The Eutrophication-related Index of Drinking Water Sources Based on the Oxidation-Reduction Potential

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Eutrophication caused by excessive nitrogen and phosphorus is an important factor affecting water quality in drinking water sources. Convenient monitoring of eutrophication in water bodies can reduce the use of pesticides and reduce energy consumption, helping to promote ecological and economic development. This study examined the relationship between water eutrophication and the oxidation-reduction potential (ORP). The results showed that various parameters related to eutrophication, such as ammonia nitrogen, total nitrogen, total phosphorus, chlorophyll-a, and cyanobacteria, had correlations with ORP. There is a close relationship between eutrophication and the concentration of cyanobacteria. When cyanobacteria blooms occur in the drinking water source, it may contaminate the drinking water. Because the conventional eutrophication index does not include the concentration of cyanobacteria, principal component analysis (PCA) was utilized to comprehensively analyze these eutrophication-related parameters and obtain the eutrophication-related index, with the cumulative contribution of principal components reaching 81.8%. Different mathematical methods such as neural network model and mathematical fitting were used to study the relationship between ORP and the eutrophication-related index. A three-segment relationship between the ORP and the index was established. This three-stage relationship was confirmed in different reservoirs.

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INTRODUCTION

With the development of the social economy, water pollution has become increasingly serious, posing a primary threat to the safety of drinking water sources. Contaminant of water sources directly affects people's health and immediate interests. For instance, long-term consumption of water containing nitrate pollutants has been associated with a significant increase in gastric cancer incidence (Fijani *et al.* 2019). Drinking water with high levels of ammonia can cause symptoms such as oral mucosal erosion, edema, and dizziness (Wang *et al.* 2018). Moreover, eutrophication of water sources, characterized by excessive growth of algae, can lead to the production of algal toxins. Drinking water contaminated with algal toxins can cause gastrointestinal diseases and even have teratogenic and mutagenic effects (Arash *et al.* 2022; Hamza *et al.* 2023). The impact of water pollution in water sources on human health is immense, underscoring the crucial importance of monitoring and early warning research on water source environments.

Monitoring of water environments in water sources is achieved primarily by detecting various water quality parameters (Mehreen *et al.* 2022). By regularly monitoring water environments, authorities can track changes in water quality parameters, such as pH levels, turbidity, dissolved oxygen (DO), as well as the presence of biological or chemical contaminants. Different physical, chemical, and biological water quality parameters can be selected to assess the water environment. Given the numerous water quality parameters, researchers often use different models to predict water quality or study the relationships between different water quality parameters (Roy *et al.* 2018; Nimisha *et al.* 2020). For instance, Choden *et al.* (2022) selected parameters such as dissolved total solids, conductivity, pH, and DO as modeling data, using a neural network model to provide water quality analysis and future predictions, thus achieving water resource protection and sustainability. Fijani *et al.* (2019) used the complete ensemble empirical mode decomposition with adaptive noise (CEEMDAN) and variational mode decomposition (VMD) algorithms, coupled with extreme learning machines (ELM) and least-squares support vector machines (LSSVM), to achieve real-time evaluation of reservoir water quality. Wang *et al.* (2019) improved the water quality prediction model based on the time series ARIMA model by introducing the Holt-Winters seasonal model and established a universal water quality prediction model with eutrophication parameters, which could significantly reduce the cost of water quality prediction and analysis in drinking water resources. Due to the lack of biological factor evaluation in water quality assessment, Zhang and Liu (2020) studied the correlation between evaluation indicators and cyanobacteria concentration and established a new cyanobacterial pollution index for comprehensive water quality evaluation. In addition, mixed models can also be used to predict changes in water quality parameters. Song *et al.* (2022) proposed a hybrid model based on ensemble learning methods, combining the complete ensemble empirical mode decomposition with adaptive noise (CEEMDAN) and improving long short-term memory (LSTM) to perform water quality prediction. This model demonstrated better predictive accuracy compared to other data-driven models. The studies described above used algorithms to analyze the relationships between water quality parameters and attempted to simplify water quality assessment through various models, focusing on predicting or evaluating water quality based on key water quality parameters. The use of mathematical models to simplify water environmental monitoring processes has shown promise and potential for application. Continued research and development in this field will further improve the accuracy and reliability of these models, leading to better water management strategies and enhanced protection of drinking water sources.

Various water quality parameters have complex relationships with each other (Nimisha *et al.* 2020). For example, Shroff *et al.* (2015) conducted a regression analysis on the water quality of Gagan River from different sites, revealing a significant relationship between parameters such as pH and conductivity. The results showed that the high conductivity suggested the presence of dissolved ions in water, which would influence the pH value. In a study conducted by Han *et al.* (2022), an increase in NO_3^- concertation led to an increase in the quantity of cyanobacteria, subsequently resulting in the occurrence of water blooms in that area. Furthermore, Zeinalzadeh and Rezaei (2017) found that the concentration of pollutants (such as nitrogen pollutants) in rivers always varied seasonally and was related to the flow rate of the river. While there are certain relationships between various water quality parameters, some parameters, such as algae, might intuitively reflect water quality. For example, the temporal variation in the composition and abundance of algal communities can provide valuable information about the trophic level and overall health of the water body. Compared to nutrient concentrations or chlorophyll a (Chla-a) values, algal communities can more comprehensively reflect changes in water quality (Gökçe 2016). Touchette *et al.* (2007) conducted water quality testing on 11 drinking water supply reservoirs in the Piedmont region of North Carolina. They found that accelerated eutrophication resulting from further watershed development is expected to promote an increase in cyanobacterial abundance. At the same time, some water quality parameters are difficult to detect in real-time, and if mathematical models can be used to establish relationships between easily monitored water quality parameters and other water quality parameters, it can greatly simplify the water quality assessment process and enable timely water quality forecasting. For example, Wang *et al.* (2018) established the air temperature-water quality model of a reservoir using an improved BP neural network method based on the changing of water quality indicators. This model can provide early warning of excessive total nitrogen in reservoir through air temperature, which can significantly simplify the water quality monitoring and prediction process.

The oxidation-reduction potential (ORP) is a parameter that describes the redox properties of all elements in an aqueous solution. During wastewater treatment, ORP is often positively correlated with water quality. Generally, higher ORP values indicate better water quality, whereas lower ORP values are always associated with poorer water quality. As a result, ORP detection is widely used in wastewater treatment plants. Monitoring of ORP can help the rapid analysis of wastewater purification reactions and water pollution status, thereby achieving efficient management of water environmental quality (Prambudy *et al.* 2019). Wang *et al.* (2022) utilized variance analysis to study the relationship between ORP and major active substances in wastewater under anaerobic conditions and they further employed multiple regression analysis to establish a mathematical model, revealing that under anaerobic conditions, ORP was positively correlated with nitrate, dissolved oxygen (DO), and chemical oxygen demand (COD), while it was negatively correlated with ammonia nitrogen, phosphate, and pH. There was also certain correlation between ORP and parameters related to water eutrophication. Liu *et al.* (2019) found that ORP (within 65 to 170 mV) was significantly and negatively correlated with total phosphorus in water body. Shao *et al.* (2023) studied the microbial community structure during the outbreak of algal bloom in different kinds of eutrophic micro water bodies and found that ORP was related to eutrophication parameters such as total phosphorus, nitrogen, and microbial communities related to algal blooms. ORP detection is easy and can be achieved through dedicated ORP meters for online monitoring (Yu *et al.* 2008; Saratale *et al.* 2018). The total phosphorus and total nitrogen include partially oxidized substances, which may increase the ORP (Wang *et al*. 2020). When the relationship between ORP and water eutrophication can be established in drinking water sources, it would enable rapid assessment and analysis of water quality, enhancing the ability of early warning systems. Based on literature analysis and the authors' previous research, a hypothesis is proposed that the relationship between ORP and eutrophication is not simply a positive or negative correlation, and there may be a phased change relationship. This hypothesis opens up new possibilities for understanding the complex interactions between ORP and eutrophication in water body. It would be important to conduct further research and data analysis to test this hypothesis and gain insights into the relationship of ORP and eutrophication in different environmental contexts.

This study aimed to establish a relationship between water eutrophication and the oxidation-reduction potential (ORP) to achieve a rapid analysis of eutrophication parameters in water bodies, allowing better monitoring of ecosystem health. Firstly, correlation analysis was used to determine the correlation between ORP and various water quality parameters. Subsequently, Principal Component Analysis (PCA) was used to reduce dimensionality and form water quality evaluation index based on water quality parameters that were highly correlated with ORP. The neural network analysis was then applied to predict the corresponding relationship between the eutrophication-related index and ORP. Finally, a mathematical formula model for the relationship between ORP and the eutrophication-related index was established using mathematical fitting methods, elucidating the underlying patterns and achieving rapid water quality warning, thereby providing a theoretical basis for reservoir management. In addition, this research method has been applied in different reservoirs to further confirm the results. Therefore, the methodology proposed in this study can be applied to other analogous water environmental systems. This study proposes different methods to establish the relationship between eutrophication and ORP and further enhances the mathematical model depicting their correlation, showcasing significant innovation.

EXPERIMENTAL

Study Area

The main research area of this study was the Shihe Reservoir. The Shihe Reservoir is located on the mainstream of the Shihe River, north of Xiaochen Village Shan Kou, in Shanhaiguan District, Qinhuangdao City, Hebei Province, China. The location of the reservoir in the north temperate monsoon climate zone has implications for its water availability and overall ecology. During the wet season, there may be higher precipitation levels, leading to increased water inflow into the reservoir. During the dry season, there may be lower precipitation levels, leading to reduced water inflow and potentially lower water levels in the reservoir. With a total storage capacity of 70 million m^3, the Shihe Reservoir serves as an important drinking water resource for Shanhaiguan region of Qinhuangdao City. The normal water level of the Shihe Reservoir is 56.70 m, and the design flood level is 56.99 m. This level ensures that the reservoir can safely manage and mitigate flood risks in the surrounding area. Shihe Reservoir has a catchment area of 28.2 km^2. The catchment area plays a crucial role in determining the amount of water that can be stored in the reservoir, as well as the overall water quality. Referring to the authors' previous research (Zhang and Liu 2020), the water sampling site under dam (119°71′28″ E, 40°03′34″N) was still chosen in this study to monitor the water quality of the reservoir outlet. The selection of this specific sampling site was based on the understanding that the water quality measured here would provide the most accurate representation of the water supply quality. By selecting this sampling site, the aim was to ensure that the collected data accurately reflect the quality of water that will be distributed to consumers.

At the same time, to confirm that the results obtained from the study can be applied in other reservoirs, Yanghe Reservoir was selected as the water sample sampling point. The Yanghe Reservoir is located in the north of Dawanzi Village, Funing District, Qinhuangdao City, Hebei Province. It covers an area of 755 square kilometers, with a total storage capacity of 386 million cubic meters and an irrigation area of 126,000 mu. The annual average rainfall is 750 mm and the annual average runoff is 169 million cubic meters, accounting for about 70% of the flood season runoff. Samples were taken at 119°2 '1 "E, 39°9' 9" N.

Sampling and Measurement Methods

The sampling method was the same as the authors' previous study. Since the surface layer water from the reservoir is used for water supply purposes, it makes sense to specifically analyze the quality and characteristics of this water. Surface water samples were collected at a depth of 0.5 meters underwater, from the sampling site, throughout the period from January 2022 to December 2023. The sampling frequency was twice a week (always Monday and Thursday). The sampling was carried out during relatively warmer periods (12:00 noon). The collected water samples were still analyzed following the China Standard for Surface Water Environmental Quality (GB3838-2002) and Water and Wastewater Monitoring and Analysis Method (fourth edition) published by the State Environmental Protection Agency. Measured parameters included chemical oxygen demand, ammonia nitrogen, nitrate nitrogen, total phosphorus, total nitrogen, chromium ion, biological oxygen demand, fluoride, cyanobacteria, and Chla. Other routine parameters including temperature, pH, DO, turbidity, conductivity, and ORP were carried out by instruments (HACH, USA). All testing was carried out in accordance with the requirements of the specifications. To ensure accuracy, the average values for each parameter were calculated based on three repeated test results. This methodology can provide a more reliable representation of the overall water quality at the sampling site.

Parametric Correlation Analysis

Correlation analysis was used to measure the linear relationship between two variables X and Y, and the correlation coefficient values range from -1 to 1. The calculation was as follows,

$$r(X,\ Y) = \frac{Cov(X,Y)}{\sqrt{Var[X]Var[Y]}} \tag{1}$$

where Cov(X, Y) represents the covariance between X and Y, Var[X] represents the variance of X, and Var[Y] represents the variance of Y.

The Pearson correlation coefficient, denoted as r(X, Y), ranging from -1 to 1, indicates the degree of linear relationship between two variables X and Y. When the correlation coefficient r(X, Y) is close to zero, it suggests that there is no linear correlation between the variables. If the coefficient r(X, Y) is close to 1, it indicates a strong linear correlation between the variables. A positive correlation coefficient (>0) implies a positive correlation, while a negative correlation coefficient (<0) suggests a negative correlation (Zhang *et al.* 2022).

Principal Component Analysis (PCA)

The Principal Component Analysis (PCA) is to achieve dimensionality reduction through orthogonal transformation of the original data. It uses a set of linearly independent principal components to represent the majority of information in the original data. The method is generally divided into the following steps (Zhu *et al.* 2021):

1) To eliminate the influence of different scales, the original data is standardized using mean normalization. This standardization method retains the variation information among variables of the same type while eliminating the interference of different scales. The calculation is as follows,

$$\mathrm{MX_{ab}} = \frac{\mathrm{X_{ab}}}{\mathrm{MeanX_a}} \tag{2}$$

where MX_{ab} represents the standardized value of the b-th data point of the a-th variable,

X_{ab} represents the original value of the b-th data point of the a-th variable, and Mean X_a represents the mean value of the a-th variable.

2) The correlation matrix P of the standardized values MX_{ab} is calculated.

3) The eigenvalues (β_a) and eigenvectors of P are calculated, and the eigenvectors are arranged in descending order.

4) The cumulative variance contribution rate to determine the number of principal components is calculated. The sum of the previous y eigenvalues accounts for the percentage of the total eigenvalues as the cumulative variance contribution K.

5) The values of principal component Fa are calculated and the overall composite score of the principal components F is obtained by Eq. 3.

$$F = \sum_{1 \leq a \leq y} \frac{\beta_a}{\beta_1+\beta_2+\beta_3+\cdots\ldots+\beta_y} F_a \quad (3)$$

The BP Artificial Neural Network Analysis

The BP artificial neural network, also known as backpropagation neural network, is a commonly used artificial neural network model. It consists of neural units as the smallest building blocks, with multiple neural units forming the input layer, hidden layers, and output layer (Shlens 2014). The information is shared among these three layers with different permissions and boundaries. To start the algorithm, a set of random weights and thresholds αi^x is generated. The term αi^x represents the weight from the j-th neuron in the previous layer to the i-th neuron in the current layer; αi^x represents the threshold of the i-th neuron in the x-th layer, where x = 1,2, ..., M, and M is the number of layers;i = 1,2, ..., S_M; j = 1,2, ..., S_{x-1}; S_x represents the number of neurons in the x-th layer. After running the neural network, the network adjusts the weights and thresholds based on the error between the output values and the actual values, in order to minimize the error tolerance. The error in the output layer can be represented as follows,

$$F(x)=[t(n)-b(n)]^T[t(n)-b(n)] \quad (4)$$

where t(n) represents the target variable matrix at the n-th iteration, and o(n) represents the output variable matrix at the n-th iteration. When the output values do not meet the set accuracy, the backpropagation (BP) neural network will propagate the error backward. Under the influence of training error, the weight correction value is calculated as follows,

$$w^x_{i\,j}(n+1)=w^x_i\, j(n)+£[w^x_{i\,j}(k)_-w^x_{i\,j}(n-1)]-\alpha(1-£)s^x_i\, b^{x-1}{}_j \quad (5)$$

The adjusted value of the threshold is

$$\alpha^x_i\,(n+1)=\alpha^x_i\,(n)+£[\alpha^x_i\,(n)-\alpha^x_i\,(n-1)]-\alpha(1-£)s_i{}^x \quad (6)$$

where $s_i{}^x$ represents the sensitivity of the i-th neuron in the x-th layer; £ ($0 \leq £ < 1$) is the momentum factor; α is the learning rate (Chen *et al.* 2020).

Data Fitting Method

Using SPSS data analysis software (IBM SPSS Statistics 27.0.1), curve estimation was performed. The software provides multiple selectable function models. When it is not clear which model fits the sample data best, several models can be simultaneously selected. SPSS automatically performs parameter estimation for the models and displays statistics such as the F-value, p-value, R^2, *etc*. Finally, the model with the highest likelihood is chosen as the regression model, and predictions are made based on that model,

RESULTS AND DISCUSSION

Correlation Analysis of Water Quality Parameters

Correlation analysis can be used to study pollution trends, explore potential sources of pollution, and provide data support for risk management. Additionally, for some water bodies, it is possible to establish related models and prediction methods for surface water resources, thereby enhancing the diversity and accuracy of surface water quality measurement (Chen *et al.* 2020). There may be a certain correlation between different water quality parameters.

Through the analysis of pH, water temperature, dissolved oxygen, turbidity, conductivity, COD, ammonia nitrogen, nitrate nitrogen, total phosphorus, total nitrogen, cyanobacteria and Chla, the water quality of the reservoir was similar to that of the year 2018 and 2019 (Zhang *et al.* 2020), and eutrophication related parameters such as total nitrogen, total phosphorus and ammonia nitrogen exceeded the requirements of national standards in some times. This reservoir faced a slight eutrophication problem during in summer and autumn. If agriculture and industry in the upstream of the water body discharges excessive N and P, this will lead to excessive algae growth in the water body, and the reservoir will face eutrophication problems. The analysis and prediction research on water quality parameters related to eutrophication was particularly important for the reservoir.

According to the test results, the ORP of Shih River Reservoir ranged from 235 to 314 mV without very significant variation. Similar findings have been also reported in other studies, such as the ORP values testing in Shanxi Reservoir, showing certain fluctuations at different time periods but in the range of 221 to 286 mV (Yang *et al.* 2023). There was a correlation between ammonia nitrogen, total phosphorus, total nitrogen, Chla, cyanobacteria concentration, and ORP, with correlation coefficients of -0.204, 0.293, 0.373, -0.320, and -0.225, respectively. This suggested that ORP can be related to these eutrophication parameters through certain methods. However, the correlation between other parameters and ORP was extremely weak. Krom *et al.* (1991) believed that external factors such as wind, rain, and flow velocity may suddenly affect the transformation process of certain substances in water bodies. This might result in weak interrelationships between water body parameters. For example, dissolved oxygen did not form significant relationships with ORP (Absolute value of the correlation coefficients was less than 0.1). This result was different from what was expected, which may be due to the large surface area of the reservoir and there were significant differences between the characteristics of reservoirs and wastewater treatment plants. And when the dissolved oxygen concentration in the water was high, nitrogen organic matter in the water and sediment would decompose under aerobic microbial action, resulting in the production of reducing agents such as ammonia nitrogen. The dissolved oxygen of the reservoir did not directly show a significant positive correlation with ORP.

Notably, there were different positive and negative correlations between pollutant concentrations (ammonia nitrogen, total phosphorus, total nitrogen, Chla, cyanobacteria concentration) and ORP, which require further analysis. Ammonia nitrogen, Chla, and cyanobacteria concentration had a negative correlation with ORP, while total nitrogen and total phosphorus had a positive correlation with ORP. The total phosphorus and total nitrogen include partially oxidized substances, which may increase the ORP (Wang *et al.* 2020). However, ammonia nitrogen refers to free ammonia and ionized ammonia in the water. Free ammonia and ionized ammonia are reducing substances that can directly affect the oxidation-reduction potential of water body. Furthermore, Chla plays a role as a reducing agent in physiological processes and is involved in the electron transfer process of photosynthesis. When the Chla content in the water is high, it consumes oxidants in the water, forming a reducing environment and reducing the oxidation-reduction potential (Long *et al.* 2006). Therefore, there may be a negative correlation between Chla content and ORP. The reproduction of cyanobacteria results in the death and degradation of aquatic organisms and the production of reducing substances (Wu *et al.* 2015). A negative correlation was observed between cyanobacteria concentration and ORP. Based on previous study, there were also correlations between these eutrophication parameters (ammonia nitrogen, Chla, cyanobacteria, total nitrogen, and total phosphorus). It is necessary to comprehensively analyze these parameters and their relationship with ORP.

Principal Component Analysis and Calculation of Eutrophication-Related Index

Principal Component Analysis (PCA) was conducted on parameters including ammonia nitrogen (Z_1), total phosphorus (Z_2), total nitrogen (Z_3), chlorophyll-a (Z_4), and cyanobacteria (Z_5). Prior to performing factor analysis, the suitability of the raw data was evaluated using the Kaiser-Meyer-Olkin (KMO) and Bartlett's sphericity test, with results presented in Table 1. The KMO value was 0.784, exceeding 0.7 (indicating suitability for factor analysis), and Bartlett's test yielded a sig value much lower than 0.05, confirming the data's suitability for factor analysis.

Table 1. KMO and Bartlet Test of Principal Component

KMO	Approximate chi square	df	Sig.
0.784	1429.131	15	0.000

Table 2. Eigenvalues and Contribution Rates of Each Component in Principal Component Analysis

Component	Eigenvalues	Contribution rates of each component	Cumulative contribution rate
1	1.939	38.787	38.787
2	1.127	22.539	61.326
3	1.024	20.487	81.814
4	0.690	13.801	95.615
5	0.219	4.385	100.00

By conducting factor analysis on these parameters, the eutrophication-related index of water quality in the reservoir could be calculated. The formulas and expressions for the three principal components are shown in Eqs. 7 through 10,

$$F_1=-0.115Z_1-0.359Z_2-0.485Z_3+0.873Z_4+0.894Z_5 \tag{7}$$

$$F_2=0.188Z_1+0.689Z_2+0.634Z_3+0.357Z_4+0.296Z_5 \tag{8}$$

$$F_3=0.939Z_1-0.364Z_2+0.101Z_3+0.011Z_4+0.019Z_5 \tag{9}$$

$$F=0.474F_1+0.275F_2+0.25F_3 \tag{10}$$

where Z_1 represented ammonia nitrogen concentration (the standardized value), Z_2 represented TP concentration (the standardized value), Z_3 represented TN concentration (the standardized value), Z_4 represented Chla concentration (the standardized value), and Z_5 represented cyanobacteria concentration (the standardized value). "F" stands for eutrophication index.

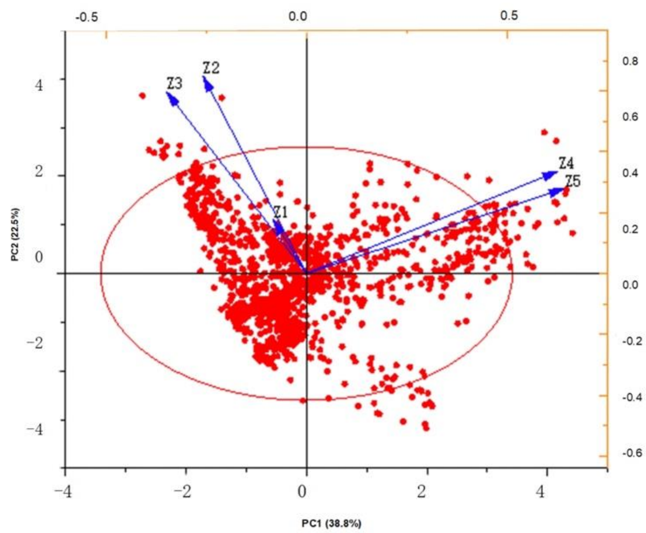

Fig. 1. Main components of Principal Component Analysis (PCA)

A rotated component matrix was obtained (Fig. 1). According to the PCA results (Fig. 1, Table 2, and Eqs. 7 through 10), the first component (F_1) exhibited the highest contribution to variance, 38.8%, which was strongly correlated with chlorophyll-a (Z_4) and cyanobacteria (Z_5), emphasizing its significance over other components. The second component contributed 22.5% of the variance, which was closely associated with total phosphorus (Z_2) and total nitrogen (Z_3). The third component contributed 20.49% of the variance, which was closely related to ammonia nitrogen (Z_1). This conclusion aligned with previous correlation analysis findings. In Fig. 1, arrows represent principal component loadings, reflecting correlation coefficients between the original variables and the principal components. Each arrow corresponds to an original feature. The arrows labeled Z_1, Z_2, Z_3, Z_4, and Z_5 denote ammonia nitrogen, total phosphorus, total nitrogen, chlorophyll-a, and cyanobacteria, respectively. The direction of the arrows indicates the orientation of the feature in the principal component space. Taking the composition of F_1 as an example, arrows for Z_1, Z_2, and Z_3 roughly shared the same direction, and arrows for Z_4 and Z_5 exhibited a similar direction. The length of the arrows represents the contribution or weight of the feature in the principal component space. Both the direction and length of the arrows are calculated through PCA of the raw data. This result was completely consistent with the formula of F_1 (Eqs. 7). At the same time, during the PCA computation using SPSS, a third principal component was identified, contributing 20.487% of the variance, leading to a subdivision into three principal components (Table 2).

Compared with other studies, Mishra conducted an analysis on 16 physicochemical and bacteriological variables. PCA was applied to extract the most significant parameters for assessing water quality changes. Four main factors were identified (nutrient factors, sewage and fecal contamination, sources of physicochemical variability, and water pollution from industrial waste and organic load), which collectively account for 90% of the total variance (Mishra 2010). Ibrahim *et al.* (2023) used PCA and Artificial Neural Network (ANN) to study the potential pollution that caused spatial variations in water quality and the results demonstrated that the PCA and ANN methods can serve as decision-making and problem-solving tools for better river water quality management. Therefore, it can be seen that the use of PCA for the comprehensive analysis of water pollution is an effective and feasible approach.

Observing the relationship between the water eutrophication-related index and the month (Fig. 2), the eutrophication index was higher during the summer, indicating poor water quality. This may be due to the elevated summer temperatures and increased light intensity, promoting the growth of aquatic plants and nutrient cycling. Additionally, the summer season typically experiences frequent rainfall. Increased precipitation results in more runoff entering reservoirs, carrying a significant amount of nutrients and pollutants into the water. These nutrients and pollutants may originate from activities such as agricultural fertilization and urban emissions, further intensifying the degree of eutrophication in the reservoir. The eutrophication problem in reservoirs requires better monitoring, which once again confirms the significance of this study.

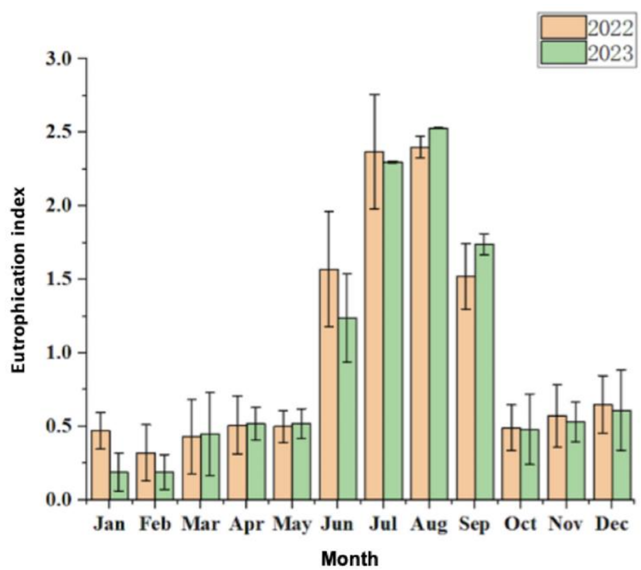

Fig. 2. Changes of eutrophication-related index in different months

Neural Network Analysis

At the same time, if some models can be used to predict and analyze water quality, it will solve the problem of delayed response to water quality changes in current water quality monitoring. For instance, Zhao *et al.* (2007) conducted a study on water quality dynamic prediction using BP neural network technology and analyzed the predictive performance of the model with the example of Yuqiao Reservoir in Tianjin City. Ye *et al.* (2019) proposed a LSTM-RNN (Long Short Term Memory -Recurrent Neural Network) network water quality parameter prediction model based on an improved RNN (Recurrent Neural Network) network structure to predict the trend of water quality change. Ma *et al.* (2021) applied the neural network model to predict the water quality status and trend of Nansi Lake. Their use of neural networks for water quality prediction showed promising results. In this study, to establish the relationship between the ORP and eutrophication-related index, the BP neural network analysis was used to predict the eutrophication index at different ORP levels. After multiple predictions, there was a certain level of error between the predicted eutrophication index and the actual eutrophication index and the error reached 15% (Table 3). Therefore, although neural network analysis could be performed, simulation analyzes in other forms should be performed to ensure reliability.

Table 3. Neural Network Prediction Analysis (Partial Data)

ORP	Actual Index	Prediction Index	Error (%)
280.88	0.57	0.58	1.72%
274.1	0.53	0.61	13.11%
275.65	0.52	0.61	14.75%
274.13	0.53	0.59	10.17%
275.74	0.52	0.58	10.34%
274.15	0.53	0.6	11.67%
277.32	0.51	0.6	15%
242.98	2.38	2.55	6.67%

The Polynomial Fitting Analysis

The polynomial fitting method can be used to establish a closed functional expression that captures the general trend and characteristics of the sample data through curve fitting. It is a type of curve fitting method commonly used in regression analysis. This fitting method can better correspond the data to the quadratic polynomial form, thus improving the prediction and analysis of the data.

It is important to note that fitting a quadratic polynomial may lead to underfitting. Therefore, before applying the quadratic polynomial fitting, it is necessary to perform an appropriate analysis on the data to ensure that the established quadratic polynomial function accurately reflects the characteristics and trends of the data. To better identify the exact relationship between variables, the distribution of the sample data in the graph should be observed and then the model that matches the function characteristics and the point distribution could be determined (Chen *et al.* 2022).

By analyzing the data on ORP and the eutrophication-related index, it was observed that a stage-wise curvilinear relationship existed between ORP and the eutrophication index (Fig. 3). Moreover, this relationship could be divided into three segments, as shown in Fig. 4.

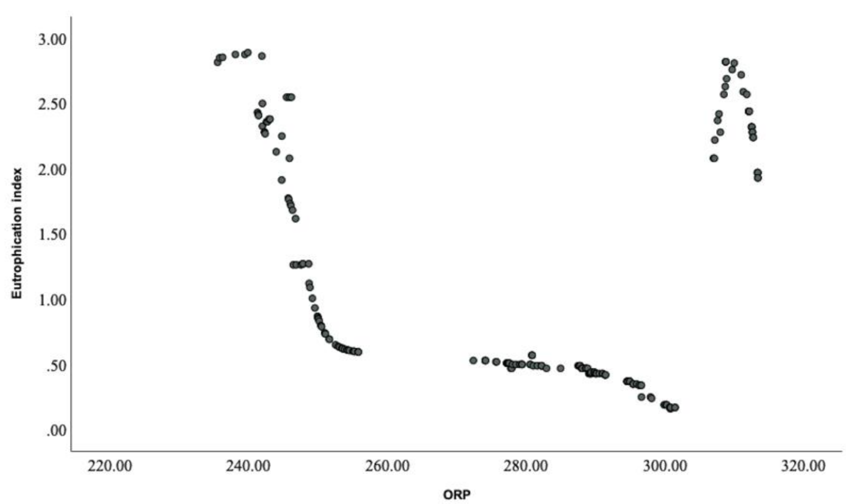

Fig. 3. Scatter plot of overall distribution between ORP and eutrophication-related index (Shihe Reservoir)

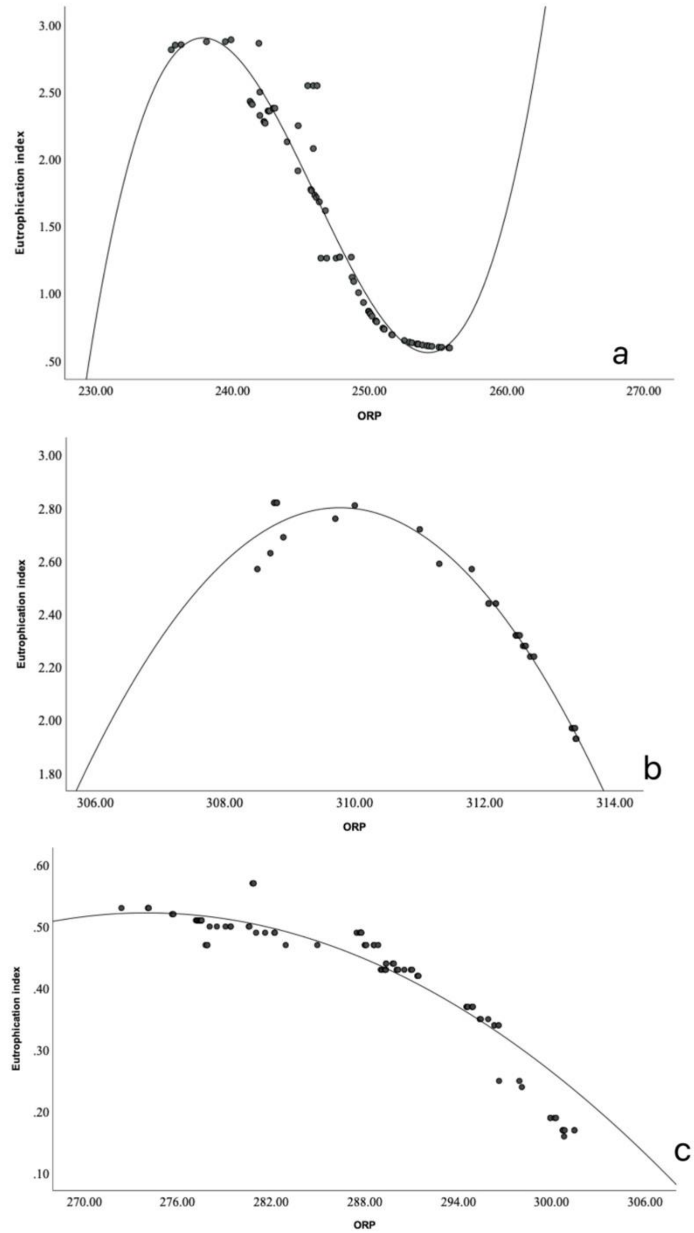

Fig. 4. Fitted Relationship between ORP and eutrophication-related index of Shihe Reservoir (a: First Segment Fit; b: Second Segment Fit; c: Third Segment Fit)

After fitting, the expressions for the three segments of the relationship between the eutrophication-related index (Y) and the ORP (x) were determined as follows:

$$Y_1 = 0.0011 \times x^3 - 0.782 \times x^2 + 192.2 \times x - 15727; R^2 = 0.943\ (230 \leq X \leq 270) \quad (11)$$

$$Y_2 = -0.0008 \times x^2 + 0.4243 \times x - 58.84; R^2 = 0.9599;\ (270 \leq X \leq 306) \quad (12)$$

$$Y_3 = -0.0781 \times x^2 + 48.448 \times x - 7507.4;\ R^2 = 0.949 (306 \leq X \leq 314) \quad (13)$$

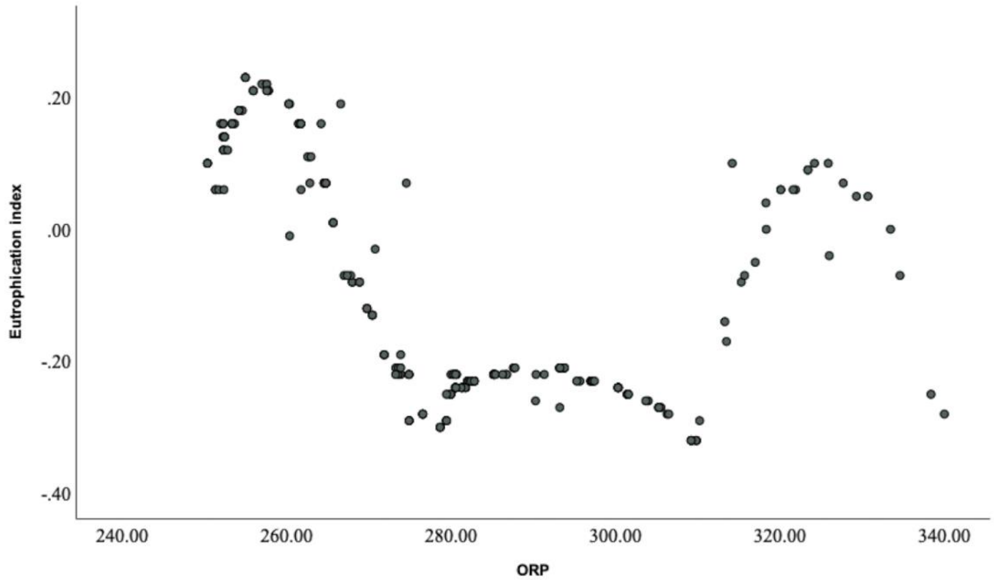

Fig. 5. Scatter Plot of Overall Distribution between ORP and eutrophication-related index (Yanghe Reservoir)

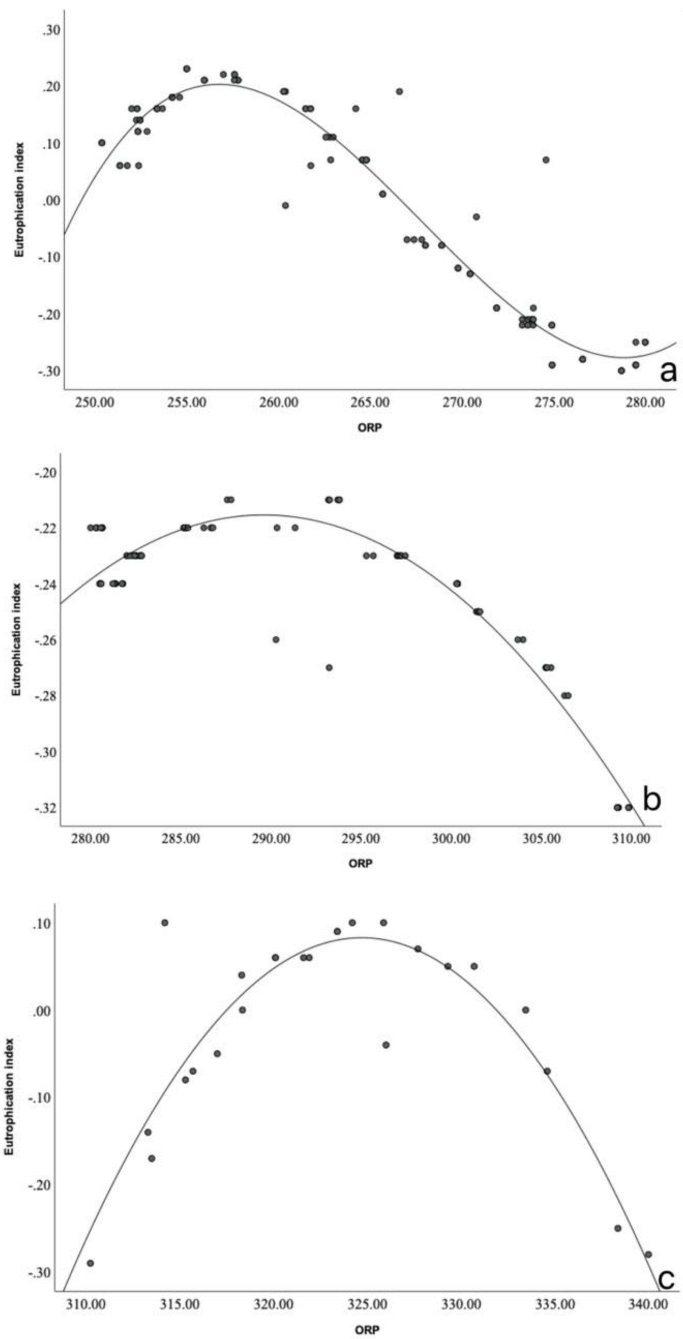

Fig. 6. Fitted Relationship between ORP and eutrophication-related index of Yanghe Reservoir (a: First Segment Fit; b: Second Segment Fit; c: Third Segment Fit)

As shown by the fitted curve, the relationship between ORP and eutrophication index (Y) exhibited three distinct segments as follows: (1) within the range of 235 to 260 mV, the eutrophication index decreased after equilibrium; (2) in the range of 260 to 308 mV, the eutrophication index gradually decreased with increasing ORP; and (3) within the range of 308 to 314 mV, the eutrophication index first increased and then decreased.

To verify this interrelationship, the same method was used to study the water quality of Yanghe Reservoir. There was a three-stage relationship between ORP and water eutrophication index (Figs. 5 and 6).

The data of Yanghe reservoir were divided into three sections as follows:

$$Y_1 = 9\times10^{-5}\times x^3 - 0.0719x^2 + 19.228x - 1710.5;\ R^2 = 0.9332\ (250 \le X \le 280) \tag{14}$$

$$Y_2 = -0.0002x^2 + 0.1446x - 21.161;\ R^2 = 0.8851\ (280 \le X \le 310) \tag{15}$$

$$Y_3 = -0.0016x^2 + 1.0388x - 168.56;\ R^2 = 0.8191\ (310 \le X \le 340) \tag{16}$$

The eutrophication index and ORP exhibited an inverse relationship, where higher ORP values corresponded to lower eutrophication index and better water quality. An increase in pollutants or the occurrence of eutrophication in water can lead to deteriorated water quality. The decomposition of these pollutants often consumes oxygen, resulting in a reduction of the oxidation-reduction potential (ORP). Hence, the eutrophication index and ORP often display an inverse relationship (Martín *et al.* 2012). However, when ORP increases, it may also indicate the presence of other oxidizing pollutants entering the water or the release of pre-existing oxidizing pollutants from sediment, leading to new water pollution. Therefore, the relationship between the eutrophication index and ORP may occasionally exhibit a positive correlation (Zhang *et al.* 2018). Additionally, flow velocity, sudden rainfall, and other biological factors in the water can also influence the ORP of the water. In this study, a stage-wise change pattern was identified, which could be used to predict water quality, especially eutrophication, using ORP in the future.

In general, Shihe Reservior and Yanghe Reservoir are both drinking water sources with eutrophication phenomena. Therefore, samples were taken from the two water sources and the same analysis was conducted. Although ORP ranges were different, there was still a three-stage shared relationship, and ORP and eutrophication index were negatively correlated in most cases. It is fully explained that the three-stage formula was still applicable in other water sources, so as to prove the feasibility of the research. This result could confirm the hypothesis proposed in the introduction section. The relationship between ORP and eutrophication is not simply a positive or negative correlation, and there may be a phased change relationship.

Although this study established a mathematical relationship between ORP and eutrophication, which could predict the trend of eutrophication in water bodies through changes in ORP, no corresponding evaluation mechanism has yet been established, and further analysis is needed in future research.

CONCLUSIONS

1. This study examined the relationship between water eutrophication and the oxidation-reduction potential (ORP) to achieve a rapid analysis of eutrophication parameters in water bodies, thus enabling better monitoring of ecosystem health. The results showed that various parameters related to eutrophication, such as ammonia nitrogen, total nitrogen, total phosphorus, chlorophyll a (Chla), and cyanobacteria, showed certain correlations with ORP.
2. Principal Component Analysis (PCA) was used to comprehensively analyze eutrophication-related parameters and obtain an index, with the cumulative contribution of the principal components reaching 81.8%.
3. BP neural network analysis was employed for water quality prediction. The results indicated that utilizing BP neural networks for predictive analysis is a promising

method.

4. A mathematical fitting method was applied to establish a three-segment relationship between ORP and eutrophication-related index, allowing the calculation of the eutrophication-related index based on the ORP value.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES CITED

Arash, A., Hiwa, F., Mahmoudian, S. M., Lotfirad, M., Iraj, S., and Hossein, S. (2022). "Selection of the best machine learning method for estimation of concentration of different water quality parameters," *Sust. Wat. Resour. Man.* 8, 172. DOI: 10.1007/S40899-022-00765-3

Chen, C., Zhang, D., Yuan, A., Shen, J., Wang, L., and Wang, S. -L. (2022). "A novel approach to predict the comprehensive EROD potency: Mechanism-based curve fitting of CYP1A1 activity by PAHs," *Sci. Total. Environ.* 843, article 157052. DOI: 10.1016/j.scitotenv.2022.157052

Chen, Y., Song, L., and Liu, Y. (2020). "A review of the artificial neural network models for water quality prediction," *Appl. Sci.* 10, article 5776. DOI: 10.3390/app10175776

Choden, Y., Chokden, S., and Rabten, T. (2022). "Performance assessment of data-driven water models using water quality parameters of Wangchu river, Bhutan. Sn. Appl. Sci. 4, article 290. DOI: 10.1007/s42452-022-05181-y

Fijani, E., Barzegar, R., Deo, R., Tziritis, E., and Skordas, K. (2019). "Design and implementation of a hybrid model based on two-layer decomposition method coupled with extreme learning machines to support real-time environmental monitoring of water quality parameters," *Sci. Total. Environ.* 648, 839-853. DOI: 10.1016/j.scitotenv.2018.08.221

Gökçe D. (2016). "Algae as an indicator of water quality," in: *Algae – Organisms for Imminent Biotechnology*, N. Thajuddin, and D. Dhanasekaran (eds), InTech Open Limited, London, pp. 81-101. DOI: 10.5772/62916

Hamza, N., Mostafa, L., Ghizlane, A., Chaouki, B., Sara, E., Yassine, E. Y., Hicham, G., Abderrahmane, R., Hamza, L., and Abdelmajid., M. (2023). "Application of eutrophication indices for assessment of the ecological quality of the Moroccan eastern Mediterranean coast: Ras Kabdana-Saïdia. E3s. Web. Cnf. 364, 9. DOI: 10.1051/E3SCONF/202336402008

Han, H., L, Y., Ma, X., Song, W., Wang, Zl., and Zhang, X. (2022). "Factors influencing the spatial and temporal distributions of green algae micro-propagules in the coastal waters of Jinmenghaiwan, Qinhuangdao, China," *Mar. Pollut. Bull.* 175, article 113328. DOI: 10.1016/J.MARPOLBUL.2022.113328

Ibrahim, A., Ismail, A., Juahir, H., Iliyasu, A. B., Wailare, B. T., Mukhtar, M., and Aminu, H. (2023). "Water quality modelling using principal component analysis and artificial neural network," *Mar. Pollut. Bull.* 187, article 114493. DOI: 10.1016/J.MARPOLBUL.2022.114493

Krom, M. D., Kress, N., Brenner, S., Gordon, L. I. (1991). "Phosphorus limitation of primary productivity in the eastern Mediterranean Sea," *L&O* 36(3), 424-432. DOI: 10.4319/lo.1991.36.3.0424

Liu Yi. (2019). "Study on phosphorus morphology and eutrophication in the overlying water and sediments of Jiuli Lake," Ph.D. Dissertation, Chi. Univer. Min. Tech.

Long, A., Chen, S., Zhou, W., Xu, J., Shun, C., Zhang, J., and Xu, H. 2006. "Distribution characteristics and interrelationships of nutrients, dissolved oxygen, pH values, and chlorophyll in the northern south China sea during autumn," *Ocean Bull.* 25, 9-16. DOI: 10.3969/j.issn.1001-6392.2006.05.002

Ma, J., Wu, Z. H., Zou, Y. j., Ren, P., and Li, Q. (2021). "Water quality prediction of Nansi Lake based on grey Markov model," *Water. Resour. Prot.* 37, 153-158. DOI: 10.3880/j.issn.1004-6933.2021.05.023

Martín de la Vega, P. T., Martínez de Salazar, E., Jaramillo, M. A., and Cros, J. (2012). "New contributions to the ORP & DO time profile characterization to improve biological nutrient removal," *Bioresource Technol.* 114, 160-167. DOI: 10.1016/j.biortech.2012.03.039

Mehreen, A., Rafia, M., and Zahid, A. (2022). "An enhanced water quality index for water quality monitoring using remote sensing and machine learning," *Appl. Sci.* 12, article 12787. DOI: 10.3390/APP122412787

Mishra, A. (2010). "Assessment of water quality using principal component analysis: A case study of the river Ganges," *J. Water. Chem. Techno.* 32, 227-234. DOI: 10.3103/S1063455X10040077

Nimisha, W., Dev, T. A., and Ha, D. L. (2020). "Comprehensive review on application of machine learning algorithms for water quality parameter estimation using remote sensing data," *Sensor. Mater.* 32, 3879-3892. DOI: 10.18494/SAM.2020.2953

Prambudy, H., Supriyatin, T., and Setiawan, F. (2019). "The testing of chemical oxygen demand (COD) and biological oxygen demand (BOD) of river water in Cipager Cirebon," *J. Phs. Cnf. Ser.* 1360, article 012010. DOI: 10.1088/1742-6596/1360/1/012010

Roy, R., and Majumder, M. (2018). "A quick prediction of hardness from water quality parameters by artificial neural network," *Int. J. Enviro. Sustai.* 17, 247-257. DOI: 10.1504/IJESD.2018.094037

Saratale, R. G., Kumar, G., Banu, R., Xia, A., Periyasamy, S., and Saratale, G. D. (2018). "A critical review on anaerobic digestion of microalgae and macroalgae and co-digestion of biomass for enhanced methane generation," *Bioresource Technol.* 262, 319-332. DOI: 10.1016/j.biortech.2018.03.030

Shao, Z., Lai, J., Yuan, H., Zheng, X., Jiang, H., Wang, C., Huang, Z., Wang, J., Wang, D., and Xu, S. (2023). "Analysis of microbial community structure changes in Different types of eutrophication microwater algal bloom outbreaks," *Acta Scientiae Circumstantiae* 43(03), 490-502. DOI: 10.13671/j.hjkxxb.2022.0299

Shlens, J. (2014). "Principal component analysis: A tutorial," *Neural. Net.* 61, 87-91.

DOI: 10.1016/j.neunet.2014.09.010

Shroff, P., Vashi, R. T., Champaneri, V. A., and Patel, K. K. (2015). "Correlation study among water quality parameters of groundwater of Valsad district of south Gujarat (India)," *Journal. Funda. Appl. Sci.* 7, 340-349. DOI: 10.4314/jfas.v7i3.3

Song, C., and Yao, L. (2022). "A hybrid model for water quality parameter prediction based on CEEMDAN-IALO-LSTM ensemble learning," *Environ. Earth. Sci.* 81, article 262. DOI: 10.1007/S12665-022-10380-2

Touchette, B. W., Burkholder, J. A. M., Allen, E. H., Alexander, J. L., Kinder, C. A., Brownie, C., James, J., and Britton, C. H. (2007). "Eutrophication and cyanobacteria blooms in run-of-river impoundments in North Carolina, USA," *Lake and Reservoir Management* 23(2), 179-192.

Wang, J., Zhang, L., Zhang, W., and Wang, X. (2019). "Reliable model of reservoir water quality prediction based on improved Arima method," *Environ. Eng. Sci.* 36, 1041-1048. DOI: 10.1089/ees.2018.0279

Wang, J., Zhang, W., Guo, D., and Pei, Y. (2018). "An intelligent predicating algorithm for air temperature-water temperature-water quality relationship in water source," *Admn. Tecnol. Environ. Monitor.* 30, 15-19+55. DOI: 10.19501/j.cnki.1006-2009.20180912.005

Wang, X., Li, J., Chen, J., Cui, L., Li, W., Gao, X., and Liu, Z. (2020). "Water quality criteria of total ammonia nitrogen (TAN) and un-ionized ammonia (NH_3-N) and their ecological risk in the Liao River, China," *Chemosphere* 243, article 125328. DOI: 10.1016/j.chemosphere.2019.125328

Wang, X., Wu, Y., Chen, N., Piao, H., Sun, D., Ratnaweera, H., Maletskyi, Z., and Bi, X. (2022). "Characterization of oxidation-reduction potential variations in biological wastewater treatment processes: A study from mechanism to application," *Processes* 10, article 2607. DOI: 10.3390/PR10122607

Wu, T. T., Liu, G., Han, S. Q., Zhou, Q., and Tang, W. Y. (2015). "Impacts of algal blooms accumulation on physiological ecology of water hyacinth," *Environ. Sci.* 36, 114-120. DOI: 10.13227/j.hjkx.2015.01.015

Yang, M., Xia, J., Cai, W., Yang, L., Zhu, X., Li, C. (2022). "Distribution of phytoplankton functional groups in a drinking water reservoir and analysis of environmental driving factors," *Journal of Hydroecology* 43(2), 37-44. DOI: 10.15928/j.1674-3075.202005160127

Ye, Q., Yang, X., Chen, C., and Wang, J. (2019). "River water quality parameters prediction method based on LSTM-RNN model," *IEEE* 3024-3028, DOI: 10.1109/CCDC.2019.8832885

Yu, R.-F., Chen, H.-W., Cheng, W.-P., and Shen, Y.-C. (2008). "Dynamic control of disinfection for wastewater reuse applying ORP/pH monitoring and artificial neural networks," *Resour. Conserv. Recy.* 52, 1015-1021. DOI: 10.1016/j.resconrec.2008.03.007

Zeinalzadeh, K., and Rezaei, E. (2017). "Determining spatial and temporal changes of surface water quality using principal component analysis," *J. Hydrol:Reg. Stud.* 13, 1-10. DOI: 10.1016/j.ejrh.2017.07.002

Zhang, C., Guo, J., Lian, J., Song, Y., Lu, C., and Li, H. (2018). "Bio-mixotrophic perchlorate reduction to control sulfate production in a step-feed sulfur-based reactor: A study of kinetics, ORP, and bacterial community structure," *Bioresource Technol.* 269, 0960-8524. DOI: 10.1016/j.biortech.2018.08.084

Zhang, W., Li, T., Tang, J., Liu, X., Liu, Y., and Zhong, X. (2022). "The profiles of chiral pesticides in peri-urban areas near Yangtze River: Enantioselective distribution characteristics and correlations with surface sediments," *J. Environ. Sci.* 121, 199-210. DOI: 10.1016/j.jes.2022.02.001

Zhang, W., and Liu, Z. (2020). "Daily water quality evaluation of reservoir and cyanobacteria pollution index calculation," *Water Supply* 21, 836-847. DOI: 10.2166/WS.2020.350

Zhao, Y., Nan, J., Cui, F., and Guo, L. (2007). "Water quality forecast through application of BP neural network at Yuqiao reservoir," *J. Zhejiang Univer. Sci*. 8, 1482-1487. DOI: 10.1631/jzus.2007.A1482

Zhu, Y., Wu, Q., and Zhan, Z. (2021). "Water quality assessment based on a coupled model of principal component analysis and artificial neural network," *Jiangsu Water. Resour.* 297, 48-54. DOI: 10.16310/j.cnki.jssl.2021.08.014

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