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Comparison of seven water quality assessment methods for the characterization and management of highly impaired river systems

Xiaoliang Ji · Randy A. Dahlgren · Minghua Zhang

Abstract In the context of water resource management and pollution control, the characterization of water quality impairments and identification of dominant pollutants are of critical importance. In this study, water quality impairment was assessed on the basis of 7 hydrochemical variables that were monitored bimonthly at 17 sites in 2010 along the rural-suburban-urban portion of the Wen-Rui Tang River in eastern China. Seven methods were used to assess water quality in the river system. These methods included single-factor assessment, water quality grading, comprehensive pollution index, the Nemerow pollution index, principle component analysis, fuzzy comprehensive evaluation, and comprehensive water quality identification index. Our analysis showed that the comprehensive water quality identification index was the best method for assessing water quality in the Wen-Rui Tang River due to its ability to effectively characterize highly polluted waters with multiple impairments. Furthermore, a guideline for the applications of these methods was presented based on their characteristics and efficacy. Results indicated that the dominant pollutant impairing water quality was total nitrogen comprised mainly of ammonium. The temporal variation of water quality was closely related to precipitation as a result of dilution. The spatial variation of water quality was associated with anthropogenic influences (urban, industrial, and agriculture activities) and water flow direction (downstream segments experiencing cumulative effects of upstream inputs). These findings provide valuable information and guidance for water pollution control and water resource management in highly polluted surface waters with multiple water quality impairments in areas with rapid industrial growth and urbanization.

Keywords Water quality assessment · Water quality identification index · Dominant pollutant · Wen-Rui Tang river

X. Ji · R. A. Dahlgren · M. Zhang
Institute of Wenzhou Applied Technology in Environmental Research, Wenzhou Medical University, Wenzhou 325035, China

X. Ji · R. A. Dahlgren · M. Zhang
Southern Zhejiang Water Research Institute, Wenzhou 325035, China
e-mail: mhzhang@ucdavis.edu

R. A. Dahlgren · M. Zhang (✉)
Department of Land, Air and Water Resources, University of California Davis, Davis, CA 95616, USA
e-mail: mhzhang@ucdavis.edu

Introduction

Surface water quality impairment continues to increase as a serious concern throughout the world. Water quality deterioration is primarily attributable to growing population and city expanding and is threatening human and ecological health, drinking water availability, and further economic development (Houser and Richardson 2010; Li and Zhang 2010; Morse and Wollheim 2014). Surface waters are especially vulnerable to pollution due to their easy accessibility for disposal of wastewaters (Singh et al. 2004). Water quality impairment results

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from both anthropogenic inputs (e.g., municipal and industrial wastewater discharges, agricultural runoff) and natural processes (e.g., chemical weathering and soil erosion) (Holloway et al. 1998; Singh et al. 2011; Shin et al. 2013). Practical and reliable assessment of water quality is required for sustainable water resource use with respect to ecosystem health and social development which, more importantly, lay a foundation for the prevention and control of surface water pollution (Simeonov et al. 2003; Shrestha and Kazama 2007).

To effectively address surface water quality concerns, it is first necessary to provide a critical assessment to evaluate water quality impairment and pollutant sources (NRC 2001). During the past decade, much research has investigated water quality impairment using different assessment methods. For example, Huang et al. (2010) used a fuzzy comprehensive assessment and multivariate statistic method to illustrate that the water quality of the main river channel was better than the tributaries in the Qiantang River (China). Similarly, Massoud (2012) evaluated the water pollution levels of Damour River (southern Lebanon) by applying a water quality index method. The results indicated that the water quality of Damour River was affected by the anthropogenic activities taking place along the river. Likewise, Xu (2005) presented a comprehensive water quality identification index (CWQII), which is a new tool for general water quality assessment of surface waters. Fu et al. (2014) used CWQII method to evaluate the water quality of Taizi River (China), and the results revealed that water quality was inferior to class V from the years 2009 to 2012. Ban et al. (2014) also determined the CWQII values of Honghu Lake (China), and found CWQII increased from the years 2001 to 2005 and kept a balance from 2006 to 2011, which suggested that the water quality had gradually improved since 2006 due to water protection measurements taken by local government since 2004.

The water quality assessment methods listed in the previous paragraph were developed under specific conditions. There is a growing awareness that it is critical to decide an optimal water quality assessment method for the particular purpose and specific watershed. Therefore, comparisons of the performance of different assessment methods are necessary to better understand the efficacy of each assessment method and to present a guideline to use these methods. This guideline will assist in selecting an appropriate method that provides practical and accurate characterization of the water quality

status. However, until now, no attempt has been made to analyze and compare the efficacy of various assessment methods and to propose the best applications of these methods for accurate and meaningful characterization of water quality, especially for highly impaired systems that are affected by multiple pollutants.

The Wen-Rui Tang River, considered in this study, is a major river system in the rural-suburban-urban interface in Wenzhou, Zhejiang Province, eastern China. The river was once the main source of industrial, agricultural, and domestic water supplies. As the economy rapidly developed in the past 20 years, much untreated domestic sewage and industrial effluents were directly discharged into the river. Today, the river often tends to be hypoxic, malodorous, and black colored (e.g., sulfide-rich waters) due to deterioration by multiple pollutants, but especially from the enrichment of oxygen-demanding substances.

In view of the above considerations, the main objectives of this work were to (1) compare the performance of the seven methods: single-factor assessment, water quality grading, the Nemerow pollution index, comprehensive pollution index, principle component analysis (PCA), fuzzy comprehensive evaluation, and a water quality identification index, for evaluating the water quality of the Wen-Rui Tang River and attempting to present the best applications for these methods depend on their characteristics and efficacy; (2) determine the important discriminant variables for the water quality assessment of the Wen-Rui Tang River; and (3) assess the temporal and spatial variations in the water quality of the Wen-Rui Tang River. It is expected that the results can provide a valuable evaluation of assessment tools for water quality agencies that can be used to guide water resource management and pollution control implementation for highly impaired surface waters.

Materials and methods

Study area

The Wen-Rui Tang River watershed (27°03′–28°36′N, 119°37′–121°18′E) is a typical coastal plain river network located in Wenzhou, China (Fig. 1). It drains a total area of 740 km^2 with a length of 36 km. The upper Wen-Rui Tang River watershed is dominated by forests and agriculture while the lower watershed, including 1100 km of associated canals, is an urban zone with a

metropolitan population of about 8 million (Lu et al. 2011). The Wen-Rui Tang River watershed is in a subtropical humid monsoon climate zone with mild, dry winters, and hot, humid summers. The annual average temperature ranges from 16.1 to 18.2 °C, and the annual average rainfall ranges from 1500 to 1900 mm with most precipitation occurring between April and October.

Twenty years ago, the Wen-Rui Tang River was the major drinking water source for Wenzhou and it served essential roles in transportation, aquaculture, and agriculture. However, due to rapid industrial growth and urbanization in recent years, the city has generated large volumes of wastewater from untreated sewage, service-oriented enterprises, and factories that are often discharged directly into the river system (Mei et al. 2014). Today, the river often tends to be hypoxic, malodorous, and black colored due to the deterioration by pollution.

Data sources

Water quality data from 17 monitoring stations measured every other month in 2010 were obtained from the Wenzhou Environmental Protection Agency. Seven water quality parameters were selected due to their continuity in measurement and importance for assessing the water quality conditions of the Wen-Rui Tang River: dissolved oxygen (DO), 5-day biochemical oxygen demand (BOD$_5$), potassium permanganate-chemical oxygen demand index (COD$_{Mn}$), ammonium-nitrogen (NH$_4^+$-N), total nitrogen (TN), total phosphorus (TP), and petroleum (Petrol). The sampling, preservation, transportation, and analysis of water samples were performed following standard methods and quality control/quality assurance protocols, and the specific methods are summarized in Table 1.

Water quality assessment methods

Single-factor assessment method

The single-factor assessment method is determined according to the principle of maximum membership grade. The category of the most impaired assessment factor is used as the comprehensive water quality classification. The monitoring results for each parameter were compared to the corresponding water quality standard for surface waters in China (GB3838-2002, see Appendix A) to determine the water quality classification for each water quality parameter. Then, the lowest classification

category (i.e., most impaired) was selected as the comprehensive water quality classification. This method is simple and convenient and can be used to directly understand the relationship between the water quality status and assessment standards. The calculation of the single-factor index method can be expressed as:

$$G = (G_i)_{MAX}$$

where G is the comprehensive water quality classification and G_i is the classification of parameter i. $(G_i)_{MAX}$ is the maximum classification for all of the parameters. According to the national water quality standards, the water quality standards for surface waters in China are characterized from I to V corresponding to water quality from clean to seriously polluted, respectively. In GB3838-2002, the class I water quality standard refers to water quality equal to the source water or national nature reserve water; class II water quality standard refers to the first-grade protection zone mainly used as the centralized drinking water source; class III is the second-grade protection zone mainly used as the centralized drinking water source and water quality worse than class III is no longer suitable for drinking; class IV water quality standard refers to water suitable for industrial uses; class V water quality standard refers to water suitable for agricultural purposes such as irrigation, and water quality inferior to class V does not support aquatic ecosystem health.

Water quality grading method

The water quality grading method identifies the water quality classification for each assessment factor according to the national water quality standards for surface waters in China (Wang and Wang 2011). Each parameter's classification is given a corresponding score (class I=10, class II=8, class III=6, class IV=4, and class V=2). Finally, the overall water quality classification is determined as the arithmetic mean for all assessment factors. The classification standard for the comprehensive water quality method is shown in Table 2. The mathematical formula for the water quality grading method is:

$$M = \frac{1}{n}\sum_{i=1}^{n} A_i$$

Where M is the mean value for all parameter scores, A_i is the score of parameter i, and n is the total number of water quality parameters.

Fig. 1 Land-use map and monitoring sites of the Wen-Rui Tang River watershed
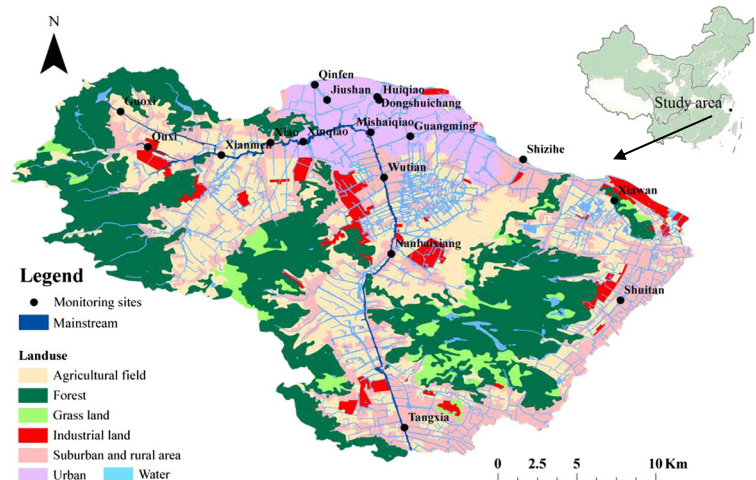
Nemerow pollution index

The Nemerow pollution index is a water pollution index taking extreme values into account using a weighted environmental quantity index and frequently used in water quality assessments around the world (Cheng et al. 2007; Liu et al. 2007). The calculation of this index takes three steps as follows:(i) identify the classification of each parameter according to the national water quality standards, (ii) determine the corresponding pollution index for each classification, and (iii) determine the water quality classification by calculating the Nemerow comprehensive index (Table 2). The mathematical formula for the Nemerow comprehensive index calculation is as follows:

$$P = \sqrt{\frac{\left(\frac{1}{n}\sum_{i=1}^{n} P_i\right)^2 + \left[(P_i)_{MAX}\right]^2}{2}}$$

where P is the Nemerow comprehensive pollution index, n is the total number of water quality parameters, P_i is the pollution index of parameter i, and $(P_i)_{MAX}$ is the maximum pollution index.

The following formulas are used to calculate P_i:

$$P_i = C_i/C_0$$

As to DO,

$$P_{DO} = \begin{cases} |C_{DOf} - C_i|/(C_{DOf} - C_0) & C_i \geq C_0 \\ 10 - 9C_i/C_0 & C_i < C_0 \end{cases}$$

C_i is the measured value of parameter i, C_0 is the desired water quality standard value of parameter i, and C_{DOf} is the saturated dissolved oxygen concentration. For the Wen-Rui Tang River, the desired water quality standard was set to be water quality standard class V (ZEPB 2010).

Comprehensive pollution index

The comprehensive pollution index has been frequently utilized for water quality assessment worldwide because of its relatively strong comprehensiveness (Hope et al.

Table 1 Analytical methods for the water quality parameters

Parameters	Abbreviations	Units	Analytical methods
Dissolved oxygen	DO	mg/L	Probe method
Potassium permanganate index	COD_{Mn}	mg/L	Permanganimetric method
5-day biochemical oxygen demand	BOD_5	mg/L	Dilution and inoculation test
Ammonium nitrogen	NH_4^+-N	mg/L	Pay reagent luminosity law
Petroleum	Petrol	mg/L	Infrared spectrophotometry
Total phosphorus	TP	mg/L	Ammonium molybdate spectrophotometric method
Total nitrogen	TN	mg/L	Alkaline potassium persulfate method

Table 2 The classification standards for water quality

Classification	Water quality grading (M)	Principal component analysis (Z)	Water quality identification index ($X_1 \cdot X_2$)	Classification	Nemerow pollution index (P)	Comprehensive pollution index (R)
I	>10	<−2.04	<2	Clean	<0.80	<0.20
II	8-10	(−2.04)–(−1.71)	2-3	Slightly polluted	0.80–2.50	0.20–0.40
III	6-8	(−1.71)–(−1.21)	3-4	Moderately polluted	2.50–4.25	0.40–1.00
IV	4-6	(−1.21)–(−0.17)	4-5	Heavily polluted	4.25–7.20	1.00–2.00
V	2-4	(−0.17)–(1.26)	5-6	Seriously polluted	>7.20	>2.00
Inferior to V	<2	>1.26	6-7	Very seriously polluted		
Malodorous and black			>7	Very seriously polluted		

1992; Khanna 2000). The ratio of the measured water quality parameter to its corresponding water quality standard value is first calculated as the "relative" pollution index. Finally, the "comprehensive" pollution index, which is a measure of the cumulative water pollution level, is determined as the arithmetic mean value from the sum of relative pollution indices. The water quality was assessed by comparing the calculated comprehensive pollution index with the classification standard (Table 2). The mathematical formula for the comprehensive pollution index is:

$$R = \frac{1}{n} \sum_{i=1}^{n} P_i$$

where R is the comprehensive pollution index, n is the total number of water quality parameters, and P_i is the pollution index of parameter i.

Principle component analysis

Principal component analysis is frequently employed for the purpose of evaluating water quality (Dalal et al. 2010). PCA is designed to convert the original variables into new, uncorrelated variables (axes), called the principal components, which are linear combinations of the original variables. The axes determined by PCA lie along the directions of maximum variance. PCA provides an objective way of calculating indices so that variation in the data can be accounted for as concisely as possible (Phung et al. 2015). It provides information on the most meaningful parameters, which describes the whole data set interpretation, provides data reduction, and summarizes the statistical correlation among water quality constituents with minimum loss of the original

information (Helena et al. 2000). The principal component can be expressed as:

$$z_k = a_{k1}X_1 + a_{k2}X_2 + \cdots + a_{kn}X_n$$
$$Z = (z_1 V_1 + z_2 V_2 + \cdots + z_m V_m)/(V_1 + V_2 + \cdots + V_m)$$

Where, z is the component score, a is the component loading, X is the measured value of a parameter, k is the component number, n is the total number of parameters, Z is the comprehensive score, V is the total variance of each component, and m is the total number of components. Five water quality classes (GB3838-2002) were considered as five special samples and the comprehensive scores of each class were used to determine the water quality classification.

Fuzzy comprehensive evaluation method

The fuzzy comprehensive evaluation is the process of evaluating an objective utilizing fuzzy set theory, which comprehensively considers the contributions of multiple related indicators according to weights and decreases the fuzziness by using membership functions (Chen et al. 2005). The evaluation was carried out in six steps as follows: (i) selecting assessment parameters and establishing assessment criteria, (ii) establishing membership functions, (iii) calculating the membership function matrix, (iv) calculating the weights matrix, (v) calculating the membership degree, and (vi) determining the final water quality classification. The classification whose membership degree is the largest is the water quality classification.

The fuzzy set comprehensive evaluation method can improve understanding of the diverse processes and complex phenomena involved in environmental studies,

which is why it has been successfully used to assess pollution levels for water quality (Lu and Lo 2002). It also resolves any fuzzy boundary problems and controls for possible effects due to monitoring errors or inconsistencies.

A. The mathematical formulas for the membership functions are as follows:

1) Water quality class I, that is $j=1$, the membership function is:

$$r_{i1} = \begin{cases} 1 & 0 \le X_i \le S_{i1} \\ \dfrac{S_{i2} - X_i}{S_{i2} - S_{i1}} & S_{i1} \le X_i \le S_{i2} \\ 0 & S_{i2} < X_i \end{cases}$$

2) Water quality classes II, III, and IV, that is $j=2, 3$, and 4, the membership function is:

$$r_{ij} = \begin{cases} 1 & X_i = S_{ij} \\ \dfrac{X_i - S_{ij-1}}{S_{ij} - S_{ij-1}} & S_{ij-1} < X_i < S_{ij} \\ \dfrac{X_i - S_{ij+1}}{S_{ij} - S_{ij+1}} & S_{ij} < X_i \le S_{ij+1} \end{cases}$$

3) Water quality class V, that is $j=5$, the membership function is:

$$r_{i5} = \begin{cases} 1 & X_i \ge S_{i5} \\ \dfrac{X_i - S_{i4}}{S_{i5} - S_{i4}} & S_{i4} < X_i < S_{i5} \\ 0 & X_i \le S_{i4} \end{cases}$$

where X is the measured value of parameter i; S_{ij-1} and S_{ij}, S_{ij+1} are the standard value of parameter i for classes j-1, j, $j+1$; and r_{ij} is the membership degree of each parameter i for each class j.

B. The mathematical formula for the membership function matrix is as follows:

$$R = \left[r_{ij} \right] = \begin{bmatrix} r_{11} \cdots r_{15} \\ \vdots \cdots \vdots \\ r_{n1} \cdots r_{n5} \end{bmatrix}$$

where r_{ij} indicates the fuzzy membership of parameter I to class j, and R is the membership function matrix which consists of water quality parameters and classes.

C. The mathematical formula for the calculation of the weights matrix is:

$$W_i = \frac{X_i}{\frac{1}{5}\sum_{j=1}^{5} S_{ij}}$$

$$a_i = \frac{W_i}{\sum_{i=1}^{n} W_i}$$

$$A = [a_1, a_2, \cdots, a_n]$$

where W_i is the weight of parameter i; a_i is the normalized form of W_i; and A is the weights matrix.

D. Water quality assessment by fuzzy membership is based on the matrix B,

$$B = A \times R = [b_1, b_2, b_3, b_4, b_5]$$

where b is the membership degree for each class. The fuzzy B is the matrix of membership for each water quality class. Water samples are classified to the class with the maximum membership.

Comprehensive water quality identification index

The comprehensive water quality identification index is a relatively new tool for general water quality assessment of surface waters. It evaluates general water quality both qualitatively and quantitatively; it classifies general water quality conditions into five classes that support aquatic communities (high quality (type I and type II), moderate quality (type III), polluted (type IV), and highly polluted (type V)) and two classes termed

inferior to class V that do not support aquatic communities termed inferior to V and malodorous and black (Xu 2005). The evaluation was performed in three steps as follows: (i) calculating the single-factor water quality identification index, (ii) calculating the comprehensive water quality identification index, and (iii) identifying the water quality classification according to the comprehensive water quality identification index and assessment criteria (Table 2).

The water quality identification index comprises integral digits and three fractional digits. The structure is as follows:

$$I_{wq} = X_1.\ X_2X_3X_4$$

The meaning and calculation method for each digit are as follows:

A. X_1 indicates the comprehensive classification of water quality, X_2 is the location of water quality within the variation range of Class X_1, so it can more specifically evaluate the water quality within a given classification unit. $X_1 \cdot X_2$ can be calculated as follows:

  1) If the classification of water quality is between class I and class V according to GB3838-2002, as to each variable except DO,

$$P_i = j + \frac{X_i - S_{ij-1}}{S_{ij} - S_{ij-1}}$$

As to DO,

$$P_i = j + \frac{S_{ij-1} - X_i}{S_{ij-1} - S_{ij}}$$

  2) If the classification of water quality is inferior to class V according to GB3838-2002, as to each variable except DO,

$$P_i = 6 + \frac{X_i - S_{i5}}{S_{i5}}$$

As to DO,

$$P_i = 6 + \frac{S_{i5} - X_i}{S_{i5}}$$

where X is the measured value of parameter i, S_{ij} is the standard value of parameter i for class j, and P_i is the single-factor water quality identification index of $j=1, 2, 3, 4,$ and 5 for classes I, II, III, IV, and V, respectively.

Finally,

$$X_1.X_2 = \frac{1}{n}\sum_{i=1}^{n} P_i$$

B. X_3 is the total number of parameters that are inferior to the water quality standard for the region. For example, a value of $X_3=1$ indicates that one parameter involved in the assessment does not meet the water quality standard for the region.

C. X_4 is used to identify if the comprehensive water quality meets the desired water quality standard for the region.

1) If the comprehensive water quality is inferior to the desired water quality standard and $X_2 \neq 0$

$$X_4 = X_1 - f$$

2) If the comprehensive water quality is inferior to the desired water quality standard and $X_2 = 0$

$$X_4 = X_1 - f - 1$$

where f is the desired water quality standard for the region.

Results and discussion

Basic statistics of water quality parameters in the Wen-Rui Tang River

The descriptive statistics of the original data for the seven water quality parameters are shown in Table 3.

DO varied greatly from 0.13 to 10.05 mg/L, with 87 and 52 % of the samples exceeding water quality standards class III (the threshold for drinking water) and V (minimum quality to support aquatic ecosystem health), respectively. The average concentration of COD_{Mn} was 4.39 mg/L; more than half of the samples (54 %) exceeded the class II water quality standard with 17

Table 3 Descriptive statistics for water quality parameters (mg/L)

Parameters	N	Mean	SD	CV (%)	Maximum	Minimum
DO	102	2.69	2.18	81.3	10.05	0.13
COD_{Mn}	102	4.39	2.05	46.7	12.40	1.3
BOD_5	102	5.15	3.74	72.6	19.00	1.00
NH_4^+-N	102	5.59	4.6	82.3	22.60	0.12
Petroleum	102	0.08	0.04	57.5	0.31	0.05
TP	102	0.43	0.24	56.8	1.56	0.03
TN	102	7.49	5.46	72.9	29.90	0.38

N number of samples, SD standard deviation, CV coefficient of variation

and 1 % exceeding class III and IV water quality standards, respectively. For BOD_5, 55 % samples met the water quality standard class III. The highest concentration of BOD_5 (19 mg/L) was 4.8, 3.2, and 1.9 times higher than class III, IV, and V water quality standards, respectively. Nitrogen pollution was the most serious pollution problem in the Wen-Rui Tang River. NH_4^+-N was the main form of nitrogen in this watershed, constituting 74.6 % of the TN concentration on average. The ratios for the mean values of NH_4^+-N and TN compared to the class V standard of 2.0 mg N/L(GB3838-2002) were 2.8 and 3.5, respectively. About 78 and 89 % of NH_4^+-N and TN concentrations, respectively, exceeded the class V water quality standard. The highest concentration of NH_4^+-N and TN were 11.3 and 15.0 times higher than the class V water quality standard, respectively. For petroleum, almost all samples complied with the class III and IV water quality standards. The mean value of TP was 0.43 mg/L, with 82, 69 and 56 % of the samples exceeding water the quality standards class III, class IV, and class V, respectively.

The coefficient of variation (CV) provides a measure of variability that eliminates the influence caused by differences of units or mean values between two or more datasets (Yang et al. 2013). As shown in Table 3, CV values ranged from 46.7 to 82.3 %, indicating that these water quality parameters were moderately to highly variable in the study area during time of the study.

Water quality assessment

Results of the seven assessment methods

Seven assessment methods were employed to evaluate the water quality classification for the 17 sampling sites of the Wen-Rui Tang River (Table 4). The mean values for the seven water quality parameters at each sampling site are shown in Appendix B. Based on the single-factor assessment method, the water quality from 16 of the 17 monitoring sites was assessed as inferior class V. The assessment results for the water quality grading method characterized the water quality of Guoxi as class III, Quxi and Jiushan as class IV, Xiawan, Tangxia, and Huiqiao as inferior class V, and all other sites as class V. Assessment results from the Nemerow pollution index indicated that the water quality of Guoxi and Quxi were clean, while the water quality of Shuitan was characterized as seriously polluted. The assessment results determined using the comprehensive pollution index method showed that the water quality of Guoxi and Quxi were slightly polluted, Xinqiao, Xianmen, Xi-ao, and Jiushan were moderately polluted, while all other sites were heavily or seriously polluted. The results of principle component analysis are shown in Table 5. The comprehensive scores of the 17 sites were compared to the comprehensive scores of 5 water quality classes to determine the water quality classification. The water quality of Guoxi and Quxi were assessed as class II, Jiushan was assessed as class III, Xinqiao, Xianmen, and Xi-ao were assessed as class IV, and all other sites were assessed as class V or inferior class V. The fuzzy comprehensive evaluation method characterized the water quality for 16 of the 17 monitoring stations as class V; Guoxi was classified as class IV. The comprehensive water quality identification index showed that the water quality of Guoxi and Quxi were classes II and III, respectively, while the water quality of 13 monitoring sites were class V or inferior class V, including three stations with malodorous and black water characteristics.

Table 4 Water quality assessment results comparing the seven assessment methods

Monitoring sites	Single-factor assessment	Water quality grading	Nemerow pollution index	Comprehensive pollution index	Principal component analysis	Fuzzy comprehensive evaluation	Water quality identification index
Xinqiao	Inferior V	V (3.43)	Slightly polluted (1.70)	Moderately polluted (0.91)	IV	V	V (5.030)
Xianmen	Inferior V	V (2.86)	Slightly polluted (1.91)	Moderately polluted (0.95)	IV	V	V (5.130)
Xiawan	Inferior V	Inferior V (1.71)	Heavily polluted (5.44)	Seriously polluted (2.48)	Inferior V	V	Inferior V (7.132) malodorous and black
Xi-ao	Inferior V	V (3.43)	Slightly polluted (1.64)	Moderately polluted (0.85)	IV	V	IV (4.920)
Wutian	Inferior V	V (2.29)	Moderately polluted (3.02)	Heavily polluted (1.72)	V	V	V (5.740)
Tangxia	Inferior V	Inferior V (1.71)	Moderately polluted (3.46)	Heavily polluted (1.78)	V	V	Inferior V (6.241)
Shuitan	Inferior V	V (2.00)	Seriously polluted (6.97)	Seriously polluted (2.76)	Inferior V	V	Inferior V (7.432) malodorous and black
Shizihe	InferiorV	V (2.00)	Heavily polluted (5.82)	Seriously polluted (2.97)	Inferior V	V	Inferior V (7.132) malodorous and black
Qinfen	InferiorV	V (2.00)	Moderately polluted (3.17)	Heavily polluted (1.83)	V	V	Inferior V (6.141)
Nanbaixiang	Inferior V	V (2.29)	Moderately polluted (3.19)	Heavily polluted (1.55)	V	V	V (5.930)
Mishaiqiao	Inferior V	V (2.00)	Slightly polluted (2.49)	Heavily polluted (1.16)	V	V	V (5.540)
Quxi	Inferior V	IV (5.71)	Clean (0.79)	Slightly polluted (0.37)	II	V	III (3.410)
Jiushan	Inferior V	IV (5.14)	Slightly polluted (1.03)	Moderately polluted (0.51)	III	V	IV (4.110)
Huiqiao	Inferior V	Inferior V (1.71)	Heavily polluted (4.46)	Seriously polluted (2.55)	Inferior V	V	Inferior V (6.531)
Guoxi	IV	III (7.43)	Clean (0.44)	Slightly polluted (0.25)	II	IV	II (2.900)
Guangming	Inferior V	V (2.29)	Heavily polluted (4.50)	Seriously polluted (2.03)	V	V	V (5.840)
Dongshuichang	Inferior V	V (2.86)	Moderately polluted (3.08)	Heavily polluted (1.53)	V	V	V (5.540)

Table 5 Factor scores and grades of sampling sites

Monitoring sites	F1 score	F2 score	Comprehensive score	Grades (serious-slight)	Water quality classification
Xinqiao	−0.25	−0.51	−0.57	13	IV
Xianmen	−0.28	−0.38	−0.54	12	IV
Xiawan	1.64	0.36	2.22	1	Inferior V
Xi-ao	−0.46	−0.49	−0.82	14	IV
Wutian	0.40	−0.48	0.25	9	V
Tangxia	0.54	0.02	0.67	7	V
Shuitan	1.50	0.16	1.94	2	Inferior V
Shizihe	1.49	−0.07	1.81	4	Inferior V
Qinfen	0.66	−0.12	0.75	6	V
Nanbaixiang	0.48	−0.37	0.40	8	V
Mishaiqiao	0.02	−0.35	−0.15	11	V
Quxi	−1.21	−0.60	−1.80	16	II
Jiushan	−0.86	−0.33	−1.23	15	III
Huiqiao	1.45	0.13	1.86	3	Inferior V
Guoxi	−1.26	−0.75	−1.94	17	II
Guangming	0.94	−0.38	0.97	5	V
Dongshuichang	0.24	−0.46	0.06	10	V
I	−1.39	−0.62	−2.04		
II	−1.24	−0.34	−1.71		
III	−0.99	0.03	−1.21		
IV	−0.85	1.72	−0.17		
V	−0.58	3.85	1.26		

Advantages and limitations of the seven assessment methods

In order to better understand and apply each assessment method referred to in this study, the advantages and limitations for the seven methods are of great significance and are evaluated as follows:

1. The single-factor assessment method is determined according to the principle of maximum membership grade. Only the maximum contributing factor (i.e., the most impaired water quality parameter) is considered in this method; therefore, all other factors were not considered in the assessment results. In the Wen-Rui Tang River, total nitrogen was generally the most impaired water quality parameter, although several other parameters were also highly impaired (e.g., dissolved oxygen, and chemical and biological oxygen demand). Thereby, this method does not fully depict the overall water quality when multiple impairments are contributing, and it is difficult to compare with water quality assessments from different areas that might have contrasting pollution issues.

2. The water quality grading method neglects the influence of the extreme contributing factors (maximum and minimum pollutant parameter values) by averaging all contributing factors within the data set. If the scores of some contributing factors are disproportionately high, then the total score will be increased making it potentially difficult to evaluate the overall water quality status among sites.

3. Both the dominant parameter and the average contribution of all factors are taken into account for the Nemerow pollution index. However, this method tends to overemphasize the influence of the maximum evaluation factor (i.e., most serious pollutant factor). Thus, the comprehensive score will be increased in situations where the index value for one evaluation factor is much higher than those of others. Hence, there exists the potential problem that the assessment results may disagree with the overall water quality status.

4. The comprehensive pollution index method provides a comprehensive water quality status, but it is based on the premise that each evaluation factor has an equal contribution to the overall water quality, which is not always reasonable in practice. In addition, this method, as well as the Nemerow pollution index, does not intuitively identify the classification of the overall water quality condition.

5. A particular problem in the case of water quality monitoring is the complexity associated with analyzing the large number of measured variables. Principle component analysis helps in the interpretation of complex data matrices providing a better understanding of water quality (Bu et al. 2010). This method not only considers water quality inferior to class V but also provides good separation for higher water quality classifications. However, PCA limitations include ignoring the degree of data dispersion and a weakness in processing nonlinear data. Thus, principle component analysis may not have good accuracy and reliability.

6. The fuzzy comprehensive evaluation method is capable of describing the fuzzy character of classified bounds for water quality and can reflect the overall water quality condition objectively. However, there are some limits to this method, such as overemphasis of extreme water quality values. In this case, some information is lost and the scientific basis for the weighting factor is not always clear. In addition, this method can not characterize water quality conditions inferior class V.

7. The water quality identification index was verified to have good accuracy and reliability as inferred by the assessment results agreeing very well with the overall field evaluation of water quality conditions. This method was considered the best choice for evaluating the water quality conditions of the heavily polluted, urban portion of the Wen-Rui Tang River due to the following characteristics. Firstly, it can fully depict the general water quality and also assesses the overall water quality conditions both qualitatively and quantitatively. Secondly, it assesses general water quality using a group of assessment items instead of using only the worst assessment item, so the assessment of general water quality is reasonable. Thirdly, it can also be used to compare general water quality with the same classification and also successfully classifies water quality conditions inferior class V, a reoccurring problem in the urban portion of the Wen-Rui Tang River.

A summary of the evaluation guidelines used to judge the efficacy and the advantages/limitations of the seven assessment methods are shown in Table 6.

According to the characteristics and efficacy mentioned above, the best applications for each assessment method are suggested as follows: (1) the single-factor assessment method can be applied to conditions when a single water quality parameter impairs water quality more seriously than others; (2) the water quality grading method can be applied to conditions where the class of each parameter is generally equal according to GB3838-2002; (3) both the Nemerow pollution index and comprehensive pollution index methods can be applied to judge if the water quality meets environmental water functions. However, the comprehensive pollution index is most reasonable when each evaluation factor has an equal contribution to the overall water quality. When a specific pollution factor plays a dominant impairment role, the Nemerow index is more suitable. (4) Principle component analysis is best applied when the relationships among water quality parameters are linear; (5) the fuzzy comprehensive evaluation method should be applied when the water quality classification for each water quality parameter is better than the class V water quality standard; and (6) when water quality is seriously polluted and many water quality parameters are worse than class V water quality standard, the water quality identification index will be the best choice to assess the overall water quality.

Table 6 The evaluation guidelines and results for performance of the seven assessment methods

Assessment methods	Evaluation guidelines					
	A	B	C	D	E	F
Single-factor assessment	√	√	×	×	×	×
Water quality grading	√	√	√	×	×	×
Nemerow pollution index	√	×	√	√	×	×
Comprehensive pollution index	√	×	√	√	×	×
Principal component analysis	×	√	√	×	√	×
Fuzzy comprehensive evaluation	×	√	×	×	×	×
Water quality identification index	√	√	√	√	√	√

A simple calculation, *B* judges overall water quality classification, *C* differentiation with the same classification, *D* judges if water quality meets environmental water functions, *E* characterizes water quality inferior class V, *F* classifies water quality inferior class V. √ meets evaluation guidelines, × does not meet evaluation guidelines

Fig. 2 Comparison of single-factor water quality identification index (mean±std.dev.)
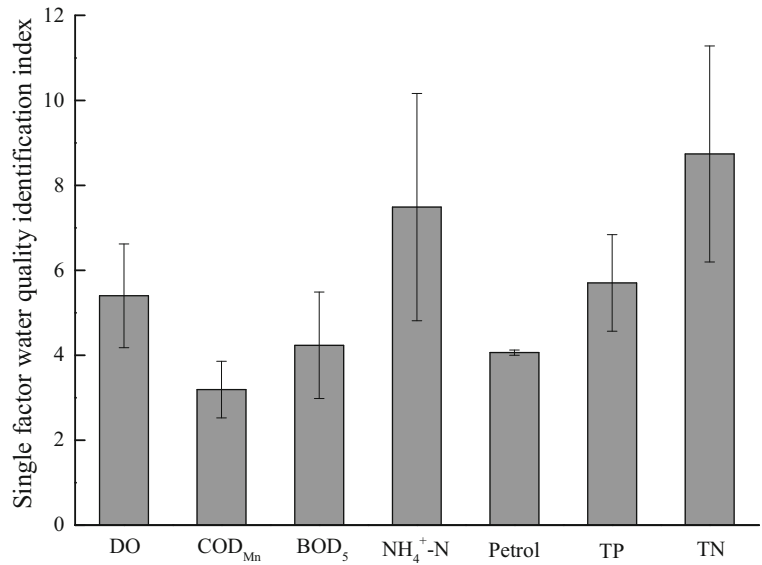
The distribution characteristics of the water quality identification index

Analysis of pollutant contributions to water quality impairment

The influence of each pollutant to water quality impairment can be obtained by calculating the average value for each water quality parameter from each single-factor water quality identification index (Fig. 2). By this approach, the most severe pollutants in the Wen-Rui Tang River were TN and NH_4^+, followed by TP and DO. This overall assessment accurately reflects the severe eutrophication and hypoxia that occur in the Wen-Rui Tang River.

Temporal variation of the water quality identification index

The bimonthly variation of water quality is shown in Fig. 3. The pollution degree was least severe in May and most severe in January. The water quality identification index was closely related to the precipitation. It implied that the precipitation was able to dilute the concentration of pollutants, thus contributing to reduced water pollution severity in the Wen-Rui Tang River, especially in flood season (Mei et al. 2014). In addition, the higher temperatures in summer promoted the activity of algae and microorganism that contributed to increased absorption and degradation of pollutants (Dierk and Michael 2008; Houser and Richardson 2010).
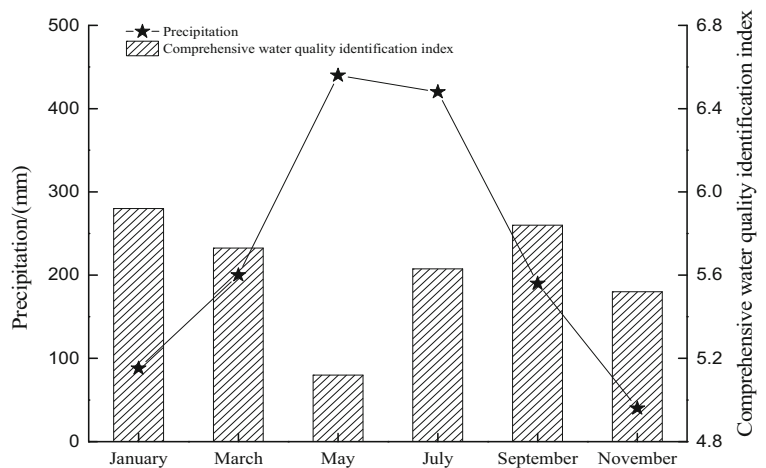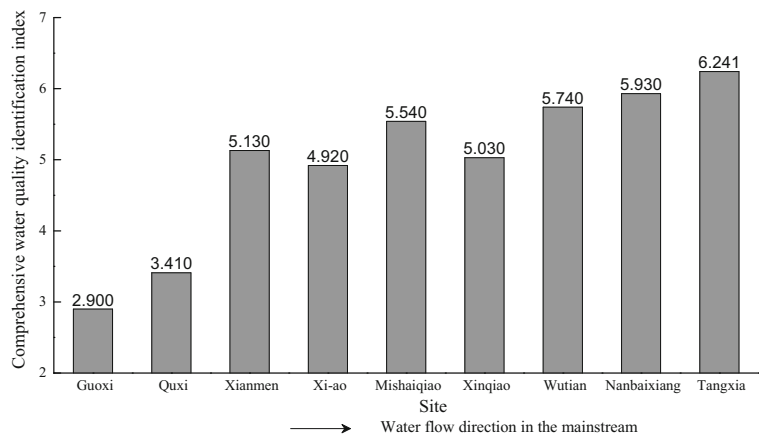
Fig. 3 Temporal variation of CWQII

Fig. 4 CWQII variation in the mainstream

Spatial variation of the comprehensive water quality identification index

The water quality classification for each monitoring site was determined according to the comprehensive water quality identification index as shown in Table 4. The mean value for the comprehensive water quality identification index of the 17 monitoring sites was 5.570, which indicates that the mean water quality condition of the Wen-Rui Tang River was class V in 2010. The degree of water pollution for the 17 sites followed the order of Shuitan (7.432)>Xiawan (7.132) and Shizihe (7.132)>Huiqiao (6.531)>Tangxia (6.241)>Qinfen (6.141)>Nanbaixiang (5.930)>Guangming (5.840)> Wutian (5.740)>Mishaiqiao (5.540) and Dongshuichang (5.540)>Xianmen (5.130)>Xinqiao (5.030)>Xi-ao (4.920)>Jiushan (4.110)>Quxi (3.410)>Guoxi (2.900). Water at Guoxi was class II indicating relatively good water quality, while the water quality at Quxi and Jiushan was assessed as class IV indicating better than the class V minimum quality necessary to support aquatic ecosystem health. These assessment results agreed very well with the field observation of overall water quality conditions. The monitoring sites that had the worst water quality conditions were Shuitan, Xiawan, and Shizihe. The water quality of Xiawan and Shuitan was the most seriously polluted due to their locations in the Longwan industrial area of Wenzhou where the water quality was affected by industrial waste water. Huiqiao, Shizihe, Qinfen, Dongshuichang, Guangming, and Jiushan were located in the main urban area of Wenzhou where various sewage discharge outlets are widely distributed. The high pollutant concentrations in these sites were determined

by both the untreated domestic sewage and the long hydrological residence times in these river branches (Lu et al. 2011). However, compared to other sites, the Jiushan site was in better water quality for the Jiushan river segment was protected for water sports (e.g., swimming and dragon boat races).

In general, the comprehensive water quality identification index increased with the water flow direction in the mainstream (Fig. 4). Guoxi and Quxi were located in upstream rural areas and displayed relatively little impact from municipal pollution sources resulting in much better overall water quality conditions. When the water flows into urban area from Xianmen, the water quality was strongly affected by domestic and service sector pollution sources. These pollutants accumulated along the water flow path in the mainstream and peaked at Tangxia, which was the most downstream site along the mainstream.

Conclusions

Both the single-factor assessment method and the water quality grading method were limited in their ability to characterize the general water quality conditions as they only consider the maximum contributing factor (i.e., the most impaired water quality parameter) and reduce the influence of the extreme contributing factors (maximum and minimum pollutant parameter values), respectively; the comprehensive pollution index, as well as Nemerow pollution index, did not effectively assess the general water quality condition because they tend to overemphasize the influence of the maximum evaluation factor (i.e., most serious pollutant factor) and are based on the

often unreasonable assumption that each evaluation factor has an equal contribution to the water quality; principle component analysis (PCA) provides a convenient tool to treat the complex data, but it does not have good accuracy and reliability because it ignores the degree of data dispersion and cannot reasonably process nonlinear data; the fuzzy comprehensive evaluation method was in good agreement with the field observations of water quality conditions at a given site; however, it was not capable of classifying water quality conditions inferior to class V. The water quality identification index was able to classify water quality inferior to class V and also assessed overall water quality in both qualitative and quantitative terms. Therefore, the water quality identification index was chosen as the best choice for evaluation of the water quality conditions of the heavily polluted Wen-Rui Tang River. Additionally, a guideline for the applications of these methods was presented in terms of their characteristics and efficacy in this study. This guideline will help decision makers and stakeholders to decide the appropriate method regarding water quality evaluation under specific conditions.

The assessment results from the single-factor water quality identification index showed that the main pollutants in the Wen-Rui Tang River were TN comprised largely of NH_4^+, followed by TP and low DO.

The comprehensive water quality identification index showed that the water quality in the Wen-Rui Tang River was seriously polluted in 2010. The temporal variation of water quality was closely related to precipitation (i.e., dilution effect). Of the 17 monitoring sites, 13 were class V or inferior to class V, with 3 sites displaying highly impaired malodorous and black waters (i.e., sulfide-rich waters). The spatial variation of water quality was associated with anthropogenic influences (urban, industrial, and agriculture activities) and water flow direction. The water quality for Xiawan and Shuitan, which were located in an industrial area, Shizihe, Huiqiao, and Qinfen, which were located in the main urban area of Wenzhou, had the worst water quality conditions. In contrast, Guoxi and Quxi located in the upstream rural areas had much better water quality conditions. Thus, the results of this study demonstrate that the water quality was generally deteriorated in the downstream portion of the mainstream due to cumulative accumulation of pollutants along the flow path. The water quality identification index methods can effectively identify sites with the most serious pollution conditions for prioritizing water quality management and remediation actions.

Appendix A

Table 7 Environmental guideline of national quality standards for surface waters, China (GB3838-2002) (units: mg/L)

Parameters	Category of water quality standards				
	I	II	III	IV	V
DO	>7.5	6	5	3	2
COD_{Mn}	<2	4	6	10	15
BOD_5	<3	3	4	6	10
NH_4^+-N	<0. 15	0.5	1	1.5	2
Petroleum	<0.05	0.05	0.05	0.5	1
TP	<0.02	0.1	0.2	0.3	0.4
TN	<0.2	0.5	1	1.5	2

Appendix B

Table 8 Average concentration of the water quality parameters at each sampling site considered in this study (mg/L)

Sites	DO	COD$_{Mn}$	BOD$_5$	NH$_4^+$-N	Petroleum	TP	TN
Xinqiao	2.87	3.57	3.37	2.84	0.05	0.49	4.44
Xianmen	3.52	3.60	4.37	3.15	0.07	0.41	5.05
Xiawan	2.17	7.10	9.50	11.42	0.11	0.75	14.55
Xi-ao	3.24	3.50	3.20	2.93	0.07	0.35	4.32
Wutian	1.35	3.98	4.23	4.68	0.06	0.48	7.65
Tangxia	1.88	6.11	4.97	8.21	0.14	0.47	9.12
Shuitan	2.58	6.23	10.22	13.41	0.09	0.29	18.92
Shizihe	1.28	5.72	7.84	13.50	0.11	0.33	15.35
Qinfen	1.57	5.48	5.50	6.67	0.08	0.58	8.18
Nanbaixiang	2.18	4.50	4.78	6.92	0.06	0.54	8.48
Mishaiqiao	1.96	4.08	4.50	3.57	0.07	0.41	6.64
Quxi	4.90	2.43	2.15	0.57	0.09	0.08	2.12
Jiushan	6.09	3.80	3.73	0.94	0.06	0.26	2.73
Huiqiao	0.94	5.73	7.88	8.71	0.13	0.69	9.37
Guoxi	6.66	2.02	1.83	0.33	0.05	0.13	1.13
Guangming	0.88	3.85	5.90	5.33	0.05	0.62	6.23
Dongshuichang	1.32	3.53	4.75	4.15	0.05	0.43	5.52

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