Neglect of Temperature and pH Impact Leads to Underestimation of Seasonal Ecological Risk of Ammonia in Chinese Surface Freshwaters

Zhen-Guang Yan,1 Jun-Tao Fan,1 Xin Zheng,1 Shu-Ping Wang,1 Xiao-Shan Guo,1 Tian-Xu Zhang,1 Su-Wen Yang2, and Yi-Zhang Zhang1

1State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China
2National Engineering Laboratory for Lake Pollution Control and Ecological Restoration, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

Correspondence should be addressed to Su-Wen Yang; environzane@163.com and Yi-Zhang Zhang; zhangyz@craes.org.cn

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Ammonia nitrogen (AN) is evaluated with fixed water quality standards (WQSs) in aquatic environment management in China. Since the toxicity of AN can be influenced by water parameters, the current evaluation is not rigorous and may result in problematic conclusions. The present study collected the ecotoxicity and exposure data of AN in Chinese surface freshwaters in 2017. The species sensitivity distribution of AN was established, and the ecological risk posed by AN in Chinese surface waters was assessed with Chinese AN water quality criteria. The results showed that mollusk species are the most sensitive taxa to AN. Ecological risk assessments on AN suggested that, in summer and autumn, when the water temperature and pH are high, the risk of AN may occur at some sites with good water quality (Class II or III). This poses a threat to aquatic organisms at these sites, especially highly sensitive freshwater shellfish. It suggested that neglect of water parameters impact may lead to underestimation of ecological risk of AN in Chinese basins.

1. Introduction

Ammonia nitrogen (AN) is considered one of the most concerning pollutants in aquatic environment because of its high toxicity and ubiquity in surface water systems [1]. Ammonia nitrogen is one of the most common pollutants in all watershed basins within China [2]. With the exception of the compound pollution index and chemical oxygen demand (COD), ammonia nitrogen is the only pollutant monitored and evaluated by the Chinese government for management of nation-controlled pollution sources and pollution control [3]. Ammonia nitrogen is produced for commercial fertilizers and other industrial applications, including the use as a source of hydrogen in metal treating and finishing and many other uses [4]. Natural sources of ammonia nitrogen include the decomposition of organic matter, forest fires, biotic ammonia excretion, and nitrogen fixation [5–7].

Ammonia can enter aquatic environments via various pathways and can be highly toxic to aquatic life [8–10]; therefore, it has received considerable attention from scientists since the 1980s [11, 12]. The chemical form of ammonia in water consists of two species: the ammonium (NH₄⁺) molecule and the unionized ammonia (NH₃) molecule. The ratio of the two species in a given aqueous solution is dependent upon the pH and temperature of the solution [13, 14]. As pH and temperature increase, the concentration of NH₄⁺ decreases and the concentration of NH₃ increases. In general, the ratio of NH₃ to NH₄⁺ in freshwater increases by 10-fold for each rise of a single pH
unit and by approximately two-fold for each 10°C rise in temperature from 0 to 30°C [14]. The concentration of ammonia nitrogen is the sum of NH\textsubscript{3} and NH\textsubscript{4}\textsuperscript{+} concentrations, and it is often expressed as total ammonia nitrogen. The toxicity of NH\textsubscript{3} is significantly greater than NH\textsubscript{4}\textsuperscript{+} toxicity, so the hypothesis that NH\textsubscript{3} increases with pH and temperature explains why toxicity of total ammonia also increases as pH and temperature increase [15].

Ammonia nitrogen, particularly the NH\textsubscript{3}, have significant toxic effects on aquatic animals. For example, the toxic effects of ammonia on fish includes gill damage [16], reduction in blood oxygen-carrying capacity [1], interference in the ability of a fish to metabolize adenosine triphosphate [17], and disruption of normal metabolic function in the liver and kidneys [18]. In order to protect aquatic organisms from ammonia hazard, the United States Environmental Protection Agency (USEPA) studied ammonia aquatic life criteria (ALC) for several decades [15, 19]. In recent years, studies have addressed the effect of ammonia toxicity on bivalves [20], particularly in freshwater mussels within the family Unionidae [21–23]; the US EPA suggested that mollusk may be the most sensitive taxa to ammonia [15], and this should be considered sufficient for the establishment of ALC for AN [24]. Following this discovery, the USEPA updated the ALC technical report and criteria values for AN in 2013 [15]. In this report, the ammonia nitrogen ALC were described as functions with two independent variables, pH and temperature. Using this framework, North American mollusks can be given sufficient protection according using the latest ALC of AN. In addition, other countries have established their own ammonia nitrogen water quality standards, such as Australia and New Zealand [25], as well as Canada [6]. Since the toxicity of ammonia nitrogen varies with the temperature and pH of the water, the standard values of ammonia nitrogen in these countries are dependent on the water quality parameters.

In order to monitor and assess surface water quality, 145 national monitoring sites were set in Chinese surface freshwaters. The water quality was assessed by comparing the monitoring data with national water quality standards (WQSs). The current Chinese WQSs for surface freshwater are divided into five levels according to water body function classification [26]. For example, the freshwater WQSs for ammonia nitrogen were set as 0.15 mg/L (Class I), 0.5 mg/L (Class II), 1.0 mg/L (Class III), 1.5 mg/L (Class VI), and 2.0 mg/L (Class V) [26]. However, these WQSs values were assigned for all Chinese surface freshwater management; no water quality parameters were considered in the WQS establishment [26]. When compared to American WQSs, Chinese WQSs for ammonia nitrogen are not rigorous enough to assess the ecological risks posed by ammonia or to protect aquatic organisms.

The present study collected the ecotoxicity data and assessed the species sensitivity distribution (SSD) of AN and monitoring exposure data of AN in Chinese major basins in 2017. The ecological risk posed by AN in China surface freshwaters was evaluated using the previously derived ALC of AN, and the results can provide valuable information for water environmental management in China.

### 2. Materials and Methods

#### 2.1. Exposure and Toxicity Data Collection of Ammonia

Ammonia nitrogen exposure data for 145 sites in 2017 were collected weekly from surface freshwater quality monitoring reports [27]. Twenty basins (ten rivers and ten lakes) were included in the report (Figure 1).

Ammonia nitrogen ecotoxicity data were derived from both the USEPA ECOTOX database [28] and published literatures. The data were screened according to the USEPA ALC guidelines [29]. Unicellular animal toxicity data were eliminated. The toxicity test duration should be two days for Daphnia and chironomid larvae and four days for other aquatic animals. The accepted endpoints for an acute test are median lethal concentration (LC\textsubscript{50}) or median effect concentration (EC\textsubscript{50}), while the accepted endpoints for a chronic test are no observed effect concentration (NOEC) or 20% effect concentrations (EC\textsubscript{20}). Both of the NOEC and the EC\textsubscript{20} are acceptable chronic toxicity endpoints for ammonia according to the US ammonia criteria document [15]. For the same species, toxicity data of sensitive life stage take priority to data of the resistant life stage. The flow-through toxicity experiment data are prioritized over static or renewal experiment data, and the data produced by measuring chemical concentration are prioritized over data produced with the nominal level of chemicals. Finally, because the toxicity of ammonia can be affected by the pH and temperature of water bodies, published ammonia toxicity data that did not include pH and temperature information were abandoned.

#### 2.2. Toxicity Data Adjustment of Ammonia Nitrogen

Temperature and pH can affect the toxicity of ammonia nitrogen; all the toxicity data were adjusted to the same baseline conditions (pH 7.0, 20°C) before data analysis. The data adjustment was performed according to the USEPA ALC document of ammonia nitrogen with the equations (1) to (4) [15]:

\[
AV_{t,7} = \frac{AV_t}{((0.0114)/(1 + 10^{7.204-pH})) + (((1.6181)/(1 + 10^{pH-7.204}))}
\]

\[
\log(\text{AV}_{t,7}) = \log(\text{AV}_{t,7}) + 0.036(T - 20),
\]

\[
CV_{t,7} = \frac{CV_t}{((0.0278)/(1 + 10^{7.888-pH})) + (((1.1994)/(1 + 10^{pH-7.888}))}
\]

\[
\log(\text{CV}_{t,7}) = \log(\text{CV}_{t,7}) + 0.028(T - 20),
\]

where \(AV_t\) and \(CV_t\) were the acute and chronic toxicity values under the given temperature and pH, respectively. \(AV_{t,7}\) and \(CV_{t,7}\) were the adjusted acute and chronic values under pH of 7. \(AV_{t,7,20}\) and \(CV_{t,7,20}\) were the adjusted values under pH of 7 and temperature of 20°C, and \(T\) was temperature.
According to the document, the raw values under the given temperature and pH were transformed to an adjusted value under a pH of 7 for toxicity data of vertebrates or an adjusted value under a pH of 7 and temperature of 20°C for toxicity data of invertebrates. After adjustment, the SSD curve was established according to [30]. If the chronic ecotoxicity data are not sufficient, the acute-chronic ratio (ACR) method [15] will be used to transfer the acute data to chronic data.

2.3. Ecological Risk Assessment of Ammonia Nitrogen. The hazard quotients (HQs) method was used to assess the ecological risk of ammonia nitrogen. HQs are equal to the measured exposure concentration divided by the long-term ALC value derived in our previous study [31]. Ammonia nitrogen posed no significant risk to the environment if HQs are less than 1.0 [32]. The risk assessment was performed with exposure data in 2017 for all 145 sites (Figure 1).

The data were processed with Excel 2010 (Microsoft, USA), and the figures in this study were prepared with Origin 9.64 (OriginLab, USA) and Adobe Photoshop 8.0.1 (Adobe Systems, USA).

3. Results and Discussion

3.1. Variations of Water Parameters in Chinese Freshwater Basins. Water quality monitoring data in 2017 were collected for twenty basins. The pH and temperature data for these basins were compared, and significant differences were observed with a range of 6.06–9.79 in pH and −1 to 33.5°C in temperature (Figure 2). The highest water pH of several basins, including Songhua River, Haihe River, and Huaihe River, was greater than 9.0, while the highest water temperature of Huaihe River, Yangtze River, Zhujiang River, Southeast rivers, and Southwest rivers was greater than 30°C (Figure 2). According to the chemical equilibrium of ammonia in water, the higher the water pH and temperature is, the more toxic the ammonia becomes [15]. Therefore, the apparent differences in pH and temperature of the twenty basins produce tremendous uncertainty if we were to assess the ecological risk of ammonia without considering the water quality parameters in routine environmental management. Previous studies have also considered the influence of water parameters on ammonia toxicity when assessing the ecological risk of ammonia in Taihu Lake or the seven Chinese major basins [33, 34].

3.2. SSDs of Ammonia Nitrogen. A total of 565 acute ammonia nitrogen toxicity and 36 chronic ammonia nitrogen toxicity data points were collected by searching the literature (Supplemental Information Table S1). Seventy-six genus mean acute values (GMAVs) and 16 genus mean chronic values (GMCVs) of AN were obtained through calculation (Supplemental Information Table S2). The fish toxicity data set is more sufficient than other taxa with 30 GMAVs and 8...
The quantities of GMCVs were relatively insufficient. In order to obtain more ammonia nitrogen GMCVs to construct the SSD, we used the ACR method to transfer the species mean acute values (SMAVs) to species mean chronic values (SMCVs). The species mean ACR values were calculated by dividing the acute value (LC50 or EC50) with the chronic value (20% effect concentration, EC20) according to the methodology provided by the ALC guidelines [29] and the ammonia nitrogen ALC technical report released by the USEPA [15]. Generally, it is desirable to use species mean ACR in the transfer process. However, species mean ACR was not always available due to the scarcity of EC20 toxicity data. So, the alternative ACR values were genus mean ACR, family mean ACR, or phylum mean ACR in the descending priority order. The applied ACR values are shown in Supplemental Information Table S3, and total GMCVs, including the published GMCVs and the calculated ACR-based GMCVs, are shown in Supplemental Information Table S2.

All GMCVs were ranked in Figure 3. Among these 79 GMCVs, the top ten GMCVs in front were all mollusks. This suggests that mollusks are the most sensitive taxa to ammonia nitrogen. These results are consistent with the USEPA ALC technical report of ammonia nitrogen conclusions [15]. Besides mollusks, many fish species are also sensitive to ammonia nitrogen, while crustaceans and insects are relatively insensitive (Figure 3). This indicates that different organisms have different levels of sensitivity to ammonia nitrogen and results in different levels of ecological risk of ammonia nitrogen to varying organisms.

3.3. Chinese Water Quality Criteria of Ammonia Nitrogen

Study on water quality criteria is a new research hotspot in China in recent years [35–39]. Based on the sensitivity of Chinese freshwater organisms to ammonia nitrogen, we have proposed China’s ammonia nitrogen ALC function in the previous study [31]. The proposed short-term (CMC) and long-term (CCC) Chinese ammonia nitrogen criteria are shown in equations (5) and (6), respectively. It can be seen from the function equations that the temperature and pH of the water body are the independent variables of the two criteria functions. Therefore, the long-term and short-term criteria values of ammonia nitrogen vary with the temperature and pH of the water (Figure 4). In general, as the water temperature and pH increase, the water quality criteria value of ammonia nitrogen keeps decreasing. It suggests that when the water body temperature ranges from 0°C to 30°C, the pH value ranges from 6.5 to 9.0, and the
The difference between the water quality criteria values of ammonia nitrogen can be up to dozens of times:

\[
CMC = \left( \frac{0.0314}{1 + 10^{7.204 - \text{pH}}} + \frac{4.47}{1 + 10^{6.788 - \text{pH}}} \right) \times \text{MIN}(10.40, 6.018 \times 10^{0.0362(25 - T)}) \tag{5}
\]

\[
CCC = \left( \frac{0.0339}{1 + 10^{7.688 - \text{pH}}} + \frac{1.46}{1 + 10^{10\text{pH} - 7.688}} \right) \times \text{MIN}(2.852, 0.914 \times 10^{0.028(25 - \text{MAX(T,T)})}) \tag{6}
\]

3.4. Ecological Risk Assessment of AN. Using the derived Chinese ammonia nitrogen ALC equation (CCC), the ecological risk of ammonia nitrogen in 145 sites in Chinese surface water bodies was assessed. The results showed that the ecological risk of ammonia nitrogen was not significant at most sites, but for 20 sites with a seasonal mean pH of more than 8.5 (including 9 in summer and 11 in autumn), half (10) of the sites had excessive ammonia nitrogen concentrations, exceeding the CCC value to varying degrees. These sites include 1 site of Songhua River, 2 sites of Huaihe River, 1 site of Southwest Rivers, 3 sites of Dianchi Lake, and 1 site of Erhai Lake (Table 1).

In general, the ecological risk of ammonia nitrogen in Dianchi Lake is the most prominent. It is worth noting that, according to the current Chinese surface water quality standards, among the above 10 risk sites, the water quality of 8 is classified as Class II and of 2 is classified as Class III. They are considered to be “good” in China aquatic environment management.

In summary, in the summer and autumn, when the water temperature and pH are high (such as temperature greater than 30°C, pH is greater than 8.5), the risk of ammonia nitrogen may occur at a site with “good” water quality (Class II or III). This poses a threat to aquatic organisms at these sites, especially highly sensitive freshwater shellfish. In recent years, investigations on benthos in Dianchi Lake have also found that benthos in Dianchi Lake is sparsely single and species diversity is significantly reduced. The dominant species of benthos in Dianchi Lake have evolved from a variety of shellfish (such as *Semisulcospira* and *Radix*) to pollution-tolerant species (*Chironomus* and *Limnodrilus*) [40]. The increase of ammonia nitrogen ecological risk may be one of the important reasons for the decline of shellfish community in Dianchi Lake.

4. Conclusions

As the exclusive chemical monitored by the Chinese government for water environment pollution control, ammonia nitrogen is evaluated with current Chinese WQS for surface
freshwater in aquatic environment management. The present study assessed the ecological risk of ammonia in 2017 in twenty basins in China with developed Chinese ALC of AN. The results indicated that, in summer and autumn, when the water temperature and pH are high, the risk of ammonia nitrogen may occur at some sites whose water quality is typically considered good. It suggested that neglecting the influence of water parameters on TAN toxicity may bring serious risk to aquatic organisms, especially for sensitive mollusk species.

Data Availability

The TAN exposure data can be derived from the weekly monitoring reports on surface water quality in China on the website http://www.cnemc.cn/sssjszzjy/, and the other data used to support the finding of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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Supplementary Materials

Table S1: the acute and chronic toxicity data of ammonia. Table S2: GMAVs and GMCVs of ammonia. Table S3: ACRs of ammonia. (Supplementary Materials)

References

[23] N. Wang, R. J. Erickson, C. G. Ingersoll et al., “Influence of pH on the acute toxicity of ammonia to juvenile freshwater


