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The characteristics of ammonia nitrogen in the Xiang River in Changsha, China

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Abstract. Changsha is a highly industrialized city in Hunan Province, China, where the water quality is of great importance to the development of economy and environment in this area. We have analyzed the characteristics of ammonia nitrogen in the Xiang River in Changsha from 2016 to 2019. The results showed that in the main stem, concentrations of ammonia nitrogen were very low and reached the third water quality level. In the six tributaries, concentrations of ammonia nitrogen have increased, especially in Longwanggang and Liuyang River, where the latter of which has a large number of industries and domestic sewage. Correlations between monthly precipitation and ammonia nitrogen concentrations were negative, besides two sites Jinjiang and Juzizhou, indicating that in most rivers, ammonia nitrogen contents had been diluted by rainfall. In general, concentrations and fluxes of ammonia nitrogen have decreased significantly during this time period, suggesting that water environment has improved greatly under the series of the clean motions by the local government.

1 Introduction

Changsha city, which is located in Hunan province, includes both rural and highly industrialized urban areas. Rapid urbanization, climate change, inadequate maintenance of water and wastewater infrastructures, and poor solid waste management may lead to flooding, water scarcity, water pollution, adverse health effects and rehabilitation costs that may overwhelm the resilience of cities [1]. In water scarce regions, the problem of water pollution and deterioration of water quality is closely related to water shortage. Surface water pollution poses serious risks to aquatic habitat and the health of aquatic life [2]. In a southern city Guangzhou in China, stream water quality around urban villages with high population densities was worse than that within business districts [3]. River water quality of densely populated catchments was more prone to deterioration [4].

Ammonia (NH_3) come from a variety of sources, including fertilizers, livestock, mining, manufacturing, and transportation industries [5, 6]. [7] reported that global anthropogenic NH_3 emissions reached about one third of the industrial ammonia production in 2010, implying a larger potential for reductions in NH_4^+-N wet deposition. [8] found that 37%-52% of the initial NH_3 concentrations were from fossil fuel emissions in Beijing.

In this study, we analyzed trends in ammonia nitrogen concentrations from 2016 to 2019 along the main stem of Xiang River in Changsha and its six main tributaries. We aim to find the current status of ammonia nitrogen in streamflow and to identify the potential pollution in the Xiang River basin in Changsha.

2 Study area

The Xiang River is the second largest tributary and is in midstream of the Yangtze River. There are six tributaries in Changsha city, including Jinjiang, Longwanggang, Weishui, Liuyang, Laodao, and Shahe rivers. The Xiang River flows from the south to the north through Changsha (Figure 1) and it is crucial to the economic, social, and cultural development of Hunan Province. The basin has the highest urbanization level, and the total basin area accounts for 43% of Hunan Province. The population and gross domestic production (GDP) of the Xiang River basin account for 60% and 75% of those of Hunan Province. In recent years, the rapid population growth has exerted many problems, such as accelerated urbanization, rapid industrial development, and extensive agricultural fertilizer and pesticide use along the Xiang River basin [9].

This study analyzes ammonia nitrogen along the Xiang River through Changsha City in China. Changsha is located in a humid subtropical monsoon climate zone. Spring and autumn are short, while winter and summer are long. Annual average temperature ranges from 16.8℃ to 17.3℃. In the coldest month, average temperature ranges from 4.5℃ to 5.4℃, while in the hottest month, average temperature ranges from 28.8℃ to 29.3℃. Most precipitation occurs from April to July. Annual average surface runoff ranges between 550 mm

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to 850 mm, average annual runoff volume is 8.265×10^3 million m^3, annual average relative humidity is 80%, and annual average evaporation is 1206.9 mm.

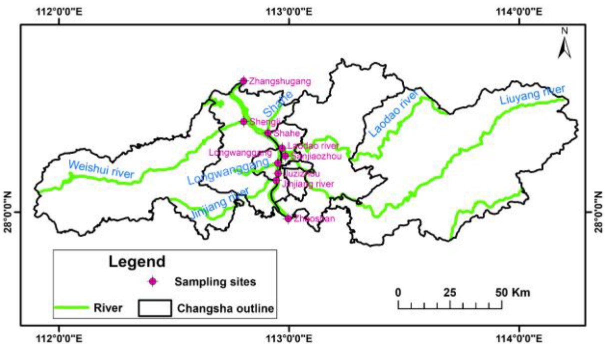

Figure 1. Location map of the study area and the sampling sites

3 Data and methods

Surface water quality data were collected by the Ministry of Ecology and Environment of the People's Republic of China and the Environmental Monitoring Centre of Changsha. There are three sampling points in the main stem of the Xiang River and six sampling points distributed along its tributaries. The samples were collected at a monthly basis and the concentration values were interpolated to daily data using a curve smoothing method (Table 1). We focused on trends and characteristics of ammonium nitrogen (NH_3-N) along the Xiang River in this study. The daily precipitation data were collected at 9 controlled stations around the Changsha city, where the daily values of precipitation were highly correlated to daily streamflow from January 2016 to December 2019. Daily streamflow was simulated by a distributed hydrologic model.

We applied the Mann-Kendall [10, 11] test to detect an existing trend with significance level. The Mann-Kendall trend test computes the test statistic S as equation (1)

$$S=\sum_{k=1}^{n-1}\sum_{j=k+1}^{n}\mathrm{Sgn}(x_j-x_k) \tag{1}$$

where n is the number of observations, x_j is the jth observation, and $\mathrm{Sgn}(.)$ is the sign function, which represents

$$\mathrm{Sgn}(x_j-x_k)=\begin{cases}+1 & \text{if } x_j>x_k\\ 0 & \text{if } x_j=x_k\\ -1 & \text{if } x_j<x_k\end{cases} \tag{2}$$

The S statistic has a mean value of 0 and a variance that is calculated using equation (3) (Kendall, 1975)

$$\mathrm{Var}(S)=\frac{n(n-1)(2n+5)-\sum_{i=1}^{m}t(t-1)(2t+5)}{18} \tag{3}$$

where m is the number of groups of tied ranks, each with t_i tied observations. Mann-Kendall's Z statistic is calculated using equation (4)

$$Z=\begin{cases}\frac{S-1}{\sqrt{\mathrm{Var}(S)}} & \text{if } S>0\\ 0 & \text{if } S=0\\ \frac{S-1}{\sqrt{\mathrm{Var}(S)}} & \text{if } S<0\end{cases} \tag{4}$$

A Z statistic value of higher than 1.96 indicates that the increasing trend is significant at the significance level of 0.05. In contrast, a Z statistic value of less than -1.96 indicates that the decreasing trend is significant at the 0.05 significance level [12].

We split the time periods to high-flow season, low-flow season, and normal-flow season. The high-flow season spans from June to September, the low flow season spans from December to March in the next year, and the normal-flow season represents all the other months, i.e., April to May and October to November.

Table 1. Sampling sites and their coordinates, time length of samples

Site name	River name	Shortening	Coordinates	Time length
Jinjianghe	Jinjiang	Jinj	112.94°E, 28.14°N	Jan 2016-Dec 2019
Sanjiaozhou	Liuyang	Liuy	112.98°E, 28.24°N	Jan 2016-Dec 2019
Laodaohe	Laodao	Laod	112.97°E, 28.28°N	Jan 2016-Dec 2019
Longwanggang	Longwanggang	Longwg	112.95°E, 28.21°N	Jan 2019-Dec 2019
Shengli	Weishui	Weis	112.80°E, 28.39°N	Jan 2016-Dec 2019
Shahe	Shahe	Shah	112.91°E, 28.34°N	Jan 2018-Dec 2019
Zhaoshan	Xiangjiang	Zhaos	112.99°E, 27.97°N	Jan 2016-Dec 2019
Juzizhou	Xiangjiang	Juzz	112.95°E, 28.17°N	Jan 2016-Dec 2019
Zhangshugang	Xiangjiang	Zhangsg	112.80°E, 28.57°N	Jan 2016-Dec 2019

4 Results

4.1. Trend analysis of daily values of ammonia nitrogen

Daily concentrations of ammonia nitrogen at the six river tributaries and the main stem of Xiang River were presented in Figure 2. Concentration of ammonia nitrogen were the lowest at Zhaoshan site, followed by Juzizhou, and were the highest at Zhangshugang site. Ammonia concentration exceeded fourth and fifth grade water quality levels at some days for Jinjiang, Laodao River, Liuyang River, Longwanggang, Shahe, and Weishui River. Zhaoshan, Juzizhou, and Zhangshugang sites were located at the upper, middle, and lower reaches of the Xiang River, separately. In general, the concentrations of ammonia nitrogen were the lowest in the main stem of Xiang River, from the upper to the lower reaches. Longwanggang site had the highest ammonia nitrogen concentration, Liuyang River had the second highest ammonia nitrogen concentration, Laodao River, Shahe River, and Weishui River had lower ammonia nitrogen concentrations, while Jinjiang River

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had the lowest ammonia nitrogen concentration in the six tributaries.

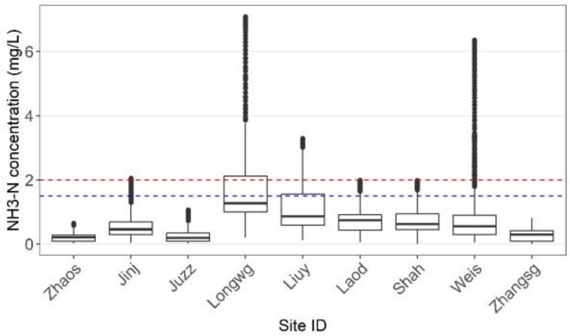

Figure 2. Boxplots of daily concentrations of ammonia nitrogen. (Boxes represent interquartile range, dots represent outliers, and the bold lines represent the median values on the graph. The dashed blue and red lines represent water quality at the fourth and fifth levels, respectively.)

From 2016 to 2019, the average daily NH_3-N flux at Zhaoshan was 38.19 t/day, increased to 49.85 t/day at Juzizhou, and increased to 60.72 t/day at Zhangshugang. The fluxes of NH_3-N at Zhangshugang come from the main stem and its tributaries. Liuyang River had the highest NH_3-N flux, Laodao and Weishui rivers had NH_3-N fluxes around 4.9 t/day, Shahe had the lowest NH_3-N flux. Longwanggang had an average NH_3-N flux of 0.62 t/day, given its relatively short length.

Table 2. Characteristics of daily NH_3-N flux (kg/day)

SiteID	Min	Mean	Max
Zhaos	1343	38191	471805
Jinj	24.97	1161.26	54749.24
Juzz	1098	49846	1114396
Longwg	22.19	620.5	5560.65
Liuy	641.7	12482	148372.2
Laod	195.8	4849.7	153978.2
Shah	0	278.3	3437.9
Weis	150.1	4985.2	137178.6
Zhangsg	0	60715	787270

Figure 3 shows Z statistics for changes in daily concentrations and fluxes of ammonia nitrogen in the main stem and the six tributaries. From 2016 to 2019, concentrations of ammonia nitrogen at Longwanggang had increased significantly at 0.05 level, while concentrations of ammonia nitrogen at the other tributary river outlets had decreased significantly. Pollutant fluxes had decreased significantly at all river outlets, suggesting that the water environment has been improved since 2016.

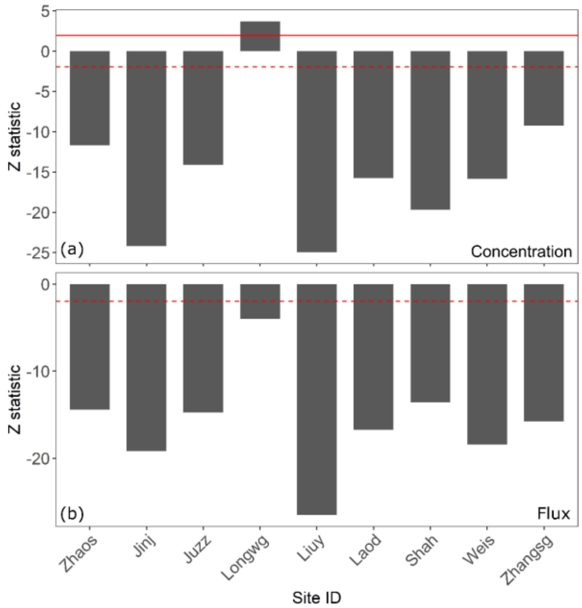

Figure 3. Z statistics for changes in concentrations and fluxes of ammonia nitrogen. (The solid and dashed red lines represent Z statistics at 1.96 and -1.96, respectively.)

4.2. Ammonia nitrogen in different flow seasons

Figure 4 shows boxplots of NH_3-N concentrations during the high-flow season. Longwanggang had the highest NH_3-N concentrations, while Liuyang River had the second highest NH_3-N concentrations, Laodao, Shahe, Weishui and Jinjiang River had close NH_3-N concentrations, while the Xiang River main stem had the lowest NH_3-N concentrations. In the high flow season, NH_3-N concentrations at Longwanggang was above the fourth and fifth grade water quality levels.

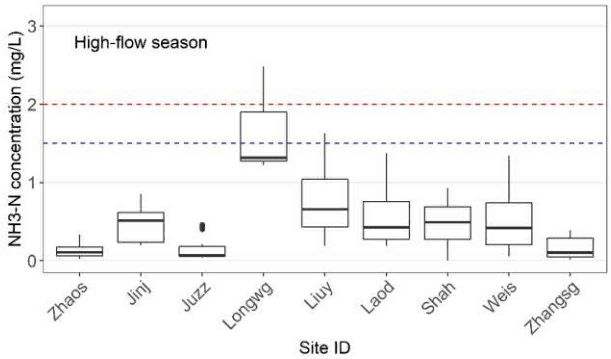

Figure 4. Boxplots of ammonia nitrogen values in the high-flow season. (Color legend refers to Figure 2)

In the low-flow season, Liuyang River had the highest NH_3-N concentrations, Longwanggang had the second highest NH_3-N concentrations, Laodao, Shahe, and Weishui River had less NH_3-N concentrations, Jinjiang River had the lowest NH_3-N concentrations in the six tributaries, and Zhaoshan and Juzizhou at Xiang River main stem had the lowest NH_3-N concentrations in all the sampling sites. In the low-flow season, NH_3-N concentrations at Liuyang River was above the fourth and fifth grade water quality levels.

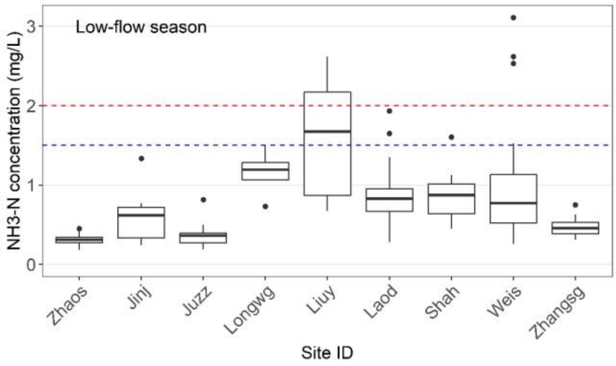

Figure 5. Boxplots of ammonia nitrogen values in the low-flow season. (Color legend refers to Figure 2.)

In the normal-flow season, NH_3-N concentrations in the Xiang River in Changsha had similar patterns with NH_3-N concentrations during the high-flow season (Figure 6). As before, NH_3-N concentrations at Longwanggag was above the fourth water quality level for some time.

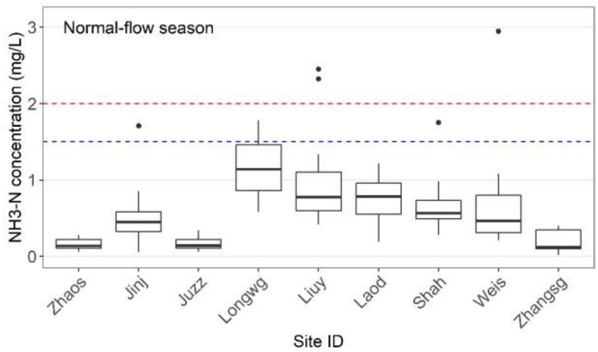

Figure 6. Boxplots of ammonia nitrogen values in the normal-flow season. (Color legend refers to Figure 2)

4.3. Correlations between precipitation and ammonia nitrogen

Daily precipitation showed a significant decreasing trend from January 2016 to December 2019. The Z statistic was -2.85 with p value less than 0.05. The Pearson correlation coefficient between monthly precipitation and NH_3-N concentrations at each sampling site was presented in Figure 7. Besides Jinjiang and Juzizhou sampling sites, the other sites all showed negative values. The negative correlations suggest that high precipitation volume could dilute NH_3-N concentrations in rivers to some degree. At Longwanggang site, monthly precipitation and NH_3-N had a correlation coefficient of -0.45 in 2019, indicating that rainfall could largely dilute pollutant contents. At the other sites, the correlation coefficients were below 0.11 or no lower than -0.23, indicating that NH_3-N concentrations had low correlations with precipitation amounts. Thus, NH_3-N concentrations may be more influenced by human activities.

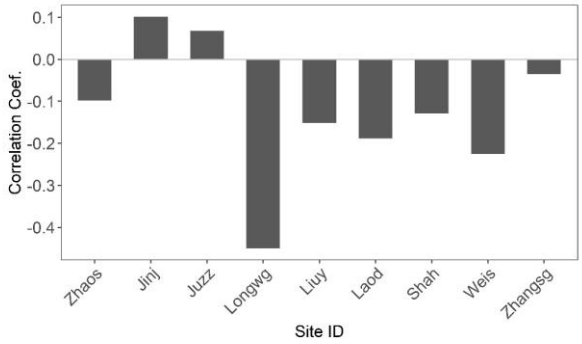

Figure 7. Bar charts of correlation coefficient between monthly precipitation and NH_3-N concentrations.

4.4. Correlations between human activities and ammonia nitrogen

The local pollutant survey has showed annual ammonia nitrogen export in the Xiang River in Changsha in 2017 (Table 3). We can see that Liuyang River has the highest number of industries available during the survey and the highest NH_3-N export amount from domestic sewage. Thus, Liuyang River has the highest NH_3-N concentrations in the low-flow season. Livestock was a significant contributing source to NH_3-N mainly in Weishui river. Domestic sewage was a significant contributing source to NH_3-N in Laodao river.

Table 3. Ammonia nitrogen export in the Xiang River, Changsha in 2017

Source	River	Num	NH_3-N export (t)
Livestock	Jinjiang	98	51.5745
	Weishui	399	131.0287
	Laodao	90	3.3486
	Liuyang	180	7.6093
Industry	Xiang River	226	116.2436
	Laodao	604	227.1666
	Liuyang	1041	157.7096
	Weishui	397	239.2252
	Shahe	69	3.6306
	Longwanggang	9	-
Domestic sewage	Xiang River	6	50.32
	Jinjiang	8	323.54
	Weishui	55	67.83
	Shahe	13	12.17
	Laodao	101	224.45
	Liuyang	54	1497.44

5 Discussions

5.1. Characteristics of daily ammonia nitrogen concentrations and fluxes

The results showed that water quality was the finest at the main stem of Xiang River. Concentrations of ammonia nitrogen were lower than the fourth grade water quality level. Except for Longwanggang, concentrations and fluxes of ammonia nitrogen have decreased significantly at the main stem of the Xiang River and its tributaries during 2016 to 2019. The results suggested that Longwanggang has water pollution problems more severe than the other rivers.

[9] presented the causes of water pollution in the Xiang River basin as four factors: (1) large-scale emissions of industrial wastewater, (2) extensive pesticide use, (3) urban sewage pollution, and (4) ineffective government control measures. Given that the government has put great emphasis on improving water environment in this city, the last factor has been eliminated. The large-scale development of livestock and poultry industry leads to the superposition of industrial and domestic pollution of the Xiang River basin. Rainfall washed off pesticides and fertilizers from the land to the river, causing an increase in pollutants [9]. With increasing population, the need of more natural resources, such as agriculture, industry, and household demand, continues to increase in a river basin in China [13].

5.2. Characteristics of ammonia nitrogen in different flow periods

The results showed that in the high-flow and normal-flow seasons, Longwanggang has the highest NH_3-N concentrations, while Liuyang River has the second highest NH_3-N concentrations, Laodao, Shahe, Weishui and Jinjiang River have similar NH_3-N concentrations, while the main stem of Xiang River has the lowest NH_3-N concentrations. In the low-flow season, Liuyang River has the highest NH_3-N concentrations, while Longwanggang has the second highest NH_3-N concentrations.

[14] stated that fertilizer application and livestock manure management could mitigate potential NH_3-N flux. [6] found that the cropland and livestock emissions are the largest contributors to ammonia emissions in national scale from 1980 to 2016, while nonagricultural sources of fuel combustion, waste treatment and ammonia escape have grown rapidly in recent years. [15] found that arable land use can deteriorate streams by increasing the non-point pollutant inputs, and can impact riparian and stream channel habitats and altering flows. [16] stated that land use intensity and socio-economic activities served as the first and second influential factors of river ecosystem health, and that seasonal differences need to be taken into account during basin management.

5.3. The impact of precipitation on ammonia nitrogen

In the Xiang River and its tributaries in Changsha, monthly precipitation and NH_3-N concentrations had positive correlations at Jinjiang and Juzizhou, but negative correlations at the other sampling sites. The correlation coefficient was -0.45 at Longwanggang, suggesting that precipitation had diluted pollutant contents in this river reach. While at the other sampling sites, the correlation coefficients were very low, indicating that NH_3-N contents were less being affected by precipitation amounts. Contrary to this study, in Yongding River within the Haihe river Basin, water quality is positively correlated to monthly precipitation [16].

5.4. The impact of human activities on ammonia nitrogen

Longwanggang had the highest NH_3-N concentrations in the high-flow and normal-flow seasons. The local survey included only a few industries, indicating that domestic sewage and livestock may be a significant source of NH_3-N in this river. [16] found that the contribution from population density was higher than that from industrial structure at the catchment scale. Furthermore, domestic sewage discharge had greater impacts on river ecosystem health than industrial activities.

6 Conclusion

In this study, we have analyzed trends in measured NH_3-N concentrations and fluxes from 2016 to 2019. The results showed that in the main stem, concentrations of ammonia nitrogen were very low and reached the third grade water quality level. In the six tributaries, concentrations of ammonia nitrogen have increased, especially in Longwanggang and Liuyang River, where the latter of which has a large number of industries and domestic sewage. Correlations between monthly precipitation and ammonia nitrogen concentrations were negative, besides two sites Jinjiang and Juzizhou, indicating that in most rivers, ammonia nitrogen contents had been diluted by rainfall. In general, concentrations and fluxes of ammonia nitrogen have decreased significantly during this time period, suggesting that water environment has improved greatly under the management of the local government.

Acknowledgements

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