

Temporal variation of water quality at the inlet of a reservoir in the Northeastern China

Yanhua Liu, Mengli Zhuang, Chengjiu Guo, Yuhua Jia*

College of Water Conservancy, Shenyang Agricultural University, Shenyang 110866, China; emails: jiayuhua@syau.edu.cn (Y. Jia), 2005500019@syau.edu.cn (Y. Liu), menglizhuang@syau.edu.cn (M. Zhuang), chengjiuguo11@syau.edu.cn (C. Guo)

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ABSTRACT

The characteristics of water quality variation from 2007 to 2018 were analyzed and evaluated with the aid of monitoring data at an inlet of Baishi Reservoir. Six indicators including 5-d biochemical oxygen demand (BOD_5), permanganate index of chemical oxygen demand (COD_{Mn}), dissolved oxygen (DO), total phosphorus (TP), total nitrogen (TN) and ammonia nitrogen (NH_3-N) were selected as water quality parameters. The Mann–Kendall trend test analysis indicated that water pollution was deteriorating in recent years. In 2018, some water quality indicators reached the highest value of the studied period. With the change of time, COD_{Mn} , TP and TN showed a significant linear increase trend ($p < 0.01$), and the increasing trend of TN was extremely significant ($p < 0.01$), indicating that TN was the most prominent pollutant. The correlation analysis results showed that the more serious the water pollution, the lower DO content, and the higher COD_{Mn} and BOD_5 demand. These results are conducive to providing scientific support for the sustainable protection of water quality in the reservoirs.

Keywords: Water quality; Phosphorus; Nitrogen; Reservoir; Water pollution

1. Introduction

Nowadays, public awareness on the evaluation, protection and restoration of water quality has raised to a great extent. However, water quality deterioration is still a challenge to the high-quality development of the economy and society. For example, according to the level of total phosphorus (TP) and chlorophyll-a in the upstream region of the Keban Dam Reservoir in Turkey, Varol [1] considered that the reservoir water was in the eutrophic status. In Dongting Lake, China, Geng et al. [2] found that concentrations of total nitrogen (TN) and the 5-d biochemical oxygen demand (BOD_5) increased significantly in the period of 1991–2018. In view of the great threat of nutrient pollution to surface water quality in Texas, the USA, Kuwayama et al. [3] considered that water quality enhancement relative to human

uses stagnated in the past three decades. These researches support the strategy of controlling external nutrient loading for maintaining the multiple functions of the water body.

Reservoirs are a kind of hydraulic engineering with the dam constructed in the river bed, which provide water resources for the beneficial purposes of agricultural irrigation, urban municipal water utilization, and drinking-water supply [4]. To date, China has established more than 86,852 reservoirs [4]. Therefore, much attention has been paid to the impacts of engineering on reservoir water quality. For example, in the Xiaolangdi Reservoir, Dong et al. [5] found that the sediment resuspension caused by water conservancy projects was responsible for the increase of concentrations and bioavailability of heavy metals. In Danjiangkou Reservoir, Zhao et al. [6] found

* Corresponding author.

that water quality after the diversion project did not significantly differ from the status before water intake. Water quality monitoring facilitates comprehension of water status and variation trends. It is treated as an essential and routine campaign for the watershed managers and decision-makers. Since water quality attributes affect its suitability for human consumption and ecosystem health, and the coupling of anthropogenic influences and natural environment increases the risk of water contamination, a holistic understanding of water quality relies on the long-term, standardized measurement and observation of the chemical, physical and biological attributes of water [7]. Although plenty of information was acquired on water quality characteristics involving seasonal variation [8], spatial variability [9], major pollutants identification [10] and methodological scheme [11,12], etc., the knowledge on long-term water quality variation remains limited, especially for the reservoir in the northeast provinces of China.

Baishi Reservoir is a large water conservancy project built-in 2000 in Liaoning Province. It undertakes the main task of supplying water to three big cities of the province every year. Thus, water quality monitoring in the reservoir is closely related to the access to safe drinking water [13], rational utilization and protection of water resources [14] and the sustainable development of the Daling River Basin. In 2001–2003, the water quality of inflowing rivers was affected by BOD_5 , ammonia nitrogen (NH_3-N), TN, chemical oxygen demand (COD_{Cr}) and other pollutants, and water quality in Daling River and Liangshui River was determined as class V according to the environmental quality standards for surface water of China (No. GB3838-2002) [15]. Li et al. [16] considered that the urgent task of reservoir management was to adopt measures to recover water quality. After years of pollution control and ecological protection, water quality in the reservoir seemed to be improved. In the periods of 2011–2015, the water quality was between class II and class III [17]. If the indicator of TN was ignored, it could be class III in 2014 [18]. This literature roughly described the improvement of water quality in the reservoir. However, they were based on the differences in observational time, sampling location and monitoring indicators. To accurately delineate the variation process of water quality in the reservoir, long-term research on the consistent observational section is needed.

Based on the above considerations, this paper used the water quality data including three oxygenated indicators (permanganate index of chemical oxygen demand (COD_{Mn}), BOD_5 and dissolved oxygen (DO)) and three nutritional indicators (TP, TN, and NH_3-N), which were collected at the inlet of Baishi Reservoir between 2007 and 2018, to analyze and evaluate the status of water quality and reveal the dynamic characteristics of water quality changes in the reservoir. The results are expected to be conducive to providing scientific support for the sustainable protection of water quality in the reservoir.

2. Material and methods

2.1. Study area

The Baishi Reservoir ($41^{\circ}40'44'' - 41.67889^{\circ}$ N, $121^{\circ}00'17'' - 121.00472^{\circ}$ E) is in the mainstream of Daling River in the

northeast China's Liaoning Province. The reservoir began to construct in May 1995, performed the closure in September 1997, carried out the impoundment in September 1999, completed the main project in September 2000, and hooked up to the power grid in April 2001. The water body has a surface area of 80 km². The total storage capacity is 1.645 billion m³, and the normal water storage is 1 billion m³. Every spring, thousands of white swans berth on the reservoir on their way to migrate to the north. In March 2009, the population of white swans amounted to 1100, making up 10% of its number in China.

Baishi Reservoir plays multiple roles in the development of the regional economy. It serves to control floods and supply water for irrigation, thus increase grain production in the area. Meanwhile, it constitutes the main source of urban water use, covering three big cities including Jingzhou, Fuxin and Chaoyang in Liaoning Province. Besides, the reservoir has functions of power generation and fishery promotion. The aerial map of Baishi Reservoir is shown in Fig. 1, which can also be found in Cheng et al. [13] and Chen et al. [19].

2.2. Data sources and description

The data used in this study were observed at the monitoring section of Zhangjiying, which is one of the water quality monitoring points of the Daling River basin. The Zhangjiying section is located in Beipiao city and is an inlet of the Baishi Reservoir. In general, the reservoir inlet is in the first line of defense against potential contaminants and the deterioration of water quality [20]. The reservoir inlet is a key position to reflect the possible or ongoing contamination as well as the performance of environmental controls. The reservoir inlet has a close relationship with the external environment, which might export pollutants frequently into the water body. Thus, the significance of water quality at the reservoir inlet is more preferential than that at other positions.

Based on environmental quality standards for surface water of China (No. GB3838-2002) [15], the water quality in the Zhangjiying section exceeded class V in 2005, belonged to class IV in 2010, and the management target in 2015 was class III. In the periods of 2007–2014, 22 indicators were measured, and the number increased to 37 since 2014. Allowing for the necessity of the research, in this study we only used the data of 6 indicators from July to October between 2007 and 2018. Such a choice would provide adequate information on the reservoir water quality status. The cases in the example were Liu et al. [21], Mi et al. [22], Yue et al. [23] and Li et al. [16], in which the number of selected indicators were 3 (DO, COD_{Mn} and NH_3-N), 4 (DO, COD, TP and NH_3-N), 5 (COD_{Mn} , BOD_5 , NH_3-N , TN and TP) and 5 (DO, COD_{Mn} , COD, BOD_5 and NH_3-N), respectively. The present literature showed that the selection of several important indicators was more efficient and effective in analyzing the causes of pollution and formulating measures of water quality improvement.

Six water quality indicators, COD_{Mn} , BOD_5 , DO, TP, NH_3-N and TN, were selected in this research. COD_{Mn} uses potassium permanganate to determine the consumption of oxidants in the treatment of water samples, thus indicating the degree of water pollution. The higher the oxidant consumption, the more serious the water pollution. BOD_5 is a surrogate of the degree of organic pollution of water.

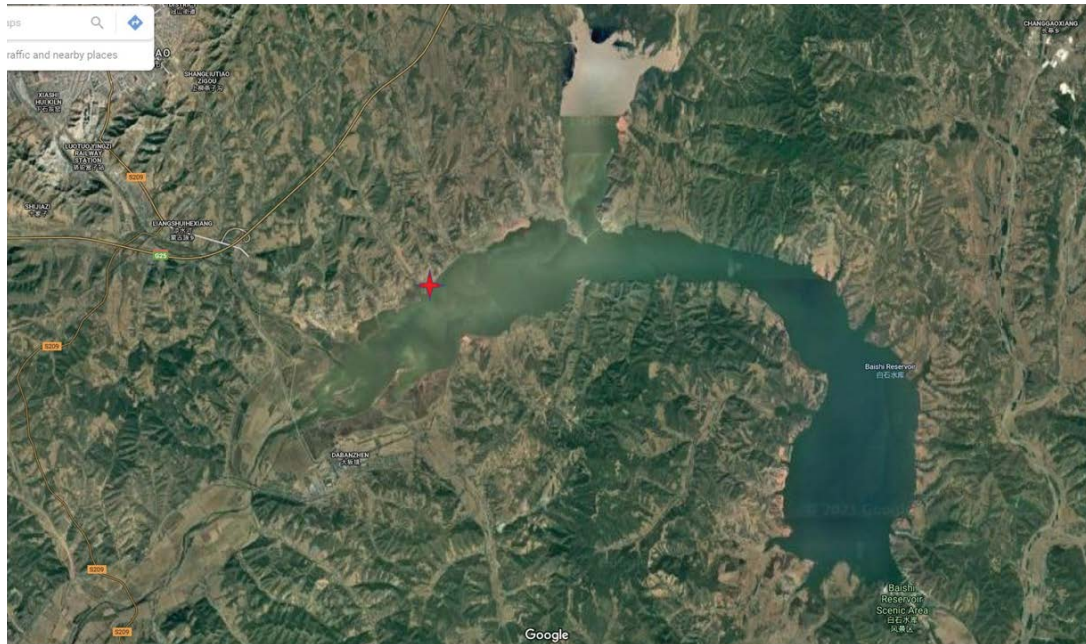


Fig. 1. The aerial view of Baishi Reservoir in Liaoning Province, China. The observational section, which is located in Beipiao city and belongs to the reservoir inlet, is marked as a red cross symbol on the map.

It refers to the amount of dissolved oxygen demanded by aerobic biological organisms, which decompose organic material presented in each water sample during 5 d of incubation at 20°C. The decomposition of organic matter in water needs to consume a certain amount of DO. The recovery of DO can measure the self-purification ability of water. Therefore, a high value of DO generally implies a relatively fast rhythm of consumption and recovery, as well as a strong self-purification capacity of the water body. Phosphorus enrichment in water is one of the major reasons for lake eutrophication [24]. TP is one of the important indicators to reflect the degree of organic pollution in water. Excessive phosphorus content in water will induce a booming growth of algae, increase oxygen consumption, and disturb the ecosystem balance of the water body. TN refers to the total amount of organic nitrogen and inorganic nitrogen in various states and is determined by the alkaline potassium persulfate oxidation–UV spectrophotometric method. In general, this pollution index keeps being effective for a long time. NH₃–N in the water presents in the form of NH₃ and NH₄⁺. The appropriate concentration of ammonia nitrogen can promote the growth of plants, while the excessive concentration will accelerate the growth of plants, thus leads to eutrophication and a serious shortage of oxygen in the water.

2.3. Statistic methods

Kolmogorov–Smirnov test was used to check whether the data conform to normal distribution. One-way analysis of variance was used to preliminarily judge whether significant differences of water quality occurred among the different years. If the difference was significant, Duncan’s multiple comparisons was used to further determine the inter-annual difference at the significance level of $p < 0.05$.

Linear fitting and Pearson correlation analysis was also employed. The main statistical analysis was completed by IBM SPSS Statistics 25.0 and Microsoft Excel software.

The Mann–Kendall test was used to determine the variation trend of water quality over lengthy periods. Mann–Kendall trend analysis is a non-parametric method to detect the variation trend of time series, its statistic S is defined as:

$$S = \sum_{k=1}^{n-1} \sum_{j=k+1}^n \text{sgn}(x_j - x_k) \tag{1}$$

where n is the length of time series, x_i and x_k are the corresponding data of time series, sgn is a sign function. Under the condition of the null hypothesis that the data has no change trend, S approximately obeys the normal distribution. Its mathematical expectation is 0, and its variance is:

$$\text{var}(S) = \frac{n(n-1)(2n+5) - \sum_{i=1}^n t_i(i-1)(2i+5)}{18} \tag{2}$$

where n is the number of associated groups, and t_i is the number of non-missed values in group i . The standardized test statistic Z is calculated by the following formula:

$$Z = \begin{cases} \frac{S-1}{\sqrt{\text{var}(S)}}, & S > 0 \\ 0, & S = 0 \\ \frac{S+1}{\sqrt{\text{var}(S)}}, & S < 0 \end{cases} \tag{3}$$

The positive value of Z indicates an upward trend and vice versa.

3. Results

3.1. Differences in water quality among the years 2007–2018

Based on the analysis of variance, the results of Duncan's multiple comparisons of water quality among different years ($p < 0.05$) are shown in Fig. 2.

At the Zhangjiying section of the reservoir, COD_{Mn} were 2.8, 2.8 and 2.6 mg/L in 2011, 2012 and 2014, respectively, and no significant differences occurred among the 3 y. However, they were significantly lower than those observed in other years. The COD_{Mn} in 2018 reached 6.2 mg/L, which was not significantly different from those in 2017 and 2016, but significantly higher than those observed in other years. BOD_5 amounted to the peak of 3.74 mg/L in 2016, which was significantly higher than those observed from 2007 to 2014 and in 2018. No significant differences were found among the periods of 2015–2017. The DO achieved the maximum (8.39 mg/L) in 2018, significantly higher than those from 2014 to 2017. Meanwhile, no significant differences were observed for DO over the periods of 2007–2013. From 2007 to 2018, there were no significant changes for TP. The TP varied from 0.02 to 0.04 mg/L between 2007 and 2014,

increased from 2015 to 2018, and reached the peak value of 0.19 mg/L in 2018. However, variance analysis for TP did not reveal significant differences among the 12 y. In 2009, the TN reached the lowest value (1.2 mg/L) in the whole study period. It fell within the range of 1.9–5.9 mg/L in other years, which rose above an acceptable level. In 2018, the TP reached the maximum of 5.9 mg/L, which was significantly higher than those of 2007, 2008, 2009 and 2011. The NH_3-N reached a peak value of 0.45 mg/L in 2016, which was not significantly different from those measured in 2007, 2018, 2009 and 2015. In 2015 and 2016, the NH_3-N was significantly higher than that in 2012, when the lowest value (0.06 mg/L) in the study period was observed.

3.2. Variation trend of water quality over the monitoring periods

The change of water quality with time was analyzed by using the Mann–Kendall method (Table 1). A positive statistic represents an upward trend, while a negative statistic represents a downward trend. At the $p < 0.05$ level, COD_{Mn} and TP were on the rise. At the $p < 0.01$ level, TN showed an upward trend. Although DO and NH_3-N

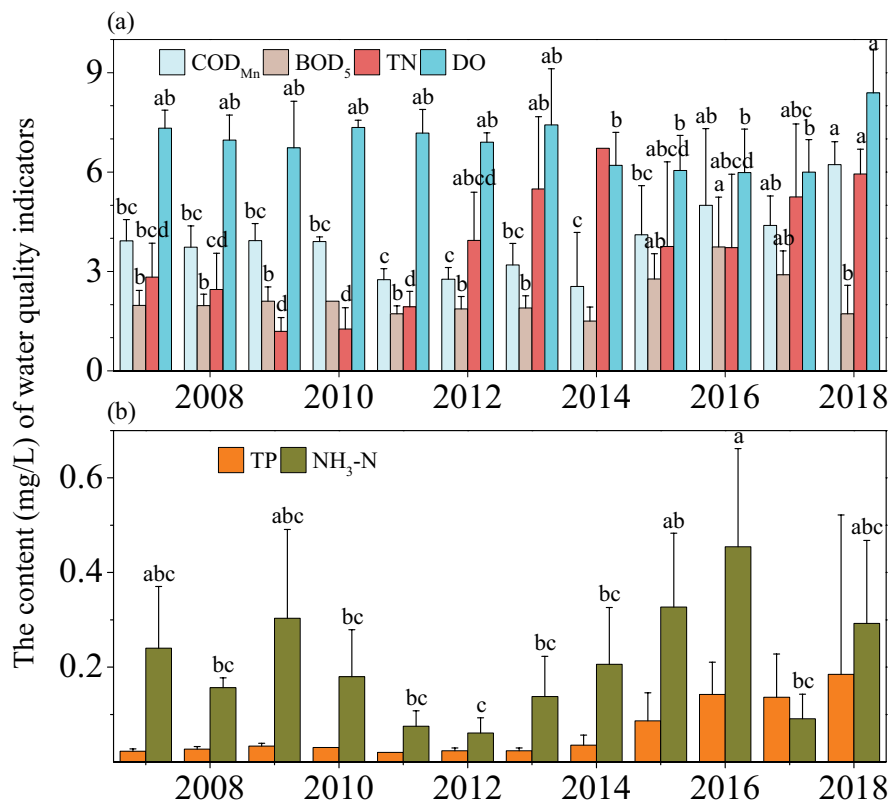


Fig. 2. Duncan's multiple comparisons of water quality indicators among the observational years 2007–2018. The symbols COD_{Mn} , BOD_5 , TN, DO, TP and NH_3-N represent permanganate index of chemical oxygen demand, the 5-d biochemical oxygen demand index of chemical oxygen demand, total nitrogen, dissolved oxygen, total phosphorus, and ammonia nitrogen, respectively. The letters that topped the bars stand for the significance level of differences ($p < 0.05$). The multiple comparisons ignored the values of BOD_5 in 2010 and TN in 2014, since only one value of BOD_5 and TN were acquired from July to October in 2010 and 2014, respectively. Additionally, the bars of TP are not marked by letters due to the result of no significant differences among the years.

Table 1
The Mann–Kendall trend analysis of water quality index

Mann–Kendall test parameters	COD _{Mn}	BOD ₅	DO	TP	NH ₃ –N	TN
Statistic (S)	636.00	395.00	–43.00	557.00	–160.00	780.00
Variance	70,151.42	83,859.10	90,736.16	78,023.65	87,946.23	63,189.18
<i>p</i> -value	0.017	0.174	0.889	0.047	0.592	0.002
Sen's slope	0.032	0.011	–0.002	0.0009	–0.0008	0.07
Kendall's tau	0.31	0.19	–0.02	0.30	–0.08	0.39

showed a downward trend, the results were not significant at the level of 0.01 or 0.05. The Kendall correlation coefficient was consistent with these results. In this study, only the data from July to October each year were used. Due to the inconsistency of time interval, the results of Sen's slope were not specifically explained here.

The relationship between water quality and observational years was linearly fitted, and the results are shown in Fig. 3. The changes of COD_{Mn}, TP and TN showed a significant linear increase with time ($p < 0.01$), and the annual increase could explain 17%, 16% and 22% of the variability, respectively. No such significant linear relationship occurred for the indicators of DO, BOD₅ and NH₃–N. The results of trend analysis were further verified by the linear fitting method, in which the upward trend of TN was extremely significant ($p < 0.01$), and the determination coefficient of its linear equation was the highest ($R^2 = 22\%$). These results indicated that TN was the most prominent pollutant at the inlet of Baishi Reservoir.

3.3. Pearson correlation among the indicators of water quality

Most correlation coefficients were significant at the level of 0.01 or 0.05. There was a negative correlation between COD_{Mn} and TN, but the correlation coefficient was not significant as showed in Table 2. Xia et al. [25] evaluated the water quality of Taihu Lake and found that there was an insignificant negative correlation between COD_{Mn} and TN. Sheng et al. [26] studied the water quality change of Xin'anjiang Reservoir from 2003 to 2012 and found that there was an insignificant positive correlation between COD_{Mn} and TN. In this study, there was a negative correlation between COD_{Mn} and DO, which was consistent with the results in Xia et al. [25] and Deng et al. [27], and similar to the results of Sheng et al. [26] and Zhu et al. [28]. There was a significant negative correlation between BOD₅ and DO, which was consistent with the calculation results of Deng et al. [27] and Zhu et al. [28]. The correlation analysis for the above indicators confirmed that the more serious the water pollution, the lower the DO, and the higher the indicators of COD_{Mn} and BOD₅. This study also showed a significant positive correlation between TP and NH₃–N, which was consistent with the results in Sheng et al. [26].

4. Discussion

Compared with the average value of Lin et al. [29], which reported the COD_{Mn} of surface water at 338 control sections from 2008 to 2013, the COD_{Mn} in this study only exceeded

the average level in 2018. The interannual change of COD_{Mn} indicated that the pollution at the inlet of Baishi Reservoir was weak in 2011, 2012 and 2014, while the water quality worsened in 2016, 2017 and 2018. The COD_{Mn} dropped from 5.0 mg/L in 2016 to 4.4 mg/L in 2017, indicating that relevant controlling measures around the reservoir had improved water quality for a short time.

In the same reservoir, Luo [30] found that COD_{Mn} and NH₃–N showed a decreasing trend based on the data of three monitoring sections: the inlet, the center, and the dam front, from 2003 to 2013. The 2006–2013 results of dam front in Xia and Zhang [14] showed that the COD_{Mn} index had an extremely significant decrease trend ($p < 0.01$), TP had a significant increase trend ($p < 0.1$) in the non-flood season, and the TN had an extremely significant increase trend in both the whole year and the non-flood season. The COD_{Mn} index, TP, and TN all presented an upward trend from 2007 to 2018. The results in this study were not completely consistent with those in Luo [30] and Xia and Zhang [14]. However, the three results indicated that the COD_{Mn} at the inlet of Baishi Reservoir presented an upward trend and mainly occurred after 2013.

According to the significance level of the trend analysis and the determination coefficients of the linear fitting equations, the most prominent pollutant at the inlet of Baishi Reservoir during the study period was TN. Guo et al. [31] found that the average concentration of TN in the reservoir in October 2013 was 1.80 ± 0.08 mg/L, and there was no significant difference in the four sections: the upstream, middle upstream, middle downstream and lower downstream. However, in this study, the TN concentration at the inlet during the same period was 5.5 mg/L. Results of carbon and nitrogen stable isotopes in Guo et al. [31] confirmed that the effects of land-orientated organic matter on the water body of Baishi Reservoir gradually weakened from upstream to downstream. These results showed that TN presented a great difference between the inlet and the monitoring sections in the middle of the reservoir, so the long-term positioning observation could not be ignored and should persist in the future.

The NH₃–N in 2015 and 2016 were significantly higher than that in 2012 when NH₃–N reached the lowest value (0.06 mg/L) in the observational period. In contrast, Chen et al. [11] found that in 2012, due to the impact of a 50 y flood, the NH₃–N in Baishi Reservoir, which was not decomposed by the current flow, quickly reached the intake of Fuxin, and the concentration reached 0.58 mg/L. This result can be explained from two aspects. Firstly, the pollutant control effort around the reservoir inlet performed well. Secondly,

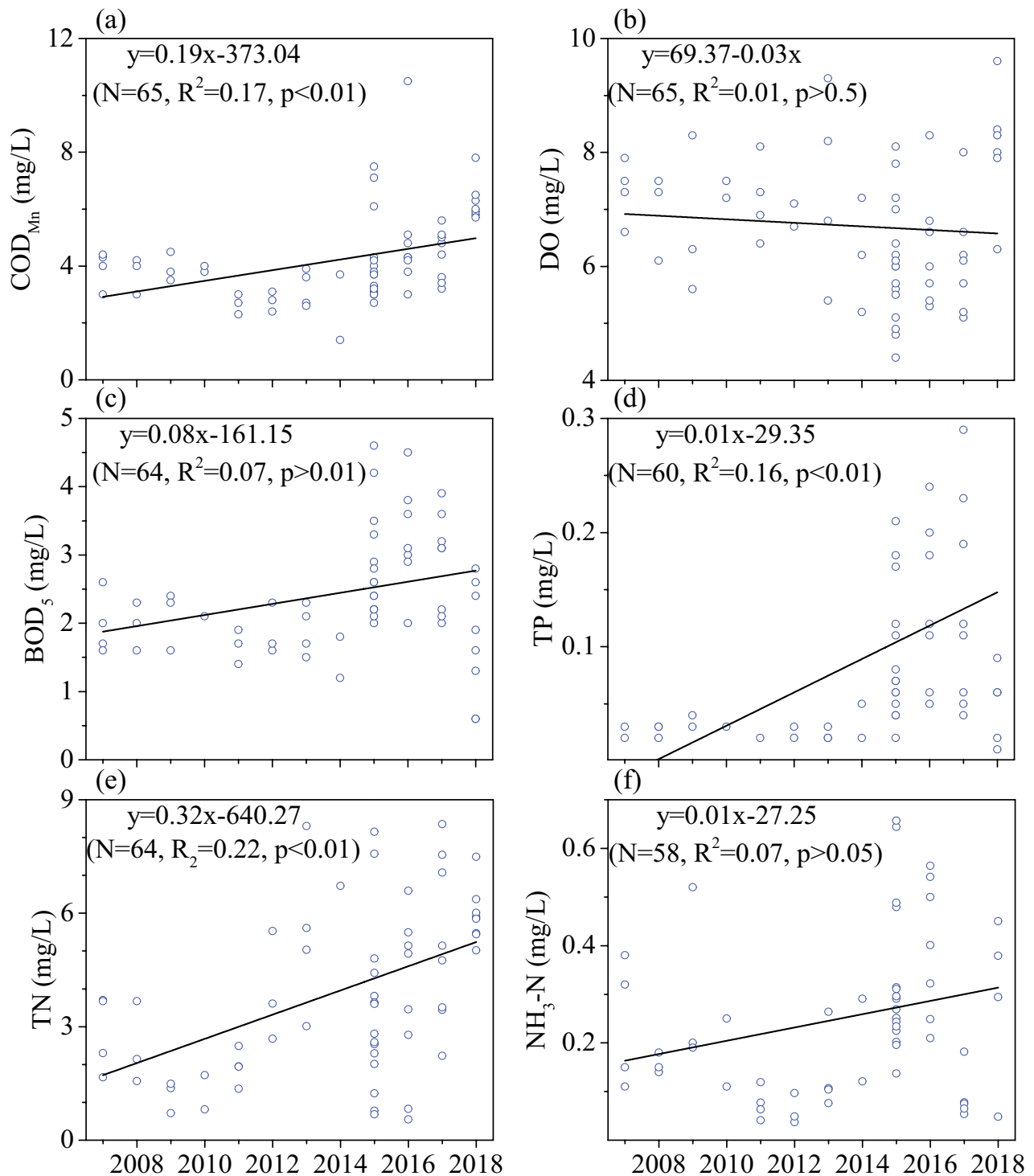


Fig. 3. The linear fitting of the relationship between the values of water quality indicators and the observational years. Y-axis in Fig. 3a–f are COD_{Mn}, DO, BOD₅, TP, TN and ammonia nitrogen (NH₃-N), respectively.

the distance between the Zhangjiying section and the Fuxin inlet was so far that the contribution of NH₃-N to the former was small. In this study, although NH₃-N was as high as 0.45 mg/L in 2016, its concentration reduced to 0.09 mg/L in 2017. This result reflected the strong ability of NH₃-N digestion and water self-purification.

The analysis results of 6 water quality indicators in this study suggested that the environmental pollution at the inlet of the Baishi Reservoir raised in recent years. The serious non-point source pollution and soil erosion upstream caused the increase of TN in the reservoir, and water quality was incapable of enhancement for a long time. When TN kept

Table 2
The Pearson correlation coefficients between water quality indexes

	BOD ₅	TN	TP	NH ₃ -N	DO
Pearson correlation coefficient					
COD _{Mn}	0.56**	-0.10	0.29*	0.36**	-0.04
BOD ₅		-0.31*	0.35**	0.33*	-0.44**
TN			0.03	-0.13	0.42**
TP				0.39**	0.18
NH ₃ -N					-0.24

Note: ** and * in the upper right corner of the number represent significance levels of 0.01 and 0.05.

high contents, it is easy for microorganisms to multiply, for plankton to grow vigorously, and for the reservoir to stay in the eutrophication state. The trend analysis showed that TP was on the rise, and the increase of TP was closely related to the collective discharge of domestic sewage and the pollutant release of bottom sediment. The results show that urban sewage treatment needs to be improved urgently, and it is necessary to dredge the sediment in the reservoir area [22,32,33]. Therefore, it is essential to take effective measures of pollution control and protect the ecological environment to improve the water quality of the reservoir and meet the requirements of drinking water.

5. Conclusions

Based on the analysis results of 6 water quality indicators at the inlet of Baishi Reservoir from 2007 to 2018, this study mainly obtained the following conclusions: Firstly, the pollution around the inlet of Baishi Reservoir was weak in 2011, 2012 and 2014, while the water pollution aggravated in 2016, 2017 and 2018. In 2018, some water quality indicators reached the maximum of the study periods, including COD_{Mn} (6.2 mg/L), DO (8.39 mg/L), TP (0.19 mg/L) and TN (5.9 mg/L). Secondly, COD_{Mn}, TP and TN showed a significant increase trend ($p < 0.01$). The results of linear fitting further verified the trend analysis, in which the rising trend of TN was extremely significant ($p < 0.01$), and the determination coefficient of the linear equation was the highest ($R^2 = 22\%$). This result indicated that TN was the most prominent pollutant. Besides, the severe status of water pollution corresponded to the low level of DO and high values of COD_{Mn} and BOD₅. Finally, it was essential to take effective measures to control pollution and protect the ecological environment to ensure the water quality of the reservoir.

Conflict of interest

We all declare that we have no conflict of interest in this paper.

Data availability statement

The data that support the findings of this study are available from the authors upon reasonable request.

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