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Relationship between catchment characteristics and nitrogen forms in Cao-E River Basin, Eastern China

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Abstract

The distribution of different nitrogen forms and their spatial and temporal variations in different pollution types of tributaries or reaches were investigated. Based on the catchments characteristics the tributaries or reaches can be classified into 4 types, including headwater in mountainous areas (type I), agricultural non-point source (NPS) pollution in rural areas (type II), municipal and industrial pollution in urban areas (type III), and combined pollution in main stream (type IV). Water samples were collected monthly from July 2003 to June 2006 in the Cao-E River Basin in Zhejiang, eastern China. The concentrations of NO_3^--N, NH_4^+-N, and total nitrogen (TN) were measured. The mean concentrations of NO_3^--N were decreased in the sequence type IV > type II> type III > type I, whereas, NH_4^+-N, total organic nitrogen (TON), and TN were in the sequence: type III > type IV > type II> type I. In headwater and rural reaches, $C_{NO_3^--N}$ was much higher than $C_{NH_4^+-N}$. In urban reaches, TON and NH_4^+-N were the main forms, accounting for 54.7% and 32.1% of TN, respectively. In the whole river system, $C_{NH_4^+-N}$ decreased with increasing distance from cities, and $C_{NO_3^--N}$ increased with the increasing area of farmland in the catchments. With increased river flow, $C_{NO_3^--N}$ increased and $C_{NH_4^+-N}$ decreased in all types of reaches, while the variations of C_{TON} and C_{TN} were different. For TN, the concentration may be decreased with the increase of river flow, but the export load always increased.

Key words: catchment characteristics; nitrogen; forms; spatial and temporal variation; Cao-E River Basin

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Introduction

The chemical composition of river water is a function of hydrobiogeochemical process acting within the watershed (Holloway and Dahlgren, 2001). Riverine nitrogen concentrations and forms are closely related to the catchment characteristics, such as anthropogenic activities, climate, geology, land use, soil type and so on (Basnyat *et al*., 1999; Watmough *et al*., 2004; Chen *et al*., 2005; Seo *et al*., 2005; Syversen and Haarstad, 2005; Williard *et al*., 2005; Filoso *et al*., 2006). Different nitrogen forms in river water have different ecological functions, and there are some different threats to aquatic life and human health. Knowledge of the state of the water quality in a river and how it changes is the first step toward establishing an efficient water management system (Perona *et al*., 1999). However, there is little overall information available on the distribution of nitrogen forms in reaches or tributaries with different characteristics in the whole river system. In fact, the variance of nitrogen form often exists in different reaches or tributaries in the same river system, especially in the basin with a high population density and strong anthropogenic activities.

In this work, a complete river system in eastern China was investigated for overall nitrogen pollution characteristics over 3 years. The primary objectives of this study were to analyze the effects of different ecological catchments coverage and anthropogenic activities on the distribution of nitrogen forms, and to evaluate their spatial and temporal variations in different types of reaches.

1 Materials and methods

1.1 Study area and characteristics of catchments

The Cao-E River Basin (29°08′–30°15′N, 120°30′–121°15′E) is located in Zhejiang Province, eastern China and encompasses about 6080 km^2. The climate is typically subtropical monsoon. The average annual precipitation is 1500 mm, and the annual mean air temperature is 16.2°C. The basin includes the Xinchang and Shengzhou, a major part of Shangyu. The population about 2×10^6 and arable

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land about 6×10^8 m^2 including 4.867×10^8 m^2 of rice paddy fields.

The Cao-E River Basin contains a main stream and 6 major tributaries (Fig. 1, Table 1). The basin encompasses tributaries with different types of pollution and reaches with different catchment characteristics. The tributaries Changle (CL), Chengtan (CT), Huangze (HZ), Yintan (YT), and Xiaoshun (XS) are dominated by agricultural non-point source (NPS) pollution. The Xinchang river (XC) is dominated by municipal and industrial pollution, and the main stream (M) suffers from combined pollution (including all types of point-source and NPS pollution). On the basis of catchments characteristics of pollution, the reaches can be grouped into four types, including type I: headwater in mountainous areas with average population density < 80 people/km^2, farmland < 15% of the catchment coverage, and almost no industry. Type II: water quality dominated by agricultural NPS pollution in rural areas with average population density range 300–400 people/km^2, farmland > 85% of the catchment coverage and gross value of agriculture output > 50% of gross domestic product (GDP) in the catchments area. Type III: water quality dominated by municipal and industrial wastewater in urban areas with average population density >1000 people/km^2, farmland < 15% for the catchment coverage, and gross value of agriculture output < 5% of GDP in the catchment area. Type IV: water in the main stream polluted by both point-source and NPS pollution.

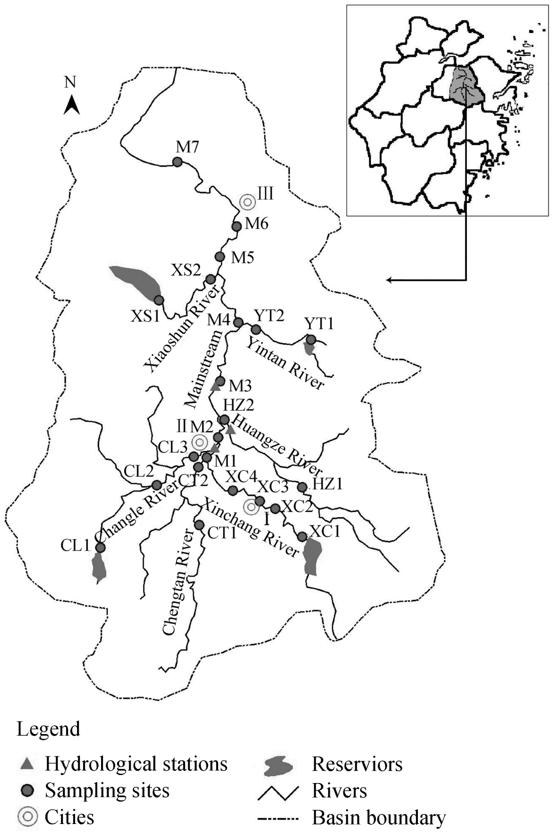

Fig. 1 Location of the Cao-E River Basin and the distribution of sampling site. I, II, and III represent Xinchang, Shengzhou, and Shangyu, respectively.

Table 1 Catchment characteristics and sampling sites in Cao-E River Basin

Tributary	Length (km)	Drainage area (km^2)	Sampling site	Pollution type
Mainstream	110.9	6079.8	M1, M2, M3, M4, M5, M6, M7	IV
Changle River	76.3	877.0	CL1	I
			CL2, CL3	II
Chengtan River	86.3	851.1	CT1, CT2	II
Xinchang Rive	70.2	532.5	XC1	I
			XC2	II
			XC3, XC4	III
Huangze River	61.1	584.0	HZ1, HZ2	II
Yintan River	33.4	97.8	YT1	I
			YT2	II
Xiaoshun River	69.3	547.9	XS1	I
			XS2	II

1.2 Methods

Water samples were collected monthly from July 2003 to June 2006. Samples were collected in a polyethylene barrel at a depth of about 0.3 m in the central stream, put into plastic bottles (2500 mL), transported to the laboratory and stored at 0–4°C until the analysis. The analyses of NO_3^--N, NH_4^+-N, TN were performed according to the standard methods (APHA, 1998). There are three hydrological stations in the basin which are used to collect discharge and precipitation data (Fig. 1). River discharge and precipitation data were obtained from the Hydrologic Bureau of Zhejiang Province, China.

Statistical analyses were performed with SPSS (version 11.5). For the annual mean concentration of each nitrogen form, the weighted mean was calculated based on the distributions of monthly water flow. Lilliefors test was used to determine whether data were normally distributed. Probabilities of differences among multiple means were generated with ANOVA when the assumption of normality was met. The degree to which specific pairs of variables differed was measured using Fisher's LSD multiple means comparison when the assumption of normality was met, and using the Mann-Whitney U-test when data were not normally distributed.

The nitrogen load was calculated on the basis of the mean concentration of nitrogen and the water flow:

$$L = \sum_{i=1}^{12} \frac{C_{ij} Q_{ij} T_i}{10^6} \tag{1}$$

$$T_i = 3600 \times 24 \times D_i \tag{2}$$

where, L (ton) is the annual load of nitrogen; C_{ij} (mg/L) is the mean concentration of nitrogen measured in month i at the sampling site j; Q_{ij} (m^3/s) is the monthly mean water flow measured at the sampling site; T_i (s) is the total time of month i; and D_i is days of the month i.

2 Results and discussion

2.1 Comparison of different nitrogen forms in different pollution types of reaches

As shown in Fig. 2, the mean concentrations of NO_3^--N were in sequence: type IV > type II > type III > type I, and the mean concentrations of NH_4^+-N, total organic nitrogen (TON), TN were in the same sequence: type III > type IV > type II > type I. In headwater (type I) and rural reaches (type II), the highest proportion of nitrogen was NO_3^--N (Table 2). In urban reaches (type III), TON was the dominant form of nitrogen and NH_4^+-N was also quite high. In combined pollution reaches (type IV), the highest proportion of nitrogen was TON followed by NO_3^--N. Comparing the nitrogen composition in different pollution types of reaches, the largest difference parameter is the ratio of $C_{NO_3^- -N}/C_{NH_4^+ -N}$ (Table 2).

Analytically, in natural water TON includes particulate and dissolved inorganic nitrogen (DIN), where DIN includes NH_4^+-N, NO_2^--N, and NO_3^--N. Generally, NO_2^--N is a negligible to DIN in surface water. According to the National Surface Water Quality Standard of China (GB3838-2002), only index NH_4^+-N is used to evaluate nitrogen pollution status in river water. This standard is adapted to urban reaches, but may not be adapted to other pollution type of reaches, especially to reaches dominated by agricultural NPS pollution in rural areas. $C_{NO_3^- -N}$ was much higher than $C_{NH_4^+ -N}$ in rural reaches. DIN (NO_3^--N + NH_4^+-N) is available directly to algae, which is one of the most important drivers of eutrophication (Alexander *et al*., 2000, Howarth *et al*., 2002).

2.2 Spatial variation of different nitrogen forms in Cao-E River Basin

A one-dimensional diagram of continuous variation of water quality (CVWQ) was used to characterize the spatial variations of water quality. In the CVWQ diagram, we take the unidimensional flow distance and the concentration of pollutant as the *X* coordinate and *Y* coordinate, respectively. In the Cao-E River Basin, the flow distance at the first sampling site XC1 of the longest tributary XC was defined as zero, and the flow distance to the other sampling sites in the tributary XC and the mainstream was the relative value. For other tributaries, the relative value was the flow distance between sampling site and influx points.

As shown in Fig. 3, the concentrations of NO_3^--N increased with the junction of type II tributaries. In contrast, the variation of NH_4^+-N was opposite to that of NO_3^--N in the river system, the concentrations of NH_4^+-N in tributaries CL, CT, HZ, YT and XS were lower than that in XC river and in main steam. NH_4^+-N decrease with increased distance from cities, and NO_3^--N increase with the increased area of farmland in the catchments. Moreover, another reason about the spatial variation of NO_3^--N and NH_4^+-N in the whole river system was the nitrification process in the river. The concentrations of TON and TN in the mainstream were higher than that in all tributaries expect the urban reach in the XC river, and there were a little fluctuation along the mainstream (Figs. 3c and 3d). It can be clearly found from the CVWQ

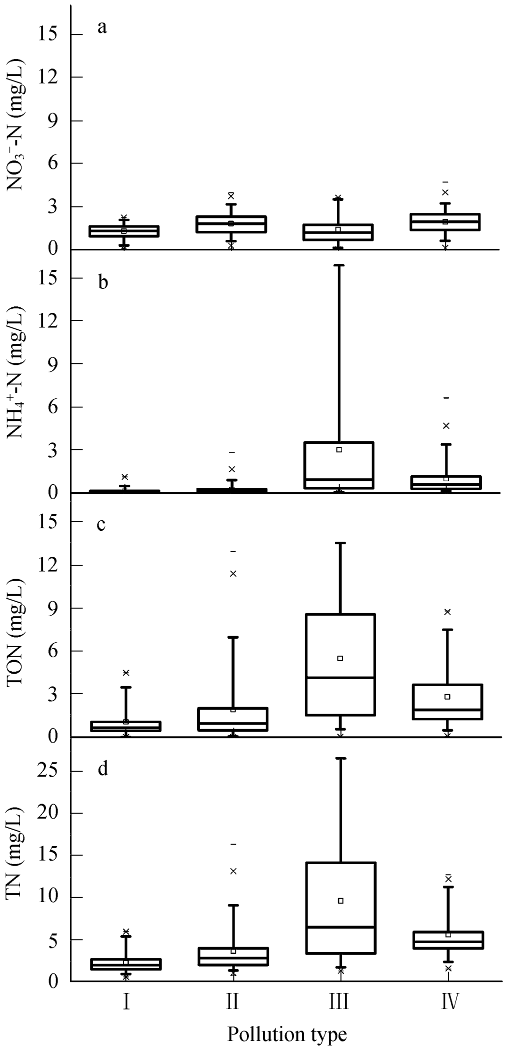

Fig. 2 Concentrations of different nitrogen forms in reaches with different types of pollution. The blank square point and the middle line in the box are the mean and median values of the observations, respectively. The upper and the lower values of the box are the 75% and 25% of the data, respectively. The error bars represent the 95% and 5% of the data and the furcations represent 99% and 1% of the data. The whiskers indicate the maximum and minimum of the observations. TN: total nitrogen; TON: total organic nitrogen.

Table 2 Characteristics of nitrogen composition in different pollution types of reaches (concentration ratio)

Reach type	NO_3^--N/TN	NH_4^+-N /TN	DIN/TN	TON/TN	NO_3^--N/NH_4^+-N	DIN/TON
I	0.536	0.046	0.582	0.418	11.600	1.392
II	0.499	0.059	0.558	0.442	8.467	1.264
III	0.131	0.321	0.453	0.547	0.409	0.827
IV	0.369	0.173	0.541	0.459	2.136	1.179

DIN: dissolved inorganic nitrogen.

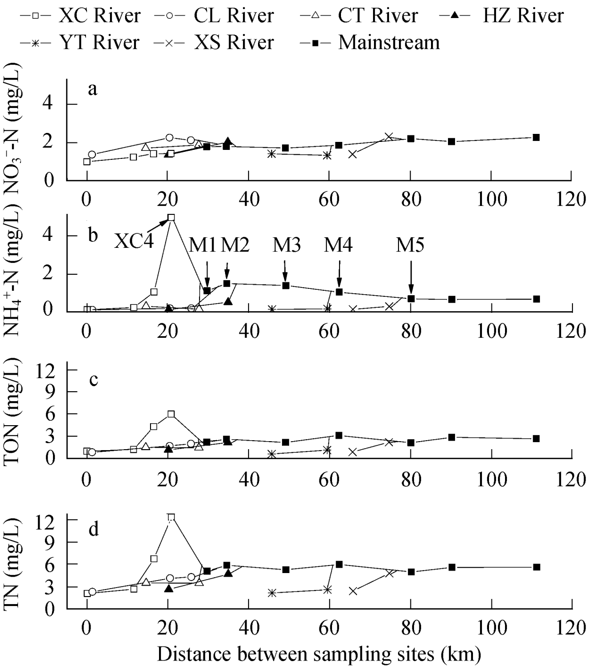

Fig. 3 Diagram of continuous variation for water quality (CVWQ) for different nitrogen forms in the Cao-E River Basin.

diagram that the most seriously nitrogen-polluted reach was in urban reaches located in Xinchang (around XC4), and the nitrogen pollution in XC river seriously affected the water quality in whole downstream.

2.3 Temporal variation of different nitrogen forms in different pollution types of reaches

On the basis of the effects of the subtropical monsoon and typhoon climate system, three hydrological categories could be assigned in the Cao-E River Basin. During the 3 years, 9 months with the lowest, and 9 months with the highest monthly average water flow were defined as the high-flow period, and the low-flow periods, respectively, and the other 18 months was considered as a mean-flow period.

The mean concentrations of the different nitrogen forms in different hydrological periods are shown in Fig. 4. The mean concentrations of NH_4^+-N in each type of reach were in the sequence: low-flow period > mean-flow period > high-flow period. In contrast, the mean concentrations of NO_3^--N were in the sequence: low-flow period < mean-flow period < high-flow period. The sequence of mean concentrations for TON and TN were different in different types of reaches.

Temporal variations of different nitrogen forms in river system were mainly controlled by two factors: the pollutant emission characteristics and the river flow (Ahearn *et al.*, 2004). In high-flow period, the transfer of large amounts of surface water and groundwater into rivers has bidirectional effects on water quality, i.e. pollutant leaching and dilution of polluted water (Gabellone *et al.*, 2005; Demars and Edwards, 2007). However, that phenomenon was not significant in urban reaches. NH_4^+-N was derived mainly from municipal and industrial pollution, and the discharge of them was relatively steady. Therefore, the mean concentrations of NH_4^+-N was high in dry periods with a low flow-rate in the river, and was low in the flooding period due to the dilution (Fig. 4). TON and TN include the form of particle nitrogen (PN). Runoff enhanced the concentration of PN in the initial period, but then dilution became the main factor. The source of PN and the proportion of PN in TN were different in different pollution types of reaches, thus the temporal variation of TON and TN was complex and different in different pollution types of reaches.

Concentration of TN might be decreased with high water flow, but this does not imply that the export load into river was decreased. The monthly mean load of nitrogen in 2004 (with the lower annual rainfall 1036.2 mm) and in 2005 (with higher annul rainfall 1404.8 mm) was estimated at sampling site HZ2, M2, and M3 that had hydrological stations. As shown in Fig. 5, although TN concentration was low in 2005, the total loads of nitrogen were high for the three reaches. In general, the emission of point-source pollution was almost not affected by rainfall and runoff, but the generation and development of NPS pollution

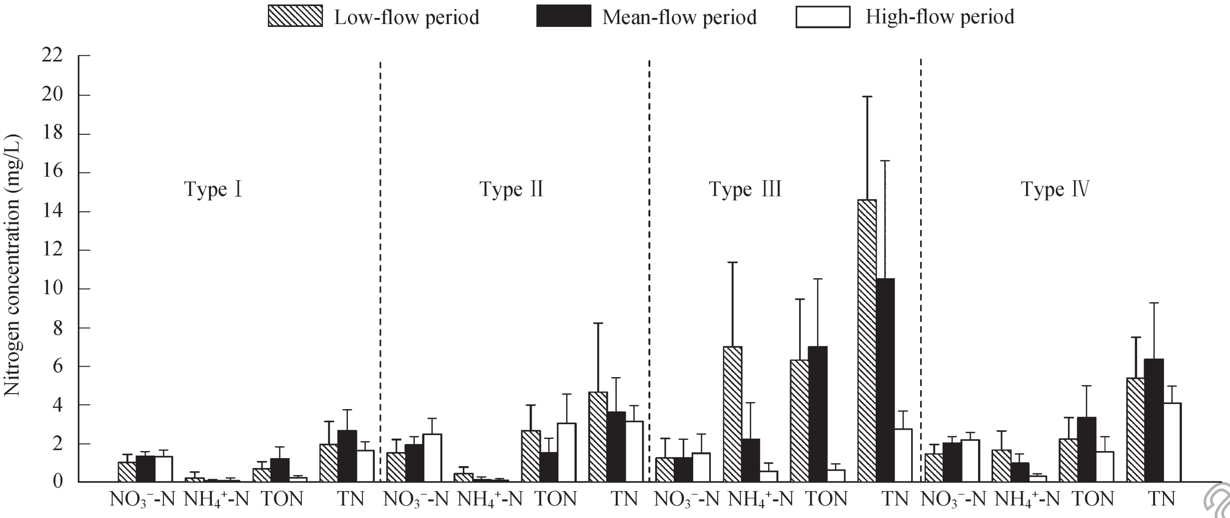

Fig. 4 Comparison of the mean concentrations of different nitrogen forms in low-flow, mean-flow, and high-flow periods in the Cao-E River Basin.

was related closely to rainfall and runoff. With increased rainfall and river flow, the concentration of TN would be decreased due to the dilution, but the export load always increased because of the leaching and erosion.

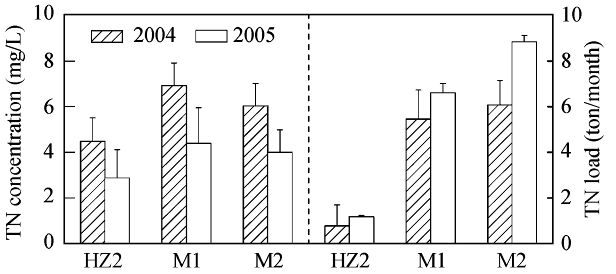

Fig. 5 Comparison of monthly mean concentration and mean load of TN in 2004 and 2005 at sampling sites HZ2, M1, and M2 in the Cao-E River Basin.

3 Conclusions

The nitrogen concentration and its dominant forms in different pollution types of reaches depend on the anthropogenic activities in the catchment. In headwater and rural reaches, high value of $C_{NO_3^- \text{-N}}/C_{NH_4^+ \text{-N}}$ was a significant characteristic of nitrogen pollution within natural forest and agricultural catchments. In urban reaches dominated by municipal and industrial pollution, TON and NH_4^+-N were the main forms of nitrogen. In the main stream, the concentrations of NO_3^--N, NH_4^+-N and TON were high due to the combination of municipal, industrial and agricultural NPS pollution.

In the Cao-E River Basin, the section with the most serious level of nitrogen pollution was in the urban reach of tributary XC, where the monthly mean concentration of TN was > 10 mg/L for the three years of study period, and it seriously affected the water quality in downstream. In the whole river system, NH_4^+-N decreased with increased distance from cities, and NO_3^--N increased with the increased area of farmland in the catchments.

The temporal variations of each nitrogen form were dependent mainly on rainfall and river flow. With increased rainfall and river flow, the concentration of NO_3^--N increased and the concentrations of NH_4^+-N and TN decreased significantly, while their loads always increased.

Acknowledgments

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