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RESEARCH ARTICLE

Spatial distribution and source apportionment of water pollution in different administrative zones of Wen-Rui-Tang (WRT) river watershed, China

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Abstract Water quality degradation in river systems has caused great concerns all over the world. Identifying the spatial distribution and sources of water pollutants is the very first step for efficient water quality management. A set of water samples collected bimonthly at 12 monitoring sites in 2009 and 2010 were analyzed to determine the spatial distribution of critical parameters and to apportion the sources of pollutants in Wen-Rui-Tang (WRT) river watershed, near the East China Sea. The 12 monitoring sites were divided into three administrative zones of urban, suburban, and rural zones considering differences in land use and population density. Multivariate statistical methods [one-way analysis of variance, principal component analysis (PCA), and absolute principal component score—multiple linear regression (APCS-MLR) methods] were used to investigate the spatial distribution of water quality and to apportion the pollution sources. Results showed that most water quality parameters had no significant difference between the urban and suburban zones, whereas these two zones showed worse water quality than the rural zone. Based on PCA and APCS-MLR analysis, urban domestic sewage and commercial/service pollution, suburban domestic sewage along with fluorine point source pollution, and agricultural nonpoint source pollution with rural domestic sewage pollution were identified to the main pollution sources in urban, suburban, and rural zones, respectively. Understanding the water pollution characteristics of different administrative zones could put insights into effective water management policy-making especially in the area across various administrative zones.

Keywords Spatial distribution · Pollution index · Source apportionment · APCS-MLR · Administrative zone · Water pollution

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Introduction

Water quality problems have posed serious threat to human health, ecology, and environment all over the world especially in developing countries (Brown and Froemke 2012; Liu et al. 2011; Saksena et al. 2008). In China, urbanization has quickened its step in the latest decades. With the growing population and fast developing economy, pollution problems become highlighted; especially when fundamental facilities (e.g., sewage networks and sewage treatment plants) cannot keep up the pace of economy development, water quality problems are getting increasingly serious. Anthropogenic contamination caused by city expanding and extensive population growth has long been criticized for their adverse effects on water quality (Mei et al. 2011; Xu et al. 2009; Su et al. 2013). But few researches investigating water quality were conducted under different administrative divisions (urban, suburban, and rural zones), especially in China, where owing to different functions and water management policies among various administrative zones, the water quality and pollution source could be different. Moreover, for a watershed, the area is usually across several administrative zones, and this would bring difficulty for water quality management and protection.

To ensure that any investment in remedial works reaps maximum improvements in most heavily polluted area at watershed scale, it is imperative that the pollution critical zones are pointed out; in other words, spatial distribution of pollutants are characterized, besides, the primary sources of each pollutant are identified both in terms of profile and contribution. Source identification and source apportionment of polluted water systems can provide basis for better water management practices to improve the quality of the waters, and thus, they deserve more attention (Howarth et al. 2002; Ma et al. 2009; Singh et al. 2005). To quantify the contributions of all sources to each measured pollutant, the receptor model absolute principal component score—multiple linear regression (APCS-MLR) method was used. It was firstly used for pollution source identification and apportionment in atmospheric environment due to its little relies on the number of sources or their compositions (Guo et al. 2004; Miller et al. 2002; Singh et al. 2008). APCS-MLR is based on the assumption that all pollutants in the receptors were the linear combination of several pollution sources; thus, it can calculate the contribution of each source. In recent years, there have been many researchers who used this model to apportion the pollution sources in aquatic systems (Su et al. 2011; Wu et al. 2009; Zhou et al. 2007b).

In the East China Sea, anthropogenic inputs of nutrients as well as organic pollutants brought along by the coastal rivers have greatly degraded the environmental and ecological quality of the Sea (Chai et al. 2006; Daoji and Daler 2004; Tang et al. 2006). Wen-Rui-Tang (WRT) river converges with the nearby rivers and then goes straight into the East China Sea. It flows through a densely populated (with a metropolitan population of about 7 million) and highly developed area of Wenzhou city, which is situated in eastern part of Zhejiang province, China. Since 20 years ago, this river has been called the “Mother River” for Wenzhou city by local people for its important functions in providing most water supply to municipal use and supporting daily life consumption (Lu et al. 2011), but due to the severe pollution conditions, the whole watershed is now under multiple water quality impairments and losing its water supplying functions.

As the knowledge of spatial distribution and pollution source apportionment for water quality in each administrative zone is very important for providing scientific information on policy-making decision for local government, the objectives of this study are (1) to understand the status quo of the water quality in WRT river watershed in different administrative zones, (2) to find out the spatial distribution of critical water quality parameters using multivariate analysis methods and pollution index method in WRT river watershed, and (3) to identify the pollution sources and apportion their contributions for each pollutant in the three administrative zones.

Material and methods

Study area

The WRT river watershed (Fig. 1) is mostly located in Wenzhou city and covers an area of 353 km^2. Due to the rapid economic development and significant population expansion, the water quality of this watershed is deteriorating these years (Lu et al. 2011), which seriously threatens the availability of potable water for local people. According to the water quality datasets collected from the 2009 and 2010 surveys by the Environmental Protection Bureau of Wenzhou city, the major water pollutants in the WRT river watershed are DO, COD, $NH^+{}_4$–N, and TN, among which nitrogen pollution is the most serious problem, which also contributes to the frequently emerging of red tides in the near coastal area.

River administrative zoning

The concept of river administrative zone was employed into this study. To investigate the spatial distribution of water quality in WRT river watershed, we divided the study area into three administrative zones of urban, suburban, and rural based on their differences in population density, land use, and land cover. Among them, the urban zone is densely populated with commercial and services activities dominated along with sparsely distributed factories. Water quality in this zone is expected to be better than water quality standard type IV under the guidance of National Water Quality Guidelines for Surface Water (State Environment Protection Bureau of China 2002a). The suburban zone is moderately populated area with intensive industrial activities (galvanization, metal processing industry, and leather industry), water quality of this zone is expected to be better than water quality standard type IV. In these two zones, treatment rates of domestic sewage are both about 70 %. Most areas of the rural zone are sparsely populated with agricultural activities to be dominant in this area. No sewage effluent network has been constructed in the rural zone and all sewage is discharged directly into the WRT river watershed without any treatment; thus, the water quality in this zone is expected to be better than water quality standard type V.

This study was conducted in the three administrative zones to investigate the spatial distribution of water quality in the WRT river watershed. We selected 12 monitoring sites in the whole watershed out of which five were within the urban zone, four were in suburban zone, and the other three located in rural zone. Understanding the relationship between water quality and administrative zones will greatly help implementing water quality improvement plans.

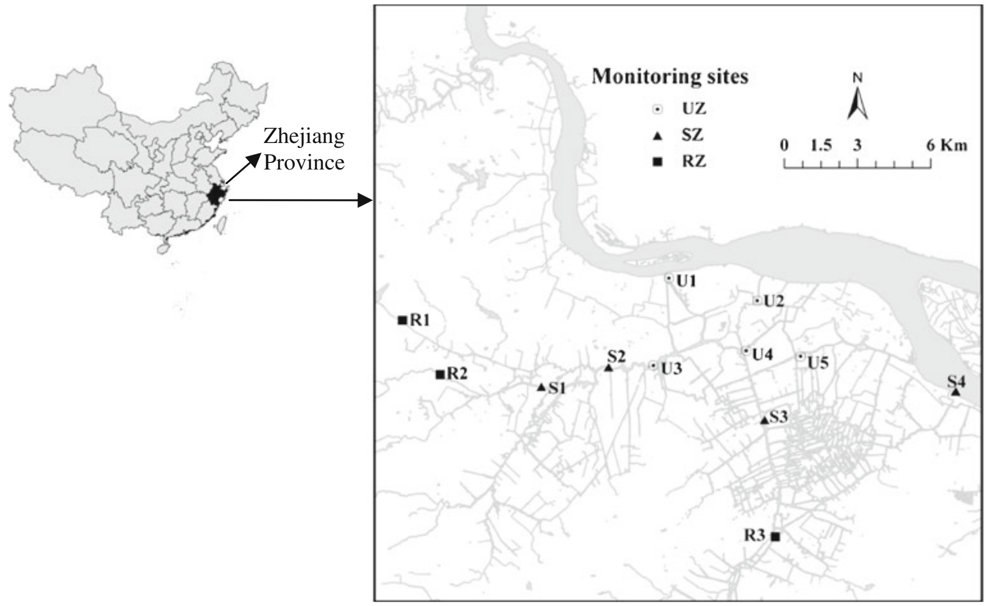

Fig. 1 Study area and monitoring sites (*UZ* urban zone; *SZ* suburban zone; *RZ* rural zone; *U1 U2*, *U3*, *U4*, *U5* monitoring sites in the urban zone; *S1*, *S2*, *S3*, *S4* are monitoring sites in the suburban zone; *R1*, *R2*, *R3* are monitoring sites in the rural zone)

Data pretreatment and chemical analysis

Water quality data from the 12 water quality monitoring sites were obtained from the Wenzhou Environmental Protection Bureau. Eleven water quality parameters of pH, electrical conductivity (EC), dissolved oxygen (DO), chemical oxygen demand (COD), potassium permanganate index (COD_{Mn}), total nitrogen (TN), ammonium nitrogen (NH_4^+–N), arsenic (As), copper (Cu), zinc (Zn), and fluorine (F^-) were measured bimonthly in 2009 and 2010. The parameters in one monitoring site (T4) in May 2010 were missing; thus, linear interpolation with the values of two nearest time points was used to complete the overall dataset. For any particular water quality parameters that were below detection limit in the samples, their values were represented by the values of their respective detection limits. The sampling, preservation, transportation, and analysis of the water samples followed the standard methods (State Environment Protection Bureau of China 2002b), to be specific, pH, EC, and DO, probe method; COD, potassium dichromate method; COD_{Mn}, acidic potassium permanganate method; TN, potassium persulfate oxidation–ultraviolet spectroscopy method; NH_4^+–N, spectrophotometric method with salicylic acid; As, Cu, and Zn, determined by atomic absorption method; F^-, ion chromatography method.

Methods

Descriptive and multivariate statistics

In order to unveil the spatial distribution pattern of the degraded water quality parameters in different administrative zones, one-way ANOVA, and Mann–Whitney *U* test were used. Normality test was performed using one-sample Kolmogorov–Smirnov test. For those parameters that were not normally distributed, box-cox transformation was conducted (Zhou et al. 2007a). Besides, homogeneity of variance test was conducted to assess the homogeneity of variance. For those normally distributed and equal-variance parameters, one-way ANOVA was applied. Least significant difference (LSD) was then chosen to conduct the multiple comparison analysis. For the non-normally distributed and/or unequal-variance parameters, a nonparameter test, the Mann–Whitney *U* test, was chosen to detect the difference of water quality datasets among the three administrative zones. To identify the sources as well as to apportion the contributions of each pollutant source, principal component analysis (PCA) and APCS-MLR were conducted on the datasets of the different administrative zones. PCA is often used to simplify the numeric matrix of dataset by reducing their dimensionality and to concentrate most information of the original dataset into several new principal components through varimax rotation with Kaiser normalization. These newly generated principal components were orthogonal, and each component could explain part of the variance of the whole dataset; thus, principal components were identified as pollution sources (Zhou et al. 2007a). APCS-MLR was then applied to estimate the pollutant contribution of each pollution source by combining multiple linear regression with the denormalized principal component score values generated from varimax rotated PCA and the measured concentrations of a particular pollutant; it was described elsewhere in detail (Su et al. 2011; Zhou et al. 2007b). After confirming the number and identity of the possible sources influencing the river water quality in the three administrative zones using PCA, source contributions were computed using APCS-MLR technique. All statistical data analyses were performed using the "Statistical Package for the Social Sciences Software-SPSS 16.0 for Windows" (Norusis 2008).

Pollution index

Pollution index (PI) (Su et al. 2011) was computed to study the spatial distribution and bimonthly variation of different administrative zones in WRT river watershed. We used the following formulas to calculate PI for surface water quality.

$$\mathrm{PI_i} = \mathrm{C_i}/\mathrm{C_{0-i}}(\mathrm{i} = 1, 2, \ldots \mathrm{n}) \tag{1}$$

$$\mathrm{PI_{DO}} = \mathrm{C_{0-DO}}/\mathrm{C_{DO}} \tag{2}$$

where PI_i is the pollution index of the ith pollutant of surface water, C_i is the actual concentration value of the ith pollutant (mg/l), C_{0-i} is the standard concentration value of the ith pollutant (mg/l), and n is the number of monitoring parameters. While for DO, as low concentration of DO reflects worse water quality, the formula is upside down (Eq. (2)) when calculating DO pollution index. When PI is >1, the water in this monitoring site is regarded as polluted by the specific pollutant or parameter, otherwise not polluted. In this study, in order to be consistent for all the three zones, C_0 was set to be the water quality standard type III concentration of Environmental Quality Standards for Surface Water (State Environment Protection Bureau of China 2002a).

Results

Basic statistics of water quality parameters in the whole watershed

The descriptive statistics of the original data for the 11 water quality parameters are shown in Table 1. For water quality comparison, the surface water quality standard of GB3838-2002 (State Environment Protection Bureau of China 2002a), the authorized guidelines available now in China, is also included in Table 1. In the guidelines, the water quality standard type I refers to background water quality that is not polluted. The water quality standard type V is the worst that is seriously polluted. Water quality worse than the water quality standard type III is no longer suitable for drinking while worse than the water quality standard type V can hardly support aquatic ecosystems.

The pH ranges complies with the surface water guidelines; therefore, pH was not included in further analysis. For EC, no regulation or standard is available in China, as EC could be used as an indicator of water quality in the areas unaffected by seawater, and higher EC indicates more ions in water, which has an adverse effect on water quality. DO concentrations varied greatly, with 85 % of the samples worse than the water quality standard type III (also known as the threshold for drinking water), 72 and 58 %, respectively, worse than the water quality standards type IV and V. For COD, more than half of the samples (53 %) exceeded the water quality standard type III. The highest concentration of COD (57 mg/l) was 3, 2, and 1.4 times higher than the water quality standards types III, IV, and V, respectively. The average concentration of COD_{Mn} was 5.0 mg/l, with most of samples complying with the water quality standard type III, with 26 and 4 % of samples exceeded the water quality standards types III and IV. As both COD and COD_{Mn} reflect organic pollution in aquatic systems and COD is usually a better indicator for severely polluted water, plus that the pollution status of COD is severer compared with that of COD_{Mn} in the study area, we selected COD instead of COD_{Mn} for spatial distribution analysis.

Nitrogen pollution is the most serious pollution problem in this watershed, with the mean values of TN and NH_4^+–N exceeded the water quality standard type V. About 91 % of the samples with TN concentration and 80 % of the samples with NH_4^+–N concentration exceeded the water quality standard type V. NH_4^+–N is the main form of nitrogen in this area, it constituted 71 % of the TN concentration on average. The highest concentration of TN and NH_4^+–N were 13 and 11 times, respectively, higher than the water quality standard type V. The badly deteriorated nitrogen pollution status may cause serious eutrophication in the watershed and subsequently been entrained to the coastal area and influence water quality there.

Apart from those organic pollution parameters and nitrogen pollution parameters, other trace elements (As, Cu, Zn, and F^-) were also analyzed for source identification purposes. All As concentrations were within the type I standard. Cu and Zn are essential for organisms; however, toxic effects were observed when their concentrations are higher than certain specific concentrations (Kavcar et al. 2009). For Cu and Zn, the concentration gap between the water quality standard types I and II is quite large that all samples did not exceed the standard type II, but over 73 and 62 % of the samples exceeded the type I standard. For F^-, nine samples exceeded the type III standard out of which four samples exceeded the type V standard, and these fluorine polluted samples happened to be in the same monitoring site, so there seems to be point source pollution in this area.

The coefficient of variation (CV) is the most discriminating factor in variability description; it can eliminate the influence caused by the difference of units and mean value between two or more datasets. As showed in Table 1, all parameters showed CV value from 3.5 % to >100 %, indicating a great variability.

Spatial distributions of water quality parameters in the three administrative zones

To study the spatial distribution pattern of water quality parameters in the watershed, the novel concept of assessing

Table 1 Basic descriptive statistics of water quality parameters in WRT river watershed

Parameters	*N*	Mean	Min.	Max.	SD	CV (%)	National surface water quality standard (GB 3838-2002)					
								I	II	III	IV	V
pH	144	7.01	6.54	7.66	0.24	3.5		6~9				
EC (μS/cm)	144	28.23	6.17	108.00	14.87	52.7		No available standard				
DO (mg/l)	144	2.57	0.04	9.66	2.27	88.4	≥	7.5	6	5	3	2
COD (mg/l)	144	22	10	57	9	41.1	≤	15	15	20	30	40
COD_{Mn} (mg/l)	144	5.0	1.3	13.6	2.5	50.0	≤	2	4	6	10	15
TN (mg/l)	144	8.10	0.38	25.30	5.20	63.6	≤	0.2	0.5	1.0	1.5	2.0
NH_4^+–N (mg/l)	144	6.35	0.06	22.60	4.80	75.7	≤	0.15	0.5	1.0	1.5	2.0
As (mg/l)	144	0.0013	0.0005	0.0035	0.0006	47.8	≤	0.05	0.05	0.05	0.1	0.1
Cu (mg/l)	144	0.022	0.002	0.348	0.033	150.4	≤	0.01	1.0	1.0	1.0	1.0
Zn (mg/l)	144	0.076	0.008	0.753	0.082	107.6	≤	0.05	1.0	1.0	2.0	2.0
F^- (mg/l)	144	0.40	0.09	1.80	0.30	80.0	≤	1.0	1.0	1.0	1.5	1.5

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

water quality based on administrative zones was implemented in our study. Based on our preliminary analysis, COD, NH_4^+–N, and As were conducted using ANOVA and LSD multiple comparison. Due to their non-normal distribution and/or unequal-variance restriction, the rest of the parameters were analyzed using the Mann–Whitney *U* test.

The comparisons of means of all parameters in the three administrative zones are shown in Table 2. Most of the water quality parameters except for Cu and Zn showed significant difference in two or all three of the three administrative zones. COD, COD_{Mn}, TN, NH_4^+–N, and EC values showed the same trend in the urban and suburban zones, and they were significantly ($p<0.05$) higher than those in the rural zone. DO concentration values were significantly different among the three zones, with concentration in the rural zone was higher than that of the suburban zone and the urban zone, and concentration in the suburban zone was significantly higher than that of the urban zone, indicating that water quality was the best in the rural zone, followed by the suburban zone, and the urban zone was the worst. The As concentration in the urban zone was significantly higher than that in the other two zones, which indicated that As in the urban zone was affected by anthropogenic sources. Concentrations of F^- in the suburban zone were significantly higher than those of the urban and rural zones; no other water quality parameter displayed this trend. This abrupt

Table 2 Comparison of the means for all parameters in three administrative zones

Parameters	Zone	*N*	Mean	Method	Parameters	Zone	*N*	Mean	Method
EC	Urban	60	27.7a[a]	*U* test	NH_4^+–N	Urban	60	7.40a	ANOVA
	Suburban	48	34.0a			Suburban	48	7.43a	
	Rural	36	21.5b[a]			Rural	36	3.14b	
DO	Urban	60	1.44c[a]	*U* test	As	Urban	60	0.0015a	ANOVA
	Suburban	48	2.26b			Suburban	48	0.0012b	
	Rural	36	4.87a			Rural	36	0.0011b	
COD	Urban	60	24.9a	ANOVA	Cu	Urban	60	0.018a	U-test
	Suburban	48	23.7a			Suburban	48	0.027a	
	Rural	36	16.1b			Rural	36	0.021a	
COD_{Mn}	Urban	60	5.63a	*U* test	Zn	Urban	60	0.064a	U-test
	Suburban	48	5.37a			Suburban	48	0.097a	
	Rural	36	3.54b			Rural	36	0.068a	
TN	Urban	60	9.13a	*U* test	F^-	Urban	60	0.33b	U-test
	Suburban	48	9.37a			Suburban	48	0.57a	
	Rural	36	4.69b			Rural	36	0.29c	

[a] Different lowercase letters behind the mean value indicate significant difference ($p<0.05$) between zones, while the same letter indicates no significant difference

high concentration in the suburban zone indicated that there existed considerable F^- source in the suburban zone. Cu and Zn did not show any significant differences among the three zones, but the mean concentrations of these two sources were higher than water quality standard type I; thus, anthropogenic sources were expected for these two elements. In general, we can conclude that for most of the parameters, water quality is worse in the urban and suburban zones than in the rural zone, and water quality in suburban and urban zones was generally alike. As the suburban zone now received much less attention on its pollution problems, this finding just give us an alarm that the suburban zone should be paid equivalent concern as the urban zone does.

From the above analysis, four water quality parameters were identified to be critical to sustain water quality either for their serious deterioration or for the large difference among the three administrative zones. For evaluating the most seriously deteriorated parameters, TN (more deteriorated than NH_4^+–N) and COD (more deteriorated than COD_{Mn}) were chosen for pollution index calculation in each monitoring site as well as each administrative zone. Additionally, DO and F^- were selected for their largest difference of means among the three administrative zones.

Bimonthly pollution index at each monitoring site and each administrative zone

PI values were used to speculate the spatial distribution of pollution status by the four critical water quality parameters in each monitoring site thus reveal the within-group variation.

TN (Fig. 2a) was the most seriously polluted parameter in this watershed throughout the sampling period with all PI values in the urban zone larger than in the suburban zone, then followed by the rural zone, among which all values were larger than 2.0, showing that the water quality in 2010 was better than that in 2009. In the urban zone, all the PI values were larger than 2.0 with sites C1, C2, and C5 having PI values >5.0, signifying a serious TN pollution. The PI in the suburban zone varied from site to site: All the sampling points in site T1 were polluted as evidenced by high PI values ranging from >10.0 to 1.0–2.0. All the sampling points in site T2 were polluted as indicated by the PI values of 1.0–10.0. For site T3, PI was within the range of 2.0–10.0. Site T4 was the most polluted among the four sites in the suburban zone with all PI values >5.0 and half of the sampling points >10.0, which shows a great threat to the drinking water quality. In the rural zone, site V1 had four sampling time points that were not polluted, while the other eight time points were within a range of 1.0–10.0. All PI values for site V2 were within 1.0–5.0. Site V3 had the worst water quality in the rural zone, with its PI values ranging from 5.0 to 10.0; this can also be caused by the exact location of the sampling sites, as site V3 locates downstream, which displays a water quality worse than the other two sites in the upstream. Overall, TN concentration in the study area showed a downward trend from 2009 to 2010.

For DO (Fig. 2b), the urban zone and suburban zone were all polluted throughout the study period, while in most of the sampling time points, the rural zone was polluted. All the five monitoring sites in the urban zone were polluted throughout the study period. In the suburban zone, monitoring site T3 was polluted throughout the study period, while the other three monitoring sites each had several months that the water was not polluted. In the rural zone, the three monitoring sites showed quite different trend; for site V1 and site V2, in most of the sampling time points, they both met the requirement of drinking water standard, while for site V3, the monitoring site was polluted throughout the study period, which is attributed to the special location, since site V3 is located downstream, which is easier polluted by pollutants from the upstream.

As to COD (Fig. 2c), it was not seriously polluted in the suburban zone or the rural zone, while in the urban zone, water was generally polluted throughout the study period. Waters in the urban zone were most polluted at all the five sites or they were at alarming status, among which site C1 and site C2 had a PI value >2.0 in several sampling time points, indicating a serious organic pollution. In the suburban zone, COD pollution was less severe with all sampling points in site T2 met the drinking water quality standard. Sites T1 and T3 each got one sampling point, while site T4 got three sampling points, which had a PI value between 1.0 and 2.0, respectively. In the rural zone, site V1 was not polluted by COD, site V2 displayed a PI value between 1.0 and 2.0 in May 2009, and site V3 showed half of its sampling points polluted during the study period.

For F^- (Fig. 2d), at the zone level, all three zones were not polluted in the study period. All the monitoring sites except for site T4 met the drinking water standard. Fluorine pollution was observed in several months at site T4. The abrupt high concentration in this monitoring site indicated a doomed F^- point source in this part of the study area especially near site T4. Further study is needed to investigate the cause of high F^- at site T4.

Pollution source identification for different administrative zones

Source identification of different pollutants was performed with PCA on the basis of different activities in the watershed area in light of previous literatures. A receptor model, APCS-MLR, was then used in pollution source apportionment.

A total of 10 parameters were employed to assist the source identification. Kaiser–Meyer–Olkin (KMO) and Bartlett test of sphericity were used to examine whether PCA was an effective method to assess the measured water

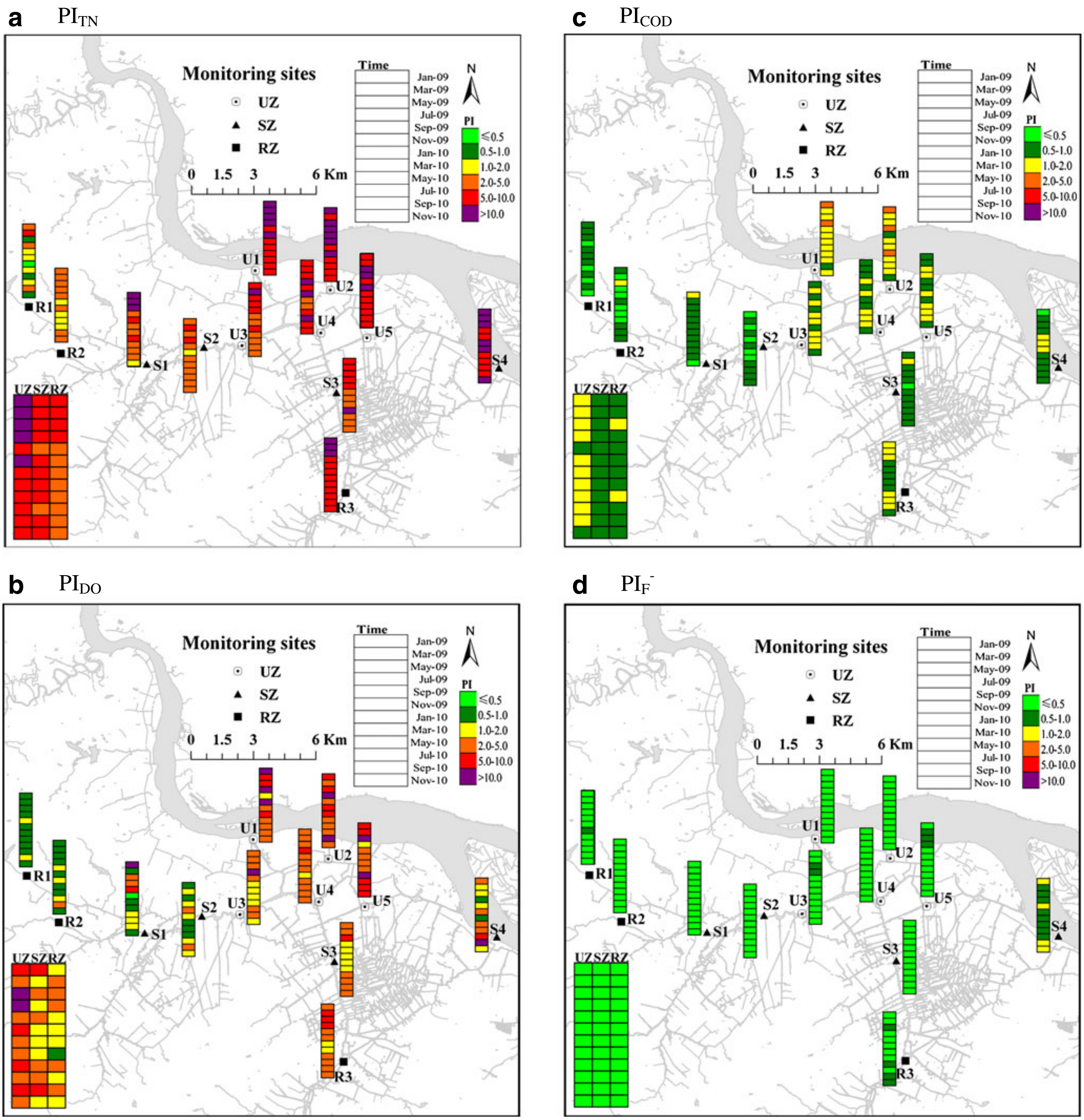

Fig. 2 Pollution index (PI) of TN, DO, COD, F^- at each monitoring site as well as each administrative zone (*UZ* urban zone; *SZ* suburban zone; *RZ* rural zone; *U1*, *U2*, *U3*, *U4*, *U5* monitoring sites in the urban zone; *S1*, *S2*, *S3*, *S4* monitoring sites in the suburban zone; *R1*, *R2*, *R3* monitoring sites in the rural zone; PI was divided into six groups, ≤0.5, 0.5–1.0, 1.0–2.0, 2.0–5.0, 5.0–10.0, and >10.0, among which PI>1.0 indicates water that has been polluted; sampling interval was bimonthly from January 2009 to November 2010)

quality parameters in the three administrative zones. KMO values for the urban, suburban, and rural zones were 0.720, 0.749, and 0.816, respectively, and Bartlett's test of sphericity values were 327, 338, and 292 ($p<0.05$), respectively, indicating PCA could be a helpful method for analyzing these three datasets. Under the guidance of eigenvalue >1 (Pekey et al. 2004), four principal components were extracted from the urban zone, three from the suburban zone, and two from the rural zone, respectively (Tables 3 and 4). According to Liu et al. (2003) and Su et al. (2011), the terms of "strong," "moderate," and "weak" loadings are used for describing factor loadings with absolute factor loading values >0.75, 0.75–0.5, and 0.5–0.3, respectively. The communalities in the extracted components show how much variance each variable

Table 3 Varimax rotated loadings of water quality parameters in the urban zone and suburban zone

Parameters	Urban zone					Suburban zone			
	Comp.1[a]	Comp.2	Comp.3	Comp.4	Communality	Comp.1	Comp.2	Comp.3	Communality
DO	−0.558	−0.049	−0.374	−0.148	0.475	−0.386	−0.077	−0.805	0.804
COD_{Mn}	0.860	0.247	−0.285	−0.008	0.882	0.751	−0.403	−0.065	0.730
COD	0.791	0.307	−0.019	−0.331	0.830	0.646	−0.528	0.154	0.720
TN	0.912	0.102	0.053	0.079	0.851	0.909	−0.054	0.050	0.831
NH_4^+–N	0.940	−0.037	0.028	0.224	0.936	0.946	0.063	0.036	0.901
As	−0.004	−0.064	0.930	−0.023	0.870	−0.427	−0.008	0.758	0.757
Cu	0.021	0.801	−0.190	−0.047	0.680	0.217	0.735	0.257	0.653
Zn	0.146	0.828	0.129	0.132	0.741	−0.027	0.841	−0.092	0.717
F^-	0.130	0.081	−0.003	0.944	0.914	0.796	0.366	0.003	0.768
EC	0.690	−0.335	0.222	0.266	0.709	0.920	0.228	−0.024	0.899
Initial eigenvalue	4.06	1.71	1.10	1.01		4.57	1.91	1.30	
Total variance %	40.6	17.1	11.0	10.1		45.7	19.1	13.0	
Cumulative variance %	40.6	57.8	68.8	78.9		45.7	64.8	77.8	

[a] *Comp* principal component

has in common with those components that have been retained. Low communality values indicate that variables do not share much variance with the extracted principal components while high values indicate that the extracted principal components represent the variables well.

For the urban zone, component 1 shows strong positive loadings on COD_{Mn}, COD, TN, and NH_4^+–N; moderate positive loadings on EC; while moderate negative loadings on DO. This component explained 40.6 % of the total variance, implying that this is typical mixed-type pollution. High loadings on TN and NH_4^+–N can be interpreted as nutrient pollution from strong anthropogenic impacts such as urban domestic sewage and public toilet sewage (there are about 300 public toilets in this zone). Meanwhile, strong positive loadings on both COD_{Mn} and COD with a moderate negative loading on DO indicated that this zone was also influenced by organic pollution from uncontrolled domestic discharges caused by rapid urbanization and commercial/-service pollution (Singh et al. 2005; Zhou et al. 2007b). Moderate positive loading on EC also confirmed the mixed

Table 4 Initially extracted and modified varimax rotated loadings for the rural zone

Parameters	Rural zone (initially extracted)			Rural zone (modified)			
	Comp.1[a]	Comp.2	Communality	Comp.1	Comp.2	Comp.3	Communality
DO	−0.741	−0.371	0.686	−0.734	−0.204	−0.373	0.719
COD_{Mn}	0.911	−0.023	0.830	0.902	0.149	−0.160	0.861
COD	0.691	0.381	0.622	0.674	0.358	0.207	0.625
TN	0.938	0.195	0.918	0.925	0.269	0.039	0.929
NH_4^+–N	0.932	0.254	0.934	0.921	0.256	0.145	0.934
As	0.081	0.814	0.669	0.074	0.285	0.921	0.936
Cu	0.190	0.771	0.630	0.141	0.897	0.148	0.846
Zn	0.372	0.654	0.566	0.331	0.747	0.154	0.691
F^-	−0.668	−0.276	0.522	−0.676	0.037	−0.504	0.712
EC	0.869	0.291	0.840	0.860	0.227	0.232	0.844
Initial eigenvalue	5.90	1.32		5.90	1.32	0.88	
Total variance %	59.0	13.2		59.0	13.2	8.8	
Cumulative variance %	59.0	72.2		59.0	72.2	81.0	

[a] *Comp* principal component

pollution sources. Based on the above analysis, component 1 represented nutrient pollution and organic pollution from urban domestic sewage and commercial/service pollution.

Component 2 explained 17.1 % of the total variance and had strong positive loadings on Cu and Zn. Previous work signified that Zn and Cu could come from metal rich materials from surface runoff during higher flows when the river level was elevated (Gozzard et al. 2011; Sodré et al. 2005). Thorpe and Harrison (2008) reviewed that Cu and Zn were ubiquitous and had been repeatedly reported to display high concentrations in brake linings. Davis et al. (2001) found that the largest contributor for Cu was brake emissions from automobiles, while for Zn, the largest contributor was runoff from tire particles of vehicles. Besides, several Zn die casting factories and mechanical processing plants locate in this zone; thus, this component might be pollution from industrial and traffic pollution.

Component 3 explained 11 % of the total variance, and it only showed high loadings on As. With the ANOVA result, we can tell that, although As concentration is quite low in the urban zone, it was significantly higher than that of the other two zones, which indicated an anthropogenic contribution. For industrial activities may change As concentration (Aksentijević et al. 2012), and in this zone, there exists leather industries; thus, we attribute this component to industrial pollution.

Component 4 explained 10 % of the total variance, and it solely showed high loadings on F^{-}. In several months for monitoring sites C3 and C5, F^{-} concentration reached the drinking water threshold (1.0 mg/l), which was attributed to fluorine pollution from domestic sewage (e.g., using refrigerators with fluorine release) in the urban zone. The communalities of most parameters in this zone were high (0.914 of F^{-} to 0.936 of NH_4^{+}–N) except for DO and Cu that had communalities of only 0.475 and 0.680, respectively, suggesting that there must be some latent sources that have not been interpreted.

For the suburban zone, three components were extracted. Component 1 explained 45.7 % of the total variance, and it had strong positive loadings on TN, NH_4^{+}–N, EC, F^{-}, and COD_{Mn}. Among them, TN, NH_4^{+}–N, and EC were the most overwhelming loadings in component 1, suggesting a serious nutrient pollution in this zone. Compared with the urban zone, higher loadings on F^{-} and lower loading on COD_{Mn} were found in the suburban zone, indicating that the organic pollution in this zone is relatively minor while fluorine pollution is more serious than in the urban zone. It was found that there are some electroplating factories and metal-processing factories locating at the upper stream of site T4, which could raise fluorine concentration in this zone. According to the above analysis, this component can be interpreted as representing the influence from suburban domestic sewage and F^{-} point source pollution.

Component 2 explained 19.1 % of the total variance. It had high positive loadings on Cu and Zn. Since there are several galvanization factories in this zone, and galvanization processes may lead to increase Cu and Zn concentration in water, this component can be considered as industrial pollution source.

Component 3 explained 13.0 % of the total variance, As alone had strong positive loading on this component. According to World Health Organization, As is found widely in Earth's crust and with levels in natural waters generally range between 1 and 2 μg/l, which is in accord with our concentration status; thus, it was attributed to As derived from geologic materials through natural weathering processes (WHO 2011; Barringer et al. 2007). The communalities of all parameters were high (above 0.700) except for Cu whose communality was only 0.653, suggesting that this zone was influenced by miscellaneous sources which had not been perfectly interpreted (Huang et al. 2010).

For the rural zone, only two principal components were extracted, but the two components explained about 72 % of the total variance. The communalities of all parameters in this zone were lowest among the three zones, with more than half of the parameters (DO, COD, As, Cu, Zn, and F^{-}) possessed a communality value <0.7, indicating that the two components automatically extracted under the guideline of eigenvalue >1 by PCA was not enough for representing most of the pollution sources. To solve this problem, we manually extracted three principle components from the complete dataset to achieve higher communalities of all parameters (Table 4). As one more component is retained, the communalities of all the parameters improved significantly, with only two parameters possessed communality values <0.7, and the total variance explained improved 8.8 % (changed from 72.2 to 81.0 %).

Component 1 explained 59.0 % of the total variance, and it had strong positive loadings on TN, NH_4^{+}–N, COD_{Mn}, and EC and moderate negative loading on DO and F^{-}. If we assumed a 500-m buffer around the monitoring sites in the rural zone, the dominant land cover was agricultural land, which indicated that component 1 mainly interpreted sources from agricultural nonpoint pollution especially from nitrogenous fertilizers (Singh et al. 2005). Strong positive loading on COD_{Mn} along with moderate negative loading on DO and F^{-} may be caused by rural domestic sewage discharged directly into the watershed without any treatment as no sewage effluent network has been constructed in the rural zone. Thus, this component is mainly attributed to be pollution from agricultural nonpoint source pollution and rural domestic sewage pollution. Component 2 explained 13.2 % of total variance, and it had strong positive loadings on Cu and Zn, as these two metals are always rich in manure, which could have been applied to farmland; thus, this component was interpreted as agricultural runoff.

Component 3 showed highest loading on As. Since the amount of As in this zone is quite low, this component is attributed to natural sources such as rock or soil weathering.

Pollution source apportionment for different administrative zones

The main sources of pollution in the urban, suburban, and rural zones are anthropogenic sources such as domestic sewage, industrial and commercial sewage, and agricultural nonpoint source pollution. From the above analysis, we can conclude that different administrative zones were influenced by different pollution sources. Besides the pollution types, we also evaluate the contribution of main sources to these pollutants (Table 5) using the APCS-MLR method (Su et al. 2011; Zhou et al. 2007b).

In the urban zone, the major pollutants were mainly related to urban domestic sewage pollution and commercial/service pollution (DO, 31.1 %; COD_{Mn}, 74.0 %; COD, 62.6 %; TN, 83.2 %; NH_4^+–N, 88.4 %; and EC, 47.6 %). Traffic and industrial pollution contributed 64.1 % to Cu and 68.6 % to Zn, and 11.2 % to EC. Industrial pollution contributed 86.6 % to As and 14.0 % to DO, while fluorine pollution from domestic sewage contributed 89.0 % to F^-, 11.0 % to COD and 5.0 % to NH_4^+–N. In the suburban zone, most sites were influenced by suburban domestic sewage and fluorine point source pollution (COD_{Mn}, 56.4 %; COD, 41.7 %; TN, 82.6 %; NH_4^+–N, 89.5 %; As, 18.2 %; F^-, 63.3 %; and EC, 84.7 %) and industrial pollution source (COD_{Mn}, 16.2 %; COD, 27.9 %; Cu, 54.0 %; Zn, 70.8 %; and F^-, 13.4 %), as well as geologic materials through natural weathering processes (DO, 64.9 %; As, 57.4 %). In the rural zone, most of the sites were influenced by agricultural nonpoint source pollution and rural domestic sewage pollution (DO, 53.9 %; COD_{Mn}, 81.4 %; COD, 45.4 %; TN, 85.5 %; NH_4^+–N, 86.2 %; F^-, 45.7 %; and EC, 73.9 %) and agricultural runoff entrained manure source (Cu, 80.5 %; Zn, 55.7 %) as well as soil weathering (As, 84.9 %; F^-, 25.5 %).

The adjusted coefficient of determination (A-R^2) values represented the fraction of variance of measured concentrations attributable to variance in the predicted concentrations. The greater A-R^2 value is, the better regression performs, and when A-R^2 value equals 1 means the regression is perfectly done with predicted values 100 % matches the measured value. In the urban zone, for most of the water quality parameters, A-R^2 values were >0.700, indicating a goodness-of-fit between the measured and predicted concentrations of water quality parameters. DO, Cu, and EC were unsatisfactorily represented with A-R^2 of only 0.437, 0.657, and 0.687, respectively. In the suburban zone, all water parameters except for Cu and Zn displayed A-R^2 values >0.70, indicating a goodness-of-fit of these parameters. In the rural zone, COD_{Mn}, TN, NH_4^+–N, As, Cu, and EC had A-R^2 values >0.800, while the rest four parameters had A-R^2 values between 0.589 and 0.693, suggesting that the MLR performed barely satisfactory in the rural zone.

Discussion

Water quality monitoring networks in China play an important role in water quality management. Administrative zoning is useful in water quality management at watershed scale, as different administrative zones have different land use types, population density, and sewage disposal practices, which can influence surface water quality. But so far, there are few reports analyzing water pollution based on administrative divisions, which lead to an ambiguous conclusion that the urban zone was the main even only region for anthropogenic water pollution, while the suburban or rural zones were not to be blamed for their pollution contributions. This study evaluated water quality based on three administrative zones, and it was found that the suburban zone with a large number of industrial enterprises and densely immigrant population can contribute as much pollution to surface water as urban zone does. Thus, the urban–suburban transition zone should become the new focus for water quality management. By recognizing this, the government can adjust its water management practices and focus not only on the urban zone as in the past did but also pay attention to the suburban zone so that the newly built infrastructure system such as sewage treatment facilities in the suburban zone can keep up with the economy development. For the rural zones, with less population, domestic waste water was not the main contributor to water pollution. In contrast, agricultural activities contributed more to nutrient pollution. It should be noted that the administrative zoning should be integrated with the exact location of the monitoring sites (e.g., the upstream or downstream) to get a better interpretation of pollution sources.

PI is a simple but effective way for measuring whether or not a water quality parameter is polluted relative to a specific water use purpose. In this study, water quality standard type III (also known as drinking water threshold) was used as the standard value for each parameter. By studying PI on each monitoring site, we can easily find out the within group variation (temporal variation) of each water quality parameter. PI is also valuable for figuring out point source of some pollutants (e.g., T4 was obviously influenced by F^- point source.)

APCS-MLR calculated the contribution of each source to each pollutant, which helps the government to develop better water quality management practices to control specific pollutants such as nutrient pollutants and organic pollutants in the watershed. Coupled with the characterized critical zone, limited resources can be applied to the most needed zones on the most deteriorated water quality

Table 5 Contribution of pollution sources to each pollutant in different administrative zones with modified PCA results

Parameters	Urban zone					Suburban zone				Rural zone			
	Comp.1	Comp.2	Comp.3	Comp.4	A-R^2[a]	Comp.1	Comp.2	Comp.3	A-R^2	Comp.1	Comp.2	Comp.3	A-R^2
DO	31.1		14.0		0.437			64.9	0.791	53.9			0.693
COD_{Mn}	74.0				0.874	56.4	16.2		0.712	81.4			0.848
COD	62.6			11.0	0.818	41.7	27.9		0.700	45.4			0.589
TN	83.2				0.840	82.6			0.820	85.5			0.922
NH_4^+–N	88.4			5.0	0.931	89.5			0.894	86.2			0.940
As			86.6		0.861	18.2		57.4	0.740			84.9	0.930
Cu		64.1			0.657		54.0		0.629		80.5		0.832
Zn		68.6			0.722		70.8		0.698		55.7		0.662
F^-				89.0	0.907	63.3	13.4		0.752	45.7		25.5	0.685
EC	47.6	11.2			0.687	84.7			0.892	73.9			0.830

[a] *A-R^2* adjusted coefficient of determination

parameters. Due to the parameter limitation, a part of latent sources were still not sufficiently identified in this study; more meaningful water quality parameters are required for getting full interpretation of those sources and the contribution of each source in future studies.

The administrative zoning and APCS-MLR source apportionment method could be implemented to other rivers due to most rivers cross several administrative zones, and the differences in water management policies in various zones can have significant different impact on water quality. Based on the information extracted from PCA and subsequently the contribution calculated from APCS-MLR, more effective water quality management plans can be implemented to critical pollution zones, thus maintain efficient and sustainable utilization of resources.

Conclusions

This study analyzed the spatial distribution and source apportionment of water pollution in a seriously polluted watershed, WRT river watershed (China) through the analysis of major pollutants (e.g., nutrients, COD_{Mn}, F^-, and toxic metals) in different administrative zones (urban, suburban, and rural zones). The main findings are as follows:

- WRT river watershed was seriously polluted by nitrogen and organic pollutants (parameters) such as TN, NH_4^+–N, DO, COD_{Mn},, and COD, among which TN is the most deteriorated one, with 91 % of the samples exceeded the water quality standard type V of GB3838-2002 (2.0 mg/l) and the highest concentration of TN is 13 times higher than the water quality standard type V.
- The spatial distribution of most water quality parameters varied among the three administrative zones through ANOVA. The pollution of most deteriorated water quality parameters (TN, NH_4^+–N, COD, and COD_{Mn}) in the urban zone and suburban zone were severer than in the rural zone.
- Pollution index at each monitoring site was proved to be useful for studying within-group variation and point source identification.
- Source identification using PCA revealed that domestic sewage, industrial pollution, and agricultural pollution were most responsible for the water pollution in urban, suburban, and rural zones, respectively.
- Source apportionment through APCS-MLR indicated that some variables received the contribution from the unidentified pollution sources. Thus, further investigation of the unknown pollution sources is needed.
- The local government should strengthen the water quality monitoring and management under fast economic development, control point source pollution from

industrial companies, accelerate infrastructure construction in suburban and rural zones, pay more attention to water quality in the urban–suburban transition zone, and advocate rational fertilization in the rural zone to protect water quality in watershed scale.

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