sensitive, and non-destructive methods [11] Nitrogen stable isotope (δ^{15}N) analysis has proved to be a reliable method and has been widely applied toward distinguishing between different pollution sources and nitrogen transformations in groundwater and surface water [12–14]. This method is based on the principle that nitrate in the water originates from different sources, such as chemical fertilizers, soil organic nitrogen, sewage/manure effluents, and atmospheric precipitation, which often possess distinct isotopic compositions (δ^{15}N) [15–18].

The Banchengzi reservoir, which was monitored in this study, is a medium-sized reservoir located northeast of Beijing, the capital city of China. It is involved with flood control, irrigation, ecological water supply, and electricity generation. In the last 10 years, the economy in this area has rapidly developed, especially in the tourist industry. Although the standard of living in this area has improved markedly, the Banchengzi reservoir suffers from increasing pollution as well as deteriorating water quality. The possible causes of water quality deterioration include anthropogenic and natural sources of pollution. Anthropogenic pollution mainly comes from agricultural non-point source pollution and other point source pollution, such as sewage and livestock excretions from villages upstream, fish cage culture in the reservoir, and more. Natural sources include phytoplankton photosynthesis in the reservoir, which may convert inorganic matter to organic matter. Nevertheless, the main cause of water pollution is still not clearly identified. Further study needs be done to determine the sources of pollution because it will be the key to controlling water quality deterioration in the reservoir and the potential ecological risks, which will have a significant impact on public health and sustainable regional development.

This work aims to identify the exact causes of water quality deterioration in the Banchengzi reservoir. Water quality data and hydro-meteorological variables of the Banchengzi reservoir from 2007 to 2012 were collected and analyzed to assess the degradation of water quality and to reveal the contributing factors by multivariable analysis. Moreover, water samples from the reservoir were collected in 2013 and analyzed to further confirm the major sources of pollution by performing three-dimensional EEM spectroscopy and nitrogen stable isotope (δ^{15}N) analysis. Finally, given the results of our study, we proposed a strategy for improving the water quality in the reservoir.

2. Methods

2.1. Study area and data-set

The Banchengzi reservoir (116˚55′-117˚02′ N, 40˚37′-40˚43′ E) is in the Mangniu river basin, located northeast of Beijing, China (Fig. 1). The catchment area is about 66.1 km^2. Developed in 1976, the total capacity of Banchengzi reservoir is approximately 102 million cubic meters, and its average surface area is 0.373 km^2. The shape of the reservoir is narrow, and is 2,100 meters long and 200 meters wide. The average depth of the reservoir is 20.5 m, which increases from upstream to downstream. Low mountains and hills are the main landform in the area with altitudes of 250–500 m. The average annual temperature of this area is 10.2℃, and more than 75% of the precipitation is during the summer (from June to August). There

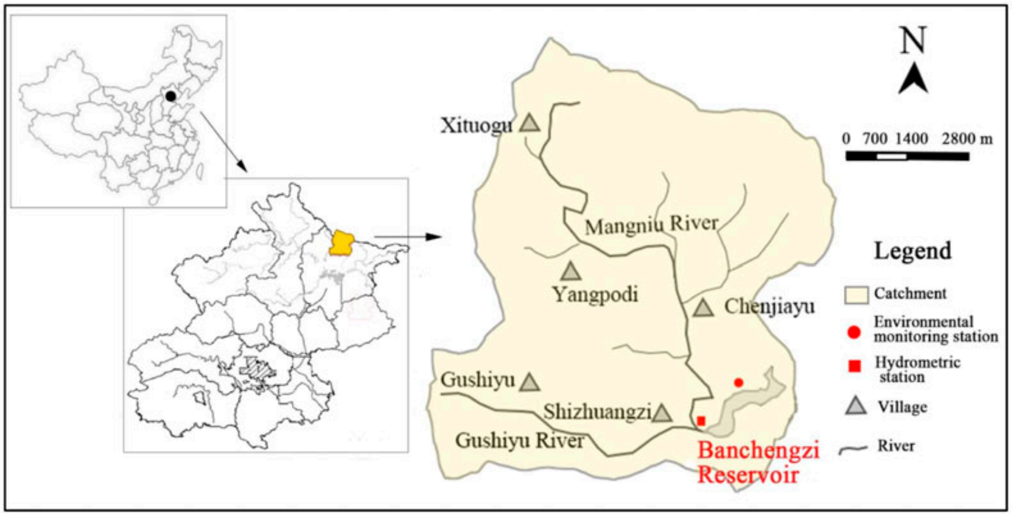


Fig. 1. Geogaphical location and water streams of Banchengzi reservoir catchment.

are five villages in the watershed area, and agriculture is the main human activity in this area.

The water quality and hydro-meteorological parameters of the Banchengzi reservoir were measured and collected by the local Environmental Monitoring Center and the hydrological station of the Banchengzi reservoir, respectively. This study used water quality and hydro-meteorological data collected monthly from 2007 to 2012 except the ice period of the reservoir in winter. These water quality variables include pH, dissolved oxygen (DO), permanganate index (COD_{Mn}), 5-d biological oxygen demand (BOD_5), total nitrogen (TN), ammonium nitrogen (NH_3-N), total phosphorus (TP), and chlorophyll a (Chl a), which were measured according to standard methods (PRC EPA, 2002). The hydro-meteorological variables include maximum daily rainfall, monthly rainfall, maximum daily inflow, monthly inflow, monthly average water storage, and temperature of the reservoir.

To estimate the trophic state of the Banchengzi reservoir, TN, TP, Chl a, and COD_{Mn} were used for the quantitative evaluation of a comprehensive trophic level index TLI (Σ) [19], which was calculated according to the equations and the parameters given in supplementary material.

2.2. Data analysis

Multivariate statistical methods including PCA, CA, and correlation analysis were performed in this study to investigate the structure of the data and to infer more complex relationships between the variables. All statistical tests were performed using the IBM SPSS 20.0 software package.

PCA was used to describe, summarize, and simplify the data-set of monthly water quality variables from 2009 to 2012 (Varimax rotation of the normalized data) by determining a set of uncorrelated orthogonal components that are calculated according to the composition of the data-set and the relationships between the variables. For clarity, loadings >0.6 were discussed as statistically significant. This is a subjective but common value for defining the factors [20,21].

CA (Ward's method of linkage, squared Euclidean distances as a similarity measure) was applied as a hierarchical agglomerative clustering of the water quality data from 2009 to 2012 based on the result of PCA. To identify the effect of hydro-meteorological variables on the water quality of the reservoir, differences between the hydro-meteorological variables of different clusters were examined by Kruskal–Wallis analysis at a 95% confidence interval ($p \leq 0.05$) in this work.

Correlations between water quality and hydro-meteorological variables were analyzed using Spearman correlations in the IBM SPSS 20.0 software package. The statistical significance was evaluated at $p \leq 0.05$.

2.3. Sampling and chemical analysis methods

Besides data collection and the analysis mentioned above, we also collected and analyzed the water samples from the reservoir twice a month from July to September 2013. Water samples from the six sites (Fig. 2), which were located at key points throughout

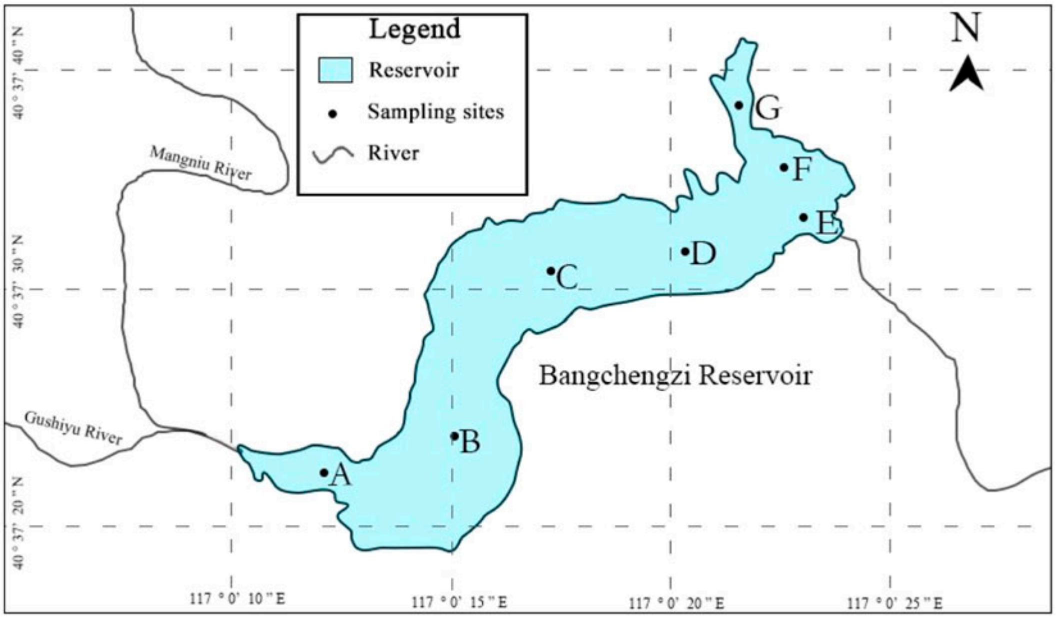


Fig. 2. Map of sampling sites locations in the reservoir. Points A, B, C, D, E, F, and G are 6 sampling sites of this study.

the reservoir, were taken about 30 cm below the water surface. Sampling and preservation were performed according to standard analytical methods for the examination of surface waters (ISO; APHA 1995; EPA 1999), which are routinely applied in water quality monitoring laboratories.

Samples were qualitatively analyzed for eight different physiochemical parameters including pH, DO, COD_{Mn}, TN, TP, NH_3-N, nitrate nitrogen (NO_3-N), Chl a, and specific UV absorbance (SUVA). Triplicate samplings were done at each selected site. The pH and DO were determined immediately at the collection site by a portable pH meter and DO meter, respectively, to minimize errors with time due to biological and chemical reactions between the atmosphere and the sample [22]. Other parameters were analyzed in the laboratory. Unless otherwise specified in the methods, water samples were collected in 3–5 L polyethylene containers, stored in the dark at 4°C, and analyzed within 24 h [10]. The analysis methods of these parameters followed the standards of environmental quality for surface water in China (PRC EPA, 2002), which are briefly presented as follows: COD_{Mn}, acidic (alkaline) potassium permanganate method; TN, method using oxidative digestion with peroxodisulfate; NH_3-N, spectrophotometric method with salicylic acid; NO_3-N, spectrophotometric method; TP, ammonium molybdate spectrophotometric method. Chl a was extracted using acetone and analyzed by a fluorometric method (detection limit 0.01 mg m^{-3}) [17,23]. SUVA values were determined as the ratio of the UV absorbance at 254 nm to the dissolved organic carbon (DOC) concentration. DOC was measured using a carbon analyzer (Shimadzu TOC-5000 A, Japan). UV254 is calculated as the extinction coefficient at 254 nm with a UV–vis spectrophotometer (Shimadzu UV1700, Japan). Chl a, DOC, and UV254 were analyzed after filtration through 0.45 μm PVDF Millipore syringe filters [20].

2.4. EEM spectrum measurement

The water samples from the reservoir were diluted to twofold after being filtered using cellulose acetate fiber filters (Millipore, 0.45 μm fiber Ø) for fluorescence measurements. The organic carbon concentration was less than 5 mg L^{-1}, which reduced the ionic strength influence on fluorescence intensity [24]. The fluorescent properties of the water samples were measured by a spectrofluorometer (F-4500; Hitachi; Tokyo, Japan). The spectra of samples and Milli-Q water (blank EEMs) were recorded at excitation wavelengths from 200 to 400 nm (increments of 10 nm) and emission wavelengths from 250 to 500 nm (increments of 10 nm). The scan speed was 600 nm min^{-1}. The slit width was 5 nm for both excitation and emission. The photomultiplier voltage was set to 400 V [25]. According to the manufacturer's suggested protocols, the spectrophotometer was corrected for excitation and emission. The sample EEMs were obtained by first subtracting the water blank EEM and then correcting for dilution. The relative standard deviation of fluorescence intensity was less than 5% for three replicated measurements of the samples.

To indicate DOM source, three optical indices were used in this study, including fluorescence index (FI), humification index (HIX), and index of recent autochthonous contribution (BIX). FI was calculated as the ratio of the emission intensity at 470 nm to the emission intensity at 520 nm with an excitation wavelength of 370 nm [26]. HIX is the ratio of the integrated area of the emission spectrum from 435 to 480 nm to that from 300 to 345 nm with an excitation at 254 nm [27]. BIX was the ratio of the normalized emission intensity at 380 nm to that at 430 nm with an excitation wavelength of 310 nm [28].

2.5. Nitrogen stable isotope ($\delta^{15}N$) analysis

To measure the nitrogen isotope ($\delta^{15}N$), samples were pretreated as follows [14,29]: Nitrate was first collected on the ion exchange column through an anion resin. Then, 2 M HCl was used to elute the nitrate from the resins. Excess $BaCl_2$ and activated carbon were used to remove SO_4^{2-}, PO_4^{3-}, and DOC. The samples were passed through a cation exchange resin and stored in a 50-ml beaker with stirring. The Cl^- was removed by excess Ag_2O, and the solution was neutralized to pH of 6. The AgCl precipitate was removed by filtration, and the solids were rinsed with distilled water. Finally, the $AgNO_3$ solution was freeze-dried for isotopic analysis. The $\delta^{15}N$ values were determined using an elemental analyzer (Flash EA1112 series, Italy) connected online to an isotope-ratio mass spectrometer (Finnigan MAT ConHo III, Germany) (precision 0.2‰). IAEA-600 (caffeine) was used as an internal standard.

3. Results and discussion

3.1. Assessment of water quality situation and trophic state of Banchengzi reservoir

Annual variation in water quality of the Banchengzi reservoir from 2007 to 2012 is shown in Fig. 3. There was a descending trend in pH and in DO concentration since 2009. As for the organic-related parameters, the concentration of COD_{Mn} increased whereas BOD_5 decreased yearly, indicating increasingly serious organic pollution in the reservoir with poorer biodegradation. Although little change could be found in the annual variation of TN, NH_3-N, and TP, the concentration of TN exceeded the boundary value (<1.0 mg L^{-1}) for the second-class drinking water preservation area of surface water quality of China (GB3838–2002).

As for the trophic state calculated in Table 1, the tropic level indices were all less than 50, which meant that they belonged to the mesotrophic state and meet the standards of the first-grade protection zone of centralized drinking water sources (Table S2). TP is the limiting factor of eutrophication, however, the tropic

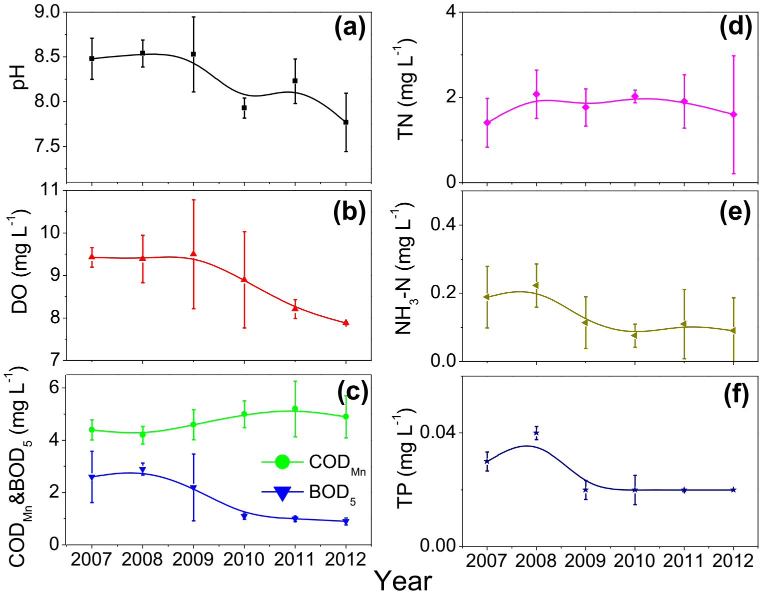


Fig. 3. Annual variation of water quality of Banchengzi reservoir from 2007 to 2012. (a) pH, (b) DO, (c) COD_{Mn}, and BOD_5, (d) TN, (e) NH_3-N, and (f) TP.

Table 1
Annual variations of trophic state of Banchengzi reservoir

	COD_{Mn}		TP		TN		Chl a			
Year	Mean ($mg\ L^{-1}$)	TLI (j)	Mean ($mg\ L^{-1}$)	TLI (j)	Mean ($mg\ L^{-1}$)	TLI (j)	Mean ($\times 10^{-3}\ mg\ L^{-1}$)	TLI (j)	TLI (Σ)	Trophic state
2007	4.1	39	0.021	32	1.41	60	1.73	31	39	Mesotrophic
2008	4.2	39	0.019	30	2.08	67	1.92	32	41	Mesotrophic
2009	4.6	42	0.020	31	1.77	64	2.01	33	41	Mesotrophic
2010	4.8	43	0.020	31	2.03	67	1.97	32	42	Mesotrophic
2011	5.2	45	0.020	31	1.91	65	2.01	33	42	Mesotrophic
2012	5.3	45	0.020	31	1.60	62	1.96	32	42	Mesotrophic

index of TN is greater than 60, which reached the mid-eutrophic state, whereas the TLI of COD_{Mn} increased from 39 to 45. The eutrophication of the Banchengzi reservoir could not be underestimated as the trend of eutrophication had been shown in recent years.

According to the measurements of water quality and the trophic state of the Banchengzi reservoir mentioned above, it is clear that the water quality of the reservoir had deteriorated yearly. This was mainly embodied by the relatively high prevalence of nitrogen pollution, increasingly serious organic pollution, and the trend of eutrophication. Therefore, there is an urgent need for source identification of pollution and effective measurements to control the water quality degradation in this reservoir.

3.2. Identification of potential pollution sources by statistics technique

PCA was used to assess the relationships between the seven water quality variables within the data-set, and principal components (PCs) with eigenvalue >1 were retained. The extracted three PCs are responsible for the data structure; they explain 74.67% of these seven water quality variables as shown in Table 2. PC1 explains 35.68% of the total variance, and has strong loadings of DO, COD_{Mn}, and BOD_5, which relate to organic pollutants. PC2 accounts for 20.77% of the total variance and is explained by pH and TP. PC3 is dominated by two nitrogen pollutant related variables, NH_3-N and TN, and it accounts for 18.22% of total variance. PC1 and PC3 have close relationship with organic pollutant and nitrogen pollutant, respectively, suggesting the need for further analysis. The relationships between the variables along these two dimensions are visualized in Fig. 4.

Hierarchical cluster analysis was performed on these three PCs, and the results show that the data can be grouped into five primary clusters (Fig. 5). The characteristics of each cluster are summarized in Table 3. Cluster one was characterized by an extremely high mean DO concentration ($11.167\ mg\ L^{-1}$) and low mean COD_{Mn} concentration ($4.467\ mg\ L^{-1}$).

Table 2
Varimax rotated principal component matrix of water quality variables

Variable	PC1	PC2	PC3
pH	0.143	**0.846**	0.044
DO	**0.851**	−0.094	0.232
COD_{Mn}	**−0.698**	0.040	0.363
BOD_5	**0.743**	0.557	0.011
NH_3-N	0.033	0.017	**−0.770**
TP	0.108	**−0.644**	0.015
TN	0.024	0.034	**0.704**
% of variance	35.68	20.77	18.22
Cum % of variance	35.68	56.45	74.67

Note: Significant contributions (loadings above 0.6) are marked in bold with underline.

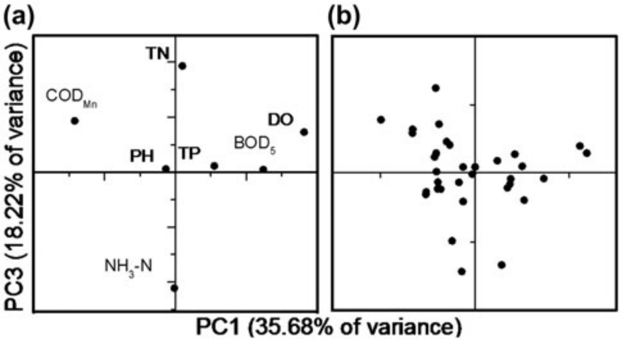


Fig. 4. (a) PCA loading plot of variables along PC1 and PC3, showing the spatial relationship of the variables along these dimensions. (b) Score plot, showing individual data points plotted in coordinate space along PC1 and PC3.

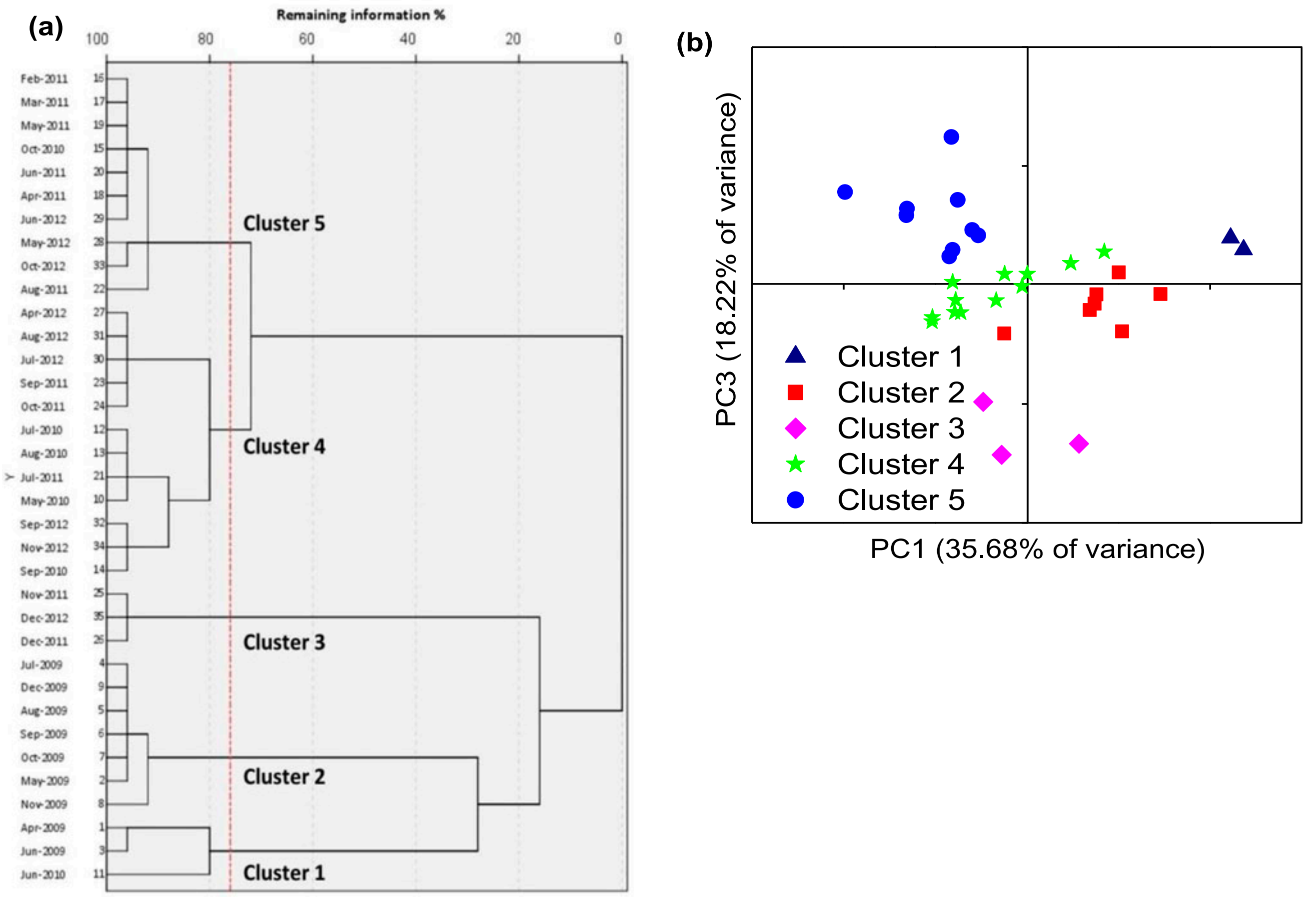


Fig. 5. (a) Hierarchical dendrogram showing the clustering of the monitoring time (linkage method: Ward's method, distance measure: Euclidean). (b) Factor plot of individuals and clusters along PC1 and PC3.

Cluster two also displayed a relatively high mean DO concentration (8.943 mg L^{-1}) and low mean concentration of COD_{Mn} (4.557 mg L^{-1}). In addition, another distinguishing feature of cluster one and cluster two was the BOD/COD ratio (0.463–0.480, respectively), which were much greater than the other three clusters and indicated the more capacity for organic matter in the reservoir to be decomposed by natural microbial activities. Thus, cluster one and cluster two described better water quality status of the reservoir. According to the hierarchical dendrogram in Fig. 5(a), cluster one and cluster two were composed of all the individual data points from 2009 (except only one from the beginning of 2010). It shows that the water quality status of the Banchengzi reservoir was relatively good in 2009, and it became worse in the following three years. The data from these three years were classified in cluster three, cluster four and cluster five. The highest mean concentration of NH_3-N in cluster three indicated that the ammonia nitrogen was the main pollutant in the reservoir during the monitoring time in cluster three. Both cluster four and cluster five describe water quality degradation of the reservoir

Table 3
Results of CA, showing the mean value of each water quality variable in each cluster

	Mean value in cluster				
	1	2	3	4	5
pH	7.873	8.687	7.773	8.003	8.053
DO	**11.167**	**8.943**	8.170	8.179	8.152
COD_{Mn}	**4.467**	**4.557**	4.200	**4.975**	**5.640**
BOD_5	**2.067**	**2.186**	1.867	0.950	0.930
NH_3-N	0.064	0.131	**0.323**	0.061	0.067
TP	0.023	0.019	0.020	0.021	0.020
TN	1.920	1.781	1.097	1.384	**2.545**
BOD/COD ratio	**0.463**	**0.480**	0.188	0.191	0.165

Notes: Defining characteristics for each cluster are highlighted in bold with underline. The unit of the variables is mg L^{-1} except pH.

characterized by low mean concentration of DO, high mean concentration of COD_{Mn}, and low BOD/COD values. Cluster five represented the worst water quality status due to its highest mean concentration of COD_{Mn} (5.640 mg L^{-1}) and TN (2.545 mg L^{-1}).

To extract detailed information about the effect of hydro-meteorological variables on water quality, boxplots of hydro-meteorological variables in clusters and the results of the correlation analysis between water quality and hydro-meteorological variables are shown in Fig. 6 and Table 4, respectively. The lowest monthly average temperature is the distinguishing feature of hydro-meteorological variables during the monitoring time in cluster three, during which time ammonia nitrogen was the main pollutant in the reservoir. Furthermore, the concentration of NH_3-N was negatively correlated with monthly average temperature ($p < 0.05$). Considering the close relationship between microbial activity and temperature, it is reasonable to speculate that the attenuated nitrification during period of low temperature resulted in the increase of NH_3-N concentration in the reservoir.

Monthly rainfall, monthly inflow, and maximum daily rainfall among the five clusters were significantly different ($p < 0.05$) according to Kruskal–Wallis analysis. This indicated that rainfall and inflow had an influence on the water quality of the Banchengzi reservoir. The monthly inflow and maximum daily inflow of cluster four and cluster five (Fig. 6(b) and (d)) were higher than the other three clusters. It seemed that the poorer water quality of these two clusters could be attributed to the large water inflow of the reservoir, which may carry high levels of contaminants. The water quality of cluster five is worse than cluster four, as mentioned above. The difference between these two clusters in hydro-meteorological variables is the increased rainfall in cluster four, which meant that rainwater carried fewer contaminants and that it is not the main cause of pollution. This result is not consistent with nonpoint source pollution, in which pollutants are carried by rainfall-runoff [30,31]. Similar results were also obtained from the correlation analysis (Table 4). The concentration of DO was negatively correlated with the concentration of COD_{Mn} ($p < 0.05$), indicating reduced DO concentrations with increasing organic pollution in the reservoir. There is a significant negative correlation ($p < 0.05$) between DO and monthly inflow, suggesting that the organic pollution became serious as water inflow increased. In contrast, no significant correlation was found between rainfall and water quality ($p > 0.05$), indicating that the rainfall had little effect on the water quality degradation of the Banchengzi reservoir.

On the basis of above statistical analyses, we drew a preliminary conclusion that both the nitrogen and organic pollution in the reservoir could principally be ascribed to exogenous pollution because of the close relationship between water quality and water inflow. The pollutants were more likely to originate from point sources upstream rather than nonpoint sources. Additionally, microbial activities such as nitrification had strong influence on contaminant degradation.

3.3. Determination of pollution sources in Banchengzi reservoir by samples analysis

In this section, we further examined the pollution source in the Banchengzi reservoir by sample analysis, which included spatial variation of water quality, fluorescence spectroscopy, and nitrogen stable isotope ($\delta^{15}N$) analysis.

Fig. 7 presents the spatial variation of water quality parameters in the Banchengzi reservoir. Pollutants might have come from upper streams of the reservoir as higher concentrations of TN and TP were detected near the entrance of reservoir. Similar concentration and spatial distributions between TN and NO_3-N were found in Fig. 7(b) and (d), indicating that nitrate is the main form of nitrogen in reservoir. Sampling site B was the nearest sampling site to the fish cage in the reservoir. The water quality of sampling site B had no significant difference from that of other sampling sites. In addition, the fish cage culture in the reservoir has stopped after 2006 according to the investigation before our study. Therefore, we excluded it as the main cause of water pollution in the reservoir.

The concentrations of Chl a in all sample sites were about 2.0 mg m^{-3}. Chl a is a well-accepted index for phytoplankton abundance and the population of primary producers in an aquatic environment. The contribution of phytoplankton photosynthesis to the organic pollutants in the reservoir was negligible due to the low concentration of Chl a [32,33]. SUVA 254 is generally positively correlated with aromaticity and the molecular weight of the organic matter. The Banchengzi reservoir had lower values of SUVA (~0.8 L m^{-1} mg^{-1}) and low aromatic content, indicating relatively low amounts of primary terrestrial material that were washed from the land to surface water by rain. The source of the organic matter was likely related to autochthonous production or *in situ* transformations [34–36].

EEM spectra were used in this work to identify organic matter composition in the reservoir, which is characterized by the wavelength of excitation/emission (λEx/Em) wavelength pair and the specific

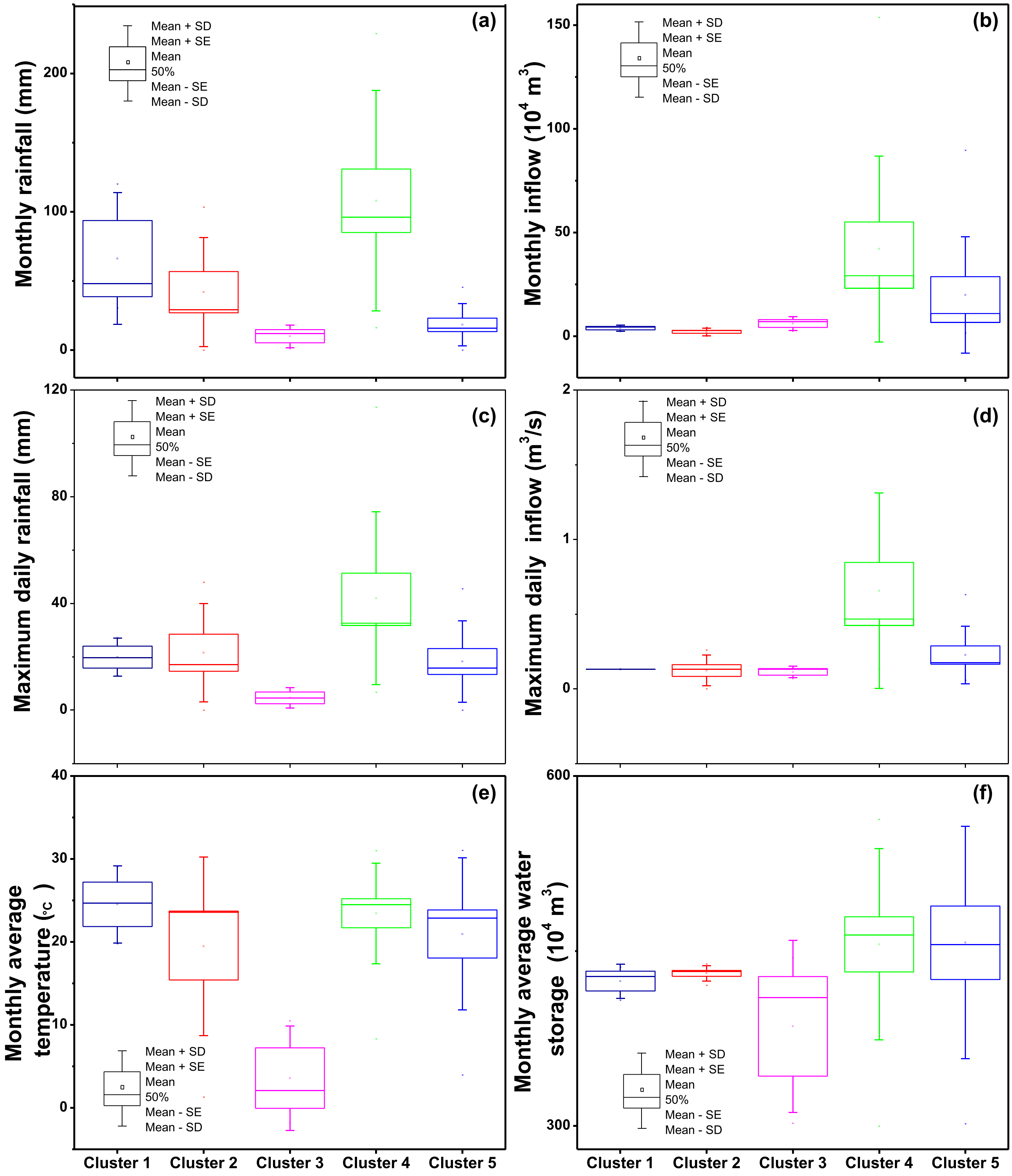


Fig. 6. Boxplot of hydro-meteorological variables including monthly rainfall (a), monthly inflow (b), maximum daily rainfall (c), maximum daily inflow (d), monthly average temperature (e), and monthly average water storage (f) in clusters.

Table 4
Spearman's correlation coefficients between water quality and hydro-meteorological variables

	pH	DO	COD_{Mn}	BOD_5	NH_3-N	TP	TN	Maximum daily rainfall	Monthly rainfall	Maximum daily inflow	Monthly inflow	Monthly average water storage
DO	0.15											
COD_{Mn}	−0.04	$\underline{-0.46}$										
BOD_5	$\underline{0.47}$	$\underline{0.65}$	$\underline{-0.36}$									
NH_3-N	0.20	0.17	−0.07	0.17								
TP	−0.24	0.07	−0.02	−0.11	0.09							
TN	0.11	0.12	0.07	0.14	−0.07	0.02						
Maximum daily rainfall	−0.16	−0.10	−0.13	0.00	−0.40	0.107	0.02					
Monthly rainfall	−0.22	−0.02	−0.16	0.00	$\underline{-0.43}$	0.293	0.13	$\underline{0.94}$				
Maximum daily inflow	−0.30	−0.29	0.07	$\underline{-0.34}$	−0.49	0.146	−0.16	$\underline{0.82}$	$\underline{0.77}$			
Monthly inflow	$\underline{-0.46}$	$\underline{-0.39}$	0.291	$\underline{-0.57}$	$\underline{-0.39}$	0.146	−0.26	$\underline{0.37}$	$\underline{0.36}$	$\underline{0.77}$		
Monthly average water storage	−0.02	−0.16	0.23	−0.19	$\underline{-0.39}$	−0.001	0.00	0.06	0.04	$\underline{0.34}$	$\underline{0.53}$	
Monthly average temperature	0.22	−0.08	−0.04	−0.14	$\underline{-0.39}$	0.010	0.28	$\underline{0.68}$	$\underline{0.72}$	$\underline{0.45}$	$\underline{0.04}$	$\underline{0.03}$

Note: Significant correlation at 95% confidence level (or at $p < 0.05$) is underlined.

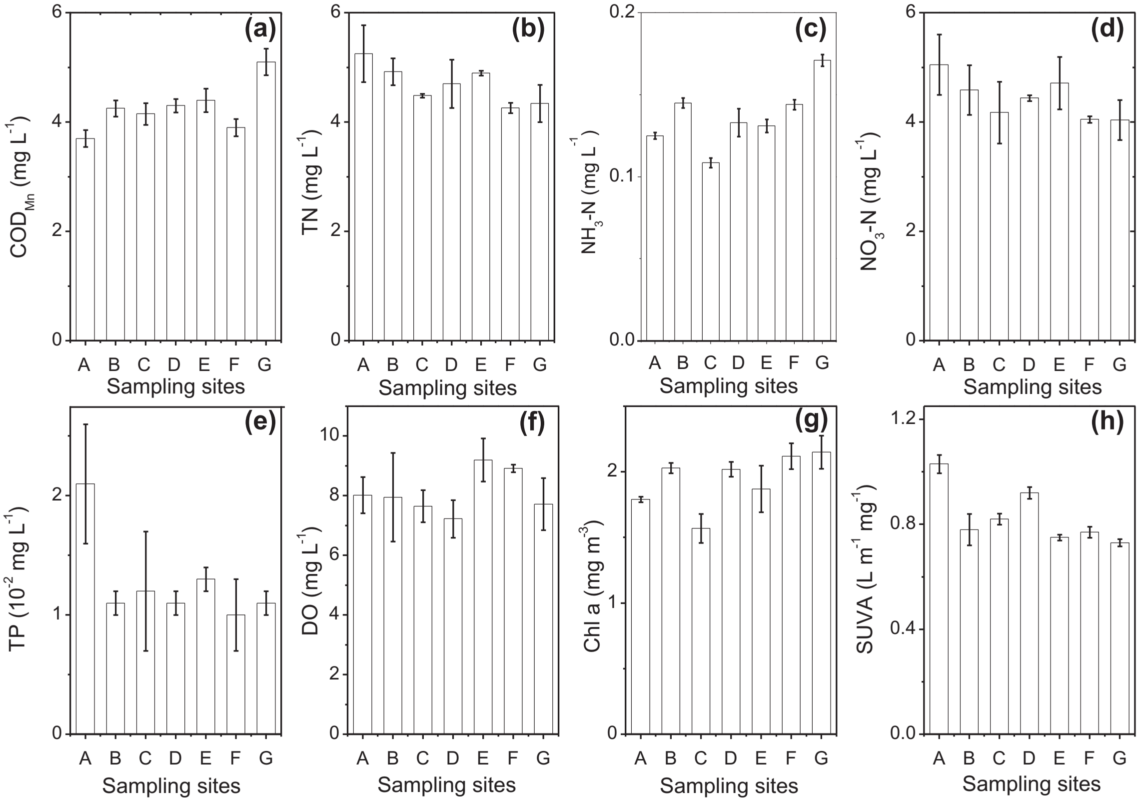
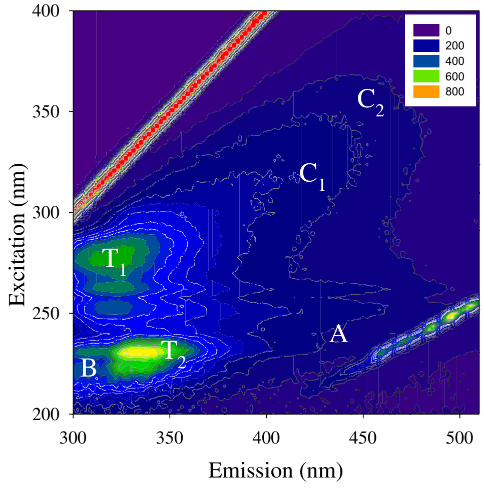


Fig. 7. Spatial variation of water quality parameters in Banchengzi reservoir: COD_{Mn} (a), TN (b), NH_3-N (c), NO_3-N (d), TP (e), DO (f), Chl a (g), and SUVA (h).

fluorescence intensity. According to previous work [24,37,38], there are six key fluorescence peaks commonly observed in freshwater aquatic samples, which have been classified as follows: Peak A–fulvic-like (λEx/Em = 237–260/400–500 nm); Peak C1–fulvic-like (λEx/Em = 320–340/410–430 nm); Peak C2–humic-like (λEx/Em = 370–390/460–480 nm); Peak B–tyrosine-like (λEx/Em = 225–237/309–321 nm); Peak T1–tryptophan-like (λEx/Em = 275/340 nm); and Peak T2–tryptophan-like (λEx/Em = 225–237/340–381 nm). According to the EEM spectra of the DOM in the reservoir (Fig. 8), three peaks, including Peak B, Peak T1, and Peak T2 were distinctly observed, indicating that the DOM is dominated by tyrosine-like and tryptophan-like organic matter. These organic matter are mainly detected in sewage-derived DOM originating from microbial activity [39]. Peaks C1, C2, and A were weak in the EEM spectra in this study, which is markedly different compared to spectra of clean reservoirs and rivers, where fulvic-like and humic-like organic matter derived from plant material predominate [40]. In addition, the optical index of the water samples from Banchengzi reservoir, including FI, HIX, and BIX, were calculated and shown in Fig. 8. A higher FI



Optical index	FI	HIX	BIX
Mean value	1.83	0.353	1.47

Fig. 8. EEM fluorescence spectra and optical index of DOM in Banchengzi reservoir, where B = tyrosine-like, T_1 and T_2 = tryptophan-like, A and C_1 = fulvic-like, C_2 = humic-like fluorescence.

value (1.83) indicated microbial and aquatic DOM sources in the reservoir, including soluble microbial products (SMP), rather than terrestrial and soil sources [28,41]. Moreover, low values of HIX (<3) and high values of BIX (>1) correspond to a predominantly autochthonous origin of DOM and to the presence of organic matter freshly released into water, rather than to strongly humified organic material from natural sources [28,41]. These results further demonstrate that the Banchengzi reservoir had been polluted by anthropogenic sources and that the organic pollution was most likely from point source pollution in the upper reaches. Biodegradable organic pollutants from sewage were degraded to form SMP by aerobic microorganisms in the aquatic environment.

Nitrogen stable isotope (δ^{15}N) analysis was applied to identify the origin of nitrogen pollutants in the reservoir. The results showed that the δ^{15}N value of the water samples from the Banchengzi reservoir was 9.53 ± 0.5‰ ($n = 5$). According to previous work, δ^{15}N value of natural soil is 0.0 ± 4.0‰, whereas a higher δ^{15}N value was obtained if the soil or water was polluted by inorganic fertilizer ($\delta^{15}N = 4.0 \pm 2.0$‰), livestock excreta ($\delta^{15}N = 7.0 \pm 3.2$‰), or domestic wastes or sewage (δ^{15}N value may range from 10 to 25‰) [18]. The relatively high δ^{15}N value of the water samples in the reservoir indicated that pollutants from natural soil or inorganic fertilizer typically carried by rainwater had little contribution to the nitrogen pollution in the Banchengzi reservoir. This indicates that non-point agriculture pollution is not the major source of nitrogen pollution in the reservoir. Nitrogen pollutants were most likely from to livestock excreta and domestic waste or sewage, which came from the villages in the watershed area and were brought into the reservoir by streams.

4. Conclusions and solutions

In this work, we present a combination of statistical analyses of water quality data, hydro-meteorological data, and chemical analyses of water samples to assess the water quality and to identify the sources of pollution in the Banchengzi reservoir. The results showed that:

(1) There was water quality deterioration and a trend of eutrophication in the Banchengzi reservoir. The main pollutants were nitrogen and organic matter.
(2) Organic and nitrogen contaminants in the reservoir were principally derived from anthropogenic point source pollution in its upstream areas, including domestic sewage leakage and livestock excreta from the villages.
(3) The biodegradable organic pollutants were degraded to form SMP by aerobic microorganisms, and the nitrogen pollutants were mostly transformed to nitrate by nitrification. These pollutants finally accumulated in the reservoir and caused water quality deterioration.

Based on the results of the analysis above, we proposed three corresponding measures to improve water quality and to protect the reservoir:

(1) A detailed investigation of the domestic sewage and livestock waste discharge should be performed to identify potential wastewater leakage from villages in the upstream areas.
(2) It is necessary to upgrade the rural sewage treatment facilities and to establish more strict emission standards to reduce pollutant discharge.
(3) Ecological restoration of the reservoir catchment, such as the construction of an artificial wetland in the upper river, will effectively contribute to contaminant degradation in the aquatic environment.

Supplementary material

The supplementary material for this paper is available online at http://dx.doi.org.10.1080/19443994.2016.1162205.

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