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Original Research

Water Pollution Characteristics and Assessment in Different Functional Zones

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Abstract

The investigation of water pollution from mainstream and dominating tributaries at different Hydrological conditions of the Qiantang River, East China, showed that water quality tends to deteriorate from upstream to downstream and possessed severe pollution levels in the dry season rather than the abundant and medium seasons. Analysis of PCA indicated that TN, NO_3^-, NH_3-N, and TP with maximum values of 18.70, 2.57, 15.50, and 0.80 mg·L^{-1} were the dominant pollution factors, therein NO_3^- accounted for the largest percentage of TN (up to 83.1% in various nitrogen species). Domestic sewage and the discharge of poultry and animal feces were the main point source pollution, and fertilizer that flushed into the river leaching from farms possessed the maximum proportion of non-point source pollution associated with NH_3-N and TP. P mainly came from sewage discharge simultaneously. In addition, the Dayuan River was the tributary with the most severe pollution and owned significantly higher TN and NH_3-N concentrations than that in mainstream and the medium values, reaching up to 3.17 and 8.99 mg·L^{-1}. Low DO concentration should be an important cause for denitrification from NO_3^- to NO_2^- and NH_3-N in the Dayuan River.

Keywords: water pollution, assessment, nutrients, different functional zones, Qiantang River

Introduction

The river serves as an important area of drinking water source, sewage disposal, agricultural irrigation, floodwater storage, and tourism. As the economy developed rapidly, large amounts of domestic sewage and industrial effluent including numerous nutrients, heavy metals, and organic pollutants were discharged into the hydrophytic ecosystems, and the water quality of many rivers has distinctly deteriorated all over the world [1-4]. River water pollution has been a worldwide environmental concern and posed serious environmental problems in surrounding areas and public health by a wide range of physical, chemical and biological processes [5].

The Qiantang River is the largest river in Zhejiang Province, one of the developed provinces of China. With the discharge of wastewater from livestock and poultry production, fishery, tourism, and shipping, etc., in the watershed, water quality of the mainstream and the tributaries was deteriorating [6]. For instance, large-scale algal blooms occured in part of the river flowing through Fuchunjiang Dam and Fuyang City in 2004, which first broke out in the Qiantang River watershed and deserves greater attention. But few detailed studies have been performed to distinguish the contribution of pollution in the Qiantang River. Existing literature mainly focused on the sedimentology and organic pollutants [7-12], so more comprehensive investigations of contamination in mainstream and tributaries will be of great importance in water environment protection of the Qiantang River.

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Materials and Methods

Study Area

The Qiantang River watershed lies in the areas of 28º10-30º48N and 117º37-121º52 E, with a catchment area of 47,100 km^2, while the area in Zhejiang Province covers around 13,901.8 km^2. The drinking water of 85% population in Hangzhou City, Fuyang City, and Xiaoshan District derives from Qiantang River. The mainstream of Qiantang River is around 524 km in length and 320 km in Hangzhou City area [13]. The annual average runoff was about 4.425×10^{11}/m^3. The consumption of water resources in this region currently has a distribution of 12% urban, 51% agricultural, and 37% industrial, and the discharge of industrial effluent, domestic sewage, and rural domestic sewage were approximate 7.04, 7.35, and 1.56×10^8 t in 2010, respectively [14].

Samples Collection

Twelve monitoring sections were set in the mainstream of Qiantang River and the water samples taken from each section were, in order, Q1-Q12. Three other monitoring sections were set in the important tributaries, i.e., Fengshui River, Puyang River and Dayuan River, and classified as Q13, Q14, and Q15. The sampling sites were chosen near the confluence of tributary and mainstream. A specific sampling location was illustrated in Fig. 1. The water samples were collected from 15 sampling sites in December 2011, and January, April, and July 2012, respectively. Q1-4, Q6-9 were located in a drinking water source protection zone, Q5 multi-function area, and Q10-15 Fishery water areas (Table 1) [15]. Dissolved oxygen (DO) was immediately measured with portable hand-held dissolved oxygen meter (HACH sension, USA) in the field, and the water samples were placed in an incubator paved with ice bags for instant analysis.

Table 1. The general situation about sampling sites.

Sampling site	River regime		Water quality goal	The water environment function region
Q 1	Fuchun River	Mainstream	II	DPZ
Q 2	Fuchun River	Mainstream	II	DPZ
Q 3	Fuchun River	Mainstream	II	DPZ
Q 4	Fuchun River	Mainstream	II	MFA
Q 5	Fuchun River	Mainstream	II	DPZ
Q 6	Fuchun River	Mainstream	II	DPZ
Q 7	Qiantang River	Mainstream	II	DPZ
Q 8	Qiantang River	Mainstream	II	DPZ
Q 9	Qiantang River	Mainstream	II	DPZ
Q 10	Qiantang River	Mainstream	III	MFA
Q 11	Qiantang River	Mainstream	III	MFA
Q 12	Qiantang River	Mainstream	III	MFA
Q 13	Fenshui River	tributary	III	FWA
Q 14	Puyang River	tributary	II	MFA
Q 15	Dayuan River	tributary	III	MFA

DPZ – drinking water source protection zone, MFA – multi-function area, FWA – fishery water areas

Physical and Chemical Characteristics Analysis

The water samples were transported to the laboratory immediately for analysis after collection. Water quality variables including permanganate index (COD_{Mn}), five-day biochemical oxygen demand (BOD_5), total phosphorus (TP), total nitrogen (TN), nitrate (NO_3^-), ammonia nitrogen (NH_3-N), volatile phenol (V-ArOH), Cyanide (CN), trace elements (As, Fe, Cu, Zn, Se, Hg, Cr, Cd, Pb, and Mn), sulphate (SO_4^{2-}), chloridion (Cl^-), petroleum, fluoride(F^-), and linear alkylbenzene sulfonates (LAS) were determined at each site. The specific methods used were presented as follows: NH_3-N, spectrophotometric method with salicylic acid; COD_{Mn}, acidic (alkaline) potassium permanganate method; V-ArOH, after distillation by means of 4-AAP spectrophotometric method; BOD_5, dilution and seeding method; petroleum, infrared spectrophotometry; TP, ammonium molybdate spectrophotometric method; TN and NO_3^-, ultraviolet spectrophotometry; the concentration of SO_4^{2-}, Cl^-, F^-, and CN^-, ion chromatography; the concentration of As, Fe, Cu, Zn, Se, Hg, Cr, Cd, Pb, and Mn were obtained by inductively coupled plasma atomic emission spectrometry (ICP-MS 7700x, USA); LAS, methylene blue spectrophotometric method. All the selected parameters were obtained in the laboratory according to the environmental quality standards for surface water of China [16].

Multivariate Analysis Methods

Principal component analysis (PCA) was widely applied to assess the sources and original variables of the contaminants [17-20]. This statistical analysis technique could reduce the dimensionality of the variables and integrate the majority of parameters with lesser factors. The varimax loadings > 0.69 were typically regarded as excellent, correspondingly, < 0.32 very poor, and all principal factors extracted from the variables were retained with eigenvalues < 1.0. The resulting clusters assisted in identifying relatively homogeneous groups of variables. All statistical calculations were performed using the SPSS 13.0 software for Windows (SPSS Inc USA).

Meanwhile, enrichment factor (EF) has been commonly used in the assessment of human contamination [21, 22]. It was calculated as the modified formula [23]:

Table 2. Descriptive statistics of the concentration variations of detectable elements in the water samples from Qiantang River (mg·L^{-1}; As, μg·L^{-1}).

Parameters		COD_{Mn}	BOD_5	NH_3-N	TP	TN	NO_3^-	F^-	AS	LAS	SO_4^{2-}	Cl^-
Dec.	Min.	1.72	0.75	0.12	0.06	2.24	1.47	0.14	0.10	0.04	15.60	5.98
	Max.	15.70	17.70	4.60	0.25	10.70	2.20	0.55	1.20	0.08	49.10	51.70
	Mean	3.04 (3.52)[a]	2.62 (4.23)	0.84 (1.06)	0.12 (0.06)	3.4 (2.04)	1.79 (0.21)	0.30 (0.10)	0.37 (0.27)	0.05 (0.01)	21.73 (10.46)	10.91 (11.65)
Jan.	Min.	1.29	1.09	0.39	0.06	1.53	0.12	0.19	0.30	0.03	14.90	7.55
	Max.	17.30	10.50	15.50	0.54	18.70	2.24	0.90	1.30	0.33	49.90	91.50
	Mean	3.36 (3.90)	3.04 (2.69)	1.80 (3.90)	0.13 (0.14)	3.29 (4.39)	1.27 (0.44)	0.32 (0.19)	0.92 (0.26)	0.08 (0.07)	22.01 (11.00)	18.45 (23.14)
Apr.	Min.	2.30	0.03	0.45	0.06	2.13	1.47	0.24	0.50	0.02	17.50	9.67
	Max.	6.02	24.30	1.86	0.41	7.27	2.57	5.25	1.00	0.08	145.00	81.40
	Mean	3.39 (0.88)	3.62 (6.00)	0.83 (0.45)	0.17 (0.08)	3.03 (1.35)	1.95 (0.38)	0.70 (1.26)	0.75 (0.11)	0.04 (0.01)	39.77 (33.67)	27.51 (18.207)
Jul.	Min.	1.21	0.03	0.35	0.14	2.69	0.04	0.22	0.40	0.03	8.45	14.40
	Max.	7.36	17.00	1.66	0.80	5.61	2.56	0.51	1.10	0.05	49.40	53.10
	Mean	2.15 (1.48)	2.07 (4.16)	0.75 (0.34)	0.22 (0.17)	3.37 (0.77)	1.96 (0.60)	0.34 (0.08)	0.50 (0.20)	0.04 (0.00)	27.24 (10.03)	21.02 (9.74)
2001-04 [b]	Min.	0.84	0.32	0.01	0.01	1.82	1.07	0.04	-	-	-	-
	Max.	11.58	8.03	7.17	0.69	3.40	8.31	2.19	-	-	-	-
	Mean	2.89	1.66	0.77	0.10	2.52	1.90	0.44	-	-	-	-
Reference values [c]		2	3	0.015	0.02	0.2	10	1	0.05	0.2	250	250

[a] Standard deviation

[b] water quality variables between 2001 and 2004, data refer to [12]

[c] Reference values, National Grade II from the environmental guideline of national quality standards for surface waters, China [24].

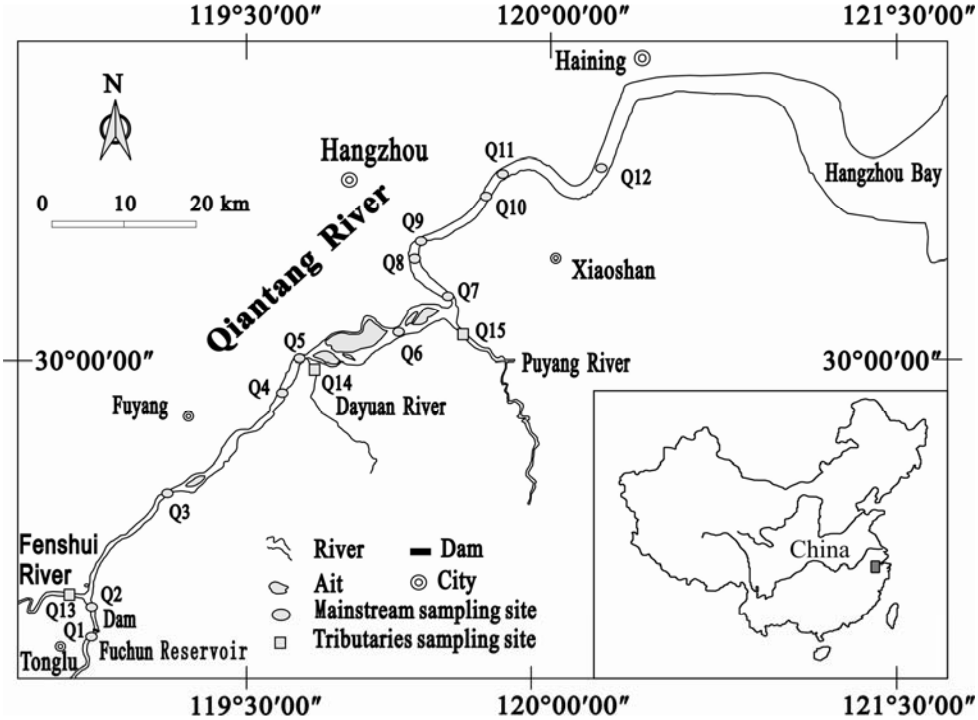

Fig. 1. The location of sampling sites in Qiantang River.

$$EF = \frac{[C_x / C_r]_{sample}}{[C_x / C_r]_{background}}$$

...where C_x refers to the concentration of the examined elements and C_r represents the concentration of the reference element in the samples and background, respectively. In this study, Class II water standard in Surface Water Environment Quality Standard were chosen as the background values [24]. Moreover, conservative element Fe was commonly used as the reference element to compensate for the influence of enrichment characters on contamination concentrations [25-27]. Generally, EF > 1 was taken to reflect higher levels of anthropogenic pollution, and EF < 1 denoted the crustal source for the elements in the samples [20, 23].

Results and Analysis

Pollution Characteristics of Sampling Sites

As seen from the data, the concentrations of the majority of trace elements (Cu, Zn, Se, Hg, Cr, Cd, Pb, and Mn), CN, V-ArOH, and petroleum were beyond the detection limit or possessed extremely low values, so they were not the significant contaminants and beyond the scope of this study. Descriptive statistics of the maximum and minimum values were presented in Table 2. For displayed variables, the concentration showed distinct difference under different hydrological conditions and at different functional areas along the river, but generally disciplinary changes were displayed simultaneously. Minimum and min. mean values presented in July and October, while maximum and max. mean values in January and April. The Qiantang was at dry season in January and April, at abundant season in July, and medium season in October on hydrology. Exceptionally, The higher concentration of TP was detected in July. Maximum values of COD_{Mn} and BOD_5 were 17.30 and 24.30 $mg\cdot L^{-1}$, and max. mean values were 3.39 and 3.62 $mg\cdot L^{-1}$, respectively. TN, NH_3-N, and NO_3^- possessed 3.29, 1.80, and 1.95 $mg\cdot L^{-1}$ in max. mean values, and reached 18.70, 15.50, and 2.57 $mg\cdot L^{-}$ in maximum values. Besides, maximum values and max. mean values of TP reached up to 0.80 and 0.22 $mg\cdot L^{-1}$. In addition, inorganic anion such as F^-, SO_4^{2-}, Cl^- exerted a similar trend, that was the maximum values and max. mean values were detected synchronously in April. There were 5.25, 145.00, 81.40 $mg\cdot L^{-1}$ and 0.70, 39.77, 27.51 $mg\cdot L^{-1}$. The maximum values and max. mean values of As and LAS were 1.30, 0.92 $mg\cdot L^{-1}$ and 0.33, 0.08 $mg\cdot L^{-1}$ and detected in January simultaneously. Contrasting with data surveyed in 2001-04, we found that the concentrations of COD_{Mn}, BOD_5, NH_3-N, TP, TN, NO_3^-, and F^- were higher than in the past, and increased by 17.3, 118.1, 133.8, 120, 30.6, 2.6, and 59.1%, which indicated that the pollution status in the Qiantang River watershed deteriorated to a greater degree, and the higher concentration of contaminants were presented at dry season apart from TP.

Principal component analysis (PCA) were taken to analyze the factor loadings of EF values of TP, Cl^-, SO_4^{2-}, F^-, TN, NO_3^-, COD_{Mn}, LAS, AS, BOD_5, and NH_3-N from each sampling site. The data was normalized and the correlation matrix of original data was obtained, then the eigenvectors were extracted from correlation matrix. The components with eigenvalues > 1.0 and cumulative variances coming to 99.966% were figured out as principal components. Table 3 displayed the factor loadings after varimax rotation. Eigenvalues of 165 eigenvectors were listed simultaneously. As shown in Fig. 2, a 3-D plot of the PCA loadings was illustrated additionally. The results of the PCA analyses showed that three components accounted for about 99.966% of the total variance in the data matrix. Component 1 was dominated by TP, accounting for 98.783% of the total variance. Component 2 dominated by TN and NO_3^-, accounted for 0.752% of the total variance. Component 3 was dominated by NH_3-N, which accounts for 0.430%. Factor loading diversity indicated that TP, TN, NO_3^-, and NH_3-N were the dominating pollution factors, namely, the primary cause bringing about pollution episodes in the Qiantang. Three relatively independent behaviors of nutrients were grouped based on PCA results.

Spatial Distribution of Nutrients

Box-and-whisker plots of the significant discriminant parameters signed out by discriminant analysis (DA) of TP, TN, NO_3^-, and NH_3-N, which were the dominating pollutions in mainstream and tributaries of the Qiantang River, were shown in Fig. 3. The maximum, minimum, and medium values of each site revealed that TP, TN, and NH_3-N concentration of Q11 were higher than others in the mainstream of the Qiantang. The median values of NH_3-N,TN, and TP were 0.94 $mg\cdot L^{-1}$, 3.47 $mg\cdot L^{-1}$, and 0.23 $mg\cdot L^{-1}$, obviously higher than other sampling sites. NO_3^- concentra-

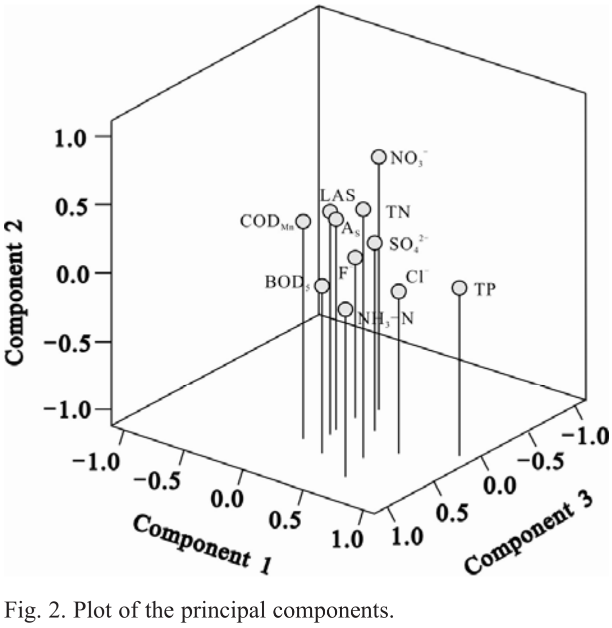

Fig. 2. Plot of the principal components.

Table 3. Component matrix and rotated component matrix after varimax rotation (PC extracted 3 factors).

Parameters	Rotated Component Matrix			Components	Initial eigenvalues		
	1	2	3		Total	% of Variance	Cumulative %
TP	**0. 989**	0.117	0.085	**1**	9185.771	**98.783**	**98.783**
Cl^-	0.651	0.071	0.296	**2**	69.969	**0.752**	**99.535**
SO_4^{2-}	0.292	0.246	0.089	**3**	40.013	**0.430**	**99.966**
F^-	0.104	0.074	0.059	4	1.408	0.015	99.981
TN	0.514	**0.698**	0.498	5	0.980	0.011	99.991
NO_3^-	0.135	**0.744**	-0.151	6	0.732	0.008	99.999
COD_{Mn}	0.019	0.478	0.509	7	0.064	0.001	100.000
LAS	0.104	0.514	0.328	8	0.010	0.000	100.000
AS	0.095	0.421	0.256	9	0.004	0.000	100.000
BOD5	0.240	0.097	0.586	10	0.004	0.000	100.000
NH_3-N	0.599	0.106	**0.794**	11	0.000	0.000	100.000

Kaiser-Meyer-Olkin measure of sampling adequacy of 60 was 0.728; Bartlett's test of sphericity with approx. chi-square came up to 451.358 and significance level of 0.000, which was significant at $p < 0.01$ level demonstrated that the data were suitable for factor analysis. Only the first three eigenvectors have been retained to suffice, reflecting the majority of information of all data.

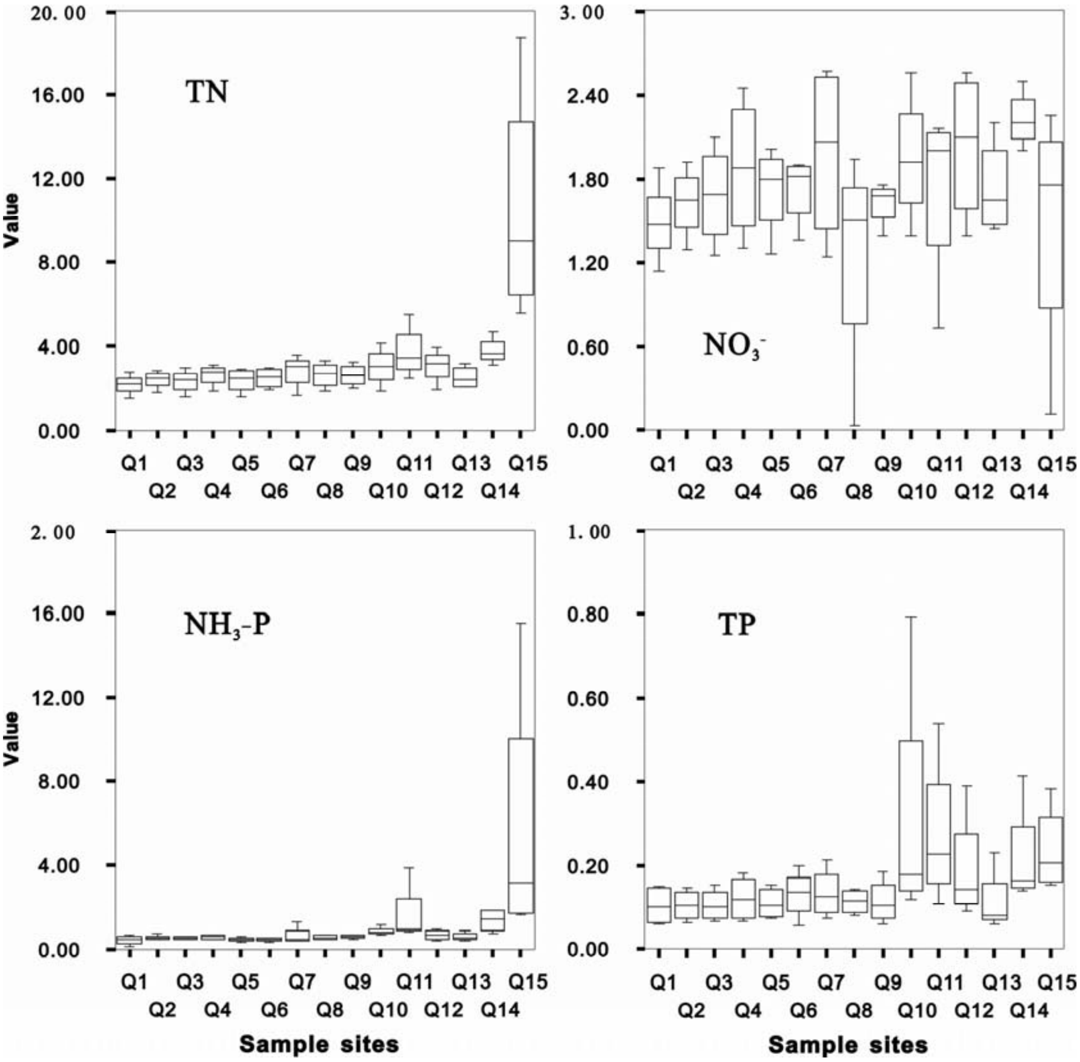

Fig. 3. Box-and-whisker plots of TN, NO_3^-, NH_3-N, and TP at different sampling sites from different functional zones of the Qiantang River.

tion detected from Q11 with 2.01 mg·L^{-1} presented higher median value than others and simultaneously slightly lower than Q12 with 2.10 mg·L^{-1}. In general, fluctuating contaminant concentrations revealed the rising trend gradually from upstream to downstream. In particular, TN, NH_3-N and TP reached relatively high levels in site Q11 then reduced somewhat.

Pollution Characteristics In Tributaries

The maximum value of pollutant content such as COD_{Mn}, BOD_5, NH_3-N, TP, TN, F^-, AS, LAS, SO_4^{2-}, and Cl^- in the Fengshui, Puyang, and Dayuan rivers, the important tributaries of the Qiantang River, were 17.30, 105.00, 15.50, 0.38, 18.70, 0.90, 1.30, 0.33, 49.90, and 91.50 mg·L^{-1}. The data were surveyed in January and distinctly higher than that in other months. In April the maximum value of TP with 2.26 mg·L^{-1} was detected. The minimum values of COD_{Mn}, BOD_5, NH_3-N, TP, TN, F^-, AS, LAS, SO_4^{2-}, Cl^-, and TP taken in July and December were 7.36, 17.00, 1.66, 0.17, 5.61, 0.41, 0.30, 0.03, 29.10, 26.90, and 1.63 mg·L^{-1}, and occupied 42.5, 16.2, 10.7, 44.7, 30.0, 45.6, 23.1, 9.1, 58.3, 29.4, and 72.1% of maximum. It was observed that the tributaries displayed the similarity to mainstream, that was the pollution level at dry season was more severe than that in the abundant and medium seasons. This was the analogy to the Yangtze River, where linear correlation was observed between nitrogen concentration under different hydrology conditions and runoff [28].

Similar to the mainstream, nutrients were the dominated contaminant in the main tributaries. Fig. 3 illustrated that the Puyang and Dayuan rivers had higher nutrient concentrations. The concentrations of TN and NH_3-N detected in sampling site Q13 distinctly exceeded other sampling sites. Medium values of TN and NH_3-N were 3.17 and 8.99 mg·L^{-1}, which were ca. 3.4 and 2.9 order of magnitude higher than Q11, situated in mainstream possessing the maximum values. Furthermore, medium value of NO_3^- concentration was 2.20 mg·L^{-1} and occupied over 5% of that in the mainstream. Finally, TP concentrations in Q14 and Q15 were slightly lower than Q10 and Q11, but much higher than water samples from mainstream. An unobvious variation of pollution levels indicated that the water quality did not deteriorate severely in the Fengshui River.

The proportions of NH_3-N, NO_3^- and other nitrogen species accounting for TN were illustrated in Fig. 4. As shown in Fig. 4, NH_3-N and NO_3^- were the dominating nitrogen species, and the summation of them occupied 55%-~100% of TN. NO_3^- possessed the highest proportions, accounting for TN and varied from 31.1% to 83.1%, and the proportions of NH_3-N ranged from 3% to 53%. A significant correlation existed between NH_3-N and TN (R = 0.941, P < 0.01). Generally speaking, NH_3-N was the most important nitrogen form in Qiantang River.

Discussion

Direct drainage (point sources) and diffuse inputs from the watersheds (nonpoint sources) resulted in the increase of contaminant concentration in the river [29]. The survey performed by Su et al. [12] demonstrated that nonpoint sources and the point sources from tributaries held the maximum proportion of pollution sources in the Qiantang River. Point sources mainly came from domestic sewage, agricultural pollution, and industrial wastewater pollution, and nonpoint sources were controlled by fertilizer leaching from farms and terrigenous sources flushing into the river [13]. The agriculture in the Qiantang River watershed was dominated by poultry and animal feces and farming, and

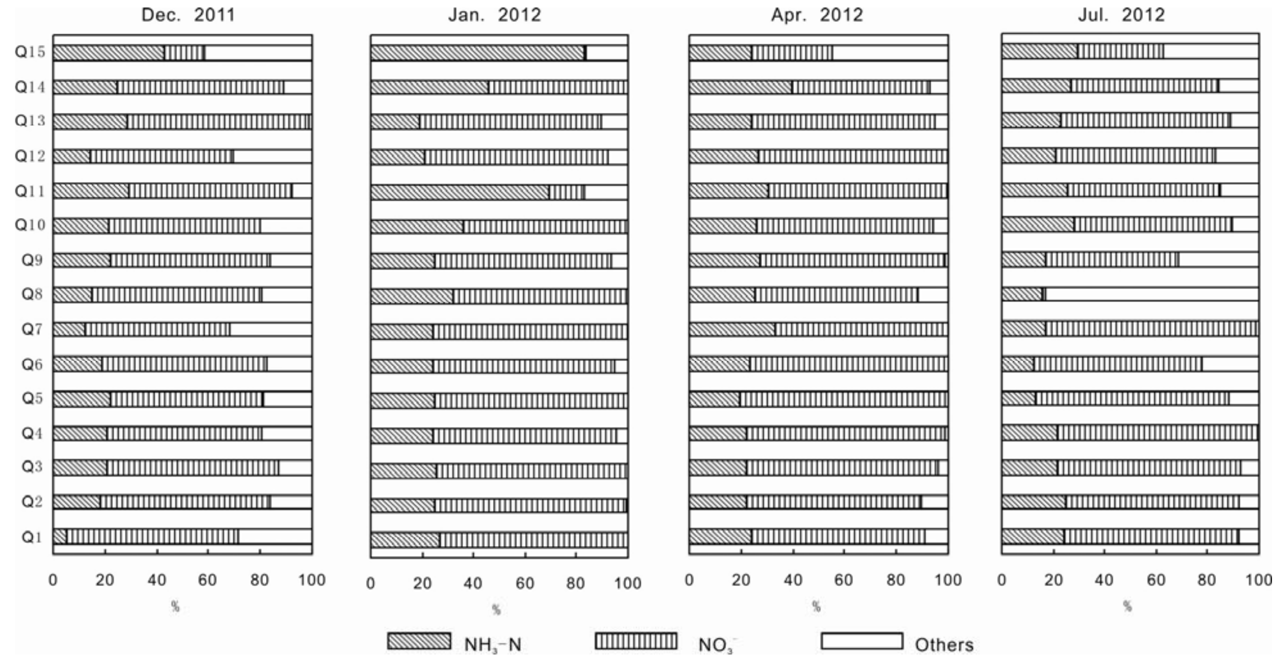

Fig. 4. Proportions of important N species accounting for total N.

Table 4. Composition of pollution loadings of different pollution source categories of Qiantang River in 2001 from Hangzhou City (t) [30].

Pollution source categories		NH_3-N (%[a])	TP (%[a])
Point sources	Industrial pollution	1,402.1 (6.7)	-
	Domestic pollution	4,486.9 (21.4)	1,004.3 (21.9)
	Livestock breeding trade	6,347.3 (30.3)	3,277.0 (71.4)
Non-point sources		8,729.0 (41.6)	-
SUM		20,965.3	4,589.3

[a] Percentage of different contamination sources accounted for the total contamination emission load.

industry structure dominated by paper products, chemical material, and chemical products bringing about chemical wastewater discharge [30]. Contaminant sources of the study region focused on Fuyang City and Xiaoshan District located in the middle and upper reaches of the mainstream of the Qiantang River.

In 2005 NH_3-N emissions reached up to approximately 2.10×10^5 t from Hangzhou City in Qiantang River and derived from runoff of the farmland loss, sanitary wastewater, industrial wastewater, and livestock and fowl wastewater. TP emissions originating from domestic sewage, livestock, and poultry production and fertilization came to 4.59×10^4 t [30]. In addition, after fertilization, soil particles principally adsorbed NH_3-N, so the nitrogen leaching loss was dominated by NO_3^-, which was transported to the river through flooding [31], all of which brought about the rise of NO_3^-, concentration. NH_3-N emissions from industrial sewage were 1,402.1 t·yr^{-1} and accounted for 4% of the summation of domestic wastewater and agricultural effluent, i.e., sanitary wastewater and agricultural effluent were responsible for the excess emissions of nutrients. NH_3-N and TP emissions from domestic wastewater and livestock and fowl wastewater accounted for 85% and 93% of the total emissions from Hangzhou City. Though discharge of nitrogenous industrial wastewater gave rise to the NH_3-N pollution, dometic wastewater and agricultural effluent were responsible for the point source pollution in Qiantang River as a whole. When NH_3-N discharged into the river, with the increase of flow velocity and DO concentration, nitrification was intensified and resulted in transition from NH_3-N to NO_3^- and aggravated the pollution from NO_3^- [32-34]. The pollution loadings and proportion of different pollution source categories of the Qiantang River in 2001 from Hangzhou City were listed in Table 4, and NH_3-N and TP emissions from livestock and fowl wastewater summed up to 6,347.3 and 3,277.0 t·yr^{-1}, while the emissions rooted in domestic sewage were 4,486.9 and 1,004.3 t·yr^{-1}, which accounted for 70.7% and 30.6%, respectively. It could be deduced that livestock and fowl wastewater was the biggest point source pollution of NH_3-N. Indiscriminate discharge of continental input possessed 8,927.0 t·yr^{-1} and accounted for 41.6% of total emissions, so fertilizer flushing into the river leaching from farms has the maximum proportion of non-point source pollution. Finally, TP emissions from domestic sewage, livestock, and poultry production accounted for 21.9% and 71.4% of total emissions. It could be concluded that the TP derived from domestic sewage was the dominated point source pollution of Qiangtang River from the sum of 93.3%.

Table 5. Ratios between the values of various contaminants in the Dayuan River and the mean values in mainstream.

Parameter	NH_3-N	TN	TP	NO_3^-
Dec.	8.7	3.8	2.3	0.9
Jan.	20.1	9.0	3.3	0.1
Apr.	2.5	2.8	1.0	1.2
Jul.	2.5	1.7	0.7	1.0
Mean	8.5	4.3	1.8	0.8

The variety of nutrients in Qiantang River indicated that contamination concentration was controlled by the runoff to a great degree, i.e., plentiful runoff diluted the nutrients obviously in abundant seasons and vice versa. The water flow through Fuchun Dam were 2,530, 368, 1,071, and 2,720 m^3/s at sampling dates on December of 2011, January, April, and July of 2012, respectively. It could be concluded that the runoff at abundant and medium seasons were more sufficient than the dry season, approximately, which could be attributed to more abundant erosion by overland runoff in abundant and medium seasons. Due to the relative regularity of discharge velocity and emission load of industrial point source and domestic sewage within the year, the low flow at dry season led to contamination not being fully diffused by enough water runoff and the concentration was higher than that in the medium and abundant seasons.

Generally speaking, the concentration of NO_3^- was higher than NH_3-N at most of the sample sites. Especially in the Dayuan River, which was contaminated severely, TN and NH_3-N concentration exceeded other rivers, but NO_3^- concentration was relatively low. Table 5 listed the ratios between the values of various contaminants in the most polluted tributary, Dayuan River, and the mean values in mainstream. It could be seen that the Dayuan River had a remarkably higher pollution level than mainstream except NO_3^-. This may be related to the intense denitrification. The DO of Q15 were 0.62, 0, 4.62, and 3.87 mg·L^{-1} in 4 sampling process and the lowest of all the sampling sites. Low DO concentration resulted in the transformation from NO_3^- to NO_2^- and even NH_3-N through denitrification [35, 36], and brought about the proportion of NH_3-N, accounting for TN higher than other sampling sites, while NO_3^- was lower. When the Dayuan River flowed into the mainstream the re-aeration of O_2 in water was intensified and DO concentration increased to over 6 mg·L^{-1}, nitrification activity of NH_3-N reinforced with the widening riverway and increasing flow velocity [37, 38]. In contrast to the relatively high background concentration coming from the upstream, the NO_3^- concentration in mainstream increased unconspicuously owning to nitrification, but the effect cannot be ignored and deserves Further attention for tributaries.

Conclusions

(1) The water quality of the Qiantang River deteriorated in comparison to the former years. Pollution levels in the dry season were more severe, and dilution due to increasing flow resulted in a lower contamination degree in the abundant and medium seasons. In generally, the contaminant concentration exerted a gradually increasing trend from upstream to downstream.

(2) The result of PCA indicated that TN, NO_3^-, NH_3-N, and TP were the dominant pollution factors in mainstream and tributaries of the Qiantang. Domestic sewage and the discharge of poultry and animal feces resulted in the main point source pollution of NH_3-N, while nitrogenous fertilizer flushing into the river leaching from farms possessed the maximum proportion of non-point source pollution, and NO_3^- accounted for the largest percentage of nitrogen species of TN. In addition, TP mainly came from sewage discharge.

(3) Nutrients were also the main contamination in Qiantang tributaries. The Dayuan River was the tributary with the most severe pollution and owned the NO_3^- and NH_3-N concentrations higher than those in mainstream. Low DO concentration was fundamentally responsible for the denitrification from NO_3^- to NO_2^-, and NH_3-N in the Dayuan.

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