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Temporal trend and source apportionment of water pollution in different functional zones of Qiantang River, China

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ABSTRACT

The increasingly serious river water pollution in developing countries poses great threat to environmental health and human welfare. The assignment of river function to specific uses, known as zoning, is a useful tool to reveal variations of water environmental adaptability to human impact. Therefore, characterizing the temporal trend and identifying responsible pollution sources in different functional zones could greatly improve our knowledge about human impacts on the river water environment. The aim of this study is to obtain a deeper understanding of temporal trends and sources of water pollution in different functional zones with a case study of the Qiantang River, China. Measurement data were obtained and pretreated for 13 variables from 41 monitoring sites in four categories of functional zones during the period 1996–2004. An exploratory approach, which combines smoothing and non-parametric statistical tests, was applied to characterize trends of four significant parameters (permanganate index, ammonia nitrogen, total cadmium and fluoride) accounting for differences among different functional zones identified by discriminant analysis. Aided by GIS, yearly pollution index (PI) for each monitoring site was further mapped to compare the within-group variations in temporal dynamics for different functional zones. Rotated principal component analysis and receptor model (absolute principle component score-multiple linear regression, APCS-MLR) revealed that potential pollution sources and their corresponding contributions varied among the four functional zones. Variations of APCS values for each site of one functional zone as well as their annual average values highlighted the uncertainties associated with cross space-time effects in source apportionment. All these results reinforce the notion that the concept of zoning should be taken seriously in water pollution control. Being applicable to other rivers, the framework of management-oriented source apportionment is thus believed to have potentials to offer new insights into water management and advance the source apportionment framework as an operational basis for national and local governments.

1. Introduction

Urbanization, increasing land development and industrial activities in the absence of adequate wastewater treatment, has contributed to water quality deterioration (Jonnalagadda and Mhere, 2001; Gupta, 2008). The increasingly evident water pollution problems have also led to serious ecological and environmental consequences (Ma et al., 2009). The concurrent environmental issues are fairly complex, involve scientific and engineering aspects, and have important social, legal, economic, and political ramifications (Weng, 2007). Most developing countries are now facing a daunting task of water

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resources management, dealing with problems of effective water pollution control and river ecosystem health maintenance. One promising way to deal with such complex problems is to consider them as an integrated river basin management issue, and bring together all participant planners, engineers, landscape architects, social and natural scientists, local officials, and others at basin scale, for the common good (Weng, 2007).

A host of factors have imposed challenge for integrated river basin management practices, especially the multi-functional use of water resources under varying hydrological, environmental, and socio-economic circumstances. The assignment of river function to specific uses, known as zoning, is a useful option to mitigate conflicts and a key prescriptive tool for visualizing human impacts on environment. Although the majority of zoning schemes were not originally designed for water pollution monitoring and management, these practices are common (Brierley et al., 2002; Sabatini et al., 2007; Cheruvelil et al., 2008). Using zoning frameworks for such purposes assumes that characteristics of river functions within zone are more similar than those across zones. And such prescriptive zoning is not a descriptive final document but an ongoing process, assuring that the management of the area is periodically updated and better planned. Despite the popular use of zoning schemes for integrated river basin management, there have been few reports to study the pollution characteristics and variations among different zones.

Since the "open-door" policy in 1978, many rivers in China have been seriously polluted due to rapid urbanization and industrialization, which exceeded the capacity of river ecosystems. For example, more than 70% of the water in the Huang, Huai and Hai River basins is polluted (Wang et al., 2008). River water pollution thus has been set high on the agenda of the Chinese government in response to a variety of environmental concerns and sustainable development needs. Environmental monitoring systems have been established since 1980s and various water quality monitoring programs carried out for decades in China. Additionally, in the new round of revision in river basin planning, enough emphasis was given to the concept of river function zoning. The fundamental goal of the river function zoning in China is to distinguish different parts of the river and make a clear division of control targets on the basis of river's natural features, social services, and ecological functions (China Ministry of Water Resources, 2007).

In such circumstances, information on temporal trends of water quality and the contributing pollution sources should be helpful for managers. Multivariate statistical methods are capable of detecting similarities among variables, and therefore allow profound interpretation of data and assessment of input contributions from various sources (Singh et al., 2005; Zhou et al., 2007; Su et al., in press). In recent years, there have been many studies on spatio-temporal patterns and source apportionment using multivariate statistical methods in environmental pollution issues (Love et al., 2004; Kuppusamy and Giridhar, 2006; Zhou et al., 2007; Huang et al., 2010). Particularly, many studies focused on physical characteristics of the measurement data and paid less or no attention on the science–policy integration. Despite their high-quality, they have not effectively advanced the source apportionment framework as an operational basis for government agencies, since the results were often difficult-to-understand for managers. Given the popular use of zoning schemes for integrated river basin management worldwide, we argue that comparison of temporal trends pollution sources in different river functional zones should significantly contribute to developing optimal control strategies and determining priorities in decision-making procedure. However, no source apportionment study, from management prospective, has been carried out under the framework of river function zoning. There is incomplete understanding of variations in contributing sources of different functional zones to reinforce the notion that the concept of zoning should be taken seriously in water pollution control.

Given the above considerations, the aim of this study is to obtain a deeper understanding of temporal trends and sources of water pollution in different functional zones with a case study of the Qiantang River, eastern coastal China. This will be done by using multiple multivariate methods, time series analysis, pollution index (PI) and geographic information systems (GIS). Specifically, our objectives are to: (1) characterize the temporal trends of water quality in different functional zones of Qiantang River between 1996 and 2004; (2) identify significant parameters and compare the pollution sources as well as their quantitative contributions in different functional zones; and (3) provide a frame of reference for policy makers to promote the river function zoning practices as well as effective water pollution control strategies in China.

2. Background

2.1. Study area

The Qiantang River, located in eastern coastal China (Fig. 1), is the largest one in Zhejiang Province. It plays a critical role in the sustainable development of Yangtze River Delta, due to its multiple functions: water supply, electricity generation, irrigation, tourism, fishery and shipping. Qiantang River basin covers around 40,000 km^2 and has a population of about 20 million. Following the opening-up policies, this area has made rapid strides in its social-economic development. In the period between 1996 and 2003, it has doubled its GDP, with GDP increasing from RMB 1586 billion in 1994–3366 billion Chinese Yuan in 2003. While the Qiantang River basin appears as one of the most rapidly advanced economic regions in China and has now become known as the world's workshop, it is widely acknowledged that the water quality of Qiantang River continues to deteriorate. Nevertheless, few detailed studies have been carried out to reveal temporal trends of different functional zones in the river. Systematic mapping of pollution sources is recommended with a view to assist environmental managers and public health officials to control river water pollution.

2.2. River functional zoning

In general, the river provides various functions: drinking, shipping, power generation, sightseeing, fisheries, etc. It needs to integrate various functions, as well as define coordination among them, to stablize river ecosystem health and promote

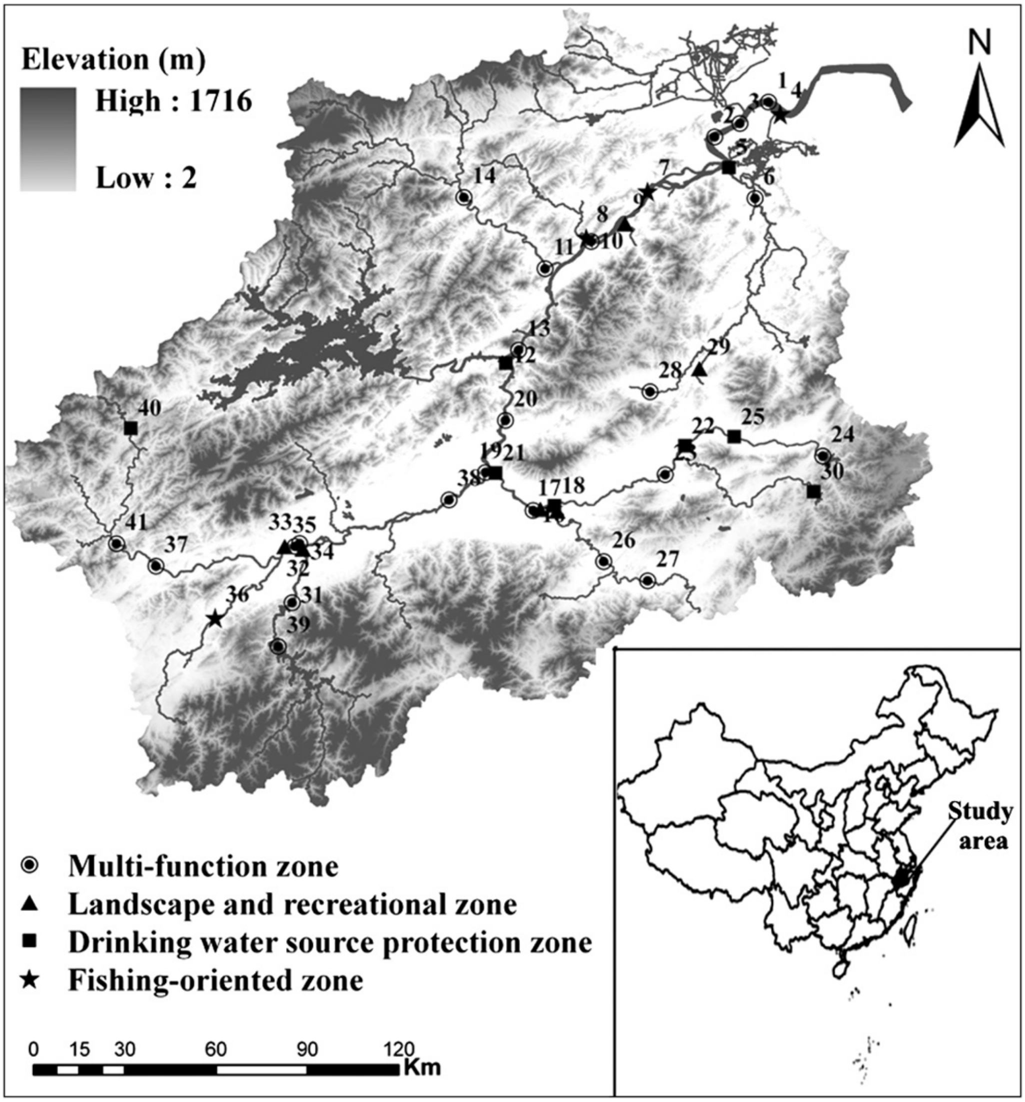

Fig. 1 – Location of Qiantang River and spatial distribution of the forty-one monitoring sites in four functional zones.

sustainable development. River function zoning is to reasonably regionalize the whole river basin according to certain indicators and standards based on natural properties (resource status, environmental conditions and geographic location) and social attributes (utilization level of water resources, demand of social advancement on water quality and quantity) of water resources. The use of river function division benefits more scientific control, supervision and management of water pollution at basin scale (China Ministry of Water Resources, 2007).

Acted in 2002, the river functional zoning has been put into practice in Zhejiang Province for eight years. Besides taking into consideration of the main principles, the river functional zoning designation of Zhejiang Province was made in attempt to link regional development, rural and urban planning, land use policy, and the development planning for various economic zones. To be specific, the corresponding river functional zones for Qiantang River were divided into six categories: natural reserved zone, fishing-oriented zone, industry-oriented zone, drinking water source protection zone, landscape and recreational zone, and multi-function zone [Zhejiang Environmental Protection Bureau (ZEPB), 2006].

Natural reserved zone refers to land and water bodies needing special protection and management, where representative natural ecosystems are dominant and rare or endangered species naturally concentrate or live. Fishing-oriented zone represents water bodies used for spawning, providing migration channels, cable feeding and breeding fish, shrimp, crab, shellfish, algae and other aquatic animals and plants. Industry-oriented zone is the area where intensely-used water intake points for industrial and mining production are located. Drinking water source protection zone indicates areas designated for providing the sources of drinking water. Landscape and recreational zone is the water with basic attributes for aquatic ecology protection and is thus suitable for sightseeing and entertainment. And multi-function zone refers to water bodies whose functions possess a lower requirement on water quality and can not be attributed to one specific function category.

3. Materials and methods

3.1. Data

Monthly data of thirteen parameters from 41 monitoring stations in Qiantang River and its tributaries were obtained from Environmental Monitoring Center of Zhejiang Province. The 13 water quality are: dissolved oxygen (DO), permanganate index (COD_{Mn}), five day biochemical oxygen demand (BOD), ammonia nitrogen (NH_3-N), volatile phenol (V-ArOH), total cyanide (TCN), total mercury (THg), total lead (TPb), total cadmium (TCd), hexavalent chromium (Cr^{6+}), petroleum, fluoride (F^-) and total phosphorus (TP) (Table 1). Six TP values and two TCN values were missing, and were replaced by virtue of smoothing. Because the distributions of V-ArOH, petroleum, Cr^{6+}, TCd, THg and TCN were skewed, the original data were Box–Cox transformed. According to the geographical distributions of the monitoring stations (Fig. 1), the 41 sites fall into four categories of functional zones: multi-function zone (Zone A), landscape and recreational zone (Zone B), drinking water source protection zone (Zone C) and fishing-oriented zone (Zone D).

3.2. Laboratory analysis

All the selected parameters were measured in the laboratory of Environmental Monitoring Center of Zhejiang Province according to the environmental quality standards for surface water of China (Wei et al., 1989) and the standard methods for observation and analysis in China (Huang et al., 1999). The specific method used is presented as follows: DO, electrochemical probe method; COD_{Mn}, acidic (alkaline) potassium permanganate method; V-ArOH, after distillation by means of 4-AAP spectrophotometric method; BOD, dilution and seeding method; NH_3-N, spectrophotometric method with salicylic acid; TCN, pyridine–barbituric acid colorimetry (isonicotinic acid–pyrazolone colorimetric method); THg, cold-vapor atomic absorption spectrophotometry; TPb and TCd, atomic absorption spectrophotometry (chelating extraction); petroleum, infrared spectrophotometry; Cr^{6+}, diphenylcarbohydrazide spectrophotometric method; F^-, ion chromatography; TP, ammonium molybdate spectrophotometric method.

3.3. Methods

3.3.1. Multivariate statistics

Discriminant analysis (DA) constructs discriminant factors (DFs) to assess the variations in water quality among different river functional zones based on three different modes: standard, forward stepwise and backward stepwise. The standard DA mode constructs DFs containing all parameters. In the forward stepwise mode, variables are added one by one, beginning with the most significant until no significant changes are obtained. In the backward stepwise mode, it is opposite: variables are removed one by one, beginning with the least significant until no significant changes occur.

Principal component analysis (PCA) extracts eigenvalues and related loadings from the covariance matrix of original variables to produce new orthogonal variables through varimax rotation, which are linear combinations of the original variables

Table 1 – Descriptive statistics of water quality variables in different functional zones of Qiantang River between 1996 and 2004 (unit: mg/L).

Parameters	Multi-function zone				Landscape and recreational zone				Drinking water source protection zone				Fishing-oriented zone			
	Mean	Min	Max	Std	Mean	Min	Max	Std	Mean	Min	Max	Std	Mean	Min	Max	Std
DO	7.62	4.80	10.15	0.91	7.60	3.83	10.71	1.30	7.23	2.44	12.58	1.52	7.67	5.56	8.77	0.79
COD_{Mn}	2.89	0.84	11.58	1.46	3.68	1.64	12.60	1.73	3.66	1.15	9.49	1.66	3.06	1.79	4.59	0.66
BOD	1.66	0.32	8.03	0.99	2.22	0.71	8.41	1.30	2.27	0.37	7.49	1.42	2.12	1.07	3.94	0.60
NH_3-N	0.77	0.01	7.17	1.05	0.96	0.17	2.98	0.72	1.47	0.01	9.21	1.74	0.75	0.22	4.71	0.74
V-ArOH	0.003	0.001	0.108	0.009	0.002	0.001	0.019	0.003	0.007	0.001	0.323	0.037	0.0015	0.001	0.002	0.001
TCN	0.003	0.001	0.016	0.0018	0.005	0.002	0.02	0.005	0.004	0.001	0.029	0.005	0.003	0.001	0.006	0.001
THg	0.0001	0.0000	0.0042	0.0005	0.0002	0.0000	0.0042	0.0008	0.0000	0.0000	0.0002	0.0000	0.0000	0.0000	0.0001	0.0000
TPb	0.011	0.001	0.25	0.031	0.008	0.001	0.085	0.017	0.011	0.001	0.1	0.014	0.002	0.001	0.006	0.001
TCd	0.0006	0.0001	0.0084	0.0012	0.001	0.0001	0.0084	0.0019	0.0007	0.0001	0.005	0.001	0.0002	0.0001	0.001	0.0001
Cr^{6+}	0.0041	0.002	0.035	0.0034	0.006	0.002	0.035	0.0059	0.004	0.002	0.017	0.003	0.003	0.002	0.004	0.001
Petroleum	0.127	0.005	1.9	0.216	0.237	0.008	3.027	0.564	0.111	0.01	0.604	0.120	0.06	0.005	0.243	0.051
F^-	0.440	0.038	2.19	0.394	0.50	0.14	1.373	0.315	0.69	0.038	2.02	0.44	0.27	0.12	1.13	0.16
TP	0.102	0.01	0.69	0.108	0.088	0.017	0.228	0.053	0.12	0.01	0.30	0.09	0.136	0.048	0.619	0.12

(Kaiser, 1958; Davis, 1986; Zhang et al., 2008). The new orthogonal variables allow data reduction with minimum loss of original information, and provide information on the most meaningful parameters for the description of the whole data set (Kaiser, 1958). In our study, PCA of the normalized variables (water quality data set) was performed to extract significant principal components and to further reduce the contribution of variables with minor significance; these PCs were subjected to varimax rotation (raw) generating original variables. Following Pekey et al. (2004), eigenvalues ≥ 1 were selected as the new orthogonal variables.

Absolute principal component score-multiple linear regression (APCS-MLR) can be applied to estimate the contribution of each pollution source to the total, by combining MLR with the de-normalized APCS values produced by PCA and the measured concentrations of the particular pollutant (Singh et al., 2005; Zhou et al., 2007; Su et al., in press). After determination of the number and identity of possible sources influencing the river water quality in four functional zones by using PCA, source contributions were computed through APCS-MLR technique in this paper. Quantitative contributions from each source for individual parameter/contaminant were compared with their measured values. All statistical calculations were performed using the "Statistical Package for the Social Sciences Software-SPSS 16.0 for Windows" (SPSS Inc., Chicago, IL).

3.3.2. *Time series analysis*

While widely used for trend analysis, Mann–Kendall's test has found its home in water science studies (Cun and Vilagines, 1997; Chang, 2008; Yang et al., 2009; Zhang et al., 2010). However, this method for trend analysis works only when the number of observed measurements exceeds ten. Besides, it can not effectively interpret the inter-level dynamics of water quality over a certain interval. To overcome the classical problems of Mann-Kendall's test, this paper used the following approach.

The first step, referred to as a graphic analysis of trend and dispersion, is to identify the major changes in the time period with box-and-whisker graphs. These plots are a graphical summary of data distribution and the outliers' presence in the data (individual points beyond the whiskers) (Tukey, 1977). The whiskers (end points of the lines attached to the box) extend out the lower and upper value of the data series. In addition, box-and-whisker diagrams can be used to identify the lack of symmetry in the distribution of data for a defined period of time (Cun and Vilagines, 1997).

The second step is to determine the presence of shifts in the mean of the water quality variables for the investigated years. Exponential smoothing (ES) is a technique that can be applied to time series data, either to produce smoothed data for presentation, or to make forecasts. It is a powerful approach to examining short-to-medium term time series up to 5 years, since no parameters have to be estimated (Temme et al., 2004). The fundamental idea is to recalculate each value of the time series by smoothing it as the weighted average of the previous observations, where the weights decrease exponentially depending on the value of the smoothing parameter (For details, see Wei, 1989).

Finally, non-parametric tests, Kruskal–Wallis test (Kruskal and Wallis, 1952) and Mann–Whitney test (Mann and Whitney, 1947), were applied to confirm whether any trends in water quality during the study period existed. For the time series that do not produce visual important variations, a Kruskal–Wallis test can be applied to study median homogeneity. This statistical method tests the null hypothesis that the medians within each series are the same. The data from all series were combined and ranked from lowest to highest. The average rank is then computed for the data in each series. Since the P value is less than 0.05, there is a statistically significant difference amongst the medians at a 95% confidence level. The tested series was chosen for each parameter considering the results of ES analysis. Mann–Whitney test is constructed by combining the two samples, sorting the data from lowest to highest value and comparing the average rank of the two series in the combined data. Mann–Whitney test has been popularly used to detect a shift or a step change in median or mean of hydro-meteorological time series such as water quality, stream flow, temperature, and precipitation (Yue and Wang, 2002). Of particular interest is the P value of the two-sided test. Since the P value is less than 0.05, there is a statistically significant difference amongst the medians at a 95% confidence level. The tested series was chosen for each parameter considering the results of Kruskal–Wallis test, in order to identify sudden changes in the study period.

3.3.3. *Pollution index*

Pollution index (Wang et al., 2008) is applied to compare temporal variations of different functional zones in Qiantang River. Eq. (1) is used to calculate the surface water quality.

$$PI = \frac{C_i}{C_0}(i = 1, 2, \dots n) \tag{1}$$

where PI is the pollution index; C_i is the actual concentration of surface water, mg/l; C_o is the standard concentration value of surface water, mg/l. When PI is greater than 1, the monitoring site is regarded as polluted; otherwise, non-polluted.

The "Environmental Quality Standards for Surface Water" of China (GB3838-2002), divides the surface water quality into five categories (see Appendix). For Qiantang River, each category of functional zones has its corresponding standard value (ZEPB, 2006). We then use the standard value for each monitoring site in the four functional zones to calculate PI value.

4. Results and discussion

4.1. *Temporal trend analysis*

4.1.1. *Significant variables*

The most significant water quality variables associated with the differences among the four functional zones were generated by DA. As shown in Table 2, the values of Wilk'lambda for each discriminant function varied from 0.598 to 0.959 and the chi-square from 9.1 to 108.2 with the p-level < 0.01, indicating that the temporal DA results were credible.

Obtained from the standard, forward stepwise and backward stepwise modes of DA, the discriminant functions (DFs) and classification matrices (CMs) were shown in Table 3. DFs from the standard stepwise mode, using 13 discriminant variables, yielded CMs correctly assigning 88.4% of the cases; DFs of

Table 2 – Results of discriminant analysis for temporal variation in Qiantang River between 2001 and 2004.

Models	DF	Wilks'lambda	Chi-square	p-level
Standard	1	0.896	108.2	0.000
	2	0.777	53.0	0.000
	3	0.598	23.1	0.00
Forward	1	0.912	86.4	0.000
	2	0.816	39.9	0.000
	3	0.703	16.5	0.000
Backward	1	0.959	64.1	0.000
	2	0.892	24.7	0.000
	3	0.743	9.1	0.000

the forward stepwise mode using 7 discriminant variables, yielded CMs correctly assigning 84.9% of the cases; and DFs of the backward stepwise mode produced similar result of 80.7% correct assignment with only 4 discriminant parameters: COD_{Mn}, NH_3-N, TCd and F^-. These DA results suggested that COD_{Mn}, NH_3-N, TCd and F^- were the most significant parameters for discrimination among the four functional zones and accounted for most of the expected variations of water quality.

4.1.2. *Temporal trends of significant variables*

Box-and-whisker plots of the significant discriminant parameters recognized by DA were shown in Fig. 2. Symmetric data would have the median to lie in the middle of the rectangle and the lengths of the upper and lower whiskers would be about the same (Cun and Vilagines, 1997). Notice in Fig. 2 that, concentrations of the four variables presented asymmetrical data almost in all the period of time between 1996 and 2004. In addition, the patterns of changes for the four variables seemed irregular and significant sudden changes were not detected. Time series yearly moving averages were applied to visualize the evolution law of water quality data from apparent irregularity. Fig. 3a showed trends of COD_{Mn} for four functional zones that behaved differently. Generally speaking, COD_{Mn} values for Zone A and D remained stable during the study period, while those for Zone B and C marked an oscillation pattern. The trend curves of NH_3-N for Zone A, C and D had similar profiles, smoothly across the period 1996–2004. NH_3-N concentrations in Zone B fluctuated within the interval 1998–2003, and became stable in other years (Fig. 3b). The concentrations of TCd reflected almost no significant changes in all zones except Zone C, with an upward from 1997 to 1999 and then a downward trend in the period 1999–2002 (Fig. 3c). No significant changed trends of F^- existed among the four functional zones (Fig. 3d).

Non-parametric tests were used to confirm the above analysis (Table 4). Results denoted that stationarities exited among the time series except the COD_{Mn} time series for Zone B and C, NH_3-N series for Zone B and TCd series for Zone D. Nevertheless, Mann–Whitney tests marked that 1999, 2001 and 2003 were not significant drop/increase points of COD_{Mn} time series for Zone C. Similarly, 1999 was not the significant drop point of NH_3-N series for Zone B. On the contrary, significant gap between 2000 and 2004 was identified for COD_{Mn} time series of Zone B, suggesting that organic pollution became more serious in this zone. In addition, 1999 and 2002 was respectively regarded as increase and drop point of TCd series for Zone C. This may be caused by increased amount of wastewater discharged from industry in 1999. Concerning about the increasing heavy metal pollution in the drinking water protection zone, the local government invested to tackle with this alarming issue. This may account for the decline in TCd concentrations in 2002.

4.1.3. *Within-group variations for different functional zones*

Aiming at comparing the within-group variations for different functional zones, yearly PI for each monitoring site was calculated and mapped with GIS. Fig. 4a indicated that COD_{Mn} of most sites in Zone A met the required standards except for site 2, 14, 26 and 39. Site 2, 14 and 26 reflected a deteriorating tendency, while site 39 was in continued polluted status. The rising trend of site 29 in Zone B and site 12 in Zone C was similar to site 2, indicating worsening water quality during the nine years. In addition, site 4 in Zone D remained in an alarming status, to which we should pay much attention.

Table 3 – Classification functions coefficients for discriminant analysis of variations in functional zones of Qiantang River between 2001 and 2004.

Parameters	Standard model				Forward stepwise model				Backward stepwise model			
	Zone A	Zone B	Zone C	Zone D	Zone A	Zone B	Zone C	Zone D	Zone A	Zone B	Zone C	Zone D
DO	10.85	11.02	10.58	11.44								
COD_{Mn}	2.20	2.21	2.00	2.29	1.32	1.28	1.66	.98	.93	1.59	1.04	1.41
BOD	3.35	4.11	3.54	4.13	2.18	3.07	2.94	3.25				
NH_3-N	.09	−.14	.19	.16	.05	−.05	.13	.11	.02	0.3	.08	.04
V-ArOH	−32.30	−34.57	−23.98	−35.36								
TCN	170.4	489.0	302.1	242.5								
THg	1.2E4	1.3E4	1.2E4	1.5E4								
TPb	12.12	−5.56	18.82	−11.27								
TCd	−6.3E3	−6.5E3	−6.4E3	−7.9E3	−4.5E3	−4.9E3	−4.6E3	−6.1E3	−2.7E3	−1.6E3	−4.8E3	−5.8E3
Cr^{6+}	210.1	345.8	50.3	172.9	211.2	395.5	69.2	170.7				
Petroleum	2.27	1.84	1.55	.94								
F^-	−2.32	−3.11	1.23	−4.37	.31	−2.06	2.78	−2.39	.64	−1.19	3.27	−1.19
TP	38.31	35.09	32.14	43.63	17.14	19.45	21.66	24.37				
Constant	−49.13	−52.90	−48.11	−54.77	−27.38	−31.97	−27.64	−31.89	−2.78	−4.35	−3.99	−2.97

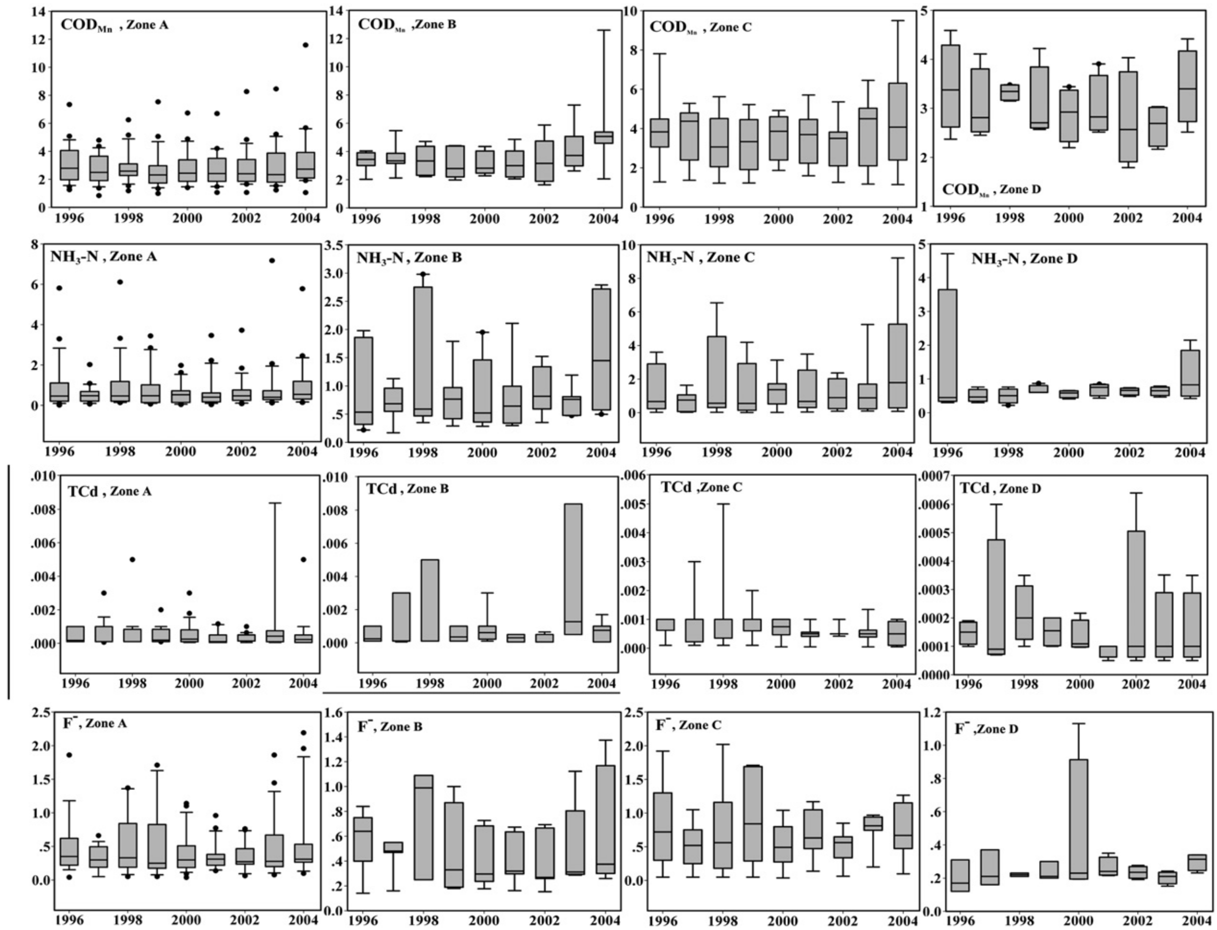

Fig. 2 – Temporal variations of COD_{Mn}, NH_3-H, TCd and F^- in different functional zones of Qiantang River between 1996 and 2004 (units: mg/l).

As shown in Fig. 4b, NH_3-N concentrations of site 2, 14, 26, 27 and 39 in Zone A, 29 in zone B, 12, 15 and 18 in Zone C, and site 4 in Zone D were very high throughout the studied period. Site 33 in Zone B had an upward trend in NH_3-N concentrations, signifying more and more serious eutrophication. Most sites were not affected by TCd pollution during 1996–2004 except some typical sites like 2, 11, 28, 35 and 39 in Zone A, 15 and 16 in Zone B, and site 40 in Zone C (Fig. 4c). Furthermore, the TCd pollution mainly occurred in 1998 and 2003 in the sites mentioned above. Fig. 4d showed that sites 14 and 28 in Zone

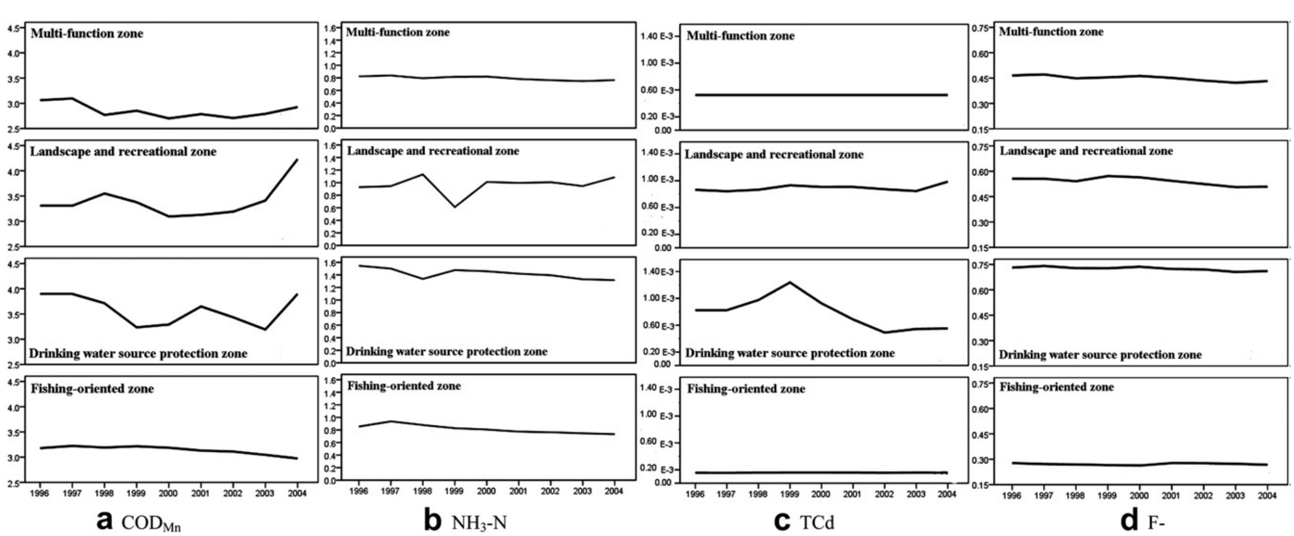

Fig. 3 – Temporal trend of COD_{Mn}, NH_3-H, TCd and F^- in each functional zone between 1996 and 2004.

Table 4 – Kruskal–Wallis test and Mann–Whitney test results for discriminant variables in functional zones of Qiantang River between 1996 and 2004.

Variable	Functional zone	Kruskal–Wallis test	P value	Decision	Mann–Whitney test	P value	Decision
COD_{Mn}	Multi-function zone	8.12	0.43	No difference			
	Landscape and recreational zone	5.46	0.03	Difference identified	87	0.003	Gap in 2000 and 2004
	Drinking water source protection zone	3.89	0.00	Difference identified	96	0.24	Not a significant value
	Fishing-oriented zone	3.37	0.39	No difference			
NH_3-N	Multi-function zone	8.46	0.36	No difference			
	Landscape and recreational zone	2.75	0.00	Difference identified	195	0.37	Not a significant value
	Drinking water source protection zone	3.56	0.67	No difference			
	Fishing-oriented zone	3.84	0.60	No difference			
TCd	Multi-function zone	7.82	0.78	No difference			
	Landscape and recreational zone	8.35	0.86	No difference			
	Drinking water source protection zone	1.56	0.00	Difference identified	37	0.00	Increase in 1999 Drop in 2002
	Fishing-oriented zone	5.38	0.64	No difference			
F^-	Multi-function zone	0.96	0.75	No difference			
	Landscape and recreational zone	3.69	0.54	No difference			
	Drinking water source protection zone	2.44	0.66	No difference			
	Fishing-oriented zone	1.84	0.81	No difference			

A had F^- pollution in most years. So was the case with sites 29 and 32 in Zone B. High F^- concentrations of site 18 in Zone C should be given special attention as high F^- concentrations in drinking water can expose public to F^- poisoning risks.

4.2. *Identification of potential pollution sources*

Before performing PCA, Kaiser-Meyer-Olkin (KMO) and Bartlett's sphericity tests were used to examine the validity of PCA. KMO results for the four functional zones were 0.805, 0.784, 0.816 and 0.775, respectively, and those for Bartlett's sphericity were 1973, 1433, 2297 and 2356 ($P < 0.05$), indicating that PCA would be useful for providing significant reductions in dimensionality. PCA with varimax rotation explained 71.2% of the total variance in Zone A, 83.3% in Zone B, 70.6% in Zone C and 81.8% in Zone D, respectively (Table 5).

According to Liu et al. (2003) and Huang et al. (2010), factor loadings > 0.75, [0.5–0.75] and [0.3–0.5] were considered to be strong, moderate and weak, respectively. For Zone A, the first varifactor (VF_1), accounting for 27.0% of the total variance, had strong and positive loadings on COD_{Mn}, BOD, NH_3-N, and V-ArOH. High concentrations of NH_3-N in surface drainage could come from various sources including natural organic matters decomposition, factories, and fertilizer applications (Hülya and Hayal, 2008). V-ArOH usually originates from chemical plants discharge, since it is widely used in plastics and organic synthesis industry. Meanwhile, the average values of NH_3-N and V-ArOH were relatively low while their maximum values were high, denoting that they could stem from some point pollution sources. Thus, with monosodium glutamate (MSG) factories and chemical plants scattered in Qiantang River basin, VF_1 can be identified as "chemical plants discharge". For VF_2, it explained 18.2% of the total variance, and had strong positive loadings on THg and TCd and a moderate positive loading on TPb. On the whole, the mean levels of the three variables were low, but those of some sites were indeed high. All the elements in this factor are likely to originate from industrial wastewaters discharged into the stream. Elements like Cd, Hg and Pb are known as markers of chemical and tannery plants (Owen and Sandhu, 2000) and electronic industries (Pekey, 2006), including electroplating, dyeing and printed circuit board manufacturing, many of which are present in the study area. According to China Environment Statistical Yearbook (2005) and Zhejiang Statistical Yearbook (2005), the total industrial wastewater discharge is estimated to more than 40000 tones. Thus, VF_2 may be interpreted as industrial wastewater pollution. VF_3, accounting for 16.2% of the total variance, had strong positive loadings on TCN and moderate positive loadings on F^- and TCd. Cyanide and Cd in water could be caused by metal mining, organic chemical industries, iron and steel factories as well as the public wastewater treatment plant. F^- is usually from cement plants, fluorine chemical factories, phosphorus fertilizer plants and smelters (Huang et al., 2010). However, the levels of TCN and TCd in Zone A, except some typical points, were both very low and corresponded to water quality class I/II;, according to GB3838-2002 (Appendix). These typical sites, associated with high F^- concentrations, were located around fluoride mines. Therefore, the pollution of VF_3 should be summed as fluoride mining. The specific geological conditions

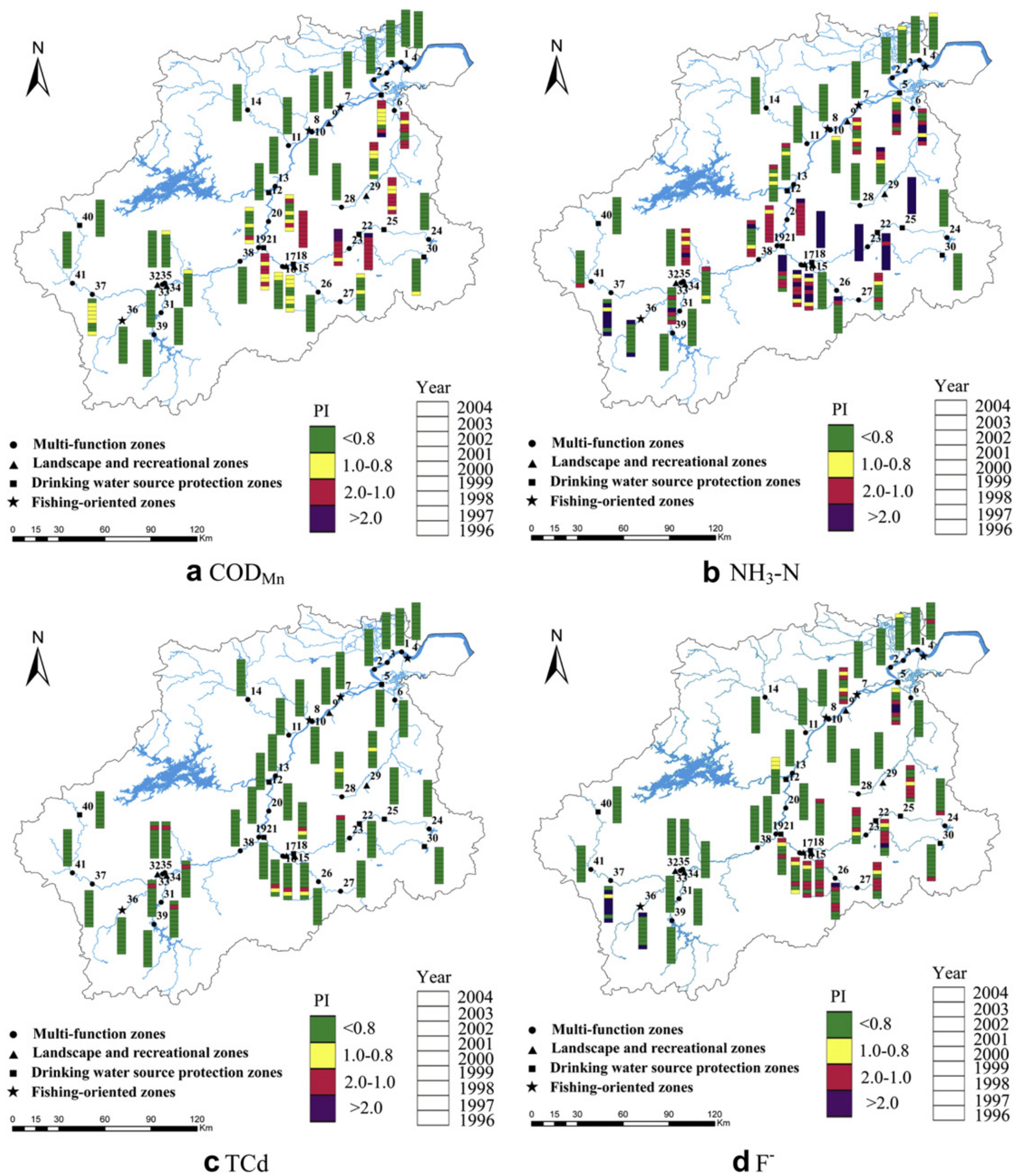

Fig. 4 – Temporal trend of PI for COD_{Mn}, NH_3-H, TCd and F^- in each monitoring site between 1996 and 2004.

make Qiantang River one of the important operating waterways of Yangtze River Deltas. Sand mining machinery and vessels shipping are generally distributed throughout the entire area for lack of corresponding bound and supervision mechanism (Su et al., in press). Therefore, VF_4, explaining 9.8% of the total variance and with only strong and positive loadings on petroleum, was attributed to vehicle exhaust and sand mining.

In Zone B, NH_3-N, COD_{Mn}, DO, BOD and TP constituted VF_1, explaining 29.1% of the total variance. VF_1 had strong and positive loadings on NH_3-N, COD_{Mn}, BOD and TP and a strong negative loading on DO. Phosphorus could originate from both point and non-point sources. Point sources comprise municipal waste treatment plants, factories, and confined livestock operations, while non-point sources mainly include soil erosion and water runoff from cropland, lawns and gardens, urban areas, small livestock confinement operations, etc (Hülya and Hayal, 2008). If we assumed a 500 m buffer around the monitoring sites in Zone B, the dominant land cover were agricultural land (45%) and forest (25%). So, in view of hydro-chemical conditions of water and land cover patterns, VF_1 can be partly identified as "agricultural non-point pollution" with the presence of NH_3-N and TP, which were mainly found in agricultural drainage water as mentioned above. Similarly, VF_1 had strong positive loadings on both COD_{Mn} and BOD, whereas, a strong negative loading on DO. It was, thus, a zone of purely organic pollution indicator parameters from uncontrolled domestic discharges caused by rapid urbanization (Singh et al., 2005; Zhou et al., 2007). Based on the above analysis, VF_1 represented nutrient pollution from strong anthropogenic impacts

Table 5 – Loadings of 13 selected variables on VARIMAX rotated factors of different functional zones in Qiantang River.

Parameters	Multi-function zone				Landscape and recreational zone				Drinking water source protection zone			Fishing-oriented zone			
	VF_1	VF_2	VF_3	VF_4	VF_1	VF_2	VF_3	VF_4	VF_1	VF_2	VF_3	VF_1	VF_2	VF_3	VF_4
DO	.207	.088	–.095	.284	–.928	–.032	.110	–.029	–.868	.238	–.034	.400	–.329	–.662	–.198
COD_{Mn}	.892	.021	.243	–.208	.830	–.022	.264	.341	.881	.076	.141	.234	.048	.757	.004
BOD	.888	.070	.112	–.191	.909	–.003	.292	.175	.932	–.055	–.052	.066	–.226	.746	–.300
NH_3-N	.877	.011	.095	–.161	.822	–.061	.243	–.218	.677	.419	.148	.155	–.062	.804	.125
V-ArOH	.817	.063	–.068	.187	.133	–.074	.619	–.185	–.026	–.111	.025	.983	–.057	.099	–.013
TCN	.096	–.027	.787	.178	.304	–.070	–.284	.458	–.038	.349	.060	.716	–.115	.497	–.207
THg	–.099	.950	–.004	.022	–.016	.988	–.052	–.090	–.071	.532	–.455	.954	.073	.037	–.108
TPb	.015	.746	–.101	.043	–.008	.988	.038	.030	–.006	.764	.005	–.004	.914	–.117	.128
TCd	.164	.934	.021	.003	–.036	.990	.021	–.028	.421	.660	.106	.064	.937	–.093	–.113
Cr^{6+}	–.039	–.065	.673	–.080	.029	–.092	.441	.783	–.070	–.218	–.516	.988	–.046	.090	–.006
Petroleum	.411	–.108	.199	.855	.241	–.003	–.231	.760	.742	–.039	–.285	.034	.299	.026	.063
F^-	.467	.027	.741	–.247	–.129	–.016	.264	.304	.146	.210	.803	–.124	.110	.003	.958
TP	.200	–.014	.583	–.461	.739	.140	.809	–.018	.896	.126	.110	–.452	.811	.158	.205
Eigenvalue	3.51	2.37	2.17	1.27	3.79	2.98	2.34	1.73	5.12	2.08	1.16	3.83	3.06	2.53	1.19
% Total variance	27.0	18.2	16.2	9.8	29.1	22.9	18.0	13.3	39.4	21.0	10.2	29.5	23.6	19.5	9.2
Cumulative %	27.0	45.2	61.4	71.2	29.1	52.0	70.0	83.3	39.4	60.4	70.6	29.5	53.1	72.6	81.8

such as domestic sewage and agricultural activities. As with VF_2 of Zone A, VF_2 (22.9% of the total variance) had strong positive loadings on TCd, THg and TPb, and was attributed to industrial wastewater discharge (Pekey, 2006). VF_3 (18.0% of the total variance) had moderately positive loadings on V-ArOH and TP, representing chemical plants discharge. VF_4 (13.3% of the total variance) had moderate positive loadings on petroleum, representing vehicle exhaust and sand mining (Su et al., in press).

The pollution pattern in Zone C was in part similar to that in Zone B. As with VF_1 of Zone B, VF_1 (39.4% of the total variance) had positive loadings on NH_3-N, COD_{Mn}, BOD and TP and negative loadings on DO, and was then attributed to non-point agricultural runoff, especially from nitrogenous fertilizers (Singh et al., 2005). VF_2 (21.0% of the total variance) had strong positive loadings on TCd and TPb, as with VF_2 of Zone B, likely representing industrial wastewater discharge (Pekey, 2006). VF_3, accounting for 10.2% of the total variance, had only positive loadings on F^-. This zone is known for high fluoride in soils and groundwater, and the pollution source can be attributed to fluoride weathering and mining.

For Zone D, VF_2 accounted for 23.6% of the total variance. High loadings of TCd and TPb were displayed, the levels of which were both very low and corresponded to water quality class I, according to GB3838-2002. So, VF_2 represented natural factors such as lithology and soil types (Huang et al., 2010). VF_3 had positive loadings on NH_3-N, likely representing agricultural runoff THg, TCN and V-ArOH were removed in the analysis because of its very low and relatively unchanged concentration (For similar issues, see Huang et al., 2010; Su et al., in press). F^- levels at almost all monitoring sites were below 1.0 mg/l in Zone D, denoting that there was no or very low pollution. Such a small amount of fluoride may be influenced by local soils entering the river together with the runoff (Huang et al., 2010). Therefore, VF_4 could be expressed as “soil weathering”.

4.3. *Source contribution using APCS-MLR*

Absolute principle component score was used to calculate source contributions after determining the number and characteristics of possible sources by PCA. Coefficients of determination (R^2) in Table 6 reflected that APCS-MLR was relatively accurate. Most sites in Zone A were primarily influenced by chemical pollution (COD_{Mn}, 73.2%; BOD, 68.1%; NH_3-N, 81.4%; V-ArOH, 59.3%), industrial wastewater discharge (THg, 65.8%; TPb, 73.6%; TCd, 59.2%), fluoride mining (F^-, 69.2%) and vehicle exhaust and sand mining (petroleum, 83.5%). For Zone B, most monitoring sites were related to domestic sewage and agricultural pollution (NH_3-N, 84.4%; TP, 81.6%; COD_{Mn}, 58.6%; DO, 64.4%; BOD, 70.8%), industrial wastewater discharge (TCd, 71.6%; THg, 77.4%; TPb, 86.4%), chemical plants discharge (V-ArOH, 65.4%; TP, 71.5%) and vehicle exhaust and sand mining. Most variables of Zone C were associated with domestic sewage and agricultural pollution, industrial wastewater discharge (TPb, 68.7%; TCd, 54.2%) and fluoride weathering and mining (F^-, 87.5%). For Zone D, most variables were related to agricultural runoff (NH_3-N, 85.3%; COD_{Mn}, 74.2%; DO, 69.9%; BOD, 70.5%) and soil weathering (F^-, 78.9%). Additionally, as shown in Table 6, unidentified sources (UIS) in all groups contributed to

Table 6 – Source contribution of each variable of different functional zones in Qiantang River.

Variables	Zone A [a]					R^2	Zone B [b]					R^2	Zone C [c]				R^2	Zone D [d]					R^2
	VF_1	VF_2	VF_3	VF_4	UIS[e]		VF_1	VF_2	VF_3	VF_4	UIS[e]		VF_1	VF_2	VF_3	UIS[e]		VF_1	VF_2	VF_3	VF_4	UIS[e]	
DO	–	–	–	–	18.7	.68	64.4	–	–	–	10.5	.72	70.0	–	–	7.5	.76	–	–	69.9	–	–	.75
COD_{Mn}	73.2	–	–	–	–	.82	58.6	–	–	–	–	.73	66.9	–	–	–	.74	–	–	74.2	–	–	.80
BOD	68.1	–	–	–	–	.74	70.8	–	–	–	7.8	.69	71.3	–	–	–	.77	–	–	70.5	–	–	.69
NH_3-N	81.4	–	–	–	1.8	.86	84.4	–	–	–	–	.83	82.6	–	–	12.8	.83	–	–	85.3	–	–	.83
V-ArOH	59.3	–	–	–	–	.73	–	–	65.4	–	–	.64	–	–	–	11.3	.71	73.5	–	–	–	7.1	.64
TCN	–	–	8.6	–	–	.66	–	–	–	–	14.6	.76	–	–	–	2.9	.69	81.6	–	–	–	–	.67
THg	–	65.8	–	–	–	.75	–	77.4	–	–	–	.80	–	–	–	–	.73	78.4	–	–	–	–	.72
TPb	–	73.6	–	–	–	.78	–	86.4	–	–	–	.75	–	68.7	–	–	.78	–	83.2	–	–	–	.81
TCd	–	59.2	–	–	–	.73	–	71.6	–	–	–	.71	–	54.2	–	–	.74	–	76.8	–	–	–	.78
Cr^{6+}	–	–	29.4	–	–	.64	–	–	–	–	8.7	.68	–	–	–	–	.71	–	–	–	–	2.9	.74
Petroleum	–	–	–	83.5	–	.80	–	–	–	79.8	–	.79	–	–	–	19.3	.70	–	–	–	–	–	.85
F^-	–	–	69.2	–	–	.84	–	–	–	–	17.8	.84	–	–	87.5	–	.81	–	–	–	78.9	18.5	.74
TP	–	–	–	–	26.9	.71	81.6	–	71.5	–	15.2	.85	77.8	–	–	25.8	.83	–	–	–	–	23.7	.69

a multi-function zone.
b landscape and recreational zone.
c drinking water source protection zone.
d fishing-oriented zone.
e UIS, unidentified sources.

pollution in Qiantang River for all water quality variables, ranging from 1.8% to 26.9%. They represented another major source of pollution besides those identified above. Therefore, field survey is in need to further identify sources of the pollution (Singh et al., 2005; Zhou et al., 2007; Su et al., in press).

4.4. *Methodological prospects*

4.4.1. *Combination of statistical methods for trend analysis: advantage and applicability*

This study used an exploratory approach, which combines smoothing and non-parametric statistical tests. This approach has several advantages: (1) its conceptual simplicity (smoothing + non-parametric tests), (2) its reproducibility with any commercial statistical software that incorporates smoothing and non-parametric tests, (3) its strong reliability (comprehensive application of non-parametric tests to conform smoothing), (4) its non-sensitivity to inequality in time record interval, non-normality in distribution, and spatial and temporal dependence of water quality data, and, (5) its internally consistency.

Though this exploratory approach is designed for short time series, it also shows promising applicability for long time series. Of importance is to note that long time series usually present seasonal patterns of temporal changes. The seasonal decomposition method can be used to divide data into a trend component and a periodical component, before applying the exploratory approach. In addition, the Mann-Kendall's test, non-parametric procedure for monotonic trend detection, can be further applied with the other tests to conform the smoothing results, when the number of observed measurements exceeds ten.

In addition, it should be mentioned that internal consistence must be checked before the combination of statistical methods is applied. The exploratory approach used in this paper presents good internal consistence given the insensitivity of non-parametric tests. However, multivariate methods employed for source apportionment are sensitive to outliers and the non-normal distributions of geochemical data. Therefore, when we apply various multivariate methods for source apportionment, appropriate data pretreatment should be taken into consideration, including estimation of missing data, examination of normal distributions and data transformation, to make sure that the combination of statistical methods is internally consistent.

4.4.2. *Pollution index: from physical numbers to practical references*

The numerical descriptions, spatial patterns and trends analysis of measurement data for water quality variables could assist in uncovering dynamics of river water pollution. However, these approaches mainly depend on the data set itself, and are thus prone to generate results that lack of practical significance. Putting into practice these physical results requires a higher level of technical expertise to facilitate optimal judgments and decisions. Besides, management of water quality today requires easy-to-understand and intellectual decision-support for national and local governments (WHO and UNICEF, 2005).

Basically, PI is a comparatively direct parameter that exhibits practical results by comparing measured values against standards. As for river functional zoning, standards of water quality are determined based on considerations of the likely adverse impact of pollutant levels. The comparison of measured values against standards implicitly conveys the message whether or not the water quality is acceptable, from a sustainable perspective. The results of this study highlighted the usefulness of PI in trend analysis. No significant trend of TCd was identified for monitoring sites in Group A. However, site 31 and 39 presented higher PI values (>1) in 2003. If we converted the practical results into physical values, the year

2003 was found to be significant gap for the nine-year time series. Consequently, we argue that, when characterizing the temporal trend of water quality, periodic reports that include time series of concentrations, and a comparison of the measured values for each pollutant against standards should be both provided.

4.4.3. *Variations in source apportionment: role of cross space-time effects*

Studies of water pollution source apportionment generally fall into the following framework. First, monitoring/sampling sites are classified into several groups according to the similarity in water quality; then pollution sources are identified via factor analysis/PCA; finally the contributions of different sources are determined using suitable receptor models (Zhou et al., 2007; Huang et al., 2010; Su et al., in press). Different from previous studies, this paper characterized the pollution sources from management prospective. Groups subject to source apportionment were clustered under the zoning framework, rather than using the physical characteristics of measurement data. This kind of source apportionment could provide direct references for managers, however, the intra-level variations within the functional zone may be relatively high. Contrarily, the traditional approach may exhibit relatively low variations within one group, but can not offer easy-to-understand information for managers. Regardless of the advantages and disadvantages of the two approaches, the comparison suggests that source apportionment is influenced by spatial scales and temporal intervals. More specifically, we gave two cases to exemplify the role of cross space-time effects.

First, we compared the results with those of Su et al. (in press). Su et al. (in press) used traditional approaches to interpret the pollution sources of Qiantang River for the period of 2001–2004. The identified pollution sources for Sites 1-3 between 2001 and 2004 were domestic sewage and agricultural pollution, industrial wastewater pollution, fluoride mineral weathering, and vehicle exhaust and sand mining. Partly different, chemical plants discharge, industrial wastewater pollution, fluoride mining, and vehicle exhaust and sand mining were interpreted as the main pollution sources in this paper. All these variations bring to light the point that the cross role of space-time effects in source apportionment can not be overestimated.

Second, we employed absolute principal component score (APCS) to quantitatively and specifically check the cross space-time effects. Since factor scores are related to source contributions, higher factor scores indicate the higher contribution of the source in the samples (Guo et al., 2009). Fig. 5 shows the annual average contributions for the extracted sources for monitoring sites of multi-function zone between 1996 and 2004. The annual average contributions for individual sources were obtained by averaging the corresponding source contributions for all the monitoring sites. The significant fluctuations of contributions for the extracted sources proved the existence of temporal variations in source apportionment. Similarly, the spatio-temporal variations in contributions of extracted sources for each monitoring site of multi-function zone (Fig. 6) also signified the space-time dependent features of source apportionment. Above analysis demonstrates that role of cross space-time effects should be taken seriously in source apportionment. Besides, APCS, which contributes to quantitative description of variations in source apportionment, can be applied to characterize the cross space-time effects.

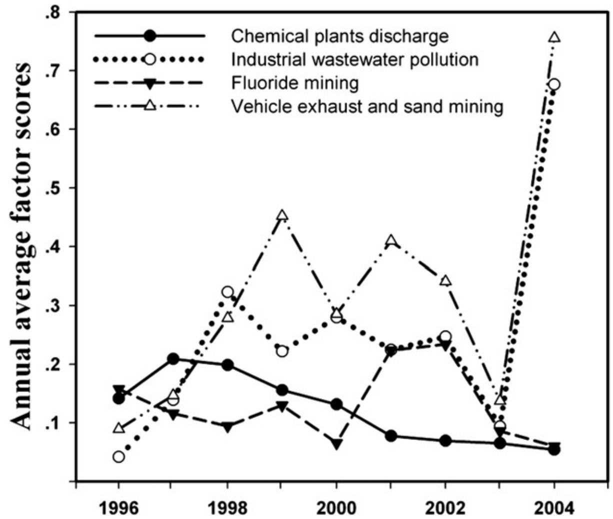

Fig. 5 – Annually temporal variations in source apportionment for monitoring sites of multi-function zone.

One limitation of this study is that the seasonal variations are not discussed. Further study related to the corresponding variations has to be carried out. Another limitation is that the monitoring sites were spatial unevenly distributed. We were not able to study other categories of functional zones, such as industry-oriented zone and natural reserved zone.

4.5. *Management implications*

The present methods for comprehensive applications of different multivariable statistics in temporal trend analysis and apportionment of water pollution source could provide a technical support for governmental agencies to implement integrated river basin management. Besides, it is designed for, but not limited, its applications at large river basin scale. Firstly, the comparison and identification of pollution sources in different functional zones would help maintain ecosystem health and make holistic policies by emphasizing the variations in different zones. Secondly, based on the information extracted from PCA, we may develop innovative planning schemes or adjust the currently used management practice to a more impartial and effective manner. The source apportionment information is also helpful for the local government to explain the dissension from the towns whose responsibility for aquatic ecosystem conservation rather than over-exploitation. Thirdly, the source contributions assessment, which determines the relative importance of different variables, could be applied to optimize future monitoring program by reducing sampling frequency, the number of monitoring sites and parameters, and thus, the subsequent cost (Su et al., in press). Finally, source apportionment framework along with function zoning and planning can be integrated into an Integrated River Basin Management Decision Support System

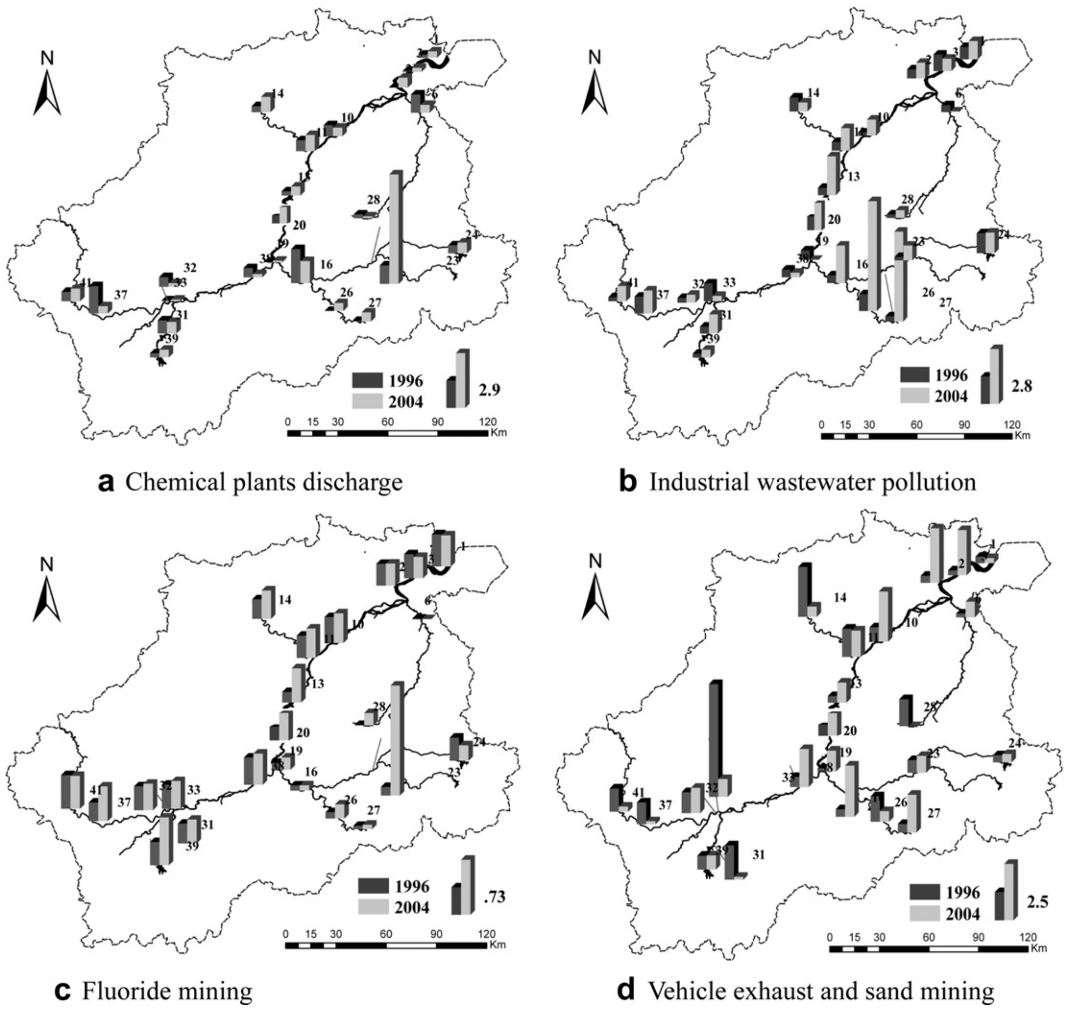

Fig. 6 – Spatio-temporal variations in absolute principal component score of extracted sources for each monitoring site of multi-function zone.

that provides a GIS platform to effectively manage land and water resources with the involvement of multiple stakeholders including governments and the general public.

5. Conclusions

This study investigated the temporal trend and identified pollution sources in different functional zones of Qiantang River using a nine-year (1996–2004) data set. COD_{Mn}, NH_3-N, TCd and F^- were discriminant variables of variations in different functional zones. An exploratory approach, which combined smoothing and non-parametric statistical tests, was used to characterize temporal trends for the four variables among different functional zones. Pollution index was further applied to analyze within-group variations in trends for different functional zones. Based on the results, we believe that this exploratory approach is not only effective for short time series but also shows promising applicability for long time series. In addition, when characterizing the temporal trend of water quality, periodic reports that include time series of concentrations, and a comparison of the measured values for each pollutant against standards should be both provided.

Sources responsible for pollution identified by PCA differed among the four functional zones. Generally, Zone A and Zone B were mainly affected by human activities, while Zone C and Zone D by natural process; point pollution was the major source for Zone A, whereas non-point source for Zone B, C, and D. Receptor-based source apportionment through APCS-MLR revealed that unidentified sources were another major latent source. Therefore, field survey is needed to identify these additional sources of the pollution. Furthermore, spatio-temporal variations in source apportionment signified the influence of spatial scales and temporal intervals. These results demonstrate that role of cross space-time effects should be taken seriously in source apportionment. Besides, APCS, which contributes to quantitative description of variations in source apportionment, can be applied to characterize the cross space-time effects.

Our work suggests that the management-oriented source apportionment under the framework of river function zoning, which could provide a technical support for governmental agencies to implicate integrated river basin management, is in great need, especially for developing countries. Based on the insight that the links between science and management should be a vital part of water science research, we argue that the advanced study of water pollution source apportionment should be more focused on the integration of source apportionment and different management frameworks, the uncertainties associated with cross space-time effects, the comparison between physical data-based and management-oriented source apportionment, and the relevance of source apportionment to integrated river basin management. In particular, how to develop or apply approach/model that presents direct practical significance has to be understood.

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Appendix A.

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

Parameters	Category of water quality standards				
	First	Second	Third	Fourth	Fifth
NH_3-N	<0.15	0.5	1	1.5	2
F^-	<1.0	1.0	1.0	1.5	1.5
COD_{Mn}	<2.0	4.0	6.0	10.0	15.0
Cr^{6+}	<0.01	0.05	0.05	0.05	0.1
V-ArOH	<0.002	0.002	0.005	0.01	0.1
DO	>90% of saturation	6.0	5.0	3.0	2.0
BOD	<3	3.0	4.0	6.0	10.0
Petroleum	<0.05	0.05	0.05	0.5	1.0
TCd	<0.001	0.005	0.005	0.005	0.01
THg	<0.00005	0.00005	0.0001	0.001	0.001
TP	<0.02	0.1	0.2	0.3	0.4
TPb	<0.01	0.01	0.05	0.05	0.1
TCN	<0.005	0.05	0.2	0.2	0.2

REFERENCES

Brierley, G., Fryirs, K., Outhet, D., Massey, C., 2002. Application of the River Styles framework as a basis for river management in New South Wales, Australia. Applied Geography 22 (1), 91–122.

Chang, H.J., 2008. Spatial analysis of water quality trends in the Han River basin, South Korea. Water Research 42 (13), 3285–3304.

Cheruvelil, K.S., Soranno, P.A., Bremigan, M.T., Wagner, T., Martin, S.L., 2008. Grouping lakes for water quality assessment and monitoring: the roles of Regionalization and spatial scale. Environmental Management 41 (3), 425–440.

China Bureau of Statistics, 2005. China Environment Statistical Yearbook. China Statistics Press, Beijing (In Chinese).

China Ministry of Water Resources, 2007. Revisions of Integrated River Basin Planning Document of Chinese Government (In Chinese).

Cun, C., Vilagines, R., 1997. Time series analysis on chlorides, nitrates, ammonium and dissolved oxygen concentrations in the Seine river near Paris. Science of the Total Environment 208 (1–2), 59–69.

Davis, J.C., 1986. Statistics and Data Analysis in Geology. John Wiley & Sons, Inc, New York.

Guo, H., Ding, A., So, K., Ayoko, G., Li, Y., Hung, W., 2009. Receptor modeling of source apportionment of Hong Kong aerosols and the implication of urban and regional contribution. Atmospheric Environment 43 (6), 1159–1169.

Gupta, D.A., 2008. Implication of environmental flows in river basin management. Physics and Chemistry of the Earth 33 (5), 298–303.

Huang, F., Wang, X., Lou, L., Zhou, Z., Wu, J., 2010. Spatial variation and source apportionment of water Pollution in Qiantang River (China) using statistical techniques. Water Research 44 (5), 1562–1572.

Huang, X., Chen, W., Cai, Q., 1999. Survey, observation and analysis of lake ecology. Standards Press of China, Beijing (In Chinese).

Hülya, B., Hayal, B., 2008. Water pollution sources assessment by multivariate statistical methods in the Tahtali Basin, Turkey. Environmental Geology 54 (2), 275–282.

Jonnalagadda, S.B., Mhere, G., 2001. Water quality of the odzi river in the eastern highlands of Zimbabwe. Water Research 35 (10), 2371–2376.

Kaiser, H.F., 1958. The varimax criterion for analytic rotation in factor analysis. Psychometrika 23, 187–200.

Kruskal, W.H., Wallis, W.A., 1952. Use of ranks in one-criterion variance analysis. Journal of the American Statistical Association 47 (260), 583–621.

Kuppusamy, M.R., Giridhar, V.V., 2006. Factor analysis of water quality characteristics including trace metal speciation in the coastal environmental system of Chennai Ennore. Environment International 32 (2), 174–179.

Liu, C., Lin, K., Kuo, Y., 2003. Application of factor analysis in the assessment of groundwater quality in a Blackfoot disease area in Taiwan. Science of the Total Environment 313 (1–3), 77–89.

Love, D., Hallbauer, D., Amos, A., Hranova, R., 2004. Factor analysis as a tool in groundwater quality management: two southern African case studies. Physics and Chemistry of the Earth 29 (15–18), 1135–1143.

Ma, J., Ding, Z., Wei, G., Zhao, H., Huang, T., 2009. Sources of water pollution and evolution of water quality in the Wuwei basin of Shiyang river, Northwest China. Journal of Environmental Management 90 (2), 1168–1177.

Mann, H.B., Whitney, D.R., 1947. On a test of whether one of two random variables is stochastically larger than the other. Annals of Mathematical Statistics 18 (1), 50–60.

Owen, R.B., Sandhu, N., 2000. Heavy metal accumulation and anthropogenic impacts on Tolo Harbour, Hong Kong. Marine Pollution Bulletin 40 (2), 174–180.

Pekey, H., Karakas, D., Bakoglu, M., 2004. Source apportionment of trace metals in surface waters of a polluted stream using multivariate statistical analyses. Marine Pollution Bulletin 49, 809–818.

Pekey, H., 2006. The distribution and sources of heavy metals in IzmitBay surface sediments affected by a polluted stream. Marine Pollution Bulletin 52 (10), 1197–1208.

Sabatini, M.C., Verdiell, V.A., Rodríguez Iglesias, R.M., Vidal, M., 2007. A quantitative method for zoning of protected areas and its spatial ecological implications. Journal of Environmental Management 83 (2), 198–206.

Singh, K.P., Malik, A., Sinha, S., 2005. Water quality assessment and apportionment of pollution sources of Gomti river (India) using multivariate statistical techniques—a case study. Analytica Chimica Acta 538 (1–2), 355–374.

Su, S., Zhi, J., Lou, L., Huang, F., Chen, X., Wu, J. Spatio-temporal patterns and source apportionment of pollution in Qiantang River (China) using neural-based modeling and multivariate statistical techniques. *Physics and Chemistry of the Earth*. doi:10.1016/j.pce.2010.03.021, in press.

Temme, C., Ebinghaus, R., Einax, J.W., Steffen, A., Schroeder, W.H., 2004. Time series analysis of long-term data sets of atmospheric mercury concentrations. Analytical and Bioanalytical Chemistry 380 (3), 493–501.

Tukey, J.M., 1977. Exploratory Data Analysis. Addison-Wesley, Reading, MA.

Wang, J., Da, L., Song, K., Li, B., 2008. Temporal variations of surface water quality in urban, suburban and rural areas during rapid urbanization in Shanghai, China. Environmental Pollution 152 (2), 387–393.

Weng, Q., 2007. A historical perspective of river basin management in the Pearl River Delta of China. Journal of Environmental Management 85 (4), 1048–1062.

Wei, F., Kou, H., Hong, S., 1989. Methods for the Examination of Water and Wastewater. China Environmental Science Press, Beijing (In Chinese).

Wei, W., 1989. Time Series Analysis: Univariate and Multivariate Methods. Addison-Wesley, New York.

WHO and UNICEF, 2005. WHO and UNICEF, water for Life. WHO and UNICEF, Switzerland.

Yang, T., Chen, X., Xu, C., Zhang, Z., 2009. Spatio-temporal changes of hydrological processes and underlying driving forces in Guizhou region, Southwest China. Stochastic Environmental Research and Risk Assessment 23 (8), 1071–1087.

Yue, S., Wang, C., 2002. Power of the Mann–Whitney test for detecting a shift in median or mean of hydro-meteorological data. Stochastic Environmental Research and Risk Assessment 16 (4), 307–323.

Zhang, C., Wu, L., Luo, Y., Zhang, H., Christie, P., 2008. Identifying sources of soil inorganic pollutants on a regional scale using a multivariate statistical approach: role of pollutant migration and soil physicochemical properties. Environmental Pollution 151 (3), 470–476.

Zhang, Q., Xu, C., Tao, H., Jiang, T., Chen, Y., 2010. Climate changes and their impacts on water resources in the arid regions: a case study of the Tarim River basin, China. Stochastic Environmental Research and Risk Assessment 24 (3), 349–358.

Zhejiang Environmental Protection Bureau, 2006. Scheme for River Function Zoning and Water Environment Zoning of Zhejiang Province Document of Zhejiang Government (In Chinese).

Zhejiang Provincial Bureau of Statistics, 2005. Zhejiang Statistical Yearbook. China Statistics Press, Beijing (In Chinese).

Zhou, F., Huang, G., Guo, H., Zhang, W., Hao, Z., 2007. Spatio-temporal patterns and source apportionment of coastal water pollution in eastern Hong Kong. Water Research 41 (15), 3429–3439.