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RESEARCH ARTICLE

Evaluation of spatial-temporal variations and trends in surface water quality across a rural-suburban-urban interface

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Abstract Water quality degradation is often a severe consequence of rapid economic expansion in developing countries. Methods to assess spatial-temporal patterns and trends in water quality are essential for guiding adaptive management efforts aimed at water quality remediation. Temporal and spatial patterns of surface water quality were investigated for 54 monitoring sites in the Wen-Rui Tang River watershed of eastern China to identify such patterns in water quality occurring across a rural-suburban-urban interface. Twenty physical and chemical water quality parameters were analyzed in surface waters collected once every 4–8 weeks from 2000 to 2010. Temporal and spatial variations among water quality parameters were assessed between seasons (wet/dry) and among major land use zones (urban/suburban/rural). Factor analysis was used to identify parameters that were important in assessing seasonal and spatial variations in water quality. Results revealed that parameters related to organic pollutants (dissolved oxygen (DO), chemical oxygen demand (manganese) (COD_{Mn}), and 5-day biochemical oxygen demand (BOD_5)), nutrients (ammonia nitrogen (NH_4^+-N), total nitrogen (TN), total phosphorus (TP)), and salt concentration (electrical conductivity (EC)) were the most important parameters contributing to water quality variation. Collectively, they explained 70.9 % of the total variance. A trend study using the seasonal Kendall test revealed reductions in COD_{Mn}, BOD_5, NH_4^+-N, petrol, V-phen, and EC concentrations over the 11-year study period. Cluster analysis was employed to evaluate variation among 14 sampling sites representative of dominant land use categories and indicated three, three, and four clusters based on organic, nutrient, and salt water quality characteristics, respectively. Factors that are typically responsible for water quality degradation (including population, topography, and land use) showed no strong correlation with water quality trends implying considerable point source inputs in the watershed. The results of this study help inform ongoing water quality remediation efforts by documenting trends in water quality across various land use zones.

Keywords Water quality · Statistical analysis · GIS · Spatial analysis · Land use · Trend analysis

Introduction

Water pollution occurs worldwide as a result of anthropogenic activities, including unprecedented population growth, urbanization, industrialization, and agricultural practices (Jones and Clark 1987; Baker 2003; Claessens et al. 2006; Li et al. 2009b). Human disturbance on water quality occurs at the watershed scale due to changes in land use/land cover, which impact the physical, chemical, and ecological characteristics of aquatic environments (Donohue et al. 2006; Chang 2007).

Due to seasonal and regional characteristics of river hydrology and water quality, identifying spatial-temporal variations and trends of water quality at the watershed scale have become a major focus of research. In previous studies, multivariate statistical techniques, such as cluster analysis (CA),

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principal component analysis (PCA), factor analysis (FA), discriminant analysis (DA), and multivariate regression analysis (MRA), combined with geographic information system (GIS) tools, were used to interpret large and complex datasets to evaluate temporal-spatial variations, predicate trends, and identify possible impact factors/sources in water quality. For example, Alberto et al. (2001) compared the results of CA, FA/PCA, and DA to evaluate both spatial and temporal changes in Suquia River (Argentina) water quality. PCA has been used to extract the factors associated with hydrochemistry variability in the Passaic River (USA) (Bengraı ne and Marhaba 2003) and seasonal correlations of water quality parameters in the lower St. Johns River (USA) (Ouyang et al. 2006). Li et al. (2009a) also used PCA and MRA to display spatial and seasonal differences and relationships to land use/land cover in the riparian zone in upper Han River (China). Multivariate statistical analysis was used to determine spatial-temporal variations and source apportionment in the Gomti River watershed (northern India) (Singh et al. 2005). Shrestha et al. (2007) used CA and DA to identify the significant parameters and optimize the monitoring network of the Fuji River (Japan). The performance of multiple linear regression models and constrained least squares models was compared for quantitatively predicting stream water quality in the Yeongsan River (South Korea) (Kang et al. 2010). Bu et al. (2010) used CA, FA, and gridding methods to illustrate that water quality deteriorated from headwater to downstream areas in the Jinshui River (China). Similarly, a variety of techniques were used to investigate the distribution of dissolved heavy metals in the Changjiang River (China) (Wang et al. 2011) and to determine spatial and temporal trends in water quality for the Han River Basin (South Korea) along with the impact from anthropogenic (land use) and natural factors (topography and soils) (Chang 2008). Results from most of these studies revealed that water quality was highly linked with land use patterns and discharge from industry, agriculture, and/or sewage. These studies demonstrated that spatial-temporal variations of water quality strongly depend on the spatial and temporal scales of analysis.

A shortcoming of many previous studies is that they do not explicitly consider the integrated effects of spatial and temporal scales. Some studies investigated temporal trends of water quality using annual mean values of all the sites or a few selected sites while ignoring spatial dependence among sites and seasonal change. Similarly, other studies investigated spatial variation of water quality using mean values from each monitoring site for the entire study period while ignoring changes in the landscape over time. Therefore, the goal of this paper was to establish a combined spatial-temporal method to comprehensively explore water quality variations occurring at the rural-suburban-urban interface. We expand on the previous work by Lu et al. (2011) and Yang et al. (2013) by extending the study period from 1 or 2 to 11 years of water quality monitoring data in the Wen-Rui Tang River watershed of eastern China. Due to rapid economic development, water quality of this river has been severely degraded. It is necessary to characterize and identify the temporal-spatial variations in water quality through long-term comprehensive investigations to achieve sustainable management and remediation of water quality conditions.

Therefore, the purpose of this study was to use a novel combined spatial-temporal analysis method to extract information over an 11-year record about (1) the similarities or differences between parameter levels for various monitoring periods and land use zones, (2) significant factors responsible for temporal and spatial variations in water quality, (3) trends in water quality during the 2000–2010 time period, and (4) the influence of possible pollutant sources (natural and anthropogenic) on water quality parameters. The results of this study will help inform ongoing adaptive management efforts aimed at water quality remediation by documenting trends in water quality across various land use zones.

Materials and methods

Study area

The Wen-Rui Tang River is located in Wenzhou, Zhejiang Province on the east coast of China and flows eastward to the East China Sea (Fig. 1a). The total length of the river with tributaries is 1,178 km, and the length of the main stem is 33.9 km. The Wen-Rui Tang River system is important for aquaculture, transportation, irrigation, and waste removal. The Wen-Rui Tang River watershed is approximately 740 km^2 with about 75 % occurring on a flat alluvial plain with elevations ranging from 3.0 to 4.2 m. The average annual rainfall of this area is 1,701 mm with approximately 70 % concentrated in the wet season (April–September). River flows reflect the seasonal variation of rainfall with annual runoff of 0.91 billion m^3. A large proportion (23 %) of the watershed is a densely populated urban and industrialized area. This area is one of the rapidly developing regions in China; during the 11-year study period (2000–2010), the population increased from 7.4 to 9.1 million, GDP increased from $13.6 to $48.2 billion, and industrial added value increased from $42 to $139 billion (Fig. 1b). Wenzhou leads the private economic development in China as the proportion of private industry output increased from 7.5 to 51 % while individual industry output decrease from 29 to 19 % (Fig. 1c). Because the installation of wastewater treatment facilities and centralized sewage collection lags behind the development rate of the urban area, about ~35 % of the city had no centralized sewage collection in 2010, and both untreated domestic sewage water and industrial effluents were discharged directly into the river in some areas. Li et al. (2013) reported that organic pollutants in the

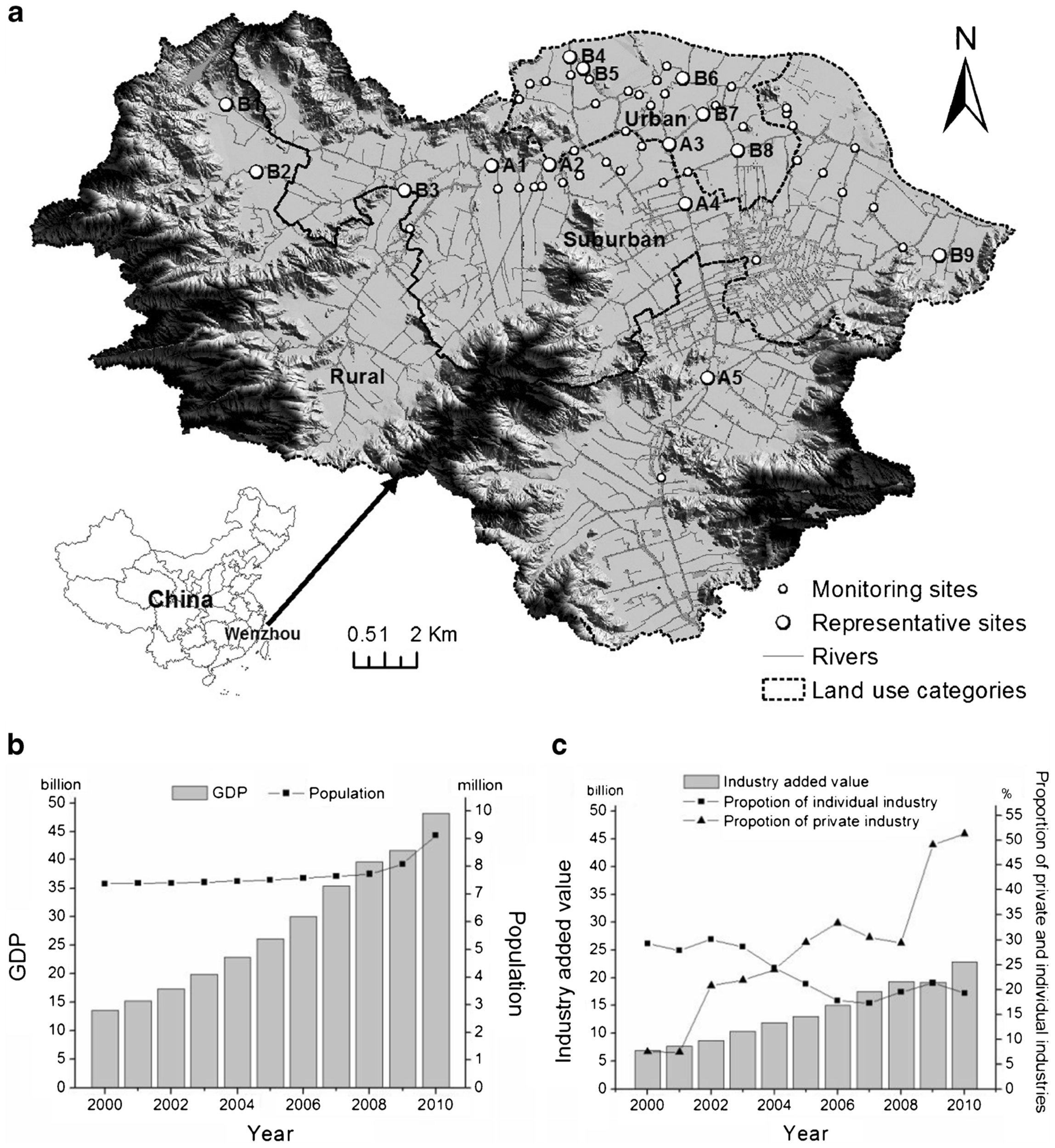

Fig. 1 Profiles of study area with **a** map of the Wen-Rui Tang River watershed, **b** population and GDP data of Wenzhou, and **c** industry output data of Wenzhou

Wen-Rui Tang River watershed mainly originate from residential point sources.

Data

Water quality data

Water quality data were obtained from 54 water quality monitoring sites established by the Wenzhou Environmental Protection Bureau (WEPB) since 2000 and the Wenzhou Water Conservation Bureau (WWCB) since 2009. There were 26 sites in the urban area, 24 sites in the suburban area, and 4 sites in the rural area. We chose 14 representative sites from the 54 sites to assess variation in water quality among dominant land use categories. These sites included five sites (A1–A5) along the main stem of the river and nine tributary sites (B1–B9). Among these 14 sites, three sites (A5, B1, and B2) were upstream in the rural area, four sites (A1, A4, B3, and B9) were within the suburban area, and the other seven sites (A2, A3, and B4–B8) were in the suburban area. The frequency of data collection from these sites was once every 4–8 weeks between 2000 and 2010. Water quality parameters included water temperature (Temp), pH, dissolved oxygen (DO), chemical oxygen demand (manganese) (COD_{Mn}), 5-day biochemical oxygen demand (BOD_5), ammonia nitrogen (NH_4^+-N), total nitrogen (TN), total phosphorus (TP), petrol, volatile phenol (V-phen), arsenic (As), chromium (Cr), lead (Pb), cadmium (Cd), mercury (Hg), copper (Cu), zinc (Zn), cyanide (CN), fluoride (F), and electrical conductivity (EC). The sampling, preservation, transportation, and analysis of the water samples were performed following standard methods (SEPBC 2002a). There were very few missing data points (less than 2 % of total samples, see Table 1), and missing values for a particular month were interpolated from the values of the same month in the previous and the following year for a given monitoring site, as well as the values from upstream and downstream sites if necessary. TN and F data were missing for the 2000 to 2003 time period.

Climate, land surface, and social-economic data

Climate data were retrieved from China Meteorological Data Sharing Service System (http://cdc.cma.gov.cn/home.do). Slope data derived from a digital elevation model (DEM) were obtained from Wenzhou Urban Planning Bureau (WUPB). Population data by census block, GDP data, and wastewater discharge and collection data for 2000–2010 were from the Wenzhou Statistical Yearbook published by Wenzhou Municipal Bureau of Statistics (WSB). Land use data were in both raster and vector formats. We used raster data from a Landsat Enhanced Thematic Mapper (ETM) at a 30-m spatial resolution to determine land use/land cover change. The vector data used for correlation analysis were originally interpreted from aerial photographs by the Land Use Survey Project of Wenzhou in 2005.

Data preprocessing

The distribution of the original water quality data was inspected using descriptive statistics, the Shapiro-Wilk test, and graphical representations (normal Q-Q plot, histogram). For the parameters that were not normally distributed, Box-Cox transformation or Johnson transformation was conducted in Minitab 15 (Minitab Inc., State College, PA) (Zhou et al. 2007). First, water quality data from the 54 monitoring sites from 2000 to 2010 were averaged across different years and seasons (dry season and wet season) to investigate the temporal water quality variations of the study area. They were also

Table 1 Min, max, and mean values and coefficient of variation (CV) of water quality data for all monitoring sites

Season	Min			Max			Mean			CV (%)		
Parameter	All	Dry	Wet	All	Dry	Wet	All	Dry	Wet	All	Dry	Wet
Temp (°C)	9.4	13.8	25.8	31.8	18.6	29.0	21.3	15.9	27.3	32.3	10.5	3.6
pH	6.80	6.96	7.06	7.61	7.38	7.38	7.21	7.21	7.24	2.2	1.7	1.2
DO (mg/L)	0.03	1.69	1.09	4.82	3.69	3.58	2.49	2.59	2.48	38.5	24.5	30.8
COD_{Mn} (mg/L)	2.19	5.58	5.26	10.61	8.64	8.30	6.69	6.88	6.56	40.6	16.9	14.9
BOD_5 (mg/L)	2.52	6.78	4.62	15.82	12.80	9.63	7.43	8.91	6.58	41.3	24.3	25.6
NH_4^+-N (mg/L)	2.66	6.04	4.61	16.04	12.81	13.01	8.07	8.90	7.42	42.2	25.9	34.3
TN (mg/L)	5.75	6.35	5.88	17.03	9.43	14.22	9.40	7.89	10.05	42.5	27.6	58.7
TP (mg/L)	0.18	0.38	0.26	5.03	1.15	1.65	0.66	0.61	0.60	94.8	41.3	65.9
Petrol (mg/L)	0.025	0.073	0.059	0.803	0.768	0.323	0.125	0.178	0.115	112.2	118.4	71.8
V-phen (mg/L)	0.001	0.002	0.002	0.050	0.017	0.008	0.005	0.006	0.004	130.8	76.4	53.7
As (mg/L)	0.001	0.001	0.001	0.006	0.004	0.005	0.002	0.002	0.002	59.7	61.5	60.5
Cr (mg/L)	0.002	0.002	0.002	0.110	0.016	0.012	0.007	0.007	0.005	200.3	73.7	72.9
Pb (mg/L)	0.001	0.001	0.001	0.021	0.011	0.006	0.005	0.005	0.004	68.0	56.7	36.0
Cd (mg/L)	1.E−04	3.E−04	3.E−04	3.E−03	2.E−03	2.E−03	1.E−03	1.E−03	8.E−04	75.7	48.5	47.6
Hg (mg/L)	1.E−05	1.E−05	1.E−05	1.E−04	6.E−05	1.E−04	3.E−05	3.E−05	3.E−05	93.8	57.6	93.1
Cu (mg/L)	0.010	0.024	0.016	0.042	0.025	0.019	0.021	0.024	0.018	41.9	3.3	12.8
Zn (mg/L)	0.032	0.063	0.063	0.136	0.083	0.079	0.072	0.073	0.071	43.8	19.5	16.4
F (mg/L)	0.224	0.366	0.328	0.464	0.374	0.450	0.379	0.370	0.389	21.5	1.5	22.2
CN (mg/L)	0.002	0.003	0.002	0.028	0.017	0.008	0.006	0.008	0.005	86.8	67.2	44.9
EC (mS/m)	14.8	28.4	18.2	53.9	44.9	36.7	31.6	34.7	29.9	26.4	15.8	18.4

The TN and F data used for statistics are during 2004–2010. $n=54$ in the Wen-Rui Tang River watershed from 2000 to 2010 averaged by months and seasons

Temp water temperature, *DO* dissolved oxygen, COD_{Mn} chemical oxygen demand (manganese), BOD_5 5-day biochemical oxygen demand, NH_4^+*-N* ammonia nitrogen, *TN* total nitrogen, *TP* total phosphorus, *V-phen* volatile phenol, *As* arsenic, *Cr* chromium, *Pb* lead, *Cd* cadmium, *Hg* mercury, *Cu* copper, *Zn* zinc, *CN* cyanide, *F* fluoride, *EC* electrical conductivity averaged across all 54 monitoring sites classified for their dominant land use type to evaluate spatial variability across land use categories (urban, suburban, and rural) (Yang et al. 2013). Second, water quality data from 14 representative sites were used for more intensive analyses. For the spatial similarity study, mean values of annual water quality data were calculated over two 3-year periods (2000s: 2000–2002 and 2010s: 2008–2010) to minimize the potential effects of interannual hydroclimatic influences. Land use types were aggregated from 22 more detailed categories by combining several similar land use types into five broader categories: developed land (urban and rural residential, transportation, commercial, industrial areas, etc.), agriculture, vegetated land (forest and grassland), water, and bare land (abandoned fields and areas with no vegetation). Percentages of the five land use types, population density, and mean slope derived from the DEM were calculated in ArcGIS 10.0 by overlapping land use, population, and slope layers to the subwatershed boundary of each monitoring site and used as a water quality index for each water quality monitoring site.

Statistical analysis

To investigate correlations among water quality parameters and relationships between the water quality parameters and impact factors, correlation analysis based on Pearson's correlation coefficients was applied (Tang et al. 2010). The use of multivariate statistical analyses, such as FA and CA for classification modeling and interpretation of large datasets, allows for the reduction of data and the extraction of information that will be helpful in water quality assessment and management of surface waters. FA was applied to evaluate the most important parameters affecting water quality. PCA was used as an extraction method and varimax with Kaiser normalization as a rotation method in FA (Li et al. 2010). CA was used to highlight similarities and differences among the sampling sites by means of Ward's method, using Euclidean distances as a measure of similarity (Kaufman and Rousseeuw 2009).

The seasonal Mann-Kendall test was used to account for the variability in water quality parameters resulting from user-defined seasons (Hamed 2009). Slope estimates for magnitude of trend (the rate of change) are the median slope of all ranked seasonal regression slopes (Chang 2008). Trends were considered statistically significant when $p<0.1$ (Shields 2009) and all significance levels were tested at $p<0.05$ and $p<0.1$ confidence levels. All the statistical analysis tests were performed with SYSTAT 12 (Systat Software, Inc., Chicago, IL).

GIS analysis

The spatial autocorrelation (Global Moran's I) statistic measures spatial autocorrelation based on both feature locations (monitoring site location) and feature values (water quality values) simultaneously (Franczyk and Chang 2009). Given a set of monitoring sites and associated water quality values, it evaluates whether the spatial pattern expressed is clustered, dispersed, or random. Moran's I value is defined as the following:

$$I = \frac{n}{\sum_{i=1}^{n}\sum_{j=1}^{n} w_{i,j}} \frac{\sum_{i=1}^{n}\sum_{j=1}^{n} w_{i,j}\left(X_i-\overline{X}\right)\left(X_j-\overline{X}\right)}{\sum_{i=1}^{n}\left(X_i-\overline{X}\right)^2} \tag{1}$$

where X_i and X_j refer to the water quality values at monitoring sites i and j, respectively; $\bar{X}$ is the mean water quality; $w_{i,j}$ is the spatial weight between sites i and j; and n is equal to the total number of monitoring sites. The Global Moran's I statistic estimates the overall degree of spatial autocorrelation for a water quality dataset. The value of I is positive if both X_i and X_j are either above or below the mean, while it is negative if one is above the mean and the other is below the mean. I values cannot be interpreted directly; they can only be interpreted within the context of the null hypothesis. For the Global Moran's I statistic, the null hypothesis states that the water quality values being analyzed are randomly distributed among the monitoring sites in the study area. When the p value is statistically significant, the null hypothesis can be rejected. The z-score is the standard deviation of the Moran's I statistic. Moran's I values can be transformed to z-scores in which values greater than 1.96 or smaller than −1.96 indicate spatial autocorrelation that is significant at the 95 % confidence level (O'Sullivan and Unwin 2003).

Results and discussions

Temporal and spatial variations of water quality

The descriptive statistics including minimum values (min), maximum values (max), mean values (mean), and coefficient of variations (CVs) for the water quality dataset averaged across different months and seasons are presented in Table 1. Water temperatures showed a characteristic annual cycle, with higher values during the summer and lower values in the winter. The mean water temperature was higher in the wet season (27.4 °C) compared with the dry season (15.9 °C). The average pH values for the samples collected over the 11 years were within the permissible standard range of 6.7 to 7.4. According to the environmental quality standards for surface water in China (SEPBC 2002b), water quality of surface waters is classified into four groups: high quality (type I and type II), moderate quality (type III), polluted (type IV), and highly polluted (type V). The descriptive statistics for surface water quality revealed that waters of the Wen-Rui Tang River were generally worse than the water quality standard type III. This also represents the threshold level for drinking source waters for some important parameters including DO, COD_{Mn}, BOD_5, NH_4^+-N, TP, and petrol. DO values varied greatly from 0.03 to 4.8 mg/L with a mean value of 2.5 due to the high biological oxygen demand resulting from organic matter and ammonia inputs from human and industrial wastes (Boyle 2003). COD_{Mn} is widely used for determining oxidizable organic matter concentrations while BOD_5 characterizes the biodegradable organic matter fraction in wastewater (Kazi et al. 2009). COD_{Mn} concentrations varied from 2.2 to 10.6 mg/L while BOD_5 concentrations ranged from 2.5 to 15.8 mg/L. The average COD_{Mn} and BOD_5 values were somewhat higher in the dry season than in the wet season because of dilution by rainfall. Nitrogen pollution is generally considered as one of the most serious pollutants in this watershed. Ammonium was the main form of nitrogen under the hypoxic-anoxic conditions with the mean NH_4^+-N values exceeding the water quality standard type V (2 mg/L) for most of the year. The averaged TP concentration was 0.6 mg/L with the highest values occurring during the dry season and exceptionally high values of 5.0 mg/L in April 2009. The concentrations of CN and F were below the permissible limit of the water quality standard type III (1.0 mg/L). Cr and Pb concentrations met the water quality standard type I (As 0.05 mg/L, Cr 0.01 mg/L, and Pb 0.01 mg/L), while Cd, Hg, Cu, and Zn concentrations only met the water quality standard type II (Cd 0.005 mg/L, Hg 0.0005 mg/L, Cu 1.0 mg/L, and Zn 1.0 mg/L). Seasonal variation in heavy metal concentrations was not obvious. Average EC values for all sites were in the range of 14.8 to 53.9 mS/m. The high EC values can be ascribed to the discharge of industrial and domestic sewage, which introduces large amounts of salts into the river system.

The descriptive statistics for the water quality parameters averaged across all monitoring sites and land use categories are shown in Table 2. There were large spatial water quality variations with pollution generally more serious in urban areas than in rural areas. The COD_{Mn}, BOD_5, NH_4^+-N, TN, and petrol concentrations followed the pattern of urban > suburban > rural, while DO concentrations showed the inverse pattern. Oxygen demand and nitrogen concentrations had high values in the urban areas as a result of river water contamination with domestic and industrial waste. TP concentrations were the highest in the suburban areas because phosphate fertilizers are frequently used in suburban orchards. Petroleum and heavy metals in this river mainly come from electroplating factories, which are most common in the suburban area, and their concentrations in suburban zones were higher than the concentrations in urban zones. Moreover, EC values were higher in suburban areas, and the extremely high EC value at B9 was caused by marine inputs from the Oujiang River during high tides.

The CVs, which represent the standard deviation normalized by the mean, were calculated to assess the variability in water quality data. In general, spatial variation was greater than temporal variation, as the temporally averaged CVs across different sites were greater than the spatially averaged values of CV across different months. Furthermore, water quality variations in the same season or in the same land use category were smaller than for the whole year or for the whole watershed.

Identification of water quality indicator(s)

All the 20 water quality parameters (Table 1) were analyzed to determine associations among water quality parameters that may be indicative of pollution source identification. The 20 water quality parameters were grouped by their correlation values; parameters in the same group were highly correlated while parameters in different groups had relatively small correlations. Results of the correlation analysis (Table 3) showed positive correlations between COD_{Mn} and BOD_5 (r=0.653) and among NH_4^+-N, TN, TP, petrol, V-phen, and EC, with especially strong correlations for NH_4^+-N (COD_{Mn} r=0.662 and BOD_5 r=0.533) and TN (COD_{Mn} r=0.688 and BOD_5 r=603). The positive correlation between COD_{Mn} and NH_4^+-N reflects inhibition of nitrification by low DO imposed by the high oxygen demand. As a result, DO was negatively correlated with NH_4^+-N, TN, and TP. The strong correlation between NH_4^+-N and TN (r=0.935) indicates that NH_4^+-N was the largest contributor to TN. Petrol showed a positive correlation with V-phen (r=0.507); EC was positively correlated with NH_4^+-N (r=0.485), TN (r=0.531), and F (r=0.416), and F was positively correlated with NH_4^+-N (r=0.454) and TN (r=0.425). There were no obvious correlations (r<0.4) among other water quality parameters.

To further characterize the nature of the water quality impairment in the Wen-Rui Tang River watershed and the relationships among the water quality parameters, the ten correlated parameters (DO, COD_{Mn}, BOD_5, NH_4^+-N, TN, TP, Petrol, V-phen, F, and EC) were selected for FA. The Kaiser-Meyer-Olkin (KMO) and Bartlett's test verified the effectiveness of FA to assess the measured water quality parameters, with a KMO value of 0.851 and a Bartlett's test of sphericity approx chi-square value of 3,381 (p<0.05). FA identified three factors with eigenvalues >0.96 (≈1) summing to 70.9 % of the total variance in the water quality dataset (Table 4). Factor 1, which accounted for 48.0 % of the total variance, was correlated primarily with COD_{Mn}, BOD_5, petrol, and V-phen and secondarily with NH_4^+-N, TN, TP, and EC, implying typical mixed-type pollution. This factor could be interpreted as "organic" pollutants influenced by point sources such as municipal and industrial effluents resulting from rapid urbanization (Singh et al. 2005). Factor 2 explained 13.3 % of the total variance with positive loadings on NH_4^+-

Table 2 Min, max, and mean values and coefficient of variation (CV) of water quality data for all monitoring sites ($n=54$) in the Wen-Rui Tang River watershed from 2000 to 2010 averaged by sites and land use categories

Zone	Min				Max				Mean				CV (%)			
Parameter	All	Urban	Suburban	Rural	All	Urban	Suburban	Rural	All	Urban	Suburban	Rural	All	Urban	Suburban	Rural
Temp (°C)	20.5	21.1	21.2	20.5	22.9	22.9	22.29	21.6	21.5	21.6	21.6	21.0	2.4	2.5	1.6	2.7
pH	6.83	6.94	6.83	7.02	7.32	7.32	7.29	7.32	7.10	7.11	7.06	7.23	1.6	1.5	1.3	2.0
DO (mg/L)	0.46	0.46	0.88	1.09	7.74	5.49	4.11	7.74	1.59	1.23	1.59	3.83	79.8	76.9	44.3	79.2
COD_{Mn} (mg/L)	2.53	3.95	4.18	2.53	20.80	20.80	15.02	6.43	7.12	7.85	6.78	4.43	48.0	54.2	32.3	39.5
BOD_5 (mg/L)	1.75	2.62	3.43	1.75	26.10	26.10	19.58	6.00	7.59	9.08	6.54	4.22	68.6	70.2	53.5	42.3
NH_4^+-N (mg/L)	0.34	1.47	4.82	0.34	39.72	39.72	22.90	8.06	10.63	12.61	9.50	4.51	67.4	72.0	39.5	90.2
TN (mg/L)	2.11	2.51	5.52	2.11	36.03	36.00	36.03	10.80	13.73	14.94	13.71	6.22	57.4	59.9	47.6	73.4
TP (mg/L)	0.12	0.28	0.21	0.12	8.70	3.70	8.70	0.73	1.17	1.20	1.26	0.39	110.0	73.0	133.9	73.9
Petrol (mg/L)	0.053	0.088	0.054	0.053	0.439	0.439	0.197	0.131	0.144	0.186	0.117	0.086	66.0	63.5	46.7	47.0
V-phen (mg/L)	0.002	0.003	0.003	0.002	0.046	0.009	0.046	0.003	0.008	0.006	0.013	0.003	140.9	53.8	136.9	34.1
As (mg/L)	0.001	0.001	0.001	0.001	0.005	0.005	0.004	0.002	0.002	0.002	0.002	0.001	52.2	57.2	48.5	18.0
Cr (mg/L)	0.002	0.002	0.002	0.002	0.096	0.017	0.096	0.021	0.011	0.005	0.019	0.009	214.1	100.7	203.1	111.6
Pb (mg/L)	0.003	0.003	0.004	0.003	0.019	0.019	0.009	0.004	0.005	0.006	0.005	0.004	68.6	85.9	36.0	13.7
Cd (mg/L)	7.E−05	7.E−04	7.E−05	7.E−04	3.E−03	1.E−03	3.E−03	2.E−03	9.E−04	9.E−04	9.E−04	1.E−03	66.7	28.9	112.4	45.7
Hg (mg/L)	2.E−05	2.E−05	2.E−05	2.E−05	6.E−05	4.E−05	6.E−05	3.E−05	3.E−05	3.E−05	3.E−05	3.E−05	34.5	20.7	44.9	19.5
Cu (mg/L)	0.012	0.012	0.015	0.012	0.047	0.026	0.047	0.026	0.021	0.017	0.028	0.021	45.3	28.2	49.7	35.4
Zn (mg/L)	0.035	0.035	0.066	0.044	0.146	0.080	0.146	0.116	0.072	0.059	0.097	0.068	42.1	22.5	36.0	61.4
F (mg/L)	0.163	0.257	0.299	0.163	1.335	0.403	1.335	0.467	0.386	0.318	0.576	0.291	73.1	14.2	87.8	54.1
CN (mg/L)	0.002	0.002	0.002	0.004	0.018	0.018	0.006	0.008	0.006	0.007	0.004	0.006	80.5	94.21	43.65	35.7
EC (mS/m)	12.8	23.9	21.2	12.8	54.1	45.0	54.1	42.0	33.7	33.7	34.6	28.0	24.7	18.5	25.7	55.4

The TN and F data used for statistics are during 2004–2010

Temp water temperature, *DO* dissolved oxygen, COD_{Mn} chemical oxygen demand (manganese), BOD_5 5-day biochemical oxygen demand, NH_4^+*-N* ammonia nitrogen, *TN* total nitrogen, *TP* total phosphorus, *V-phen* volatile phenol, *As* arsenic, *Cr* chromium, *Pb* lead, *Cd* cadmium, *Hg* mercury, *Cu* copper, *Zn* zinc, *CN* cyanide, *F* fluoride, *EC* electrical conductivity

Table 3 Pearson correlation coefficients between the water quality parameters

	Temp	pH	DO	COD_{Mn}	BOD_5	NH_4^+-N	TN	TP	Petrol	V-phen	As	Cr	Pb	Cd	Hg	Cu	Zn	F	CN	EC
Temp	1																			
pH	−0.020	1																		
DO	−0.079*	0.243**	1																	
COD_{Mn}	−0.001	0.123*	**−0.413****	1																
BOD_5	−0.167*	0.109*	**−0.422****	**0.653****	1															
NH_4^+-N	−0.124*	−0.055	**−0.485****	**0.662****	**0.533****	1														
TN	−0.105*	−0.051	**−0.505****	**0.688****	**0.603****	**0.935****	1													
TP	−0.021	0.051	**−0.402****	**0.388****	**0.451****	**0.359****	**0.423****	1												
Petrol	−0.040	−0.077*	−0.198*	**0.414****	**0.348****	0.289**	**0.335****	0.108*	1											
V-phen	−0.086*	0.054	−0.164*	**0.549****	**0.399****	**0.336****	**0.426****	0.136*	**0.507****	1										
As	0.222**	−0.020	−0.072*	0.118**	0.110**	0.043	0.026	0.015	**0.390****	0.135*	1									
Cr	−0.021	−0.005	0.000	0.033	0.015	−0.013	−0.023	−0.007	0.059*	0.089**	0.012	1								
Pb	−0.010	0.031	−0.013	0.110*	0.089**	0.040	0.071*	−0.063*	0.112*	0.196*	0.064*	−0.028	1							
Cd	−0.132*	−0.006	−0.105*	0.116*	0.107**	0.091*	0.122*	0.108**	0.036	−0.002	−0.059*	−0.032	0.145*	1						
Hg	0.035	0.040	0.041	0.017	−0.009	−0.069*	−0.056	0.047	−0.039	0.023	0.096**	0.080*	0.032	−0.049	1					
Cu	−0.042	−0.021	−0.050	0.287**	0.171**	0.169**	0.177**	0.247**	0.135*	0.250**	0.137*	0.193*	0.093*	0.057	0.141*	1				
Zn	−0.159*	−0.119*	−0.188*	0.202*	0.164**	0.155*	0.174**	0.196*	0.100**	0.051	−0.013	0.021	0.184*	**0.399****	0.078*	0.283**	1			
F	0.077*	0.026	−0.187*	0.252**	0.154*	**0.454****	**0.425****	−0.037	0.079*	0.051	−0.045	−0.035	0.033	0.033	−0.075*	−0.039	0.109*	1		
CN	−0.119*	−0.007	−0.026	0.105*	0.066*	0.117*	0.112*	0.124*	−0.002	0.076*	−0.035	0.067*	0.016	0.057*	0.013	**0.331****	0.048	−0.043	1	
EC	−0.182*	0.230**	−0.202*	**0.425****	**0.306****	**0.485****	**0.531****	0.277**	0.146*	0.191*	−0.030	0.075*	−0.045	0.141*	−0.057*	0.160*	0.108*	**0.416****	0.066*	1

The absolute values of those in bold are exceeding 0.30

Temp water temperature, *DO* dissolved oxygen, COD_{Mn} chemical oxygen demand (manganese), BOD_5 5-day biochemical oxygen demand, NH_4^+*-N* ammonia nitrogen, *TN* total nitrogen, *TP* total phosphorus, *V-phen* volatile phenol, *As* arsenic, *Cr* chromium, *Pb* lead, *Cd* cadmium, *Hg* mercury, *Cu* copper, *Zn* zinc, *CN* cyanide, *F* fluoride, *EC* electrical conductivity

*$p<0.05$ level; **$p<0.01$ level (one-tailed)

Table 4 Varimax rotated loadings of water quality parameters

	Factor 1	Factor 2	Factor 3	Communality
DO	0.020	**−0.854**	−0.0183	0.764
COD_{Mn}	**0.621**	0.457	0.373	0.734
BOD_5	**0.711**	0.410	0.191	0.710
NH_4^+-N	0.357	**0.597**	**0.631**	0.883
TN	0.394	**0.555**	**0.612**	0.837
TP	0.387	**0.697**	−0.104	0.646
Petrol	**0.695**	−0.007	0.108	0.494
V-phen	**0.789**	0.170	0.062	0.655
F	−0.081	−0.002	**0.878**	0.778
EC	0.336	0.101	**0.684**	0.590
Eigenvalue	4.796	1.327	0.969	
% of variance	47.958	13.272	9.689	
Cumulative %	47.958	61.230	70.918	

The absolute values of those in bold exceeding 0.50 are dominant components in each factor

DO dissolved oxygen, *COD_{Mn}* chemical oxygen demand (manganese), *BOD_5* 5-day biochemical oxygen demand, *NH_4^+ -N* ammonia nitrogen, *TN* total nitrogen, *TP* total phosphorus, *V-phen* volatile phenol, *F* fluoride, *EC* electrical conductivity

N, TN, and TP and a strong negative loading on DO. Factor 2 suggests "nutrient" pollution, which could be caused by nonpoint sources such as agricultural runoff and/or domestic sewage discharged directly into the watershed without treatment. Factor 3 explained 9.7 % of the total variance and had a strong correlation with F and moderate correlations with NH_4^+-N, TN, and EC. Factor 3 represents pollution sources high in salts, such as wastes from industrial processing.

In summary, water quality parameters with a communality value greater than ~70 % were considered to be important parameters (indicators) contributing to variations in water quality. Results revealed that DO, COD_{Mn}, BOD_5, NH_4^+-N, TN, TP, and EC were the most important water quality indicators for characterizing the water quality of the Wen-Rui Tang River (Table 4).

Temporal trends of water quality

The annual changes of water quality parameters divided into wet/dry seasons and urban/suburban/rural areas for all monitoring sites are shown in Fig. 2. Petrol and V-phen concentrations have decreased significantly since the early 2000s. Petrol concentration dropped from 0.8 to about 0.05 mg/L and V-phen from 0.02 to below 0.002 mg/L, which met the water quality standard type III. This significant decline resulted from point source pollution control of industries by the local government since the beginning of the 2000s. Obvious downward trends in COD_{Mn}, BOD_5, and NH_4^+-N especially in the early 2000s and the late 2010s reflect sewage collection and treatment improvements. TP concentrations were highest between 2002 and 2006, when they exceeded the water quality standard type V (0.4 mg/L). The highest values for F concentration appeared in 2006 but did not meet the minimum standard for type I water quality (1.0 mg/L).

Most of the water quality indicators showed seasonal variability during the study period. The trend lines for the dry season were above the trend lines for the wet season for most of the water quality parameters, which meant that the water quality was better during the wet season. During the wet season, nitrogen levels were lower due to dilution by higher rainfall levels (Fig. 2). The wet season was also characterized by relatively low COD_{Mn} and BOD_5 concentrations because of dilution and decomposition of organic matter. However, NH_4^+-N and TN concentrations in both wet and dry seasons exceeded the water quality standard type V (2 mg/L) by a factor of 2–5 times, and BOD_5 and COD_{Mn} values also fell within the range of highly polluted type V waters. These contaminants, which are primarily derived from anthropogenic sources, cause high pollution levels during both seasons. Low DO values always appeared in the wet season when the river levels were high. High EC levels occurred during the dry season in conjunction with low river levels. Salt inputs originated from human activities (domestic and industrial waste) as well as subsurface flows, which are rich in salt concentrations due to the marine origin of the watershed bedrock. Furthermore, EC concentrations in the surface waters displayed a negative correspondence with rainfall, with a moderately strong relationship. This suggested that the low conductivity during the wet season results from rainfall dilution.

These water quality indicators also showed regional variability during the studying period. In general, the water contamination levels followed the pattern urban > suburban > rural for most of the water quality indicators due to population intensity, but the fastest water quality improvement was also in the urban area. NH_4^+-N and TN concentrations in the suburban area exceeded the concentrations in the urban area since 2004. Higher COD_{Mn} and BOD_5 in the suburban area were also depicted. Fluoride concentration was higher in the suburban area than in the urban area caused by industrial wastewater discharged into the rivers in the suburban area around site B9. The EC levels across the rural-suburban-urban interface reflect the changes of ion concentrations, including F^- and NH_4^+.

The seasonal Mann-Kendall test examined the trends in water quality parameters for each site in dry and wet seasons during the 11 years from 2000 to 2010 (Table 5). The downward or upward trends were detected at both $p<0.1$ and $p<0.05$ levels of significance by means of Sen's slope, resulting in 52 % of the cases showing no significant detectable trends during the 11-year study period. Downward trends in water quality were detected at some sites for DO (14 % of

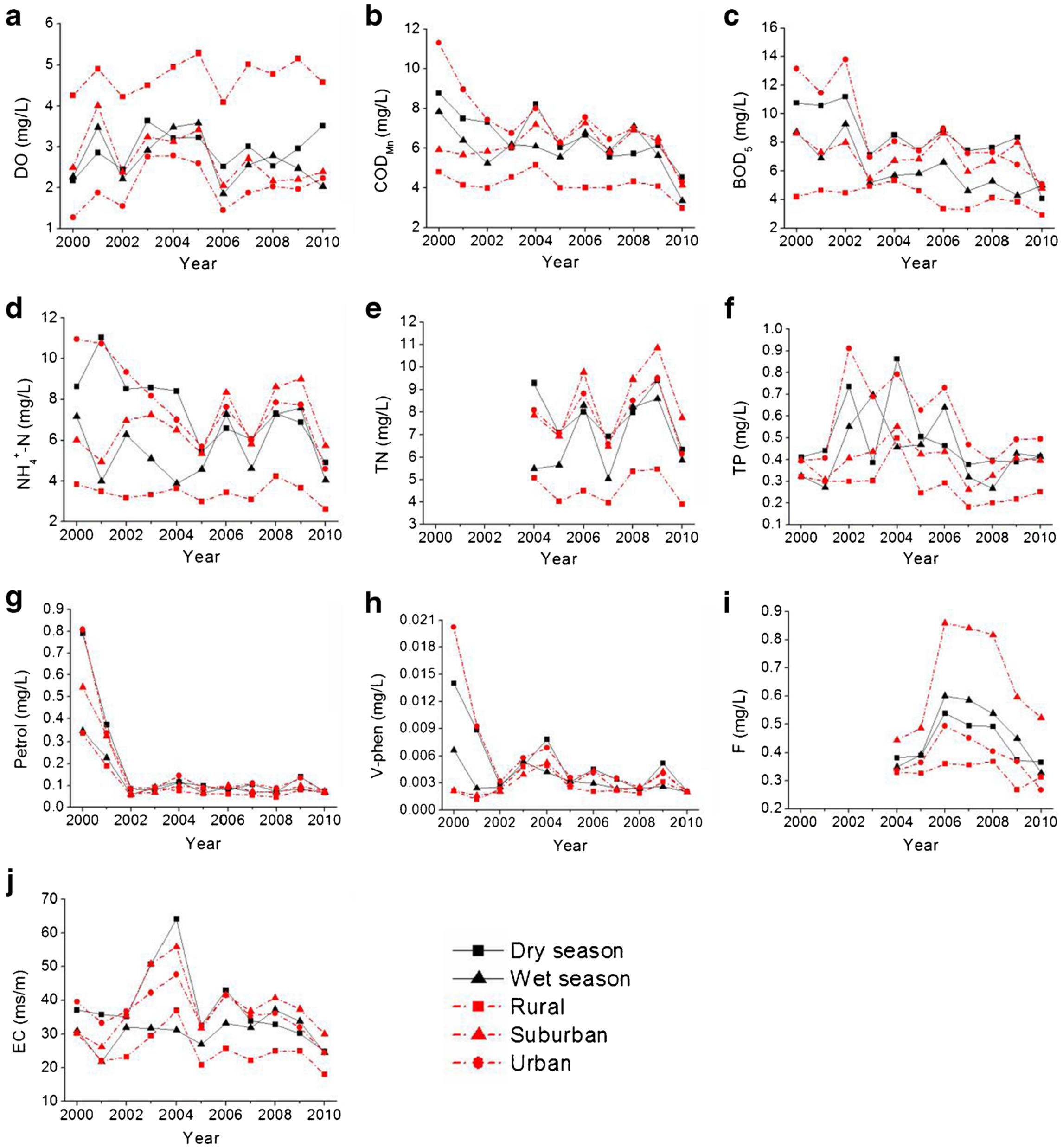

Fig. 2 Temporal changes in **a** DO, **b** COD$_{Mn}$, **c** BOD$_5$, **d** NH$_4^+$-N, **e** TN, **f** TP, **g** petrol, **h** V-phen, **i** F, and **j** EC concentrations in different seasons and different land use categories from 2000 to 2010

sites), COD$_{Mn}$ (57 % of sites), BOD$_5$ (79 % of sites), NH$_4^+$-N (57 % of sites), TP (36 % of sites), petrol (50 % of sites), V-phen (43 % of sites), F (7 % of sites), and EC (43 % of sites). In contrast, upward trends were observed at some sites for DO (7 % of sites), COD$_{Mn}$ (7 % of sites), BOD$_5$ (7 % of sites), NH$_4^+$-N (14 % of sites), TN (7 % of sites), petrol (7 % of sites), V-phen (7 % of sites), F (7 % of sites), and EC (7 % of sites).

DO showed opposing trends at various sites. Improving trends (higher DO) were found at A3, located in the central park of the city region, which means that the water quality was improving there. In contrast, degrading trends (lower DO) were found at A5, located in the agricultural region, and B9, located in the industrial area. More than half of the sites showed significant degrading trends in COD$_{Mn}$, including A3 and A4, which were the monitoring sites in the main stem, B2, which represented upstream tributaries, and B4–B8, which were the monitoring sites in the urban area. Only B9 showed a moderate upward trend in COD$_{Mn}$. Even more sites showed downward trends in BOD$_5$; however, some were less obvious (A1, A2, and B3). Those sites with downward trends in COD$_{Mn}$ also showed downward trends in NH$_4^+$-N. However, the trend for NH$_4^+$-N at B1 and B9 was rising. There were no significant trends in TN except for an upward trend at B9. This implied that the TN does not increase or decrease, but the chemical form of nitrogen is transformed. TP

Table 5 Z values for trend study of water quality in dry and wet seasons for 14 representative monitoring sites, 2000–2010

	DO	COD_{Mn}	BOD_5	NH_4^+-N	TN	TP	Petrol	V-phen	F	EC
A1	1.669	0.459	−2.252*	0.392	−1.153	−1.816	−1.499	1.128	−1.092	0.459
A2	−0.482	−0.146	−3.284**	0.112	−1.452	0.045	−1.042	0.397	−0.857	−0.751
A3	3.062*	−5.053**	−5.648**	−4.347**	0.470	1.827	−3.395**	−3.198**	−1.094	−3.754**
A4	1.636	−3.003**	−6.049**	−3.215**	−0.512	−2.388*	−3.623**	0.872	−1.047	−3.686**
A5	−2.286*	−0.516	−0.224	1.389	−0.214	−2.086*	−1.029	0.451	−0.855	−0.661
B1	−1.759	−0.516	0.585	4.175**	0.342	−0.426	−0.088	4.512**	−0.776	2.151*
B2	1.860	−3.574**	−4.313**	−4.425**	−0.769	−4.474**	−4.190**	−1.598*	−1.036	−3.586**
B3	−0.594	0.616	−1.984*	0.314	0.214	1.737	−1.954	1.828	−0.171	1.266
B4	0.325	−4.863**	−2.521*	−4.302**	−0.812	1.647	−3.530**	−4.857**	−2.335**	−4.605**
B5	1.904	−3.452**	−5.547**	−3.194**	0.790	−0.303	−1.986*	−2.369*	−0.837	−1.860
B6	0.829	−4.213**	−2.645**	−2.679**	0.320	1.065	−1.925	−4.964**	−1.373	0.157
B7	−0.594	−4.124**	−5.121**	−3.473**	−1.452	−2.387*	−3.015**	−1.414	−0.855	−3.272**
B8	1.289	−4.975**	−5.692**	−4.817**	−1.431	−4.863**	−4.561**	−4.068**	−0.171	−4.918**
B9	−3.932**	1.961*	3.216**	4.874**	2.927**	1.883	4.894**	−0.913	3.160**	2.914**

DO dissolved oxygen, COD_{Mn} chemical oxygen demand (manganese), BOD_5 5-day biochemical oxygen demand, NH_4^+ -N ammonia nitrogen, *TN* total nitrogen, *TP* total phosphorus, *V-phen* volatile phenol, *F* fluoride, *EC* electrical conductivity

*$p<0.1$ level; **$p<0.05$ level (two-sided trend)

concentration declined at A4, A5, B2, B7, and B8. Since COD_{Mn}, BOD_5, and NH_4^+-N were primary indicators of water quality in the Wen-Rui Tang River, this means that overall water quality has improved in many parts of the Wen-Rui Tang watershed during the past 11 years.

The decrease in petrol and V-phen concentrations across the entire watershed must be highlighted. Although B9 showed an upward trend in petrol and B1 showed an upward trend in V-phen, these two pollutants have been largely controlled in the watershed. An upward trend for F was found at B9, which contributed to elevated fluoride levels in the remainder of the downstream watershed. Nearly half of the sites exhibited declining trends for EC, except for B1 and B9, which also had increasing NH_4^+-N concentrations.

Spatial similarity of monitoring sites

Fourteen representative water quality monitoring sites (consisting of different land use characteristics) were subjected to CA to explore spatial trends based on organic pollutants (COD_{Mn}, BOD_5, Petrol, and V-phen), nutrients (NH_4^+-N, TN, and TP), and salt concentrations (NH_4^+-N, F, and EC) (Fig. 3). Based on these organic pollutants, CA generated a dendrogram grouping the 14 sites into three clusters (Fig. 3a). Cluster 1, composed of sites B1 and B2, represented a relatively low pollution region. Both stations were in the upper branches of the Wen-Rui Tang River upstream from municipal pollution inputs. These sites receive primarily domestic wastewater from villages and agricultural pollution. Cluster 2 corresponded to moderate levels of organic pollution found at eight stations (A3–A5, B3, B5, and B7–B9). These sites received variable amounts of urban waste, industrial waste, and pollutants from upstream sources. Cluster 3 consisted of sites B4 and B6 and corresponded to the most heavily polluted waters. These sites received wastewater from local sources and upstream sources. The water in this region was prone to being malodorous and black (i.e., sulfide-rich) due to sulfur inputs from tidal marine sources when the Qinfen and Huiqiao gates were open to exchange waters between the Wen-Rui Tang River and Oujiang River. The 14 sites were also grouped into three clusters based on nutrient characteristics (Fig. 3b). As with the organic pollutant CA, cluster 1 (A1 and A2), cluster 2 (A1–A5, B3, B5, B7, and B8), and cluster 3 (B4, B6, and B9) corresponded to relatively low, moderate, and high pollution regions, respectively, from nitrogen and phosphorus inputs. Four clusters were generated based on the salt (EC) concentration (Fig. 3c). Like the organic pollutants and nutrient groupings, sites B1 and B2 were grouped into cluster 1 with low pollution. The main stem sites A1–A4, the upstream site B3, and site B7 near the Cultural Park were grouped into cluster 2. Site B9 was grouped alone into cluster 4 due to its relatively high NH_4^+-N and F concentrations and high EC. The remaining sites that had moderate salt concentrations were assigned to cluster 3.

The Global Moran's *I* values and z-score values generated by spatial autocorrelation analysis showed moderate or strong positive spatial autocorrelation in water quality for EC in the 2000s and for DO and COD_{Mn} in the 2010s; in addition, there was a negative spatial autocorrelation for TP in the 2010s (Table 6). The positive spatial autocorrelation suggested that

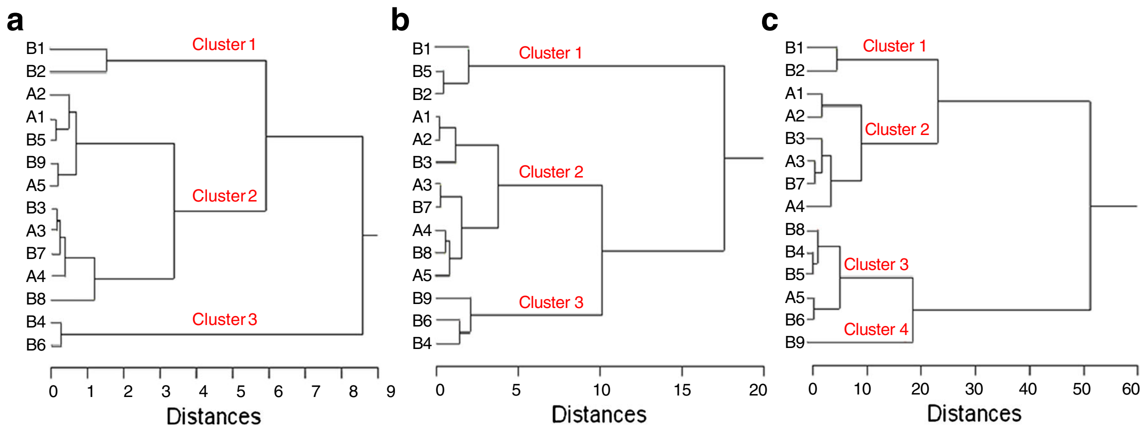

Fig. 3 Dendrogram of water quality monitoring station clusters for **a** organic pollutants, **b** nutrients, and **c** salt factors

monitoring sites adjacent to each other exhibited similar levels of water quality impairment while the negative spatial autocorrelation indicated the existence of spatial heterogeneity among monitoring sites. The increased Moran's *I* values for DO, COD_{Mn}, and EC over the 11-year study period implied that water quality varied with regional activities, while the decline in the Moran's *I* value for TP meant that TP pollution has become more localized. Figure 4 illustrates the location of the spatial autocorrelation sites. The z-score values were greater than 1.96 at B1 for EC in the 2000s and greater than 1.96 at B1 and B2 for DO and COD_{Mn} in the 2010s. This indicated that these relatively good water quality sites were similar to their nearby sites, while z-score values were less than −1.96 at B1 and B2 for TP in the 2010s, indicating that TP values at these sites were negatively correlated with neighboring sites.

The spatial autocorrelation and grouping of the monitoring sites provide a method for optimizing monitoring site selection. They also offer a reliable classification of surface waters in the whole watershed in such a way that only representative sites from each cluster can be selected for rapid water quality assessment.

Impact factors of water quality

Over the 11-year study period, urban development spread to the south and east of the watershed, and notable changes in land conversion from agriculture to urban residential were completed, particularly around site B9. When spatial variations in water quality were investigated, all the water quality data from the 14 representative monitoring sites were used to establish a detailed spatial distribution of water quality characteristics. Not all the sampling sites had complete data available for all water quality parameters, so the estimation of water quality did not involve petrol, V-phen, or F. We chose seven likely water quality impact factors, such as watershed-scale population density, average slope, and five land use categories, as the spatial variables. Pearson correlation values between water quality parameters and impact factors are shown in Table 7. Slope and vegetated land were not correlated with any water quality indicators because sampling sites were located mainly on the developed alluvial plain area of the watershed. Population density had a significant negative relationship with DO, consistent with human sources of organic materials. TP was positively related with bare land and

Table 6 Moran's *I* values of water quality in 2000–2010, 2000s, and 2010s for all stations

Year		DO	COD_{Mn}	BOD_5	NH_4^+-N	TN	TP	Petrol	V-Phen	F	EC
2000–2010	–	−0.10	−0.11	−0.03	−0.14	−0.17	−0.34	−0.28	−0.11	−0.07	−0.01
	z-score	−0.15	−0.20	0.31	−0.39	−0.54	−1.51	−1.12	−0.21	0.02	0.37
2000s	–	0.11	0.25	0.24	0.01		−0.31	−0.30	0.12		0.35
	z-score	1.14	1.93	1.80	0.52		−1.38	−1.31	1.34		2.52*
2010s	–	0.43	0.33	−0.04	0.16	0.06	−0.54	−0.05	−0.02	0.07	0.16
	z-score	3.05**	2.49*	0.2	1.39	0.77	−2.82**	0.15	0.36	1.94	1.53

DO dissolved oxygen, *COD_{Mn}* chemical oxygen demand (manganese), *BOD_5* 5-day biochemical oxygen demand, *NH_4^+ -N* ammonia nitrogen, *TN* total nitrogen, *TP* total phosphorus, *V-phen* volatile phenol, *F* fluoride, *EC* electrical conductivity

*$p<0.05$ level; **$p<0.01$ level (two-sided trend)

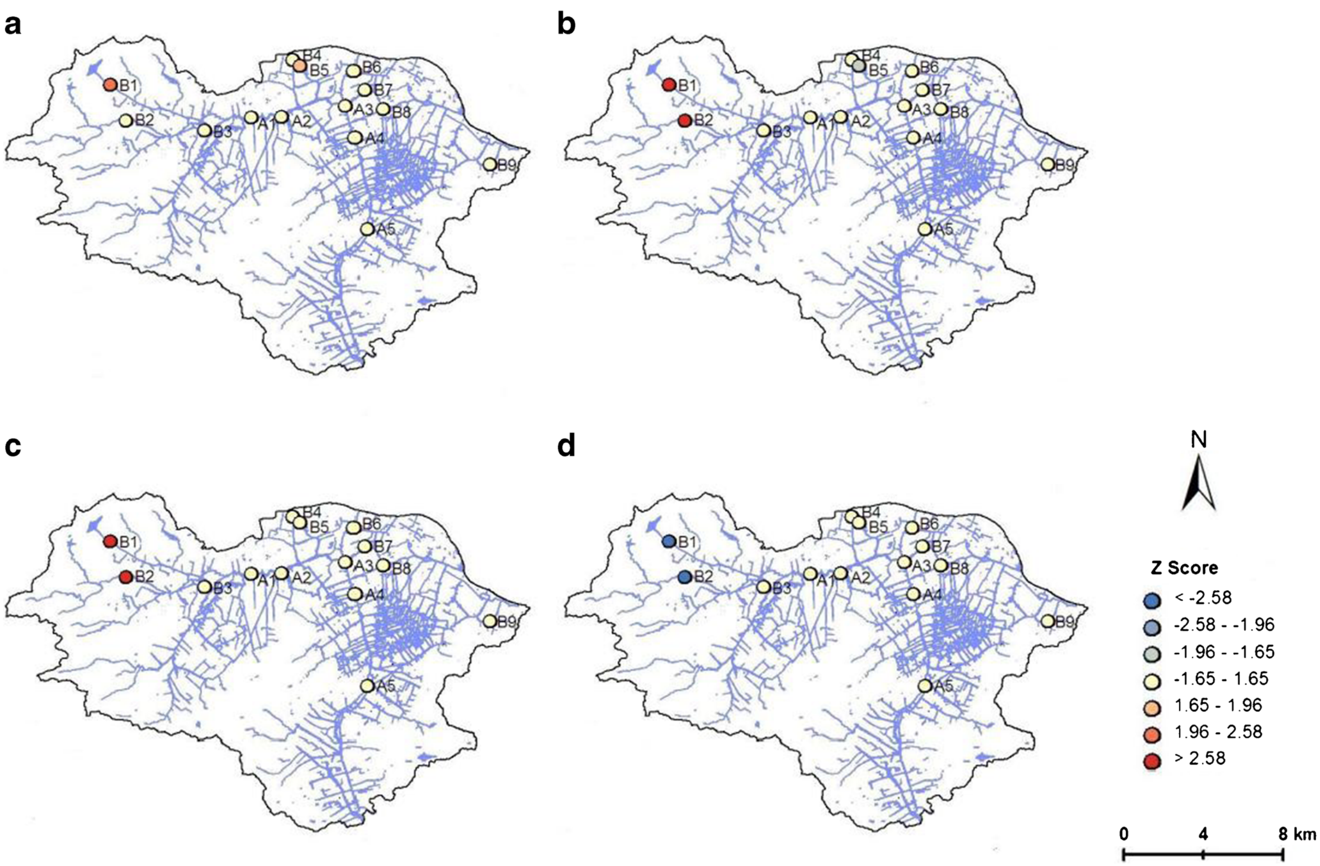

Fig. 4 Spatial autocorrelation of water quality monitoring sites for **a** EC in the 2000s, **b** DO, **c** COD_{Mn}, and **d** TP each in the 2010s

population density in the dry season. Developed land displayed a negative correlation with DO and a positive correlation with BOD_5 in the wet season due to pollution inputs from surface runoff. It was remarkable that agriculture

Table 7 Pearson correlation coefficients between the water quality parameters and population density, slope, and land use

	POD	SLO	DEV	AGR	VEG	WAT	BAR
Dry season							
DO	−0.468**	−0.007	−0.155	0.233	0.005	0.012	−0.154
COD_{Mn}	−0.149	0.163	0.000	−0.093	0.150	0.031	0.207
BOD_5	−0.110	0.076	−0.088	0.008	0.133	0.067	0.245
NH_4^+-N	−0.014	0.175	0.116	−0.202	0.146	−0.060	0.255
TN	0.100	0.164	0.209	−0.254	0.093	−0.148	0.224
TP	0.285*	0.199	0.025	−0.089	0.165	−0.066	0.423**
EC	−0.159	0.05	−0.105	−0.028	−0.003	0.241	0.108
Wet season							
DO	−0.335*	−0.029	−0.325*	0.348**	−0.097	0.239	−0.046
COD_{Mn}	0.118	0.155	0.23	−0.296*	0.094	−0.143	0.259
BOD_5	0.165	0.085	0.309*	−0.358*	0.012	−0.152	0.080
NH_4^+-N	0.134	0.103	0.261	−0.316*	0.098	−0.158	0.175
TN	0.135	0.176	0.223	−0.278*	0.076	−0.139	0.233
TP	0.254	0.217	0.148	−0.233	0.110	−0.073	0.290*
EC	−0.166	0.032	−0.186	0.052	0.006	0.290*	0.107

POD population density, *SLO* average slope, *DEV* % developed land, *AGR* % agriculture, *VEG* % vegetated land, *WAT* % water, *BAR* % bare land
*$p<0.05$ level; **$p<0.01$ level (one-tailed)

had negative correlations with many water quality indicators including COD_{Mn}, BOD_5, NH_4^+-N, and TN, especially in the wet season. This indicates that the amount of agricultural nonpoint pollutants mobilized by rain was less than that retained by the agricultural vegetation. Population density had a strong correlation with developed land ($r>0.6$), which means that one of these two variables is likely a redundant variable. However, relationships between water quality indicators and the selected impact factors were not strong (generally $r<0.4$). This implies that other impact factors, such as point source pollution, add to the complex characteristics of water pollution in the Wen-Rui Tang River watershed.

Management practice for water quality improvement

Linking the increasing socioeconomic trends (Fig. 1) along with the spatial-temporal changes of local water quality during the 11-year study period indicates that domestic sewage discharged into the river is a primary cause of river contamination. The local government recognized this important pollutant source and imposed a series of practices for river remediation at the beginning of the 2000s. Significant progress has been made in industrial restructuring through conversion of individual hand-crafting workshops to industrial-scale enterprises. These efforts have resulted in an increase of GDP and a reduction of wastewater discharge, especially heavy metals and petrol. The improvements in COD_{Mn}, BOD_5, NH_4^+-N, petrol, and V-phen in the Wen-Rui Tang River watershed, particularly in the urban area, are attributed to the installation of additional wastewater treatment capacity during the 2000s. After the first large-scale wastewater treatment plant was built in 2002, the wastewater collection rate has been improved from less than 20 % in 2000 to 65 % in 2010 (Fig. 5). However, the wastewater collection rate has not significantly improved since 2004 because the sewage pipeline network construction has not been fully implemented.

For better water quality management and remediation, the expansion of the sewage pipeline network is critical. The newly built pipeline could transport domestic and industrial wastewater to treatment plants, which would reduce the point source pollution from urban and industrial areas. In addition, best management practices (BMP), such as treatment wetland, riparian plantings and buffer strips, and river bank stabilization, should be implemented to control nonpoint source pollution.

Conclusions

Multivariate statistical analyses combined with GIS were used to identify spatial and temporal variations in water quality over an 11-year study period and to examine relationships between water quality and watershed characteristics, such as population density, topography, and different land uses in the Wen-Rui Tang River watershed, China. The following conclusions were supported from these analyses:

1. Water quality of the Wen-Rui Tang watershed varied in both temporal and spatial dimensions, and the spatial variation was greater than temporal variation. Water quality impairments were more serious in the dry season than in the wet season when comparing the spatially averaged values of each water quality parameter across different months. This implies that the dilution effect from increased precipitation was larger than the enhanced runoff effects. Urbanization and industrialization have resulted in water quality deterioration throughout much of the watershed.

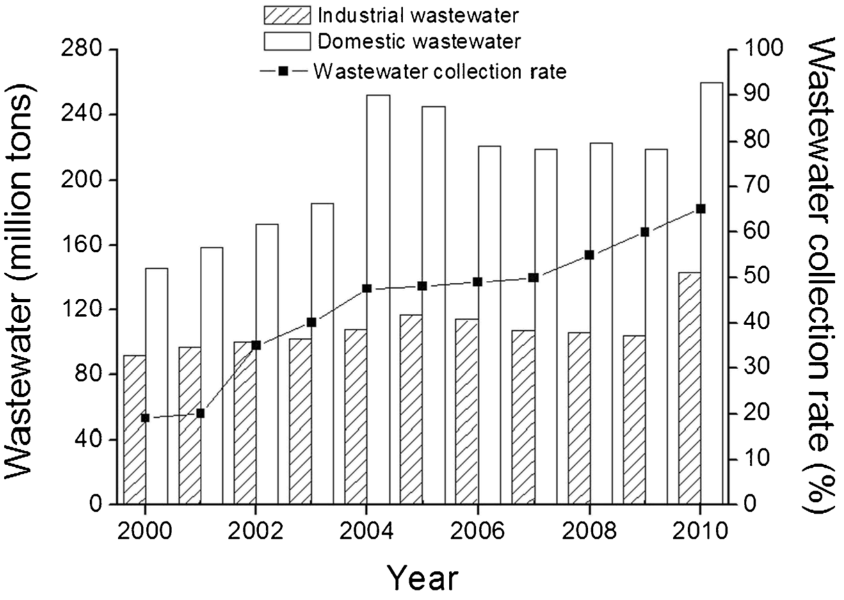

Fig. 5 Industrial and domestic wastewater and wastewater collection rate in Wenzhou during 2000–2010

Water quality impairment by heavy metals was worse in suburban areas than in rural and urban areas due to the many industrial complexes built within the suburban area.

2. Results of FA revealed that DO, COD_{Mn}, BOD_5, NH_4^+-N, TN, TP, and EC were the most important indicators of degraded water quality in the Wen-Rui Tang River. Almost all these water quality indicators were below the limits for the water quality standard type III for the entire year. Nitrogen pollution was the most serious pollution problem in the watershed with NH_4^+-N and TN concentrations exceeding the water quality standard type V (2 mg/L) in most areas.
3. Although seasonal and regional variations existed, trend analysis demonstrated some reductions in COD_{Mn}, BOD_5, NH_4^+-N, petrol, and V-phen concentrations across the watershed during the 11-year study. This significant decline depended largely on point source pollution control of industrial and sewage wastes by the local government, such as wastewater treatment plant installation and industrial restructuring, since the beginning of the 2000s. In contrast, river water quality around site B9 deteriorated due to the construction of an economic development zone during the study period.
4. CA separated 14 representative sampling sites into three clusters based on organic pollutants, three clusters based on nutrients, and four clusters based on salt (EC) concentrations. The sampling sites in the same clusters have common characteristics, while spatial autocorrelation analysis demonstrated that DO and COD_{Mn} concentrations became more regional while TP concentrations became more localized over the 11-year study period.
5. An eastward and southward shift of the economic center of the city resulted in enhanced deterioration of water quality in these portions of the watershed. The relationships between water quality and population density, topography, and land use type were not as strong as expected. The lack of stronger relationships implies that point source pollution was a dominant contributor to various pollutants in the watershed.

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