Preliminary aquatic life criteria development and ecological risk assessment of ammonia in seven major river basins in China

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Abstract: Ammonia is one of the basin indices which are nation-controlled in the water environmental management. In order to assess the differences of ammonia criteria in different basins, 7 major basins are used for the study object, including Songhua River, Liaohe River, Haihe River, Yellow River, Huaihe River, Yangtze River and Zhujiang River, referring the water environmental criteria technology of the United States Environmental Protection Agency, based on the effects of water characteristics on the ecotoxicity of ammonia, and in summer and non-summer situation, aquatic life criteria is derived for ammonia. The results showed that: (a) The differences between the criteria values in different basins and different seasons were significant. The differences between the criteria values in different basins were greater than 6 times, while those in different seasons in the same basin were greater than 2 times. (b) The summer acute and chronic criteria for Huaihe River were 0.37 mg/L and 0.06 mg/L while the non-summer values were 0.81 mg/L and 0.15 mg/L. Both the summer and the non-summer values were lowest in all of the seven basins. (c) The preliminary assessment of Ammonia exposure ecological risk indicated that was the lowest in Zhujiang River, and it was much lower in Songhua River, Liaohe River and Yangtze River, and was higher in Yellow River, and the highest in both Haihe River and Huaihe River. Haihe River has 7 sections while 2 in high risk, and Huaihe River has 27 sections while sixteen in high risk. According to the differences of the criteria values for ammonia in seven basins in different seasons and difference of ammonia ecological risk assessment, it is suggested that it should be managed by different policies.

Keywords: seven basins; ammonia; aquatic life criteria; ecological risk assessment; risk quotient

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The water quality criteria (WQC) were used as the scientific basis for the water quality standard. United States, European Union and other countries have carried out the WQC studies for many years and formed a relative mature technology system of water quality criteria and standards. The WQC study in China is relatively backward, and the relevant standards still refer to foreign standards mainly. Because of some differences in different countries or regions, both the characteristics of water environment(such as temperature, pH, hardness, ρ(DO), etc.) and the differences of aquatic biota in different areas could cause different criterion values of the same pollutant[1, 2]. Therefore, some domestic scholars carried out the native WQC studies recently, based on the native characteristics of water environment and aquatic biota, and they proposed some local pollutant criteria values, such as 2, 4-dichlorophenol[3], 2, 4, 6-Trichlorophenol [4], Nitrobenzene [5], metals [6, 7], ammonia [8] and etc., which provided scientific basis for the scientific revision of water quality standards in China.

Ammonia is one of the important indicators of water environment monitoring in China, and its main source is the production that is decomposed by microbial action from the nitrogenous organic compound in domestic sewage, some industrial wastewater and agricultural drainage[9]. In 2013, "China Environmental Status Bulletin"[10] pointed out that the total amount of ammonia was one of the most important water pollutants in China whose amount reached 245.7×10^4 t nationwidely. Ministry of Environmental Protection (MEP) issued "Planning of Water Pollution Prevention and Control in Key Drainage Basins (2011-2015)"[11], which proposed the target of the total quantity control of ammonia directly: ammonia emission would be controlled in 120.7×10^4 t by 2015. Therefore, it is very important to aim at developing the typical basin WQC and water quality standard for ammonia in China, which could both provide a theoretical basis for further reduction of the total quantity of ammonia emission and be important for the protection of the basin ecological safety in China.

In 2013, the United States Environmental Protection Agency (U.S. EPA) published the newest technical document "Aquatic Life Ambient Water Quality Criteria For Ammonia -Freshwater", which was combined with the latest international research results and proposed new ammonia[12] WQC benchmark functions and the reference value. In China, the current ammonia water quality standards refer to foreign WQC mainly [13], and there is no specific basin water quality standard now. A large number of studies [14-20] by scholars at home and abroad indicate that under different pH and different temperature conditions, the toxicity effects of ammonia on aquatic organisms are different. The China is vast in territory, where the climatic conditions and water quality conditions of different basins have obvious differences and these may bring significant impact on WQC of ammonia. Some researchers have developed the WQC of ammonia in Liaohe River basin and Taihu basin, and found that WQC values in different basins reflected the difference [8, 21, 22]. However, the development of specific basin WQC was rarely reported because our parameter data of major basins were based on the state monitoring water quality. This study is on the basis of previous studies, both deriving the WQC for ammonia under different season conditions in Songhua River basin, Liaohe River basin, Haihe River basin, Yellow River basin, Huaihe River basin, Yangtze River basin and Zhujiang River basin and desiring to provide a reference for the differential management of the water environment in China.

1 Materials and methods

1.1 Source of water quality paramenters and ammonia environmental exposure data

PH data and ammonia monitoring data came from MEP's website "Water quality automatic monitoring weekly report of key section of major river basin" (http://datacenter.mep.gov.cn/report/getCountGraph.do?type=runQianWater, from December 31, 2012 to December 8, 2013, and Recorded 1 times the pH and ρ(ammonia) data from total 90 sections of the 7 basins each 4 weeks, and pH of each basin selected the average value of the 3 highest values of all sections.

Water temperature data came from the Local Records of seven basins [23-29] and literature [30-33], and the basins which have no record will be based on its average temperature by literature method [34]. Water temperature will be divided into summer water temperature and non-summer water temperature in the study, in which the summer water temperature means that the average water temperature from June to August and the non-summer water temperature means the average water temperature of the others. If the data is not incomplete, it could use the average water temperature of April, July, October and January to replace the average water temperature of four seasons, while the water temperature of the frozen winter period is calculated at 4 °C.

1.2 Deriving the WQC for ammonia in basins

At present, the method of deriving the WQC for ammonia is mainly based on "Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses" [35], which was published by U.S. EPA in 1985. Functional relation of water temperature and pH refer to the document "Aquatic Life Ambient Water Quality Criteria for Ammonia – Freshwater" [12] which was published by U.S. EPA in 2013.

The study refers to the results [8] from previous researchers to derive the WQC for ammonia in seven basins.

Criteria maximum concentration (CMC) is as the following:

$$CMC = 0.643 \times \left(\frac{0.0489}{1+10^{7.204-pH}} + \frac{6.95}{1+10^{pH-7.204}}\right) \times MIN(10.40,\ 6.018 \times 10^{0.036 \times (25-T)}) \quad (1)$$

Criteria continuous concentration (CCC) is as the following:

$$CCC = 0.502 \times \left(\frac{0.0676}{1+10^{7.688-pH}} + \frac{2.912}{1+10^{pH-7.688}}\right) \times MIN(2.852,\ 0.914 \times 10^{0.028 \times (25-MAX(T,7))}) \quad (2)$$

where, T stands for the water temperature, ˚C.

1.3 Ecological risk assessment of ammonia exposure

Risk quotient (RQ) method is used to assess the ecological risk of ammonia in seven basins [36]. RQ is a simple and conservative approach to the risk characterization, which characterizes the ecological risk of pollutants through comparing the environmental exposure concentrations (EEC) with WQC. The calculation method is as the following:

$$RQ = EEC/WQC \quad (3)$$

where, EEC stands for the environmental exposure concentrations, mg/L; WQC stands for the water quality criteria, mg/L.

The study used the data of ρ(ammonia) measured from all the sections of the 7 basins as EEC, and each 4 weeks recorded once, respectively the first week, the fifth week, the ninth week, the thirteenth week, the seventeenth week, the twenty-first week, the twenty-fifth week, the twenty-ninth week, the thirty-third week, the thirty-seventh week, the forty-first week, the forty-fifth week and the forty-ninth week. When the ecological risk is assessed, the exposed time would correspond to the seasonality of WQC. Judging the ecological risk level according to the value of the risk quotient, when $RQ < 1$, there is nearly no risk; when $1 \le RQ < 10$, there is risk; when $RQ \ge 10$, there is the highest risk [36, 37].

1.4 Date analysis

The study used SPSS software 18.0 to analyze the significant differences of CMCs and CCCs in the summer season and non-summer season of ammonia, and samples with normal distribution used independent samples t test while samples in no conformity with normal distribution used Mann-Whitney test in non parametric test.

2 Results and analysis

2.1 WQC values for ammonia in seven basins

According to the pH and water temperature in summer season and non-summer season of 7 basins, the CMCs and CCCs in summer season and non-summer season of ammonia were calculated separately. The results were shown in Tab. 1. It can be known that the differences of the WQC values of ammonia in different basins were great, and WQC in Huaihe River basin was lowest in seven basins while the difference of CMCs in Huaihe River basin and Zhujiang River basin was more than 6 times; the differences of the WQC values of ammonia in the same basin during different seasons were also great, and the differences of the CCCs of ammonia in the same basin during different seasons, such as Songhua River basin, Haihe River basin, Yellow River basin and Huaihe River basin, were more than 2 times at all. Using software to analyze the significant differences of CMCs and CCCs in summer season and non-summer season of ammonia, the results were as follows: the CMCs of ammonia in summer season of ammonia were not conformed to the normal distribution, so it used Mann-Whitney test in non parametric test, and the results showed that there was no significant difference between two groups($P>0.05$); the CMCs in summer season and non-summer season of ammonia were consistent with normal distribution, so it used independent samples t test, and the results showed that the difference was significant between two groups($P<0.05$).

Tab. 1 Aquatic life criteria for ammonia in the seven basins

Basin	pH	Water temperature /℃		Criteria values in summer /(mg/L)		Criteria values in non-summer /(mg/L)	
		Summer	Non-summer	CMC	CCC	CMC	CCC
Songhua River	8.57	21	11	1.80	0.24	2.23	0.45
Liaohe River	8.64	23	13	1.34	0.18	1.96	0.35
Haihe River	8.94	29	13	0.48	0.08	1.16	0.22
Huaihe River	9.18	28	14	0.37	0.06	0.81	0.15
Yellow River	8.80	28	14	0.66	0.10	1.47	0.25
Yangtze River	8.71	23	17	1.18	0.16	1.72	0.24
Zhujiang River	8.11	28	19	2.45	0.32	5.16	0.57

2.2 Ecological risk assessment of ammonia exposure in 7 basins

According to the CCCs in summer season and non-summer season of ammonia in seven basins, RQ method was used to assess the ecological risk of the measured ρ(ammonia) in monitoring sections of each basin. The results were shown in Tab. 2.

Tab. 2 Amount of basin sections with risk or high risk

Basin	Section number	Ecological risk	Non-summer										Summer		
			1 weeks	5 weeks	9 weeks	13 weeks	17 weeks	21 weeks	37 weeks	41 weeks	45 weeks	49 weeks	25 weeks	29 weeks	33 weeks
Songhua River	16	In risk	8	7	8	8	6	3	4	3	2	3	11	8	8
		In high risk	0	0	0	0	0	0	0	0	0	0	0	0	0
Liaohe River	9	In risk	4	3	2	2	2	3	3	2	3	2	5	5	4
		In high risk	0	0	0	0	0	0	0	0	0	0	0	0	0
Haihe River	7	In risk	3	2	2	3	2	2	3	2	2	3	4	3	4
		In high risk	2	2	2	1	1	0	0	0	1	1	2	2	2
Huaihe River	27	In risk	19	20	19	14	19	20	21	20	20	21	22	19	21
		In high risk	6	7	7	8	5	4	2	3	2	2	4	8	6
Yellow River	12	In risk	7	9	9	8	7	2	6	3	5	7	9	8	10
		In high risk	3	3	2	1	1	2	0	1	2	3	2	2	1
Yangtze River	21	In risk	13	13	14	6	7	2	3	5	8	10	5	6	7
		In high risk	0	0	0	1	0	0	0	0	0	0	0	0	0
Zhujiang River	8	In risk	1	1	1	1	1	1	0	1	0	2	1	1	1
		In high risk	0	0	0	0	0	0	0	0	0	0	0	0	0

Note: Because of the large amount of data and limited length, it only showed the numbers of sections in risk or in high risk in seven basins.

The results of ecological risk assessment showed that: the water quality situation in Zhujiang River basin was the best in 7 basins, and Guiyang Shizui section at the forty-ninth week and Guangzhou Changzhou section in part of the month were in risk, and the others had no risk. Those in Songhua River basin, Liaohe River basin and Yangtze River basin were moderate, and most sections in majority months had no risk and a few sections were in risk; There was no high risk in the sections of Songhua River basin and Liaohe River basin, while Leshan Minjiangdaqiao section in Yangtze River basin was in high risk at the thirteenth week with RQ of 15.17 and that might be due to a one-time centralized discharge by some enterprises in this month. The water quality in Yellow River basin was relatively poor, and Haidong Minheqiao section, Yuncheng Hejindaqiao section and Weinan Tongguandiaoqiao section were in higher risk during majority months. The highest risk occurred in Yuncheng Hejindaqiao section, where ammonia concentration exceeded 68 times in the forty-ninth week, and other sections were in risk during majority months, only a few with no risk. The water quality situation in Haihe River basin and Huaihe River basin were the worst. Haihe River basin has 7 monitoring sections, that the most serious pollution occurred in Tianjin Sanchakou section and Liaocheng Chenggouwan section, which continued in high risk during most months and other sections were in risk about half of the month; Huaihe River basin has 27 monitoring sections while 16 in high risk, the others almost in risk, and only a few sections in some months were in no risk. Fuyang Zhangdaqiao section, Bozhou Yanji section and Suzhou Yangzhuang section were nearly in high risk at half a year, and the highest risk occurred in Fuyang Zhangdaqiao section, with RQ up to 159.17 at the twenty-fifth week, and it was hundreds of times over than other basins.

3 Discussion

3.1 Selection of the method for deriving basin WQC

At present, there are 3 types of Species Sensitivity Distribution (SSD) model used for WQC: the Species Sensitivity Rank (SSR) method based on log trigonometric function model[38], the method based on log normal distribution function[39], and the method based on log logistic distribution function[40]. On the basis of WQC for ammonia, the mainstream SSD model does not consider the influence of water quality parameters, so the SSD model is not suitable for deriving WQC for ammonia. US EPA established the methodology of aquatic life ambient water quality criteria for ammonia based on the empirical mathematical model, and released the latest version of the ammonia criteria technical documents in 2013. Therefore, this study mainly draw lessons from the ammonia criteria technical documents by USA, and derived the WQC for ammonia under different season conditions in 7 basins.

In addition, the data for water species distribution in different basins are not detailed enough, which is temporarily unable to support the establishment of the function formula of the WQC for ammonia separately in each basin, so this study used a unified functional relationship to derive the WQC for ammonia. With the further development of the research on the ammonia toxicity in the native species in China, if we have specific function formulae of different basins, the studies on the difference of the WQC for ammonia in different basins can be further promoted.

3.2 Selection of the data for pH and water temperature in seven basins

PH data came from MEP's website "Water quality automatic monitoring weekly report of key section of major river basin", including totally 90 sections from 7 basins and these can reflect the pH level of 7 basins basically. Considering the current monitoring site distribution of main basins may have differences, which do not fully reflect the true pH level of basins, the data could be supplemented and corrected by adding monitoring sites and other methods in the future. In addition, since the basins may have accidental emergencies and cause an abnormal elevation of pH values at some time point, and in order to reflect the true pH level of seven basins and ensure the reliability of data, we select the average value of the 3 highest values of all sections in this study.

The geographical area of each basin has large span and the difference between the upper reaches and lower reaches is large, which lead to a great difference in water temperature at different sections of the same basin. Because of the different topography and water depth, the temperatures of the different water layers have a greater difference. Therefore, there is some uncertainty of the basin water temperature selection in the summer season and non-summer season. In order to reduce the uncertainty, following conservative principle, this study refers to local records or relevant published articles as a relatively reliable source of data, and makes a preliminary estimate of the average water temperature in the summer season and non-summer season of 7 basins. In the future, with the development of research, we can carry out the studies for the measurement of water temperature in some basins or the studies on section level and water layer level, which could further reduce the uncertainty of water temperature data.

3.3 Comparative analysis of the WQC values for ammonia in 7 basins and other WQC values

From Tab. 1 we can see that the WQC for ammonia in different basins was very different at different water temperature and pH conditions. Considering the geographical distribution of the basins, it indicated that the WQC values of higher latitude and lower latitude basins (Songhua River basin, Liaohe River basin, Zhujiang River basin) were greater than those of the middle latitude basins (Haihe River basin, Yellow River basin, Huaihe River basin, Yangtze River basin); considering the seasonal distinction, it indicated that the WQC values in the non-summer season were greater than those in summer season. The largest difference was in Huaihe River basin and Zhujiang River basin, and the differences of CMCs in summer season and non-summer season were 6.9 times and 6.4 times respectively, and the differences of CCCs were 6.9 times and 6.4 times respectively. The difference of CMCs was greater than CCCs, and the difference of WQC in summer season was greater than that in non-summer season. The reason is that the pollution of Huaihe River basin is very serious, with water pH of 9.18 and it has the highest value in 7 basins; and Zhujiang River basin water quality is better, with water pH of 8.11 and it has the lowest value in 7 basins. Based on reasons above, great difference of CMCs and CCCs is caused between 2 basins under the same summer average water temperature condition (6.62 times and 5.33 times, respectively). Non-summer average water temperature in Zhujiang River basin is higher than that in the Huaihe River basin, and the difference of CMCs and CCCs between two basins is slightly less than that in summer. Supposing the non-summer water temperature of two basins unchanged, and adjusting pH to the same level, the differences of CMCs and CCCs were 1.05 times and

1.38 times respectively. Therefore, it can be inferred that the difference of pH is the main important factor of the river basins. In addition, the differential analysis results showed that the CMCs of a few basins was relatively closed with each other and with no significant difference, so that we can use a unified threshold in principle except that the basins can be used cautiously with too large difference; the CCCs had significant difference, therefore, it had important significance and necessity to implement the management of ammonia according to different basins and different seasons in China.

According to the previous research results[8] and similar data from the United States[12], in the range of pH from 6.5 to 9 ,and the temperature from 0 °C to 30 °C, the WQC values were from 0.403 to 38.9 mg/L (CMCs) and from 0.066 4 to 3.92 mg/L (CCCs) respectively in China, while the values were from 0.299 to 57.0 mg/L (CMCs) and from 0.037 1 to 2.24 mg/L (CCCs) respectively in the United States. Compared with each other, the CMC and CCC in summer season of Huaihe River basin in this study were both less than the range of Chinese WQC values for ammonia, which were in the range of WQC values in the United States. Because of the calculation formula of ammonia in this study was directly used by the previous research results, without being derived in different basins respectively, in the case of the Huaihe River basin's pH beyond 9, and the result of the calculation was less than the WQC values in China. If the pH value is expanded to 9.18, the range of CMCs will become 0.309 to 38.9 mg/L and the range of CMCs will be from 0.052 to 3.92 mg/L, and the WQC values for ammonia in summer season of Huaihe River basin will be covered in the range of Chinese WQC values for ammonia, so the difference of the calculation results is reasonable. In addition, there have differences in the distribution and research status of aquatic organisms between China and the United States. The calculation of CMCs and CCCs for ammonia adopted the data of 67 genus and 12 genus respectively in the United States, which were much more than 27 genus and 7 genus in China. Furthermore, data of the most sensitive genus in the process of calculation in the United States (*Lampsilis*, 0.344 mg/L [12]) was far lower than data of the most sensitive genus in China (average value of shellfish, 0.914 mg/L [8]), which lead to the WQC values for ammonia in the United States lower than those in China.

According to "Environmental quality standards for surface water" (GB 3838-2002), the ρ(ammonia) standard limit values of Class I to Class V surface water are 0.15, 0.5, 1.0, 1.5 and 2.0 mg/L[41] respectively. Compared with the results of this study, the current standard limit values of the surface water ammonia in China are too general and lack of practical operability. According to water standard for ammonia, the CCCs in summer season and non-summer season in seven basins are almost divided into Class I and Class II, while the CMCs are most divided into Class II to Class IV, so the CCCs can be used as a reference for more detailed ammonia water quality standards in future and the CMCs can be used to apply to the water quality emergency management in China.

3.4 Ecological risk assessment of ammonia exposure in 7 basins

The risk level of ammonia exposure in 7 basins showed the same trend of pH. When the basins had lower pH values, the ammonia risk level was lower (in the Zhujiang River basin, Songhua River basin, Liaohe River basin and Yangtze River basin), and to the contrary, when the basins had higher pH values, the ammonia risk level was greatly increased (in the Yellow River basin, Haihe River basin and Huaihe River basin). From the geographical distribution of the basins, it indicated that the risk level of higher latitude and lower latitude basins was less than that of the middle latitude basins, which presented a trend that was opposite to the WQC values in 7 basins. From the seasonal distinction, it indicated that there had no significant impact on the risk of different months by seasonally calculating RQ in 7 basins. Through analyzing the reasons, due to the impact of pH, the WQC values will be smaller when pH values are higher, and it might lead to differences in risk levels of the same ammonia exposure concentrations. But Haihe River basin and Huaihe River basin had the highest RQ values that exceeded the ρ(ammonia) standard limit values tens of times or even a hundred times, much larger than those of other basins. In addition, affected by temperature factors, the WQC values in summer season were lower than those in non-summer season, and the risk assessment results showed that there had no significant impact on the risk of different months by seasonally calculating RQ. Therefore, we infer that the basin risk level is mainly affected by the concentration of environmental exposure (actual monitoring of ammonia concentration), and the basin risk level is high while ρ(ammonia) is high, and the basin risk level is low while ρ(ammonia) is low. This inference is almost the same as that for the water quality of major basins that is reported by "China Environmental Status Bulletin" in 2013[10]. A slight difference is that in "China Environmental Status Bulletin", it's reported that the water pollution of Haihe River basin is the most serious in 7 basins, but because there are only 7 sections' monitoring data in Haihe River basin, while Huaihe River basin have 27 sections , the number of cross sections which in high risk and RQ values of Haihe River basin are both lower than that of Huaihe River basin. The uncertainty due to monitoring site layout can be further improved in the follow-up study.

It is suggested that according to the results of risk assessment, it should be managed according to different basins and different seasons. For the basins at low risk or no risk, we can carry out water quality routine monitoring; for the basins at risk, in addition to the routine monitoring, the risk assessment should be carried out regularly, and if the risk is increased, the corresponding management measures should be taken to reduce the risk level in time; for the basins and sections at high risk, we need to carry out comprehensive analysis on the pollution situation, and to reduce the risk to a lower level through a series of measures, such as real-time monitoring, strict control, total quantity control and so on.

4 Conclusions

A) The differences between the criteria values in different basins and different season were both significant. The differences between the criteria values in different basins were greater than 6 times, while those in the same basin during different seasons were more than two times. The summer CMC and CCC for Huaihe River were 0.37 mg/L and 0.06 mg/L while the non-summer values were 0.81 mg/L and 0.15 mg/L, respectively. Both the summer and the non-summer values were lowest in all of the 7 basins. The results of difference analysis showed that the CMC had no significant difference in summer and non-summer season, but the CCC had. It is suggested that according to the differences of the criteria values for ammonia in 7 basins, it should be managed according to different seasons and different policies.

B) The results of ecological risk showed that: Zhujiang River basin had better water quality, and the ecological risk was lowest in all basins; those in Songhua River basin, Liaohe River basin and Yangtze River basin were moderate, with some sections in risk; the water quality in Yellow River basin was relatively poor, with majority sections in risk and some sections in high risk; and the highest risk occurred in Haihe River basin and Huaihe River basin, and Haihe River basin had 7 sections while 2 in high risk, and Haihe River basin had 27 sections while 16 in high risk.

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七大流域氨氮水生生物水质基准与生态风险评估初探

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摘 要：氨氮是我国流域水环境管理的国控指标之一，为评估不同流域的氨氮基准差异性，以七大流域（松花江流域、辽河流域、海河流域、黄河流域、淮河流域、长江流域和珠江流域）为研究对象，基于水质参数对氨氮毒性的影响，借鉴 US EPA(美国国家环境保护局局) 水环境基准技术方法，分夏季和非夏季 2 种情况推算了各流域氨氮水生生物基准值. 结果显示：a）流域和季节的不同导致氨氮基准值的差异均很明显，不同流域的氨氮基准值差异可超过 6 倍，同一流域不同季节的氨氮基准值差异可超过 2 倍。 b)淮河流域夏季和非夏季氨氮基准值均为最低，夏季氨氮急、慢性基准值分别为 0.37 和 0.06 mg/L，非夏季分别为 0.81 和 0.15 mg/L。c) 氨氮暴露生态风险初步评估结果表明，珠江流域风险较小；松花江流域、辽河流域、长江流域次之；黄河流域风险较大；海河流域和淮河流域风险最大，海河 7 个断面中有 2 个存在高风险，淮河 27 个断面中 16 个存在高风险. 根据各流域不同季节氨氮基准值及氨氮暴露生态风险的差异，建议对不同流域、不同季节实行差异化管理。

关键词：七大流域；氨氮；水生生物基准；生态风险评估；风险商值法