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Seasonal variation of nitrogen-concentration in the surface water and its relationship with land use in a catchment of northern China

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Abstract: Surface waters can be contaminated by human activities in two ways: (1) by point sources, such as sewage treatment discharge and storm-water runoff; and (2) by non-point sources, such as runoff from urban and agricultural areas. With point-source pollution effectively controlled, non-point source pollution has become the most important environmental concern in the world. The formation of non-point source pollution is related to both the sources such as soil nutrient, the amount of fertilizer and pesticide applied, the amount of refuse, and the spatial complex combination of land uses within a heterogeneous landscape. Land-use change, dominated by human activities, has a significant impact on water resources and quality. In this study, fifteen surface water monitoring points in the Yuqiao Reservoir Basin, Zunhua, Hebei Province, northern China, were chosen to study the seasonal variation of nitrogen concentration in the surface water. Water samples were collected in low-flow period(June), high-flow period(July) and mean-flow period(October) from 1999 to 2000. The results indicated that the seasonal variation of nitrogen concentration in the surface water among the fifteen monitoring points in the rainfall-rich year is more complex than that in the rainfall-deficit year. It was found that the land use, the characteristics of the surface river system, rainfall, and human activities play an important role in the seasonal variation of N-concentration in surface water.

Keywords: non-point source pollution; nitrogen concentration; seasonal variation; land use; Yuqiao Reservoir Basin, China

Introduction

Surface waters can be contaminated by human activities in two ways: (1) by point sources, such as sewage treatment discharge and storm-water runoff; and (2) by non-point sources, such as runoff from urban and agricultural areas. Non-point source pollution is especially difficult to detect since they generally encompass large areas in drainage basin and involve complex biotic and abiotic interaction(Bao, 1996). With point-source pollution effectively controlled, non-point source pollution has become the most important environmental concern in the world(Alm, 1990; Line, 1998; Gardi, 2001; Sharpley, 1994; Bao, 1996). In the developing countries such as China, the rapid population growth leads to the increasingly application of fertilizer and pesticide for grain provision, that have resulted in soil nutrient enrichment and eutrophication in the surface water(Lu, 1998; He, 1998; Wang, 1999; Yang, 1999). One of the driving factors of eutrophication is nutrient enrichment from the agricultural land in the catchment. When the plants, animals and microbial biota are unable to utilize all the available N, the ecosystem may be considered N-saturated, that might cause eutrophication. Stream nitrogen levels have being increased in China since 1980 as a consequence of demographic, industrial and agricultural development(Yang, 1999; Bao, 1996). Modern agricultural practice and the marked increase in fertilizer-N usage, have been strongly linked with increased nitrate concentration in runoff in recent years. Stream nitrogen concentrations generally exhibit a complex pattern and numerical tools have to be used to generalize scare experimental results while taking into account the high variability of the watershed features(Lek, 1999; Bhaduri, 2000).

Non-point-source pollution, in contrast to point-source pollution, arises from sources that are normally associated with agricultural, silvicultural, and human activities in a watershed(Osborne, 1988; Alm, 1990; Line, 1998). Agricultural activities have been identified as the major sources of NPS pollutants (sediments, animal wastes, plant nutrients, crop residues, inorganic salts and minerals, pesticides) (Udawatta, 2002; Johnson, 1997; Myers, 1995; Yang, 2003) and are known to have major impacts on water quality. Land-use change, dominated by human activities, has a significant impact on water resources and quality. This includes impacts on non-point source(NPS) pollution, which is the leading cause of degraded water quality in the world(Osborne, 1988). Actually, runoff from different types of land use may be enriched with different kinds of contaminants(Tong, 2002) and enter the waterbody contributing to water pollution. It is well understood in general terms that land-use change, and rapid urbanization in particular, has significant impacts on hydrology, both in terms of water quality and quantity over a range of temporal and spatial scales(Bhaduri, 2000). The complex effects of land use change, climate change, and their potential interaction on hydrochemical response ensures that understanding and predicting nitrogen responses is difficult (Ferrier, 1995). Some model simulation results indicated that the land use, or different landscapes plays a very significant role in non-point source pollution(Peterjohn, 1984; Hood, 2003; Li, 2001). Compared with agricultural areas, the woodland act actually in landscape as a sink or an active transformation zone and the residential/urban/built-up areas have been identified as strong contributors of nitrate, and as the proportion of forests increases (or nonforested area decreases), nitrate levels downstream will decrease(Basnyat, 1999).

The formation of non-point source pollution, is related to not only the sources such as soil nutrient, the amount of fertilizer and pesticide applied, the amount of refuse, but also depends on their spatial sites and the spatial complex combination of land uses within a heterogeneous landscape(Basnyat, 1999; Nikolaidis, 1998; Chen, 2002). It was hypothesized that variations in nutrient levels in different basins were due to the variation in the LULC combinations with the other contributing factors both in space and time scale. The complex of land uses inside the basins should help explain the differences in stream water quality and their temp-spatial variation (Basnyat, 1999). Although nitrate level increase in the surface water due to land use/cover change have been well recognized in the world (Johnson, 1997; Nikolaidis, 1998; Bhaduri, 2000; Honisch, 2002; Ren, 2003; Li, 2000), there is limited information regarding the effect of different land-use/land-cover (LULC) mixed, as well with the complex landscape factors in stream pollutant concentrations, in particular in the developing counties. It is important to estimate the long-term impacts of land-use change on water quantity and quality that are dominantly controlled by the cumulative effects of smaller storm events rather than by rare high-magnitude storm events.

Non-point source pollution is doing more and more harm to agriculture industry, water resource, watershed hydrographic process and habitat of hydrobiology. Due to the fact that some correlation exits between population loading and land use, there is always potential for improving water quality with proper land-use management practices if the role of different land-use combinations within a contributing areas are known. Changing land use and land management practices are therefore regarded as one of the main factors in altering the hydrological system,

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Foundation item: The National Natural Science Foundation of China(No. 49971072; 49831020); * Corresponding author surface water supply yields, as well as the quality of receiving water (Changnon, 1996). Although the influence of the spatial pattern of land uses at the watershed level and their relationship to water quality has drawn the attention of numerous researchers (Osbotne, 1988; Ferrier, 1995; Johnes, 1997; Bhaduri, 2000; Honisch, 2002; Tong, 2002; Ren, 2003), a clear understanding of this relationship still remains elusive.

In this study, the objective are: (1) to identify the temporal and spatial variation of nitrogen concentration in surface water in a traditional Chinese agricultural area; (2) to correlate the temp-spatial variation of nitrate level with the complex spatial combination of environmental factors, such as the rainfall, land use, surface river system, human activities and landforms.

1 Study area

Yuqiao Reservoir Basin is located in the upper part of the Jiyun River (39°56'-40°23'N and 117°26'-118°12'E) and covers parts of Hebei Province and Tianjin Metropolitan area, the third largest city in China, covering about 2052 km^2 (Fig.1). This catchment is characterized by a temperate territorial semi-humid climate, the annual average temperature is about 10.4—11.5℃, and annual mean precipitation is 749 mm which occurs mostly as rainstorm from July to August. The hilly regions of 500 m asl in this catchment account for 24.5% of the total area. Yuqiao Reservoir is an important regulation pool for extracting water from the Luanhe River for Tianjin's industrial, agricultural, and daily use.

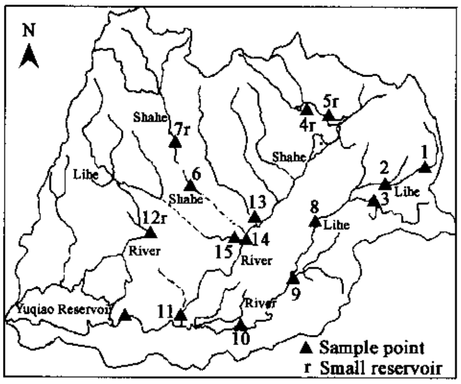

Fig.1 Location of Yuqiao Reservoir Basin in China and sample points

The rivers in Yuqiao Reservoir Basin belong to Zhouhe River, a branch of Jiyun River which originates from Yanshan Mountain and enters Bohai Sea. Three main branches, originated from northern and northeastern mountainous areas, are Lihe River, Shahe River and Linhe River. About 33 reservoirs had been constructed since 1957, and the surface river system was changed. Most of them are distributed in northeastern, northern and northwestern hilly areas, and few are located in the central and southern part. Lihe River, as one of large rivers, is used as the trunk channel to transport water from Luanhe River to Yuqiao Reservoir. Shahe River and Linhe River are seasonal rivers by discontinuous water supply. General characteristics of these three rivers are described in Table 1.

Table 1 Characteristics of main drainages in Yuqiao Reservoir Basin, China

Drainage	Length, km	Coverage, km^2	Mean runoff, $\times 10^8$ m^3	Runoff variability coefficient, Cv	Average slope, degree
Shahe River	70	887	2.45	0.64	13.8
Lihe River	76	560	5.98*	0.55	6.9
Linhe River	47	254	0.44	0.64	22.2

Note: * Including the volume of water transported from Luanhe River

Soils in this area are brown forest soil, infant brown forest soil and fluvoaquic soil, which are distributed regularly from the northern mountainous areas to the southern plains. The brown forest soil is mostly distributed in the low and moderately-high hills in the northern part, and further divided into four sub-units as mountain brown forest soil, infant brown forest soil, sod brown forest soil and skeletic brown soil. The fluvoaquic soil, as azonal soil, is mainly distributed in the lower hills and flat plain close to the Yuqiao Reservoir in the southwestern part. As the predominant soil, the cinnamon soil is widely distributed in the low hill and rolling hilly area, and flat plain. It comprises luvic cinnamon soil, infant cinnamon soil, calctic cinnamon soil and cultivated meadow cinnamon soil. Since this soil has a thick layer, rich organic matter and well-developed porosity, it was widely used as agricultural purpose.

The study area was used as an agricultural area about one thousands years ago, and was used as royal cemetery by Qing Dynasty three hundreds years ago. As a traditional agricultural area, the woodland and grassland account for 54.22% of the total area, while the agricultural land is about 31.81%. Most woodland and grassland distributed in the northern hilly area and the farmland is in the lower flat plain at the lower reach of the rivers. Crops planted in this area are maize, winter wheat, rice, peanut and tobacco as annual farming system in the northern hilly area, tri-farming system within two years in the central part, and biannual farming system in the southern part.

Since Yuqiao Reservoir Basin is close to Beijing and Tianjin Metroplitan areas, human disturbance is strong and agriculture is developed. In 1998, the total population is about 703400 and the population density is about 343 persons/km^2 that is above the average level in China (115 persons/km^2). Most of the people lives in the lower flat plain and few of them are living in the hilly area. Grain and fruit production play a predominant role and take up more than 80% of the total GDP.

2 Data sources and methodology

2.1 Data source

Monitoring data used in this study include meteorological data and water quality data. The former one was collected form the local meteorological station. Water quality data was obtained by sampling and analysis from 1999 to 2000. The thematic data available are remote sensing TM images (1995, 1996), topo-map of 1 : 250000 and 1 : 100000.

2.2 Water sampling and analysis

Based on landscape features and catchment characteristics, Yuqiao Reservoir Basin was divided into 28 sub-units. Among them, fifteen watersheds are found with permanent surface runoff or reservoir/ponds at the outlet. These 15 watersheds with available surface water are chosen as the monitoring waterbody. Water samples were collected at the outlet in the dry season (June), the rainy season (August), and the mean-flow season (October) from 1999 to 2000 by using 1000 ml poly-plastic containers and kept airproof for immediate analysis at the local environmental monitoring station. Analytical determinations included pH, chemical oxygen demand, biological oxygen demand, ammonium (NH_4), nitrate (NO_3), suspended solid particles and phosphate (PO_4). The pH was determined using a pH meter with a glass electrode method; COD_{Mn} was determined by titration with acidic potassium permanganate; BOD_5 was determined by titration, after treatment with a culture box using the dilution and inoculation method; ammonium-N was determined using Nessler's reagent colorimetry; nitric-N was determined by phenol disulfonic acid photometry; and phosphates were determined by ammonium molybdate spectrophotometer. The last three contaminants were all determined by Spectrophotometer-721. The SSP was determined by turbidimeter with photometry. In this study, the nitrogen concentration (including ammonium-N and nitric-N) was chosen to study the effect of land use on the water quality

2.3 Land use interpretation and mapping

A land use interpretation and mapping was conducted based on a landsat TM image (1995 and 1996), and then a land use map was prepared based on the topo-map of 1:250000 (Fig.2). Then, land use attributes in Yuqiao Reservoir Basin were derived by using GIS (Table 2). Fourteen land use types identified are ascribed into six groups: woodland, grassland, orchard, farmland, urban/residential land and others. Concerning the coverage of each monitoring site, the area of land use was calculated based on the corresponding coverage of the upper reach of the monitoring point. However, if a reservoir (small ponds excluded) was situated in the upper reach of the monitoring point, the area covered by the reservoir will be excluded when calculated the land use area since the surface runoff from the uppermost reach of the river will be collected by the reservoir and their land use would not contribute to the water quality.

Table 2 The characteristics of land use and related environmental factors in the Yuqiao Reservoir Basin, China

Subwatershed	Area, hm^2	Land use type, %						Applying amount per unit, kg/hm^2		Population density, person/km^2	Topography	Characters of hydrographic net
		WD	GD	OD	CD	UD	Others	Fertilizer	Pesticide			
1	2432.39	90.53	3.93	/	4.17	~	1.37	39.33	0.18	216	Highland	Water-extraction channel
2	7768.72	60.55	22.83	/	12.53	3.62	0.47	250.19	1.39	457	Highland	Water-extraction channel
3	4956.39	59.17	22.85		14.38	3.44	0.16	235.50	1.98	416	Highland	Seasonal rivers
4	4928.02	71.48	11.22	11.10	5.4	0.10	0.80	39.99	0.11	207	Low mountain	Seasonal rivers, reservoir(s)
5	5184.07	75.19	2.43	12.48	3.6	0.21	6.09	35.83	0.09	210	Hill, basin	Seasonal rivers, reservoir(s)
6	2575.96	/	39.81	16.74	35.781	4.24	3.39	836.70	16.58	407	Low mountain	Seasonal rivers, reservoir(s)
7	17117	50.67	40.03	3.85	5.24	/	0.24	284.59	0.36	437	Low mountain	Seasonal rivers, reservoir(s)
8	23041	45.75	21.65	0.34	25.77	6.12	0.37	1023.17	6.37	508	Hill, plain	Water-extraction channel
9	34323	38.73	16.91	0.23	34.83	8.99	0.32	1133.17	4.38	561	Hill, plain	Water-extraction channel
10	44270	36.10	13.65	3.75	37.17	9.08	0.25	1002.5	4.52	486	Hill, plain	Water-extraction channel
11	51990	13.88	16.31	15.71	43.74	9.85	0.54	1254.81	2.56	486	Plain	With perennial running water and obvious seasonality
12	8001	71.75	5.58	1.73	20.40	0.44	/	280.03	0.45	299	Hill, plain	Seasonal rivers, reservoir
13	5837	12.09	47.79	20.99	17.99	1.12	/	1542.77	27.94	507	Mountainous, basin	Seasonal rivers
14	51429	12.39	18.24	16.95	42.17	9.70	0.60	865.83	17.23	550	Plain	With perennial running water and obvious seasonality
15	17864	4.97	24.50	6.27	55.60	7.42	1.23	1309.33	14.10	422	Mountainous, basin	Perennial running water, supplied by underground water

Notes: WD-woodland; GD-grassland; OD-orchard; CD-cropland; UD-urban area/residential area

Table 3 Annual distribution of rainfall in Yuqiao Reservoir Basin, China, mm

Month	1999		2000		Average (1980—2000)	
	Precipitation	Accumulation	Precipitation	Accumulation	Precipitation	Accumulation
January	0.0		15.8		15.6	15.6
February	0.0	0.0	0.0	15.8	13.2	28.7
March	11.7	11.7	6.9	22.7	13.6	42.3
April	50.3	62.0	19.2	41.9	9.9	52.3
May	13.5	75.5	84.8	126.7	6.8	59.1
June	71.3	146.8	44.9	171.6	7.5	66.6
July	109.1	255.9	73.9	245.5	147.1	213.6
August	14.6	270.5	278.0	523.5	322.4	536.0
September	60.6	331.1	60.6	584.1	124.4	660.4
October	0.8	331.9	47.6	631.7	37.4	697.8
November	27.0	358.9	2.0	633.7	28.0	725.8
December	0.3	359.2	2.80	636.5	22.2	748.0

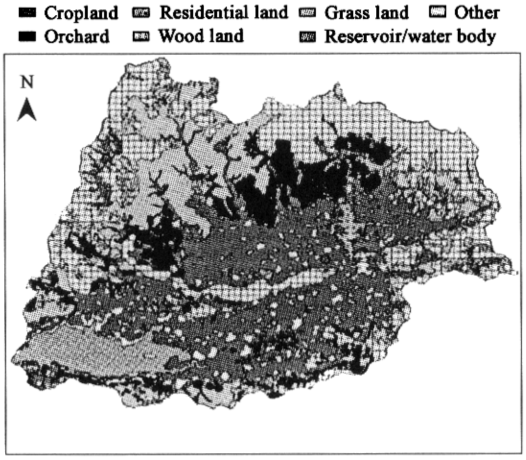

Fig.2 Current land use in the Yuqiao Reservoir Basin, China

3 Results

3.1 The characteristics of rainfall from 1999 to 2000 in the study area

Table 3 shows the general distribution of rainfall in the study area. The mean annual rainfall is about 748 mm, while it is only 359.2 mm in 1999 and 636.5 mm in 2000. The rainfall of 1999 is about 52% less than the average year, and the rainfall during rainy season (July to September) is much lower than usual. In 2000, apart from the rainfall is a little lower in July and September than that in the same period of average year, it is almost similar to the average year. The year 1999 may be called rainfall-deficit year and the year 2000 be called rainfall-rich year compared with 1999.

3.2 Seasonal change of N-concentration in surface water of rainfall-deficit year

Table 4 indicates the seasonal variation of ammonia nitrogen and nitrate nitrogen concentration in the surface water. It was found that the ammonium nitrogen had a high value in the low-flow period, then is the high-flow period and mean-flow period. The spatial variation of ammonia nitrogen in the surface water is high in the low-flow period, and then in the high-flow period and mean-flow period. In constrast, the nitrate nitrogen has a higher value in the mean-flow period, and then is the high-flow period and the low-flow period. The standard deviation of the nitrate nitrogen in both years is changed from high to low as the same order, mean-flow period > high-flow period > low-flow period. And furthermore, it was found that the concentration of nitrate nitrogen in the low-flow period is much lower than the ammonia nitrogen. This result implied that in the low-flow period, the ammonium nitrogen could be the major source of the surface water pollution, and in the high-flow period and mean-flow period, the nitrate nitrogen may become the major contributor of degrading surface water quality.

3.3 Seasonal change of N-concentration in surface water in rainfall-rich year

Since active surface runoff and underground runoff in the rainfall-rich year, the seasonal change of N-concentration in the surface water is complex. Generally, the concentration of nitrogen whether in the ammonia or in the nitrate specification, is much higher than that in the rainfall-deficit year (Table 4). However, the seasonal change of the ammonia and nitrate nitrogen has the same trend to that in the rainfall-deficit year. For the ammonium nitrogen, the concentration in the surface water is low-flow period > high-flow period > mean-flow period, and for the nitrate nitrogen, the high-flow period > mean water period > low water period. As such, the standard deviation of the concentration of ammonium nitrogen has a high value in the low-flow period compared with the other two water-flow periods, and no much difference was observed among the concentration of nitrate nitrogen.

Table 4 The characteristics of nitrogen concentration in the surface water of different monitoring points of Yuqiao Reservoir Basin, China

Monitoring points	Ammonia nitrogen, mg/L							
	1999				2000			
	Low-flow period	High-flow period	Mean-flow period	Average	Low-flow period	High-flow period	Mean-flow period	Average
1	0.27	0.032	0.05	0.117	0.082	0.03	0.02	0.044
2	0.28	0.06	0.05	0.13	1.551	0.03	0.02	0.534
3	0.09	0.08	0.03	0.067	0.055	0.09	0.02	0.055
8	0.44	0.06	0.08	0.193	3.76	1.6	0.13	1.83
9	0.76	0.39	0.27	0.473	8.559	1.37	0.07	3.333
10	0.89	0.73	0.22	0.613	0.069	0.64	0.07	0.26
4	0.16	0.1	0.08	0.113	0.256	0.32	0.03	0.202
5	0.24	0.11	0.06	0.137	1.069	0.03	0.28	0.46
6	0.05	0.02	0.11	0.06	0.025	0.03	0.02	0.025
7	0.13	0.04	0.03	0.067	0.256	0.12	0.06	0.145
11	0.26	0.06	0.06	0.127	0.069	0.73	0.08	0.293
12	0.34	0.1	0.1	0.18	0.402	0.7	0.24	0.447
13	0.18	0.83	0.1	0.37	2.592	0.83	1.03	1.484
14	2.04	0.32	1.32	1.227	3.346	0.23	1.4	1.659
15	0.14	1.01	0.02	0.39	0.149	0.4	1.4	0.65
Average	0.418	0.263	0.172	0.284	1.483	0.477	0.325	0.761
Sdv	0.507	0.329	0.325	0.310	2.333	0.499	0.505	0.928
	Nitrate nitrogen, mg/L							
1	0.086	1.61	0.896	0.864	1.17	1.31	1.49	1.323
2	0.042	1.7	1.11	0.951	0.6	2.32	1.997	1.639
3	0.093	0.91	2.187	1.063	3.48	1.48	2.85	2.603
8	0.028	1.47	1.338	0.945	0.49	5	3.02	2.837
9	0.039	1.65	1.479	1.056	0.65	1.84	1.046	1.179
10	0.052	2.03	1.126	1.069	0.75	1.218	0.632	0.867
4	0.014	0.038	0.292	0.115	0.051	2.57	3.26	1.96
5	0.028	0.19	0.369	0.196	0.283	0.39	0.377	0.35
6	0.052	2.14	2.567	1.586	3	0.11	4.481	2.53
7	0.017	1.56	1.196	0.924	0.49	0.93	2.362	1.261
11	0.052	1.09	1.306	0.816	0.99	0.665	0.681	0.779
12	0.028	0.98	0.76	0.589	0.28	6.098	1.802	2.727
13	0.075	0.11	1.106	0.43	3.24	0.052	0.047	1.113
14	0.033	1.28	4.191	1.835	0.39	2.133	0.242	0.922
15	0.079	0.047	0.634	0.253	1.03	2.036	0.413	1.16
Average	0.048	1.120	1.370	0.846	1.126	1.877	1.647	1.55
Sdv	0.025	0.724	0.986	0.481	1.138	1.696	1.327	0.793

3.4 The correlation between the environmental factors and the nitrogen concentration

Table 5 displays the results on partial coefficients between the environmental factors and the nitrogen concentration by stepwise regression. It was found that the ammonia nitrogen has a good relationship with the environmental factors other than the nitrate nitrogen.

In the rainfall-deficit year, the concentration of ammonia nitrogen in the low-flow period has a significant correlation with the residential land, however, the correlation with the other factors is poor. It is found that the fertilizer has a good relationship with the concentration of ammonia nitrogen in the high-flow period, and there is no relationship between the environmental factors and the ammonium nitrogen in the mean-flow period. Regarding the nitrate concentration, it was found that the population density has a significant effect in the mean-flow period in the rainfall-deficit year.

In the rainfall-rich year, the concentration of ammonia nitrogen has a significant correlation with the population density in the low-flow period, the application of fertilizer in the high-flow period, and the application of pesticide in the mean-flow period. However, it was found that the cropland has a good relationship with the concentration of nitrate nitrogen in the low-flow period, and no relationship between the environmental factors and the concentration of nitrate nitrogen in the other seasons.

Table 5 The partial coefficient between the environmental factors and nitrogen concentration, mg/L

			WD	GD	OD	CD	UD	Others	Fertilizer	Pesticide	Population density
1999	NH_4	Low-flow period	0.215b	-0.248b	0.123b	-0.273b	0.577a	-0.104b	-0.292b	0.115b	0.043b
		High-flow period	0.133b	-0.096b	-0.075b	0.018b	-0.190b	-0.066b	0.67a	0.237b	-0.306b
		Mean-flow period	/	/	/	/	/	/	/	/	/
	NO_3	Low-flow period	/	/	/	/	/	/	/	/	/
		High-flow period	/	/	/	/	/	/	/	/	/
		Mean-flow period	-0.181b	-0.016b	0.289b	0.086b	0.134b	0.199b	-0.341b	0.231b	0.544a
2000	NH_4	Low-flow period	0.387b	-0.340b	-0.186b	-0.217b	-0.024b	-0.235b	-0.056b	-0.093b	0.533a
		High-flow period	0.744b	-0.381b	-0.516b	-0.260b	0.015b	-0.465b	0.602a	-0.518b	0.087b
		Mean-flow period	0.018b	-0.468b	-0.017b	0.265b	0.150b	0.237b	-0.028b	0.718a	-0.86
	NO_3	Low-flow period	0.015b	0.600a	0.072b	-0.043b	-0.095b	-0.026b	-0.024b	0.217b	-0.188b
		High-flow period	/	/	/	/	/	/	/	/	/
		Mean-flow period	/	/	/	/	/	/	/	/	/

Notes: WD-woodland; GD-grassland; OD-orchard; CD-cropland; UD-urban area/residential area; the "a" behind the number means the coefficient is at significant level but the letter "b"

4 Discussion

4.1 The effects of rainfall on the nitrogen concentration

As one of important factors affecting the non-point source pollution, different types of rainfall may result in different runoff processes that will bring the pollutants into the surface water. From this study (Fig.3 and Table 4), it was found the temp-spatial pattern of N-concentration is quite different between the rainfall-deficit year and the rainfall-rich year. The seasonal change of N-concentration in the rainfall-deficit year are small compared with the rainfall-rich year, and the spatial variation (standard deviation) of the N-concentration in the rainfall-deficit year is smaller than that in the rainfall-rich year. The most seasonal variation in surface water quality are driven by climatic and biotic factors and are therefore largely governed by the processes that are taking place in the terrestrial part of the watershed such as natural or human induced vegetation cover changes. This is largely due to that the surface runoff is limited during the rainfall-deficit year while it is rich during the rainfall-rich year. With rich surface runoff occurred, a lot of randomly-distributed pollutants on the ground, for example, the soil particles with rich nutrient, mining waste, daily garbage in the residential area, etc., may be brought into the surface water which give rise to a high variation of N-concentration. However, in the rainfall-deficit year, the pollutants entered the water body is limited due to low surface runoff. This implied that in the high-variation surface-run-off areas, much more sample points are required to understand the non-point source pollution dynamics other than in the rainfall-deficit or low-variation surface run-off areas.

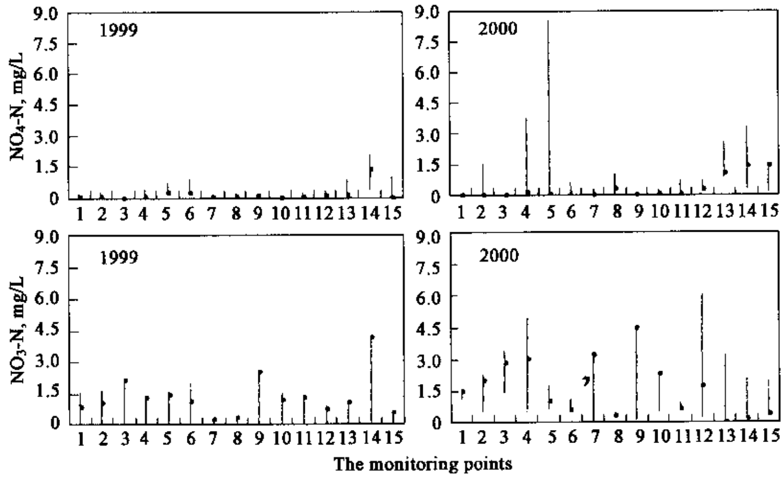

Fig.3 The distribution of nitrogen concentration in the surface water of 15 monitoring sites

The average value of ammonia nitrogen concentration (Fig.3, Table 4) of all the monitoring sites in the rainfall-deficit year is lower than that in the rainfall-rich year, and so does the standard deviation. However there is no much difference for the average value of the nitrate nitrogen concentration, as well as the standard deviation. This may reveal that the temp-spatial variation of the non-point source pollution during the rainfall-rich year is more complex, and much more complicated sources existed in rainfall-rich year compared with that in the rainfall-deficit year. That needs us to pay much attention when studying the non-point source pollution in humid area and in the complex landscape area.

4.2 The correlation between the seasonal change of nitrogen concentration and the environmental factors

Stepwise regression analysis (Table 4) showed that in most cases, the concentration of the ammonia nitrogen in the surface water can be explained by the environmental factors other than the nitrate nitrogen, particularly in the rainfall-rich year. The concentration of ammonia nitrogen, was significantly related to residential area in the low-flow period in the rainfall-deficit year and the population density in the low-flow period in the rainfall-rich year. This implies that the surface water quality in the low-flow period is probably affected by the point source pollution related to the human activities, since little surface run-off was happened. However, the most significant factor contributing to the ammonia nitrogen during the high-flow period was the application of fertilizer. This is because that a large volume of surface run-off in the high-flow period may bring a lot of pollutants to the water body which is strongly affected by the fertilizer application both in the rainfall-deficit and rainfall-rich year. This means that much more non-point source pollution has contributed to the surface water quality.

The contributing factors to the concentration of nitrate nitrogen are quite different from the ammonia nitrogen. The concentration of nitrate nitrogen in the surface water has a significant relationship with the population density in the mean-flow period in the rainfall-deficit year and with the cropland proportion in the low-flow period in the rainfall-rich year. However, in the other water-flow periods, the correlation between the environmental factors and the concentration of nitrate nitrogen was not close. Even though the contribution of agricultural activities to the non-point source was known, the complex combination of the environmental factors both in the time and space make it hard to identify the major contributing factor of the surface water quality in different water-flow period.

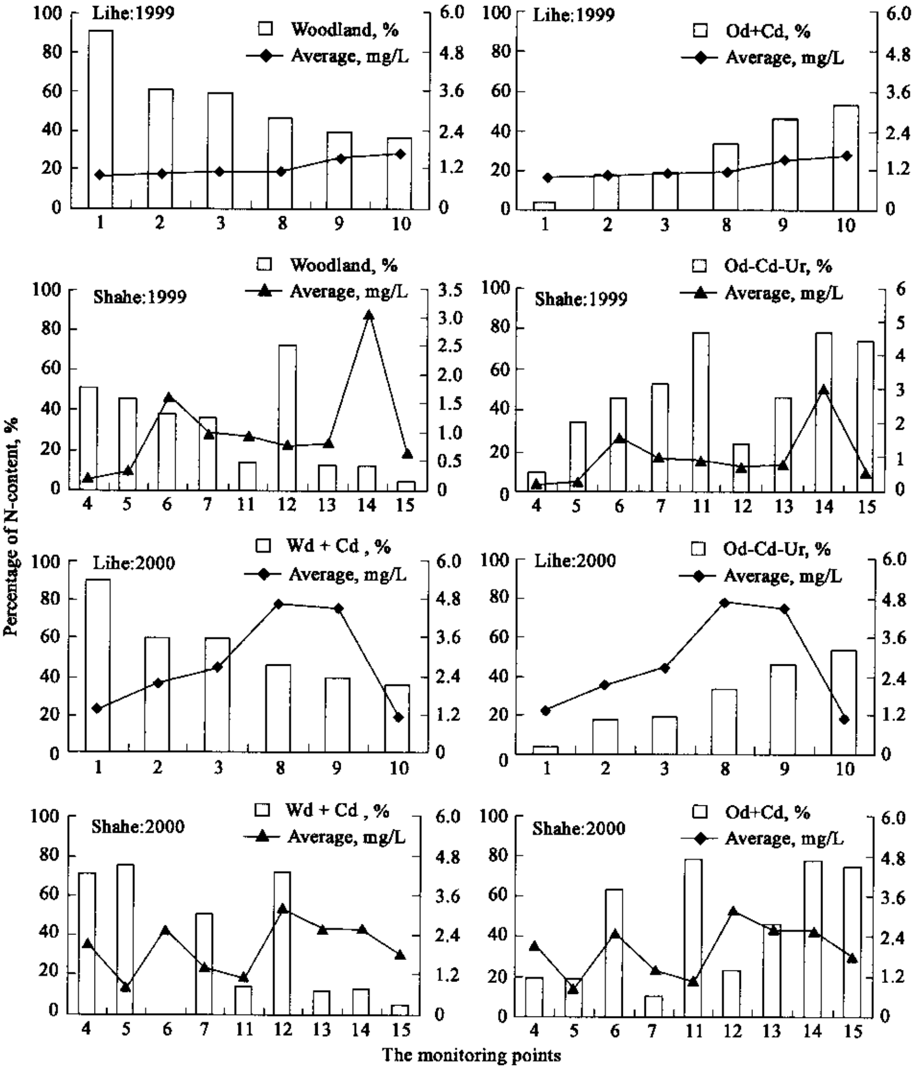

Fig.4 The relationship between the land use and nitrogen concentration in the surface water of Lihe River and Shahe River

Notes: The value of N-concentration is the average of all the three water flow periods in the years; Od-Cd-Ur means the area of orchard, cropland and residential land in total

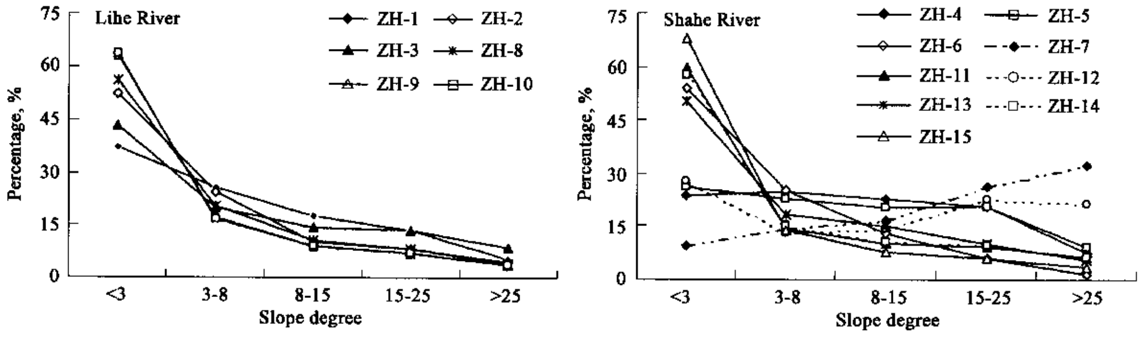

Fig.5 The distribution of slope degree in each watershed

4.3 The effects of land use on seasonal variation of N-concentration in surface water

Nitrate leaching increases as land use changes from moorland through forest, and grassland to arable agriculture. It also varies with season, disturbance and site characteristics (Ferrier, 1995). Fig.4 and Fig.5 indicate that the N-concentration (combination of ammonia and nitrate nitrogen) has a closely negative relationship with the proportion of woodland/grassland in the Lihe River drainage but not in the Shahe River drainage. Sollins *et al*. (Sollins, 1980) indicated that the forest density and forest types affect nitrogen fixation and uptake that will induce less nitrogen loss from the woodland area, and the grassland in most case acts more like a transformation zone on the nutrients loss (Basnyat, 1999). Many studies (Osborne, 1993) indicated that on an annual basis, forested buffers were able to reduce more concentrations of nitrate more than grassland buffers(Pearce, 1997; Hutchins, 1999; Sabater, 2003). Thus in this study, we focus on analyzing the relationships between the N-concentration and the woodland other than the proportion of grassland.

At the same time, a positive relationship between the N-concentration and cropland-orchards-residential land is found in Lihe River other than in Shahe River drainage. This may be affected by the catchment characteristics. After agricultural land, the three landscape factors that appeared important in determining water quality were forested land use, the standard deviation of slope, and the silt-clay deposit. Orchard has also made a positive contribution to the stream nutrient levels(Basnyat, 1999), and sometimes may have more than the farmland. In the study area, the fertilizers applied in the orchard, particularly in the chestnut land, are much higher(1—1.5 times) than that in the cropland for a good harvest. In fact, since the orchard normally distributed in the sloping area, the nutrient loss within the orchard land might be higher than that in the cropland. As same in the urban land, water pollution in urban and urbanizing areas occurs from both point and non-point sources(Bhaduri, 2000). The residential land was proved to have the greatest effect on water quality(Sliva, 2001). Therefore, the orchard and residential land have been assigned a weight respectively by 1.25 and 1.50 compared with cropland when analyzing the relationships between the N-concentration and the total proportion of cropland, orchard and residential land.

The poor relationship between the N-concentration and the land use in the Shahe River drainage is due to that the nitrogen concentration in the surface water is affected by point source pollution and the complex landscape apart from the land uses.

4.4 The effects of catchment characteristics on N-concentration dynamic in surface water

Actually, the catchment characteristics such as topography, configuration and hydrological conditions may affect the surface water quality(Sliva, 2001). In this study, the sample points in the Lihe River showed a good relationship between land use and N-concentration than that in the Shahe River drainage. First, the Lihe River, as a conduit to transport water from Luanhe River to Tianjin, runoff is relatively stable compared with that in the Shahe River, as may induce a low variation on N-concentration. Second, as Lihe River is located in the southern study area where residential area is limited. The N-concentration in the surface water is dominantly influenced by the agricultural activities. However, in the Shahe River drainage, apart from the land use, sometimes the N-concentration might be affected by point source pollution due to human activities in the residential area. Third, the areas passed by Lihe River are a relatively homogeneous landscape compared with that in the Shahe River drainage where slope degree is varied greatly and surface runoff is changed seasonally(Fig.5). All these will result in a large variation of N-concentration in the surface water. Fouth, catchment shape plays an important role on the seasonal variation of N-concentration in the surface water(Chen, 2002; Lek, 1999). It was known that the dendric river system would induce higher-variation on run-off other than the long-shaped river system as Lihe River.

4.5 The effects of land use pattern on N-concentration dynamic in surface water

In fact, apart form the land use type, the spatial pattern of land use have some impacts on the non-point source pollution. Several researchers have addressed the issue of whether land use near streams and rivers is a better predictor of water quality than land use over the entire catchment (Osborne, 1988; Hunsaker, 1995; Johnson, 1997). Basnyat *et al*. (Basnyat, 1999) believed that the contributing zone, defined as the area surrounding the stream that as a result of land use practices and other human activities, may contribute much nutrients and other NPS pollutants to surface water. These areas are closest to the stream and any disturbance in these areas will have profound impacts on stream water quality.

That N-concentration was better explained by interactions with the land use in the Lihe River drainage rather than in the Shahe River drainage, may be related to landscape features and the spatial distribution of land uses within different watersheds. The landscape characteristics of different watersheds in Lihe River drainage are almost similar but not in the Shahe River drainage. Lihe River is situated in the low hills and highland, however, the sample points 4, 5, 7, and 12 are all located in the low-high mountainous area while sample points 6, 11, 13, 14 and 15 are located in the flat plain surrounded by low hills. Concerning points 4, 5, 7 and 12, although there are woodland or grassland, it may not play many roles on pollutant detention since they are mostly located in the remote mountainous area and close the river channel are often the orchard and cropland. This may cause a poor relationship between the land use and N-concentration.

5 Conclusions

From this study, it was found that the seasonal variation of nitrogen concentration was different between rainfall-rich year and rainfall-deficit year. This implied that we have to take much care when studying the non-point source pollution in the rainfall-rich year or high-variation rainfall places. Since non-point source pollution is affected by many factors, and no clear formation mechanism is found, there are some difficulties in studying and controlling non-point source pollution, it may be better to take more attention on the pollutants source control.

The landscape pattern and catchment characteristics have some effects on the non-point source pollution. We found that the water quality in the homogeneous landscape area has a good relationship between the land use and N-concentration while a heterogeneous landscape will give a diverse reaction on N-concentration. It was suggested the landscape characteristics have to be considered when studying the non-point source pollution or make a modeling. Also, the variation of N-concentration within a watershed is closely related to the catchment characteristics (Chen, 2002; Lek, 1999).

The spatial distributions of different land use surely have some impacts on the water quality. However, how to define the land use pattern within a watersheds and correlated the spatial pattern with the water quality is still a turf work to do. Much more attention has to be paid on the effects of land use and its spatial pattern on the water quality.

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