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Spatial and temporal variations of water quality in Cao-E River of eastern China

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Abstract: Evaluation and analysis of water quality variations were performed with integrated consideration of water quality parameters, hydrological-meteorologic and anthropogenic factors in Cao-E River, Zhejiang Province of China. Cao-E River system has been polluted and the water quality of some reaches are inferior to Grade V according to National Surface Water Quality Standard of China (GB2002). However, mainly polluted indices of each tributary and mainstream are different. Total nitrogen (TN) and total phosphorus (TP) in the water are the main polluted indices for mainstream that varies from 1.52 to 45.85 mg/L and 0.02 to 4.02 mg/L, respectively. TN is the main polluted indices for Sub-watershed I, II, IV and V (0.76 to 18.27 mg/L). BOD_5 (0.36 to 289.5 mg/L), COD_{Mn} (0.47 to 78.86 mg/L), TN (0.74 to 31.09 mg/L) and TP (0 to 3.75 mg/L) are the main polluted indices for Sub-watershed III. There are tow pollution types along the river including nonpoint source pollution and point source pollution types. Remarkably temporal variations with a few spatial variations occur in nonpoint pollution type reaches (including mainstream, Sub-watershed I and II) that mainly drained by arable field and/or dispersive rural dwelling district, and the maximum pollutant concentration appears in flooding seasons. It implied that the runoff increases the pollutant concentration of the water in the nonpoint pollution type reaches. On the other hand, remarkably spatial variations occur in the point pollution type reaches (include Sub-watershed III, IV and V) and the maximum pollutant concentration appears in urban reaches. The runoff always decreases the pollutant concentration of the river water in the seriously polluted reaches that drained by industrial point sewage. But for the point pollution reaches resulted from centralized town domestic sewage pipeline and from frequent shipping and digging sands, rainfall always increased the concentration of pollutant (TN) in the river water too. Pollution controls were respectively suggested for these tow types according to different pollution causes.

Keywords: spatial and temporal variations; water quality; point pollution; nonpoint pollution; Cao-E River

Introduction

Rapid increases of industrialization, urbanization, and population in the last few decades have caused a dramatic increase in the demand for river water, as well as significant deteriorations in water quality throughout the world (Chun *et al.*, 2001; Wong and Wong, 2003). River hydrology is a complex system; water quality in river is always balanced with the pollutant discharge, dilution and decontamination. However, over-discharge pollutant will result in water quality deterioration. Therefore, the ability of self-decontamination of water in river is determined by both the hydrology characteristics of the reach and the pollution characteristics (Perona *et al.*, 1999; Ferrier *et al.*, 2001; Ho *et al.*, 2003). In river monitoring, it was frequent to face the problems that whether a variation of measured parameters should attribute to pollution (spatial, manmade) or to natural (temporal, climatic) changes in the river hydrology and how water quality varied in different human activities with similar natural changes (especially for rainfall). Also, it was necessary to determine which parameters or pollution sources were the most significant to describe such spatial and temporal variations (Ferrier *et al.*, 2001; Alberto *et al.*, 2001; Jonnalagadd and Mhere, 2001). Obviously, the knowledge of the state of water quality in rivers and the changes created by human activities is the first step towards establishing an efficient water management system (Perona *et al.*, 1999).

In recent twenty years, increasing amounts of total sewage discharged from domestic and industrial sources discharged to rivers and/or agricultural lands with only low-level or even no treatment (Moon *et al.*, 2001) so that many rivers showed the water quality deterioration or water pollution in China (Chen and Xian, 2000; Xu, 2002; Zhang *et al.*, 2002; Sun *et al.*, 2002; Wang *et al.*, 2002; Zhang *et al.*, 2003; Cheung *et al.*, 2003). But very little research has been directed to the spatial and temporal variations for river water quality and assoeted discussion on an entire river basin scale. The aim of this paper was to investigate the main pollution parameters and analyze spatial and temporal variations under different human activities with similar natural factors for the typical river system in eastern China, Cao-E River system.

1 Study river basin description

Cao-E River system locates in the most developed regions of China, Shaoxing area, Zhejiang Province. It contained six major tributaries (Fig.1 and Table 1) through Ningbo and Shaoxin plains in Zhejiang Province. Each tributary represents a different pollution type such as industry, agriculture, rural and town domestic pollution, and so on. The

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river system is located at longitude of 120°30'—121° 15' and latitude of 29°08'—30°15', and covers a total area of 6080 km^2. It flows 197 km northwards with gradient of 0.3% into Hangzhou Bay. The upper portion of the Cao-E watershed includes mountainous streams and rivers, while the lower portion of the watershed includes a mixture of tidal and fresh water. Cao-E watershed includes the Xinchang and Shengzhou counties and part of Shangyu, Shaoxing, Dongyang and Panan counties, with 2×10^8 people and arable land of 60000 hm^2 including rice paddy of 48670 hm^2. The annual precipitation is about 1500 mm for total basin recorded at the weather station in Xinchang and Shengzhou counties and Shangyu City (Fig.2), the annual mean temperature is about 16.2℃ and solar radiation is 1970 h with spatial variations in the watershed. The average depth of the rivers is about 7.42 m and the total water resource is about 451×10^6 m^3.

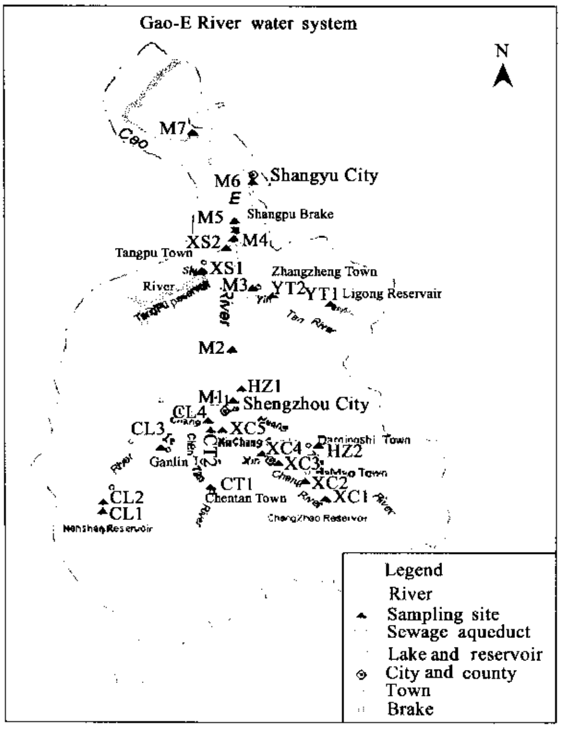

Fig.1 Sampling sites along the Cao-E River system

2 Materials and methods

2.1 Sampling and investigation

Sampling stations located at 25 sites (Fig.1) throughout the Cao-E River watershed. The advantage of this approach was that it provides detailed information from catchment, which can be used to assess the influence of geology, soils, land use, instream processes and point source inputs on water quality (Eyre and Pepperell, 1999). There was a brake between sampling site M4 and M5 for the prevention of tide, which was opened from Feb. to Mar. in 2004. Site M2 was added after Nov. 2003. Water samples were collected from about 30 cm below the water surface near the center of the river and put into polyethylene jars (2.5 L) for the lab measurements from Nov. 2003 to Oct. 2004. Sample collection took place once monthly.

Table 1 Characteristics and sampling sites for entire river system

River name	Length, km	Drainage area, km^2	Sampling code
Mainstream	110.9	6079.8	M1, M2, M3, M4, M5, M6, M7
Chentan River (Sub-watershed Ⅰ)	86.3	851.1	CT1, CT2
Changle River (Sub-watershed Ⅱ)	76.3	877.0	CL1, CL2, CL3, CL4
Xinchang River (Sub-watershed Ⅲ)	70.2	532.5	XC1, XC2, XC3, XC4, XC5, XC6
Huangze River (Sub-watershed Ⅳ)	61.1	584.0	HZ1, HZ2
Xiaoshun River (Sub-watershed Ⅴ)	69.3	547.9	XS1, XS2
Yintanxi River (Sub-watershed Ⅵ)	33.4	97.8	YT1, YT2

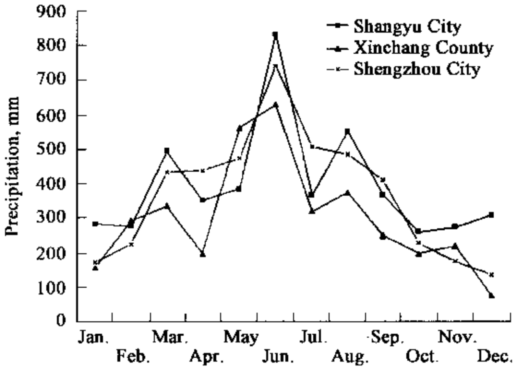

Fig.2 Average precipitation of ten years for three main regions in Cao-E River Basin

The basic information of economy, land-use and population for each village and town in the watershed were investigated one by one during the water quality monitoring. The areas were divided according to catchment to vest them in different sampling sites. The average river flux of the past years (1990—2000) offered by Zhejiang Province Government Irrigation Works Bureau. Six hydrological and meteorologic seasons were defined for the watershed according to the flow quantity, precipitation and temperature. First flood season (FS Ⅰ) exists from May to Jun. (warm and wet) and second flood season (FS Ⅱ) exists in Sep. (hot and wet), first average season (AS Ⅰ) exists from Feb. to Apr. (lukewarm and moist) and second average season (AS Ⅱ) exists in Oct. (warm and moist), first dry season (DS Ⅰ) exists from Nov. to Jan. (cold and dry) and second dry season (DS Ⅱ) exists from Jul. to Aug. (hot and dry).

2.2 Measurements and analytical methods

2.2.1 Measurement methods

Dissolved oxygen (DO), water temperature (T), pH and conductivity electrode (EC) with temperature correction were measured using a hand held multi-parameter instrument named Multi 340i SETs (WTW), and turbidity was measured in site using Turbiquant® 1000IR (WTW) during water sampling. Chemical measurements were accomplished in the lab within 24 h after water sample collection. Chemical and biological measurement of water quality parameters include chemical oxygen demand (COD_{Mn})(GB 11892), 5-d biochemical oxygen demand (BOD_5)(GB 7488-87), total nitrogen (TN) and dissolved nitrogen (DN) (GB 11893-89), total phosphorus (TP) and dissolved phosphorus (DP) (GB 11893-89) were measured according to China Standard Method. The NH_4^+-N content was measured using the Astoria Analyzer System (AAS, Brown Rupee Co., Ltd. of Germany) after filtration through a 0.45-μm filter (Hailing Medicine Co., Ltd. of Zhejiang Province, China). The NO_3^--N content measured by the absorbance of sample at 220 nm (A220) and 275 nm (A275) by visible and ultraviolet spectrophotometer (Shanghai Spectrum Instruments Co., Ltd, China) after filtration through a 0.45-μm filter, and the results were given by the equation: A220-2 × A275 (Wei *et al.*, 2002).

2.2.2 Statistical analyses methods

Multivariate analysis technique, principal component analysis (PCA), aid in reducing the complexity of large-scale data sets are widely used in water quality studies (Ferrier *et al.*, 2001; Smarta *et al.*, 1998; Alberto *et al.*, 2001; Da Silva *et al.*, 2001; Bengraïne and Marhaba, 2003), mainly due to the need of obtaining appreciable data reduction for analysis and decision. The basic features of PCA are data reduction and data grouping with little information loss or not affecting the result. It is particularly valuable when a chemical, physical, or biological interpretation of the data grouped in varifactors is possible. Principal component analysis and correlation analysis were undertaken using DPS (Data Processing System for Practical Statistics; Tang and Feng, 1997) to identify relationships between different catchments (different human activities and hydrological conditions) and water quality variables.

3 Results and discussion

3.1 Summary of water quality

Table 2 summarized the values of the measurements for the river water samples from 25

Table 2 Summary statistics for all measurements on the entire river system

Water quality	Mainstream				Sub-watershed Ⅰ				Sub-watershed Ⅱ				Sub-watershed Ⅲ			
indices	Average	SDV	Min	Max	Average	SDV	Min	Max	Average	SDV	Min	Max	Average	SDV	Min	Max
BOD_5, mg/L	5.49	2.99	0.64	19.65	1.83	1.46	0.2	9.9	2.22	1.19	0.58	5	48.6	65.4	0.4	289.5
COD_{Mn}, mg/L	6.43	3.63	1.099	23.67	2.86	1.64	0.49	8.33	2.53	1.5	0.58	6.04	17.8	19.7	0.5	78.86
NO_3^--N, mg/L	1.45	0.96	0.007	3.758	1.15	0.8	0.15	2.99	1.26	0.76	0.13	2.64	1.02	0.82	0	3.533
NH_4^+-N, mg/L	1.35	1.33	0	6.62	0.17	0.18	0	1.01	0.37	0.59	0	2.3	3.57	5.2	0	19.58
TN, mg/L	8.57	7.86	1.52	45.85	5.11	5.69	0.9	25.7	5.75	5.98	1.53	24.4	10.7	8.68	0.7	31.09
DN, mg/L	5.87	3.57	0.053	17.41	3.61	3.5	0.08	14.7	3.69	3.23	0.26	12.6	8.56	7.75	0.7	30.07
TP, mg/L	0.41	0.79	0.02	4.02	0.07	0.05	0	0.19	0.18	0.21	0.01	1.05	0.4	0.6	0	3.75
DP, mg/L	0.1	0.16	0	0.8	0.04	0.05	0	0.18	0.06	0.08	0	0.38	0.15	0.18	0	0.75
DO, mg/L	5.74	3.54	1.27	17.6	10.4	3.25	2.2	17.9	9.71	1.97	6.42	13.6	5.68	4.08	0	16.34
EC, μS/cm	1264	2741	185	14420	132	48.1	74	230	123	35.5	97	277	555	540	63	2040
pH	7.32	0.52	6.74	9.16	8.03	0.8	6.91	9.69	7.79	0.56	7.16	9.09	6.99	1.11	3.04	10.12
T, ℃	18.6	7.75	7.5	32.1	19.5	7.72	6.8	33.6	19.5	8.09	7.9	34.1	19.4	7.92	5.97	34.1
Turbidity	167	170	2.72	714.1	5.22	5.27	0.91	32	51.4	63.8	4.17	257	23.2	25.4	0.97	164

Water quality indices	Sub-watershed Ⅳ				Sub-watershed Ⅴ				Sub-watershed Ⅵ			
	Average	SDV	Min	Max	Average	SDV	Min	Max	Average	SDV	Min	Max
BOD_5, mg/L	1.63	1.17	0.1	5.14	2.00	0.74	0.95	3.92	2.29	1.47	0.08	5.04
COD_{Mn}, mg/L	2.63	1.76	0.6	9.31	4.01	2.7	1.05	13	3.59	3.69	0.48	15.5
NO_3^--N, mg/L	1.31	0.84	0.1	3.13	1.31	1.01	0.15	3.72	1.17	0.65	0.12	2.19
NH_4^--N, mg/L	0.38	0.62	0	2.82	0.21	0.23	0	0.88	0.15	0.13	0	0.44
TN, mg/L	5.84	5.51	1	22.8	5.03	4.38	0.78	16	4.57	4.42	0.76	18.3
DN, mg/L	3.56	3.33	0.8	13.5	3.61	3.7	0.71	15.6	3.4	3.34	0.66	12.8
TP, mg/L	0.17	0.12	0	0.44	0.35	0.74	0	3.27	0.22	0.32	0	1.45
DP, mg/L	0.06	0.08	0	0.39	0.07	0.14	0	0.65	0.06	0.06	0	0.22
DO, mg/L	8.61	2.2	4.5	13.1	7.8	2.78	1.01	12.2	9.13	2.32	3.26	13.1
EC, μS/L	134	41.2	82	211	149	60.74	84	253	77.3	12.4	62	101
pH	7.28	0.2	6.6	7.6	7.53	0.61	6.9	9.05	7.32	0.66	6.14	8.92
T, ℃	19.1	7.61	7.8	31.4	18.8	7.97	7.5	31.8	17.2	8.4	4.7	31.4
Turbidity	65.1	36.9	10	152	92	137	1.14	579	154	281	3.94	1111

Notes: 1. The dataset of each statistical was from the different month and sampling site; 2. the dataset of each tributaries and mainstream from upstream to downstream was collected together for summary statistics; SDV. standard variation; Min. minimum; Max. maximum stations, which describes with average, standard variation (SDV), minimum (Min) and maximum (Max) in different tributaries and mainstream. As showed in the results, perfect and steady water quality occurred in upstream, large SDV values and variations between Min and Max existed in each tributaries and mainstream, while inferior and unstable water quality occurred in midstream and/or downstream. Yearly mean values for each tributaries and mainstream indicated that water quality belong to inferior Grade V (assessing water quality grade in terms of the most inferior index) according to the National Environmental Quality Standard for Surface Water issued by State Environmental Protection Administration of China in 2002. However, mainly polluted indices or parameters of each tributaries and mainstream were different. TN and TP were the main polluted indices for mainstream that varies from 1.52 to 45.85 mg/L and 0.02 to 4.02 mg/L, respectively. Both maximum of TN (at M7) and TP (at M6) occurred at downstream. According to the differences of main polluted indices, two types could be distinguished with single polluted index and multiple polluted indices. The former included Sub-watershed I, II, IV and V since TN is the main polluted indices, and the latter is showed in Sub-watershed III since BOD_5, COD_{Mn}, TN and TP are the main polluted indices. In the Sub-watershed III, the main pollution source came from some badly industrial output.

3.2 Water quality variations

3.2.1 Nonpoint pollution type

Table 3 and 4 summarized the results of principal components and correlation analyses for mainstream, Sub-watershed I and Sub-watershed II, respectively. Four principal components (PCs) or latent factors were optimal because addition of more other PCs contributed very little to the total explained variance. PCs1 mainly included nitrogen and phosphorus pollution. It was the most important factor, because it described 26.8%, 42.2%, 30.5% of total variations of the system for mainstream, Sub-watershed I and Sub-watershed II, respectively. Correlation analyses showed that nitrogen pollution dominated by population, agriculture, forestry and fishery, while phosphorus dominated mainly by farming land. Different forms of nitrogen and phosphorus have positive correlation with the water flux in the river. It can be inferred that nonpoint source (agriculture and domestic pollution) is the main cause for nitrogen and phosphorus pollution by runoff and leaching because the water flux very significantly related to rainfall for these three rivers (r=0.91, P<0.01). A significant negative correlation between DO and flux implied that dissolved oxygen consumption increased with biologic processes and biochemistry reactions of pollutant that contain abundant nitrogen and phosphorus. Thereby, a conclusion can be drawn that the water quality in mainstream, Sub-watershed I and Sub-watershed II is mainly controlled by nonpoint pollution.

Table 3 Principal component analysis results for mainstream, Sub–watershed I and II

Principal components	Mainstream	Sub-watershed I	Sub-watershed II
PCs1	TP, DP	NO_3^--N, NH_4^+-N, TN, DN, TP, DP	TN, DN, DP
PCs2	pH, EC, DO	BOD_5, COD_{Mn}, EC	NO_3^--N, TP, pH
PCs3	TN, DN	pH	BOD_5, NH_4^+-N,
PCs4	COD_{Mn}, BOD_5, NO_3^--N	Temperature	EC
Cumulative variance, %	77.2	84.8	79.9

Table 4 Correlations $^{(r)}$ for mainstream, sub–watershed I and II

Water quality indices	Farming land, hm^2	Total population (ten thousand)	Agriculture production (ten thousand RMB Yuan)	Forestry production (ten thousand RMB Yuan)	Fishery production (ten thousand RMB Yuan)	Flow,m^3/s
NH_4^+-N, mg/L	n.s.	0.88^{**}	0.85	0.84^{**}	0.81^{**}	0.82^{**}
TN, mg/L	n.s.	n.s.	n.s.	0.78^{**}	n.s.	0.96^{**}
DN, mg/L	n.s.	0.80^{**}	0.80^{**}	0.92^{**}	0.79^{**}	0.90^{**}
TP, mg/L	0.79^{**}	n.s.	n.s.	n.s.	n.s.	0.89^{**}
DP, mg/L	0.75^{**}	n.s.	n.s.	n.s.	n.s.	0.95^{**}
DO, mg/L	n.s.	0.71^{**}	n.s.	-0.75^{**}	n.s.	-0.91^{**}

Notes: ** P<0.01, n=12; n.s. representative "no significant" for the correlation; yearly average of water quality index for each sampling site was used to correlations analysis

3.2.1.1 Mainstream

According to water quality evaluation, the river water was to inferior Grade V, and TN and TP were the most serious polluted indices for mainstream. There were remarkably temporal variations for TN and TP (Fig.3). Tow peaks existed for TN and they were synchronous with river flux variations, i.e., in FS I (average peak value is 10.4 mg/L) and FS II (average peak value is 26.7 mg/L) TN was closely related to the water flux (r =0.96, P<0.01). It implied that nitrogen loss to surface water might directly result from runoff, or infiltration through the root zone (Zebarth *et al.*, 1999). Especially, in flood season, soil loss contributes to the increase of nitrogen content in river water (Chen and Fu, 2000). However, there are few variations in spatial scale except FS II (Fig.4), which also reveals TN is controlled by nonpoint pollution in the mainstream. The largest value of TN in temporal scale appears in FS II that is the rainstorm season after concentrative agriculture measures period (DS II). Some research proved that fertilizers or manure nitrogen is not completely absorbed by the crops and most of the residual or surplus nitrogen is discharged into ground water through sub-surface drainage (Krishna *et al.*, 2004). On the other hand, the largest value in spatial scale appeared between M4 and M5 located in the middle of mainstream and M7 located in the end of mainstream. Dry farming is the main land use type along the reach from M3 to M5, where the runoff from agricultural farms is a major source of nitrogen entering river, lake and coastal water (Woli *et al.*, 2004). A big city (Shangyu) locates between M6 and M7, and the population density exerts another important influence on fixed nitrogen concentrations in river systems (El-Kaddah and Carey, 2003).

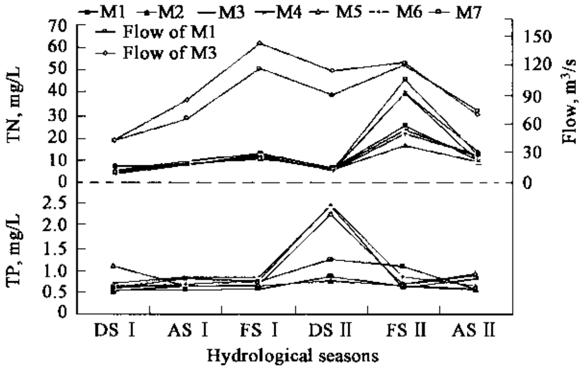

Fig.3 Temporal variations of TN and TP in the mainstream of Cao-E River

DS I. first dry season; DS II . second dry season; FS I. first flood season; FS II . second flood season; AS I. first average season; AS II . second average season

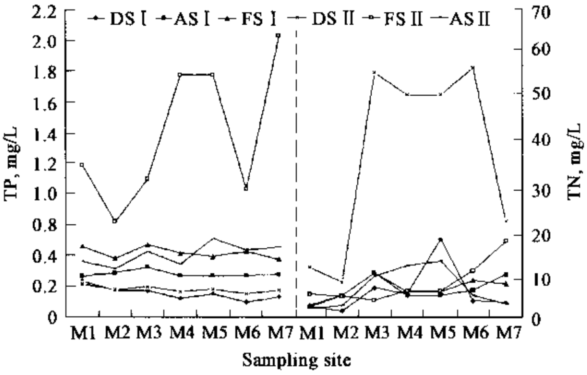

Fig.4 Spatial variations of TN and TP in the mainstream of Cao-E River

There were very high temporal variations for TP concentration in mainstream, however, there is only one peak in temporal scale and it appeared in DS II (average peak value is 1.3 mg/L). Intensive arable farming practices in DS II resulted in the higher phosphorus pollution, especially for pesticides, since the land receives higher phosphorus loads through spreading of slurry, silage effluent and other fertilizers (Robson and Neal, 1997). During the summer dry season, lower water flux in the river and higher domestic west water emission to the river, especially near the city, might be the other important reasons for the peak of TP appearing in the DSII.

3.2.1.2 Sub–watershed I

Four PCs for description of the data come from Sub-watershed I and describe 84.8% of the total variance of the system. PCs1 includes agriculture and domestic pollution (NO_3^--N, NH_4^+-N, TN, DN, TP, DP) that describes 42.2% of the total variance. PCs2 indicates organic pollution (BOD_5, COD_{Mn}) and inorganic pollution (EC) that describes 21.3% of the total variance. PCs3 (pH) and PCs4 (temperature) contain acidity factor and temperature parameter, which only describe 13.1% and 8.2% of the total variance, respectively.

Fig.5 indicated the temporal variations of TN and TP in Sub-watershed I. It showed that there was one peak in the temporal scale for TN (average peak value is 20.6 mg/L) and TP (average peak value is 0.17 mg/L), respectively, and both of them appeared in FS II . However, there are few spatial variations for these main polluted indices in Sub-watershed I, which also reflected the characteristics of nonpoint pollution. The influence of non-point sources on water quality relates to different land management practices such as the type and percentage of vegetation covering (including riparian zones), drainage and fertilizer application rates (Eyre and Pepperell, 1999). Discharges from dispersive livestock facilities in the countryside and the use of detergents (Perona *et al.*, 1999) might be another important sources since livestock rejectamenta mainly used as manure for arable field and daily necessities washing of life directly occurred in the river in local area. Centralized wastewater treatment systems were not available because of the high costs of piping and the wastewaters generally rather dilute (Kazuo and Masahiro, 1998). These patterns and reasons create the characteristics with one peak value in FS II and few spatial variations for TN and TP in Sub-watershed I.

3.2.1.3 Sub-watershed II

Four PCs for the description of the data come from Sub-watershed II, they describe 79.9% of the total variance of the system. PCs1 (TN, DN, DP) and PCs2 (NO_3^--N, TP) include agriculture influence that describe 30.5% and 22.8% of the total variance, respectively; PCs3 and PCs4 include complex influence which is controlled by PCs1 and PCs2.

In terms of the investigation in field, the main land-use along Sub-watershed II is agriculture field (paddy field, nursery and vegetable field). Fig.6 shows

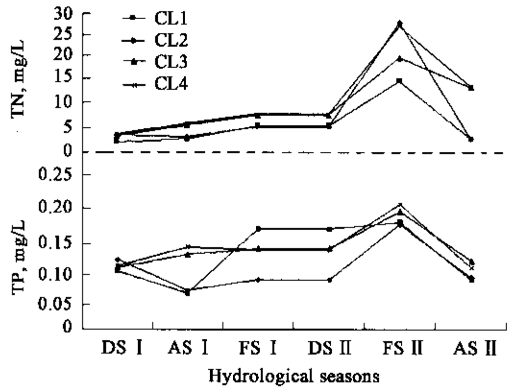

Fig.5 Temporal variations of TN and TP in Sub-watershed I of Cao-E River

that there were two peaks for the temporal variations of TN and TP in Sub-watershed II, and the average peak values were 7.3 mg/L in FSI and 23.0 mg/L in FS II for TN and 0.24 mg/L in FSI and 0.16 mg/L in FS II for TP, respectively. The mechanisms of phosphorus transportation and transformation in land-river system were much different from that of nitrogen. Phosphorus was much easy fixed by soil solid than nitrogen dose, and higher pH (average pH value is 8.1 in CT1 and 7.5 in CT2) value lead to inorganic phosphorus being co-precipitated with calcium as calcite (Hanrahan *et al.*, 2003) in river. Some rock such as volcanic, especially for basalt, contain high concentrations of phosphorus and could be released in particular conditions (Eyre and Pepperell, 1999). Basalt is just the rock type distributed along the Sub-watershed II. While, there were few spatial variations for these main polluted indices in Sub-watershed II, which resulted from the agriculture nonpoint pollution.

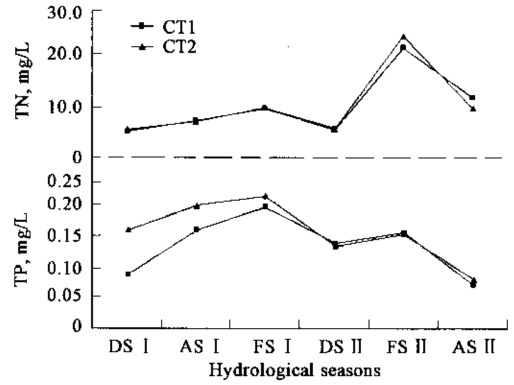

Fig.6 Temporal variations of TN and TP in Sub-watershed II of Cao-E River

3.2.2 Point pollution type

Table 5 shows the results of principal component analysis for the water quality indices in Sub-watershed III, Sub-watershed IV, and Sub-watershed V. PCs1 for all the three tributaries mainly included organic pollution (BOD_5, COD_{Mn}, DO) and it described 26.4%, 46.8% and 33.7% of the total variances for each Sub-watershed system, respectively. PCs2 mainly included nitrogen and phosphorus pollution and it described 18.6%, 15.9% and 17.5% of the total variances of each system, respectively. The correlation analysis results (Table 6) showed that both town population and industry production values positively correlated to water quality parameters. However, the main function of flow in these three tributaries was dilution and decomposition, and dissolved oxygen concentration increased with flow. In fact, sewage pipe system had been upbuilt in the towns along the river but had no any treatment for the domestic sewage by now. Therefore, a conclusion was that the main pollution type for these three tributaries was the point source by town domestic and industry.

Table 5 Principal component analysis results for Sub-watershed Ⅲ, IV and V

Principal components	Sub-watershed III	Sub-watershed IV	Sub-watershed V
PCs1	BOD_5, COD_{Mn}, DO, EC	BOD_5, COD_{Mn}, DO, TN	BOD_5, COD_{Mn}, DO
PCs2	TN, DN, TP	NO_3^--N, NH_4^+-N, TP	NO_3^--N, TN, TP
PCs3	Turbidity, temperature	DN	Temperature
PCs4	NO_3^--N	DP, turbidity	NH_4^+-N, turbidity
Cumulative variance, %	82.4	81.5	83.8

Table 6 Correlations$^{(r)}$ for Sub-watershed Ⅲ, IV and V

Water quality parameters	Town population (ten thousand)	Industry production value(ten thousand RMB Yuan)	Flow, m^3/s
BOD, mg/L	0.99^{**}	0.92^{**}	-0.79^{**}
COD_{Mn}, mg/L	0.99^{**}	0.91^{**}	-0.82^{**}
NH_4^+-N, mg/L	0.99^{**}	0.92^{**}	-0.79^{**}
TN, mg/L	0.99..	0.89^{**}	-0.78^{**}
DN, mg/L	0.98^{**}	0.93^{**}	-0.81^{**}
TP, mg/L	n.s	n.s.	-0.84^{**}
DP, mg/L	0.95^{**}	0.80^{**}	-0.79^{**}
DO, mg/L	-0.96^{**}	-0.93^{**}	0.88^{**}

Notes: ** $P<0.01$, $n=12$; n.s. representative "no significant" for the correlation; yearly average of water quality index for each sampling site was used to correlations analysis

3.2.2.1 Sub-watershed Ⅲ

Fig.7 describes spatial variations of DO, TN and TP in Sub-watershed III, respectively. Dissolved oxygen concentration decreases from 10.6 mg/L at XC1 to 2.2 mg/L at XC4, and then increased to 6.5 mg/L at XC5 (Fig.7). Peak value of TN appeared at XC4 with 19 mg/L, while the peak value of TP appeared at XC3 with 0.85 mg/L. No remarkably temporal variations occurred for DO, TN and TP in the river. The results indicated that there were some huge and very stable pollution sources near XC4. XC1 locates in the Changzhao Reservoir, which is an important drinking water source for Xinchang County and water discharge was strictly controlled. It creates perfect and stable water quality at XC1 (water quality belong to Grade I). XC3 and XC4 locate at the city zone of Xinchang County and XC5 locates at the downstream. Along the Xinchang County from XC3 to XC4, several kilometer distances only, yearly sewage discharge quantity reached to 14.3 $\times 10^3$ t. These patterns create the remarkably spatial variations in Sub-watershed III. Dissolved oxygen is an very important water quality parameters and there was a balance between exchange of oxygen at the water surface reaeration and removal for satisfying microbial and chemical oxygen demands either in the water column or through interaction with the bed sediments (Williams *et al.*, 2000). TN and TP was significantly negative correlated to DO, the correlation efficient was r=-0.78 (P<0.01) and r=-0.75 (P<0.01), respectively. The consumption of the oxygen content in water body was for the oxidation of the nitrogen compounds NH_4^+ and NO_2^- (Lehmann and Rode, 2001). DO concentrations increased from XC4 to XC5 that reflect the self-decontamination capacity of river.

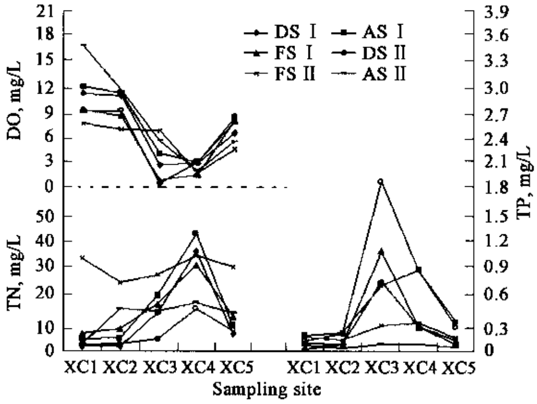

Fig.7 Spatial variations of DO, TN and TP in Sub-watershed III of Cao-E River

3.2.2.2 Sub-watershed IV

There are two sampling sites in Sub-watershed IV, which located in the middle and downstream of the river, respectively. Although point source was the main cause for this tributary and organic pollutant is the main PCs according to PCA and correlation analysis, organic pollution indices, including BOD_5, COD_{Mn} and DO, were all lower than the critical value of Grade III in surface water quality standard. But TN seriously exceeds the critical value of Grade V with yearly average of 7.45 mg/L. There are remarkable variations for TN in both temporal and spatial scale. Digging sands for the construction industry with very high density in spatial and temporal scale was the main source for the water pollution. Therefore, it is difficult to merely distinguish point or nonpoint pollution cause according to main water quality indices through PCA, and field investigation for pollutant source is necessary.

3.2.2.3 Sub-watershed V

In Sub-watershed V, the index of TN was the main problem for the water quality. As shown in Fig.8, the variations of TN concentration were much in evidence in temporal scale in the Sub-watershed. TN concentrations arrived at 14.0 mg/L during FS II but 2.0 mg/L only in DS I. A quantity of industrial point source (with sewage export quantity of 6500 t/a), domestic sewage discharge, and frequent sand shipping along the river were the main three sources of the pollution in Sub-watershed V. A remarkable spatial variations for the TN concentration in the river could be found, too, since XS1 locates at the outlet of a reservoir (Tangpu Reservoir) and XS2 was just after a big town (Tangpu Town). Domestic pollutant transport increased with rainfall and finally discharge through sewage pipeline outlets (but no treatment), which results in strong temporal variations. Tangpu Reservoir is the most important drinking water source for Shangyu City and the water discharge is strictly controlled for keeping a clear water quality. But the water resource in the reservoir was always not enough to supply the city, which resulted in almost no fresh water to import the river by the reservoir, and the relative lack of persistent freshwater inputs suggested that stochastic rain events might be an overriding factor in anthropogenic nutrient loading (White *et al.*, 2004).

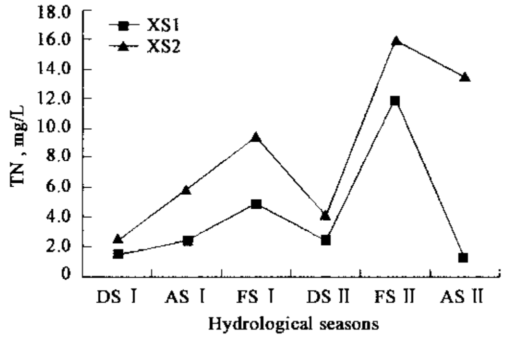

Fig.8 Variations of TN in Sub-watershed V of Cao-E River

3.3 Pollution control suggestions

As shown in Table 7, water quality variations and pollution characters for each tributary and mainstream were quite different. Therefore, pollution control must be distinctively performed for different reaches.

Control of the application quantities and the application methods of the fertilizer and other agricultural chemicals were the most important measures to prevent the fields nonpoint pollution, especially in raining season, because the non-point pollutant entered the water body always by runoff, infiltration and leaching. Human and livestock rejectamenta mainly used as organic manure for local arable field, therefore, construction of a vegetable buffer zone nearby the river is necessary, since 89% of nitogen and 80% of phosphorus can be resorted by buffers (Chen and Fu, 2000).

Source control is chief method for industrial sewage. Construction of sewage treatment plant with subsequent of total amount control of water quality is imperative under the situation (Ma *et al.*, 2002), especially for villages and township enterprises and town domestic sewage. Wetland is also efficient for pollution control since many kinds of pollutant, such as BOD_5, TN, TP, chemical oxygen demand (COD), can be removed with high removal rate (Li and Jiang, 1995; Mithchell *et al.*, 1995), which means that heavy pollution corporations should be transferred to the suburb where distributes quantity of wetlands such as natural pool and billabong in local area, especially for Sub-watershed III.

Table 7 Summary of water quality variation and pollution characters for Cao–E River

River name	Polluted indices	Spatial variations	Temporal variations	Sites of extremums	Seasons of extremums	Pollution sources
Nopoint pollution						
Mainstream	TN	A few except during FS II	Remarkably	M4, M5	FSI, FS II	Agriculture and city domestic pollutants
	TP	A few except during DS II	Remarkably	M3, M4, M5, M6	DS II	
Sub-watershed I	TN	A few	Remarkably	—	FS II	Agriculture,dispersive domestic and livestock pollutants
	TP	A few	Remarkably	—	FS II	
Sub-watershed II	TN	A few	Remarkably	—	FS I, FS II	Agriculture pollutants
	TP	A few	Remarkably	—	FS I, FS II	
Point pollution						
Sub-watershed III	DO(COD_{Mn} and BOD_5)	Remarkably	A few	XC4	—	Pharmacy wastewater
	TN	Remarkably	A few	CX4	—	
	TP	Remarkably	A few	XC4	—	
Sub-watershed IV	TN	Remarkably	Remarkably	HZ2	FS I, FS II	Sands digging
Sub-watershed V	TN	Remarkably	Remarkably	XS2	FS I, FS II	Industrial and domestic wastewater, and shipping

Note: - No remarkable extremums

4 Conclusions

Cao-E River had been polluted, and the water quality of some reaches, included the mainstream and the sub-watershed III, belong to Grade V every month according to National Surface Water Quality Standard of China (GB2002). Tow pollution types, i.e., point and nonpoint source pollution, were assorted for each tributary and mainstream according to the difference of pollution sources and the variations pattern of water quality indices. The pattern with remarkably temporal variations but a few spatial variations for the concentrations of pollutants might be a nonpoint source pollution type, especially if the pollutant concentration was correlated closely to water flow or rainfall. In nonpoint source pollution reaches, rainfall often "thickens" the pollutant concentration of the river water, which means that the pollutant concentration in the river increased with the flow or rainfall increase. Hydrological variations of the river strongly influence temporal variations of river water quality, so it is necessary to analyze water quality variations in terms of different hydrological seasons (based on flows, rainfall and temperature in this study). On the other hand, remarkably spatial variations of water qualities indices implied that might be a point pollution reach. Rainfall would dilute the pollutant concentrations of water in the river. But for the point pollution reaches resulted from centralized town domestic sewage pipeline and/or from frequent shipping and digging sands, rainfall always increased the concentration of pollutant (TN) in the river water.

For pollution control, raining seasons were the most important periods to prevent the nonpoint pollution by decreasing and improving the agricultural chemical applications. Construction of a vegetable buffer zone nearby the river might decrease a mass of nitrogen and phosphorus that would enter the river. The sewage treatment plant with subsequent of total amount control of water quality is imperative for the control of point source pollution in river, especially for the point source pollution control of villages and township enterprises and town domestic sewage.

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