Chemosphere 202 (2018) 136–144

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Ecological risks posed by ammonia nitrogen (AN) and un-ionized ammonia (NH_3) in seven major river systems of China

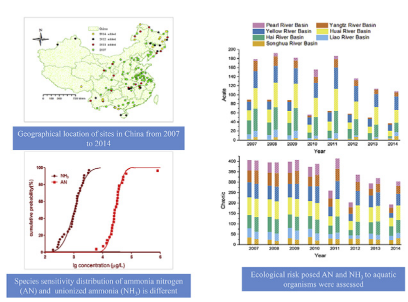
Li Zhang [a], Elvis Genbo Xu [b], Yabing Li [a], Hongling Liu [a,*], Doris E. Vidal-Dorsch [c], John P. Giesy [a,d,e]

[a] State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, Jiangsu 210023, China
[b] Department of Chemical Engineering, McGill University, Montreal, Quebec, H3A 0G4, Canada
[c] VDA LCS Consulting Services, Costa Mesa, CA 92626, USA
[d] Toxicology Center and Department of Veterinary Biomedical Sciences, University of Saskatchewan, Saskatoon, SK S7N 5B3, Canada
[e] School of Biological Sciences, University of Hong Kong, SAR, China

HIGHLIGHTS

- Ammonia nitrogen (AN) and un-ionized ammonia (NH_3) were investigated in seven river systems in China.
- Seasonal distributions of AN and NH_3 were different.
- The Hai, Huai, Yellow River Basin were more polluted than the others.
- NH_3 posed greater acute ecological risk than AN, while chronic risk posed by both were deemed to be great.
- Concentrations and risks of AN and NH_3 have been decreasing during recent years.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 August 2017
Received in revised form
3 March 2018
Accepted 15 March 2018
Available online 15 March 2018

Handling Editor: Jian-Ying Hu

Keywords:
Eutrophication
Nutrients pollution
Unionized-ammonia toxicity
Ecological risk assessment

ABSTRACT

Previous studies showed that continuous exposure to ammonia nitrogen (AN) contributed to regional losses of benthic invertebrate diversity in China. Yet, the overall ecological risk of AN to aquatic organisms in major riverine systems of China has not been appropriately studied. Our research then investigated temporal (seasonally/yearly) and spatial distributions of AN and un-ionized ammonia (NH_3) in major Chinese river basins using historic data generated between 2007 and 2014, and developed risk assessment criteria. Our results showed that the highest average AN concentrations occurred during winter (0.82–2.76 mg/L) and the lowest during summer (0.36–0.78 mg/L). NH_3 exhibited the opposite trend with the highest average concentrations mostly observed during spring (15.13–92.84 μg/L) and the lowest concentrations mainly during winter (10.53–45.43 μg/L). Both AN and NH_3 concentrations steadily increased and reached maximum levels in 2008 (AN: 1.22 mg/L and NH_3: 50.65 μg/L), and then decreased. Temporal trends showed that the Yellow, Hai, and Huai river basins had the highest AN and NH_3 concentrations. Subsequently, conventional (hazard quotients) and probabilistic (joint probability curves) methods were applied to assess the hazards and risks posed by AN and NH_3. The results showed

* Corresponding author.
E-mail address: hlliu@nju.edu.cn (H. Liu).

https://doi.org/10.1016/j.chemosphere.2018.03.098

that the probability of exceeding the acute toxicity threshold for 5% of species (exposed to AN or NH_3) was less than 13.3% and gradually decreased over time. To protect aquatic organisms, an acute criterion of 51.4 μg NH_3/L and a chronic criterion of 1.14 mg AN/L at pH = 7.5, 20 °C were developed and are recommended for future risk assessment studies.

1. Introduction

Ammonia nitrogen (AN) is very common in treated and untreated wastewater discharged into lakes and rivers through point and non-point sources (Constable et al., 2003; Armstrong et al., 2012). In freshwater systems, AN is composed of the ammonium ion (NH+ 4) and un-ionized ammonia (NH_3) that are normally found in equilibrium. Higher temperatures and pH increase the ratio of NH_3 to NH+ 4 (Mayes et al., 1986; USEPA, 1999). The study of environmental AN is important because it is known to adversely affect various kinds of aquatic organisms (USEPA, 1999), such as vertebrates (Armstrong et al., 2012), invertebrates (Mummert et al., 2003), algae (Kallqvist and Svenson, 2003), and microbes (Anthonisen et al., 1976), and these effects could alter the ecosystems' structure and function. Due to a rapid economic development in the past few decades, AN pollution in surface waters has become a common phenomenon, increasingly raising public concerns in China.

According to data provided by the Chinese Ministry of Environmental Protection (http://www.mep.gov.cn/hjzl/), annual emissions of AN exceeded 2.3 million tons between 2011 and 2014. Thus, environmental AN has become a major riverine contaminant in systems such as the Yellow and the Hai river basins (MEP, 2013). Previous research suggested that AN posed the highest risk of out of nine common contaminants to the Keelung River in Taiwan (Chen, 2005). Another assessment of the ecological risk posed by wastewater AN showed that 8% of the time NH_3 concentrations in Hamilton Harbor (Ontario, Canada) could cause 10% mortality to rainbow trout and 36% of the time NH_3 concentrations could cause a 20% reduction in reproduction or growth (Constable et al., 2003).

To protect aquatic organisms from exposure to AN, guidelines and criteria based on NH_3 or AN rather than NH+ 4 have been established around the world (USEPA, 1999; Constable et al., 2003). For example, Australian and New Zealand set a criterion of <30 μg/L NH_3 at pH 8.0 (warm-water) (ANZECC & ARMCANZ, 2000); while Canada and England have more rigorous standards of 19 and 15 μg NH_3/L (CCME, 2000; Johnson et al., 2007). To protect fish reproduction and food supplies, the Chinese government recommends a threshold of 20 μg NH_3/L for commercial fisheries (SEPA, 1989). China uses a 6-grade water quality classification. Grade-1 is the highest water quality, and water quality lower than grade-5 is not used for crop irrigation. Integrated AN wastewater discharge standards for most enterprises (excluding the dye and petrochemical industries) allow grade 3 and 4 water to enter the environment, representing 15 and 25 NH_3 mg/L concentrations (SEPA, 1998). Although AN wastewater concentrations are immediately diluted when discharged to receiving waters, NH_3 concentrations can still cause adverse effects on aquatic organisms, especially at higher pH (Passell et al., 2007). Recent research efforts have been initiated in China to evaluate AN ecological risk and to establish criteria (Yan et al., 2011; Wang et al., 2016c; Yang et al., 2017). However, little is known about country-wide AN and NH_3 concentrations and their associated risk to major river systems in China.

The seven major water systems in China are of the most economic and ecological importance, including the Songhua, Liao, Hai, Huai, Yellow, Yangtze, and Pearl Rivers, with a total drainage area of 4.4 million km^2 throughout the country. These river basins are known to be contaminated to various degrees by industry, urbanization, and agriculture (http://www.mep.gov.cn/hjzl/). Each river basin has unique geographical, hydrodynamic and physical characteristics, and their water quality is affected by local conditions (Qu and Fan, 2010; Wang et al., 2016a). The objectives of this study are: 1) To investigate seasonal, spatial and temporal AN and NH_3 concentrations in seven major Chinese rivers; 2) To derive acute and chronic NH_3 criteria based on sensitivities of aquatic species native to China; and 3) To apply a multi-tiered assessment (using deterministic and probabilistic methods) to assess the ecological risk of AN and NH_3.

2. Materials and methods

2.1. Exposure concentrations of AN and NH_3

Historical concentration values of AN in Chinese surface waters from 2007 to 2014 were collected from weekly reports from the Ministry of Environmental Protection of the People's Republic of China Data Center (http://datacenter.mep.gov.cn/). The total number of sites for which data were available for the period of 2007–2014, was 98, 98, 98, 98, 111, 131, 131 and 145, respectively (Supporting information Fig. S1).

Concentrations of NH_3 were calculated by use of the Henderson-Hasselbach relationship (Equations (1) and (2)) (USEPA, 1999, 2013).

$$f_{NH3} = 1/(1 + 10\hat{\ }(pK - pH)) \tag{1}$$

$$C(NH_3) = C(AN)^{*} f_{NH3} \tag{2}$$

where: pH = negative log10 of the hydrogen ion activity (-Log $[H^+]$); pK is the acid dissociation constant for water (Equation (3))

$$pK = 0.09018 + 2729.92/(273.2 + T) \tag{3}$$

where: T is water temperature in °C, which is derived from air temperature.

Values of pH were collected from weekly reports from the Ministry of Environmental Protection of the People's Republic of China Data Center (http://datacenter.mep.gov.cn/).

Measurements of air temperature at the main cities (including capital cities and independent municipalities) from 2007 to 2014 were collected from the China Statistical Yearbook (http://www.stats.gov.cn/tjsj/ndsj/). According to equations (1)–(3), pH was the most important NH_3 concentration factor when compared to water temperature. Also, water temperature was more stable relative to pH. Previous studies were conducted to test NH_3 prediction variations comparing air temperature- or water temperature-based methods, suggesting that monthly air temperatures can be used to derive water temperatures for NH_3 prediction (Erickson and Stefan, 1996; Mohseni and Stefan, 1999). Therefore, we used air temperatures at the sampling sites to calculate corresponding water temperatures (Equations (4) and (5)).

$$T_{water} = 0(-20^{\circ}C \leq T_{air} \leq 0^{\circ}C,) \quad (4)$$

$$T_{water} = 0.898\ T_{air} + 3.47T_{air} + 3.47(T_{air} > 0^{\circ}C,) \quad (5)$$

where: T_{air} is the air temperature, T_{water} is water temperature.

Concentrations of AN were converted to concentrations of NH_3 (Equations (1)–(3)). Concentrations of AN and NH_3 did not meet assumptions of normality and homogeneity of variance, so the Mann-Whitney, a non-parametric test was used to compare concentrations among years and river basins. (Origin Lab; version 2015; www.originlab.com).

2.2. Toxicity data and generation of species sensitivity distribution (SSD)

Toxic potency and sensitivity data for aquatic organisms to AN were collected from the U.S. Environmental Protection Agency (USEPA) database (USEPA, 2013) and the CNKI database (http://www.cnki.net/). Data were screened to ensure that they met a number of requirements, such as exposure duration(s) and testing methods (Stephan et al., 1985), and whether the selected species were endemic to China. Toxicity data, expressed as AN, were converted to NH_3, based on pH and temperature.

Additional toxicity values were collected from the peer-reviewed literature. Lethal or effect concentrations affecting 50% of the test population (LC_{50} or EC_{50}) values were selected as acute measurement endpoints. Chronic toxicity data were limited, so acute to chronic ratios (ACRs) were used to derive a chronic criterion for NH_3. According to USEPA methods (Stephan et al., 1985), data on the toxicity of NH_3 to *Daphnia magna, Cyprinus carpio,* and *Lepomis macrochirus* were used to derive ACRs (USEPA, 2013). Genus mean acute values (GMAV) were used to construct a species sensitivity distribution (SSD) (Wheelera et al., 2002) and then fitted with three parametric regression models (log-normal, log-logistic and Weibull) to derive an acute criterion.

The Kolmogorov-Smirnov (K-S) test was applied to determine whether log-transformed data were consistent with a normal distribution ($p > 0.05$ means normal distribution). Relative goodness of fit for three models was tested using the Akaike Information Criterion (AIC). Smaller values of AIC indicated better goodness of fit (Bozdogan, 1987). Values for protecting 95% species from effects (HC_5) and its 95% confidence intervals were derived from the regression model with the minimum AIC value. Considering the choice of species and reduction of uncertainty, the acute criterion was obtained by dividing the HC_5 of the model by an application factor (safety factor) of 5.0 (Jin et al., 2014). Toxicity data for AN were collected from Yan et al. (2011). All statistical analyses were conducted with R software (R Development Core Team, http://www.rproject.org/).

2.3. Assessment of ecological risk posed by an and NH_3

The risk that AN and NH_3 pose to the ecosystems can be assessed by comparing their environmental concentrations to criteria developed to provide various protection levels (Solomon et al., 2000). Criteria can be derived from concentrations that produce effects such as mortality, impaired growth, or reproduction in different species (Calow and Forbes, 2003; Malaj et al., 2014). Probabilistic ecological risk assessments (PERAs) consider both uncertainty of exposure and distributions of effects (Solomon et al., 2000) and have been applied to a number of studies to account for actual concentration variability in surface waters and to quantify effects on ecological structure or function (Wang et al., 2009; Jin et al., 2014; Liu et al., 2016).

A deterministic approach (hazard quotients, HQs) was calculated (Equation (6)) to describe potential adverse effects of AN and NH_3 in seven river basins. By comparing proportions of HQ in each category: $HQ \geq 1$ (Greater effect), $0.3 < HQ < 1$ (Lesser effect), $HQ \leq 0.3$ (*De minimis* effects) (Jin et al., 2015a), the year and river basin with the greatest proportion of HQs exceeding 0.3 for AN and NH_3 were identified.

$$HQ = \frac{MEC}{acute\ (chronic)\ \ criteria} \quad (6)$$

Measured Environmental Concentrations (MEC) of AN at each location were compared to acute and chronic criteria for AN (Yan et al., 2011), which were based on toxicity data of species endemic to China. Subsequently, the MEC of NH_3 were compared to criteria derived from this study (Section 2.2).

Joint probability curves (JPC) and areas under the JPC were used to describe risk by comparing probabilities of exposure and effect of AN and NH_3 using the Probabilistic Risk Assessment Tool (PRAT) (Solomon et al., 2000). The closer the joint probability curve was to the axes, the less the joint risk of exposure and effects (Solomon et al., 2000). The shapes of joint probability curves were used to determine the relative-contribution-probability contributed by exposure and response aspects of the probabilistic assessment. The area under the curve gave an overall estimate of the joint probability for adverse effects. The risk was directly proportional to the joint probability, which was a function of exposure probability and effects.

3. Results and discussion

3.1. Seasonal variation of AN and NH_3

When comparing the seasonal concentrations, the highest average AN concentrations were observed during winter, while the lowest concentrations were found during summer. The average AN concentrations in winter ranged from 0.82 mg/L (2014) to 2.76 mg/L (2008), while in summer the average AN concentrations ranged from 0.36 mg/L (2014) to 0.78 mg/L (2008). A summary of all the average concentrations can be found in Fig. 1 and in the Supporting Information, Table S1.

Reduced metabolism of nitrifying bacteria due to lower temperature, as well as reduced dilution of wastewater due to lower river water level in winter (dry season) could contribute to the higher concentrations of AN in winter over summer (Siripong and Rittmann, 2007; Cho et al., 2014). In contrast, during summer (wet season) the AN concentration might be diluted by the large amounts of precipitation which seems to be corroborated by our results and those of other studies (Chen et al., 2004). A similar seasonal AN concentration distribution pattern was previously observed in the Wei River (Wang et al., 2016b). The result of other researchers showed that besides natural factors such as rainfall and water, temperature, anthropogenic factors such as nitrogen-containing wastewater, and runoff fertilizers could also influence seasonal AN concentration patterns (Gong et al., 2015; Wang et al., 2016b; Rattan et al., 2017).

The NH_3 concentrations also varied seasonally. The highest average NH_3 concentrations were mostly observed during spring (15.13 μg/L in 2014 to 92.84 μg/L in 2008), while the lowest NH_3 concentrations were observed mainly during winter (10.53 μg/L in 2014 to 45.43 μg/L in 2008; Fig. 1 and Supporting Information Table S2). The main reason for such seasonal distributions of NH_3 concentrations could be the higher temperatures and pH levels during spring than in winter. In addition, higher temperatures could enhance algae growth rates and increase AN consumption as

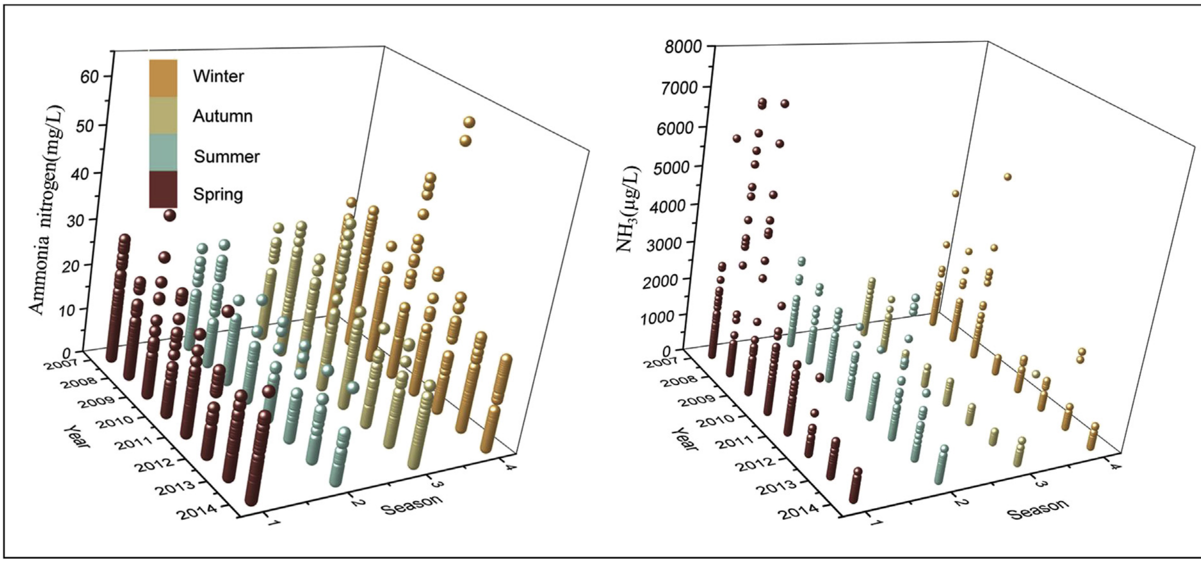


Fig. 1. Seasonal variability of concentrations of AN and NH3. Seasonal values were taken between the years 2007–2014.

a nitrogen source. Such changes seem to have resulted in higher pH (Constable et al., 2003) and decreased AN concentrations at the same time. A previous study showed that high spring NH_3 concentrations (and sometimes during the summer) increased toxicity levels and also led to river eutrophication (Chen et al., 2010). The seasonal AN and NH_3 variability highlight the need to seasonal AN control and management.

3.2. Temporal variations of AN and NH_3

Concentrations of AN and NH_3 gradually increased with the highest concentrations observed during 2008, and then decreased. The average concentrations of AN and NH_3 were 1.22 mg/L and 50.65 μg/L in 2008. The lowest AN and NH_3 average concentrations were observed in 2014 and the values were 0.55 mg/L and 14.13 μg/L (Supporting Information Table S3–S4). The concentrations of AN in 2007 and 2009 were not significantly different from those in 2008, while in other years, the concentrations of AN were significantly lower ($p < 0.05$) than those observed in 2008 (Fig. 2). Unlike AN, NH_3 concentrations measured in other years were all significantly lower than those measured in 2008.

Such general decreasing trends of AN and NH_3 could be explained by multiple factors. First, the 11th Five-Year Plan in China considered AN emissions a primary contaminant of concern in some river basins (MEP, 2009, 2010). Aiming to improve the deteriorating water environment, the Chinese government later promulgated additional policies to reduce AN emissions by 10% during the 12th Five-Year Plan (State Council, 2012). In order to meet the emissions target, central and regional governments established and updated sewage treatment facilities. In addition, the central and regional governments also took actions to reduce AN contamination caused by agricultural practices, especially in the livestock and poultry industries (State Council, 2011). Furthermore, the result of the structural decomposition analysis showed that the same measures adopted during the 11th Five-Year Plan, including improving end-of-pipe abatement efficiency and phasing out of less advanced treatment, could address industrial wastewater emissions caused by economic growth during 12th Five-Year Plan (Zhang et al., 2015).

3.3. Spatial variation of AN and NH_3

The highest average concentrations of AN and NH_3 were observed in Hai river basin, followed by those in the Yellow and Huai river basins (Fig. 3). Average AN concentrations in the Hai river basin ranged from 0.55 to 2.27 mg/L and the NH_3 averaged from 11.74 to 186.47 μg/L. The relatively higher concentrations in the Hai river basin were likely associated with its greater urbanization. It was estimated that 45% in this area was urbanized with a population of 145 million (Wang et al., 2014). The large AN load discharged into the Hai river basin has become a major water quality control concern (Wang et al., 2014). In addition, relatively high pH in the Hai river basin, which ranged 7.67–8.54 between 2001 and 2010 (Peng et al., 2015), resulted in greater NH_3 concentrations.

Similarly, the Yellow river basin is also an area of high urbanization. Previous studies indicated that wastewater and fertilizer runoff could be major AN sources (Xia et al., 2001; Chen et al., 2004; Gong et al., 2015). Average NH_3 concentrations ranged from 20.14 to 65.87 μg/L in the Yellow river basin. The pH values in the Yellow river basin were relatively high could have also contributed to the high NH_3 concentrations.

Average AN concentrations in the Huai river basin ranged from 0.85 to 2.74 mg/L. These concentrations pattern were similar to those found in previously published results (Yang et al., 2016). The main AN contributors in the Huai river basin were likely concentrated animal feedlot operations (CAFOs) and sewage treatment plants (STPs) (Yang et al., 2016). The large spatial variability of AN and NH_3 concentrations in the different river basins strengthens the need for regional governments to develop regional plans and management strategies, and to identify and control the major local pollution sources.

3.4. Assessment of potential toxicity of NH_3

A total of 32 toxicity data sets were selected for the assessment of acute effects. The most sensitive genus to acute NH_3 effects was *Siniperca* (fish). The most tolerant genus was *Gobiocypris* (fish; Supporting Information Tables S5–S6). NH_3 fish toxicity could cause: an abnormal proliferation of gill tissues (Lang et al., 1987), ATP cycle suppression in brain and weakened immune system

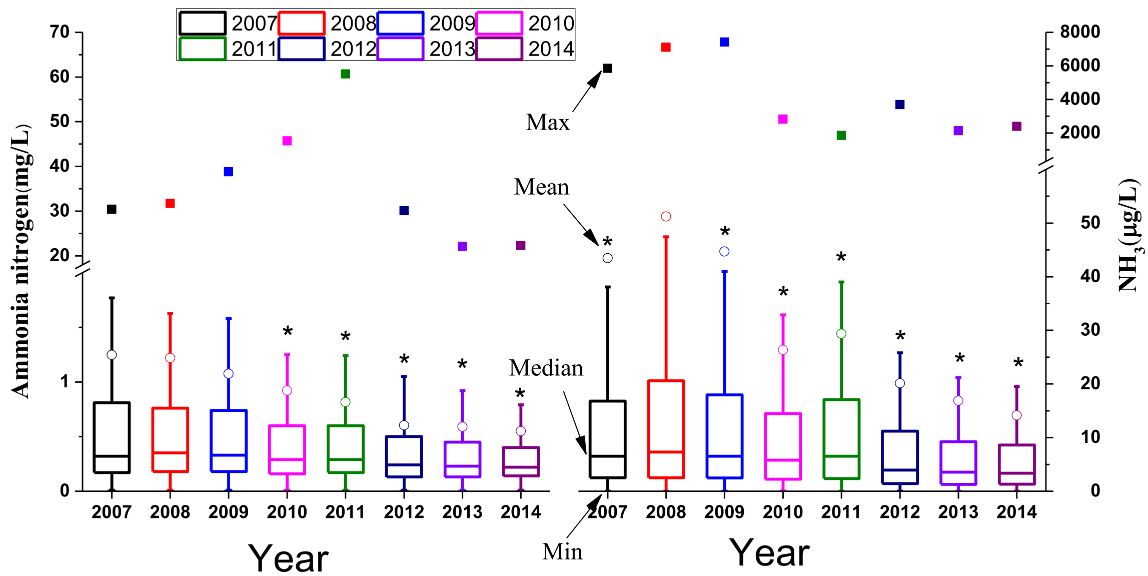


Fig. 2. Concentrations of AN and NH3 in seven major river systems of China from the years 2007–2014. The analysis was conducted using the Mann-Whitney test. The 2008 data was used as control group for AN and NH3, ("*" $p < 0.05$). Boxplots represented the concentration distribution of AN and NH3 from 2007 to 2014. Error bars represented the lowest datum still within 1.5 interquartile range of the lower quartile, and the highest datum still within 1.5 interquartile of the upper quartile.

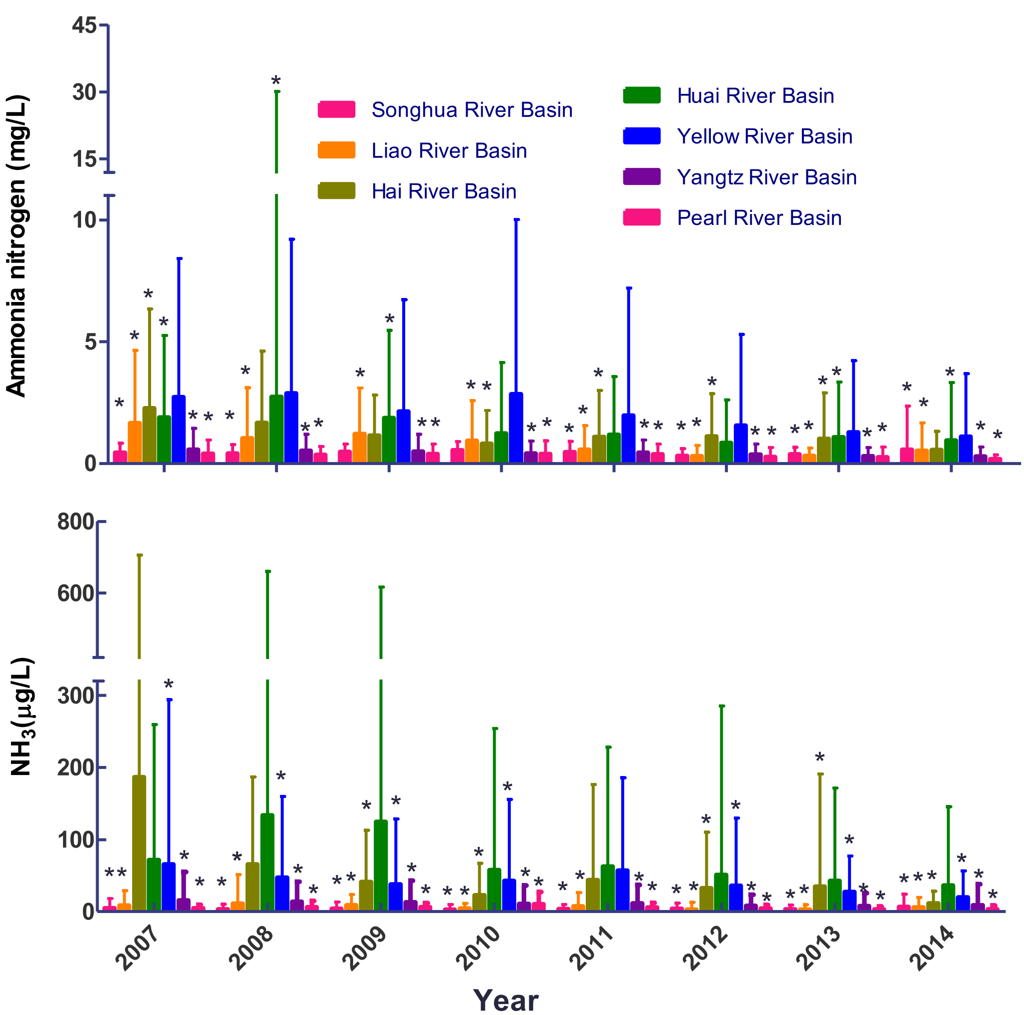


Fig. 3. Average AN and NH3 concentrations and standard deviations by year. Colors represented the seven riverine systems investigated in this study. Average were tested using the Mann- Whitney test. The Yellow river basin data was used as the control group for AN analysis. For NH3 Huai river basin data were used because it had the greatest average concentration. "*" represented a difference between average values ($p < 0.05$). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Goodness of fit for three models and thresholds (HC5) with 95% confidence intervals for acute toxicity data.

Model	AIC	K-S test for normality	HC_5 with 95% CI (μg/L)	Acute criterion (μg/L)
log-logistic	22.67	0.8633	295.12(186.21–478.63)	NO
log-normal	21.53	0.699	292.42(199.53–446.68)	NO
Weibull	19.27	0.9918	257.04(165.96–426.58)	51.41

defenses (Camargo and Alonso, 2006), and the disturbance of the energy metabolism pathway equilibrium via activation of N-methyl-Daspartic acid (NMDA) receptors in the central nervous system (Randall and Tsui, 2002), among other adverse effects.

Three statistical models (Log-logistic, Log-normal, and Weibull) were used to construct the SSDs based on acute lethality. The Weibull model resulted in the smallest AIC value (18.27), compared to 22.67 (Log-logistic) and 21.53 (Log-normal), which was selected to calculate acute criterion (Table 1 and Support Information Fig S2). The ACR analysis data used to calculate the chronic criterion can be found in the Supporting Information (Table S6). Acute and chronic criteria for NH_3 to protect aquatic organisms were 51.4 μg/L and 13.6 μg/L, respectively. These criteria were lower than the criteria (acute: 118.0 μg/L, chronic: 45.9 μg/L) previously derived by other researchers (Li et al., 2017). However, the acute and chronic values were higher than the long-term predicted no-effect concentrations (acute: 6.8 μg/L, chronic: 1.1 μg/L) proposed by the European Chemicals Bureau (Johnson et al., 2007). Considering the specific sensitivities of organisms (Wu et al., 2010; Jin et al., 2015b), NH_3 criteria only derived with Chinese species could better protect native organisms from AN exposure.

Variations among water quality parameters of the river basins investigated in this study might have resulted in different spatial AN concentrations, as well as different toxicity levels (Wang et al., 2016c). Therefore, in the present study, a site-specific criterion for AN was derived for each of the seven river basins, taking into account pH and temperature values at each sampling site as stated in the methodology section. The site-specific criteria were design to be protective of aquatic organisms inhabiting in specific rivers (Yan et al., 2011).

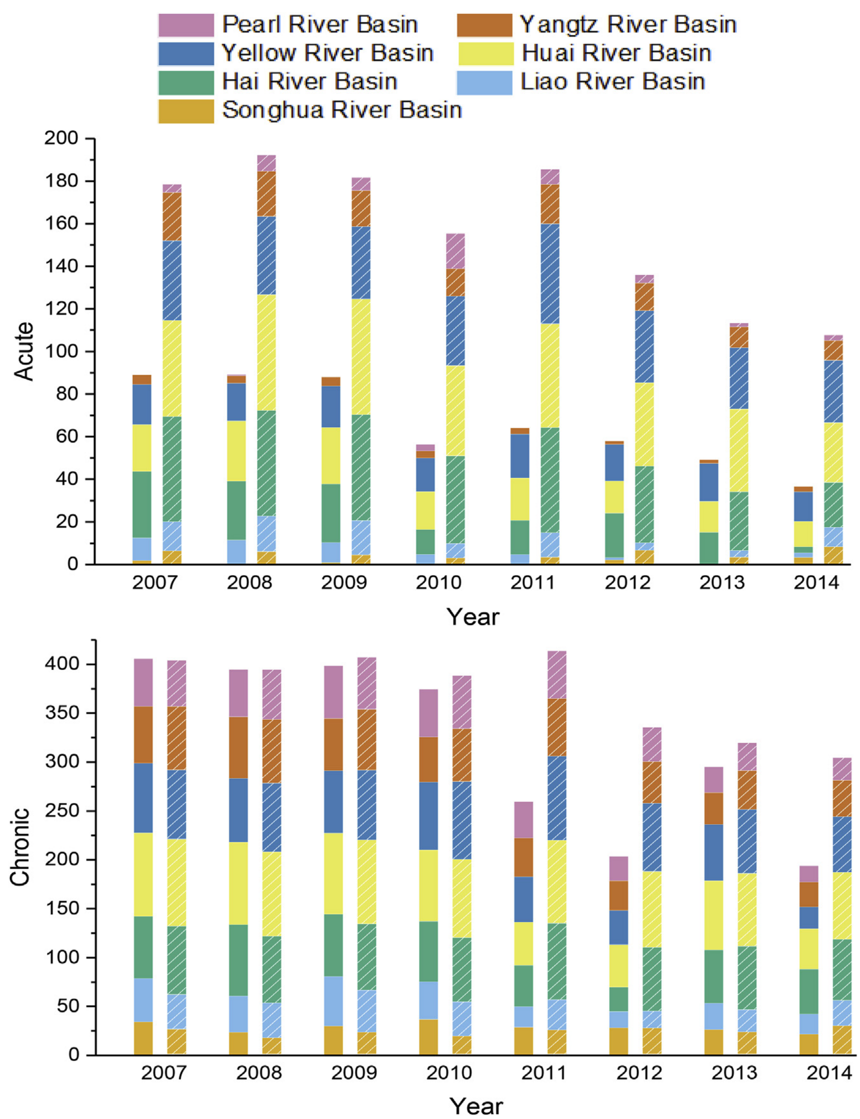


Fig. 4. Proportions of samples with acute and chronic hazard (HQ > 0.3) of AN and NH3 in the studied rivers. Data are shown yearly from 2007 to 2014 (the histogram with white diagonal lines represents NH3).

3.5. Ecological risks posed by an and NH_3

A multi-tier ecological risk assessment of AN and NH_3 was conducted using deterministic (HQ) and probabilistic methods. The result of such analysis showed that up to 32.5% of samples from the Hai river basin in 2007 and 54.3% of samples from the Huai river basin in 2008 had acute HQ > 0.3 due to AN or NH_3 exposure (Fig. 4). Data samples with chronic HQ > 0.3 ranged from 16.5% in the Pearl river basin to 85.3% in the Huai river basin for AN, 16.4% in the Songhua river basin to 89.1% in the Huai river basin for NH_3. Furthermore, probabilities of acute lethality due to exposure to AN or NH_3 were calculated. The results showed that the probability of exceeding the acute toxicity threshold for 5% of species exposed to AN and NH_3 were <13.3%. In fact, such probability gradually decreased from 13.3% to 0.0001% between the years 2007–2014 for AN and from 10.4% to 0.02% for NH_3 (Fig. 5).

Acute HQs resulting from NH_3 were generally higher than those of AN, although similar chronic HQs were observed for NH_3 and AN across China (Fig. 4). This could be due to the lower acute toxicity potency of AN comparing to that of NH_3 (Kallqvist and Svenson, 2003; Alonso and Camargo, 2004). The concentrations of NH_3 can fluctuate within few hours due to varying temperature and pH, which led to a rapidly changing toxicity of NH_3 in the environment (Maltby, 1995). It was known that acute exposures to very low concentrations of NH_3 could still result in cumulative adverse effects, depending on the inter-exposure period and whether that period of exposure was sufficiently long to allow the repair of damage by regeneration of α-keto-glutarate in the brain (Mitz and Giesy, 1985; Milne et al., 2000). In this study, the acute criterion of 51.4 NH_3 μg/L is recommended for use when assessing acute AN risk and a chronic criterion of 1.14 mg AN/L at pH = 7.5, 20 °C is recommended for assessing chronic AN effects.

Among the investigated river basins, the potential adverse effects in the Hai, Huai, and Yellow river basins were greater than those of the Songhua, Yangtze, and Pearl river basins. The higher risks caused by AN and NH_3 in the Hai, Huai and Yellow river basins were the result of higher AN concentrations. The AN and NH_3 risks identified by the present study highlighted the need for regional and season-specific management of AN. The decreasing AN and NH_3 concentrations over years was consistent with the results of the HQ analysis, suggesting an improving water quality of the major rivers. Results of this multi-tier risk assessment confirmed that the HQ method can readily screen the chemicals that have potential adverse effects on organisms, and probabilistic approaches can refine the assessment to better inform the decision-makers.

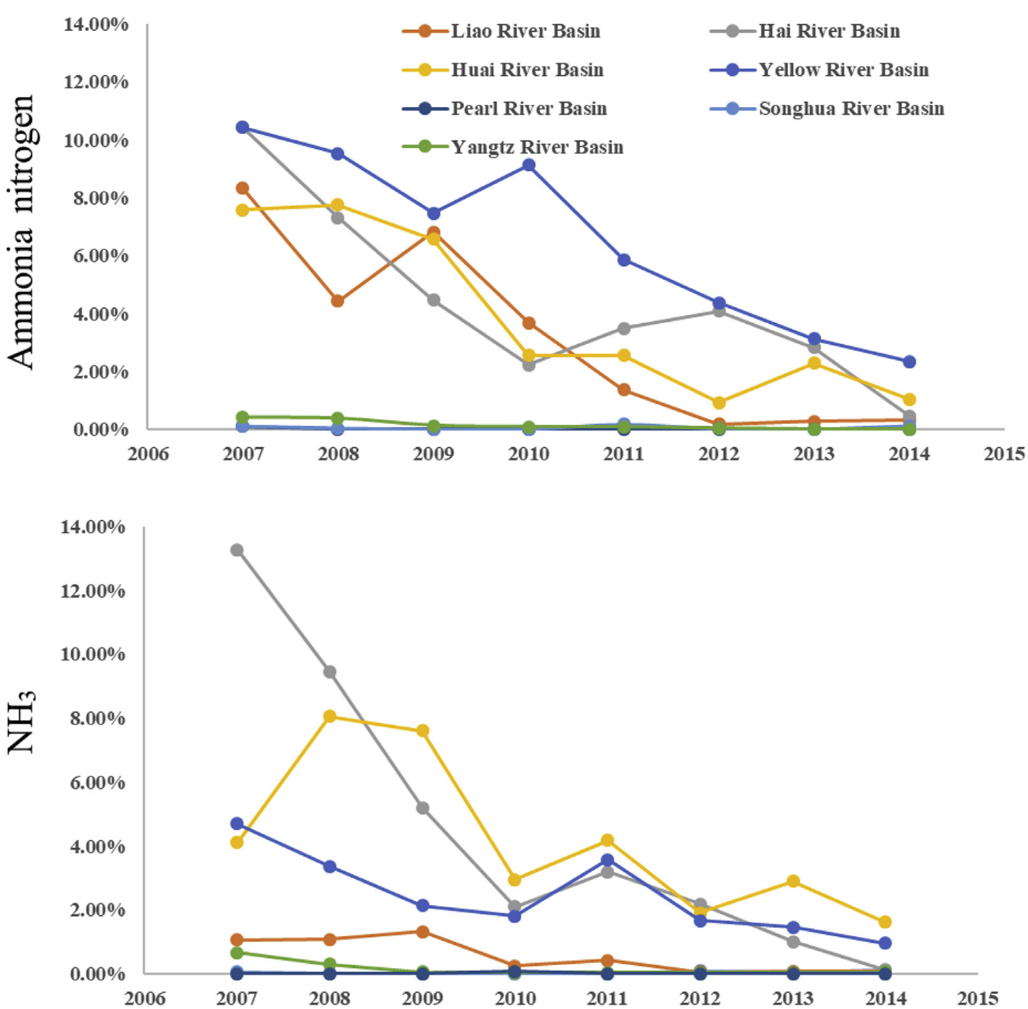


Fig. 5. Probabilities of exceeding the acute toxicity threshold for 5% of species exposed to AN or NH3 in seven Chinese rivers, the data represent values from the years 2004–2015.

3.6. Uncertainty analysis

In the present study uncertainties in risk assessment were mainly associated with the representativeness of data for the toxic potency of various species to NH_3 and systematic errors in measuring or predicting NH_3 concentrations. Although species native to China were considered to better representing the regional situation, the species chosen could not fully represent the target community to protect. Because a limited number of species were used in developing the SSDs, the resolution of the criterion to protect species was less than ideal. Another limitation was that toxicity values used for risk calculations were derived from laboratory toxicity tests, which might not realistically mimic the acclimations and adaptations of wild animals (Maltby, 1995; Dehedin et al., 2013), although an application factor of 5.0 was used to reduce the uncertainty to some extent (Jin et al., 2014).

Systematic errors such as measuring instruments accuracy and methods also existed. Limited knowledge and information included the interactions among organisms and limited monitoring equipment. In addition, surface water temperatures at sampling sites were not available from the original water quality reports, thus they were translated from air temperatures for corresponding sites. Furthermore, nitrogenous contaminants, such as nitrites, could also have influenced AN and NH_3 concentrations through biotransformation (Luo et al., 2016).

4. Conclusions

Concentrations distributions and ecological risks of AN and NH_3 to aquatic organisms native to China were investigated in seven major river systems of China from the years 2007–2014. The highest AN seasonal concentrations were observed during winter, while the highest NH_3 concentrations were observed during the spring in most years. The average yearly concentrations AN and NH_3 were found the highest between the years 2007 and 2008 and started to decrease in the year 2011. The Hai, Yellow and Huai river basins had the highest AN and NH_3 concentrations and associated hazards. Risk assessments indicated low acute risks of AN and NH_3 exposures. However, the chronic risks of AN and NH_3 were both high, suggesting a high likelihood of adverse effects on native aquatic organisms after long-term exposure to AN in all the studied rivers. An acute criterion of 51.4 μg NH_3/L and chronic criterion of 1.14 mg AN/L at pH = 7.5, 20 °C are recommended to protect aquatic organisms from the adverse effects posed by AN.

Acknowledgments

This work was co-financially supported by the National Natural Science Foundation (No. 21677073 and 21377053). Prof. Giesy was supported by the "High Level Foreign Experts" program (#GDT20143200016) funded by the State Administration of Foreign Experts Affairs, the P.R. China to Nanjing University and the Einstein Professor Program of the Chinese Academy of Sciences. He was also supported by the Canada Research Chair program and a Distinguished Visiting Professorship in the School of Biological Sciences of the University of Hong Kong.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2018.03.098.

References

ANZECC, ARMCANZ, 2000. National water quality management strategy paper No. 4. Australian and New Zealand environment and conservation Council and agriculture and resource management Council of Australia and New Zealand, canberra, Australia. Australian and New Zealand Guidelines for Fresh and Marine Water Quality 1, 1–314.
Alonso, A., Camargo, J.A., 2004. Toxic effects of unionized ammonia on survival and feeding activity of the Freshwater Amphipod Eulimnogammarus toletanus (*Gammaridae, Crustacea*). Bull. Environ. Contam. Toxicol. 72, 1052–1058.
Anthonisen, A.C., Loehr, R.C., Prakasam, T.B., Srinath, E.G., 1976. Inhibition of nitrification by ammonia and nitrous acid. Water Pollut Control Fed 48, 835–852.
Armstrong, B.M., Lazorchak, J.M., Murphy, C.A., Haring, H.J., Jensen, K.M., Smith, M.E., 2012. Determining the effects of ammonia on fathead minnow (*Pimephales promelas*) reproduction. Sci. Total Environ. 420, 127–133.
Bozdogan, H., 1987. Model selection and Akaike's information criterion (AIC): the general theory and its analytical extensions. Psychometrika 52, 345–370.
Calow, P., Forbes, E.V., 2003. Peer reviewed: does ecotoxicology inform ecological risk. Environ. Sci. Technol. 37, 146A–151A.
Camargo, J.A., Alonso, A., 2006. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: a global assessment. Environ. Int. 32, 831–849.
CCME, 2000. Canadian water quality guideline for the protection of aquatic life ammonia. In: Canadian Environmental Quality Guidelines, 2000. Canadian Council of Ministers of the Environment, Winnipeg, Canada, pp. 1–8.
Chen, C.S., 2005. Ecological risk assessment for aquatic species exposed to contaminants in Keelung River, Taiwan. Chemosphere 61, 1142–1158.
Chen, J.S., He, D.W., Zhang, N., Cui, S.B., 2004. Characteristics of and human influences on nitrogen contamination in Yellow river system, China. Environ. Monit. Assess. 93, 125–138.
Chen, G., Cao, X., Song, C., Zhou, Y., 2010. Adverse effects of ammonia on nitrification process: the case of Chinese shallow freshwater lakes. Water Air Soil Pollut. 210, 297–306.
Cho, K.H., Kim, J.O., Kang, S., Park, H., Kim, S., Kim, Y.M., 2014. Achieving enhanced nitrification in communities of nitrifying bacteria in full-scale wastewater treatment plants via optimal temperature and pH. Sep Purif Technol 132, 697–703.
Constable, M., Charlton, M., Jensen, F., McDonald, K., Craig, G., Taylor, K.W., 2003. An ecological risk assessment of ammonia in the aquatic environment. Hum. Ecol. Risk Assess. 9, 527–548.
Dehedin, A., Piscart, C., Marmonier, P., 2013. Seasonal variations of the effect of temperature on lethal and sublethal toxicities of ammonia for three common freshwater shredders. Chemosphere 90, 1016–1022.
Erickson, T.R., Stefan, H.G., 1996. Correlation of Oklahoma Stream Temperatures with Air Temperatures. Project Report 398. St. Anthony Falls Laboratory, University of Minnesota, Minneapolis, Minnesota.
Gong, Y., Yu, Z., Yao, Q., Chen, H., Mi, T., Tan, J., 2015. Seasonal variation and sources of dissolved nutrients in the Yellow river, China. Int. J. Environ. Res. Publ. Health 12, 9603–9622.
Jin, X., Wang, Y., Jin, W., Rao, K., Giesy, J.P., Hollert, H., Richardson, K.L., Wang, Z., 2014. Ecological risk of nonylphenol in China surface waters based on reproductive fitness. Environ. Sci. Technol. 48, 1256–1262.
Jin, X., Liu, F., Wang, Y., Zhang, L., Li, Z., Wang, Z., Giesy, J.P., Wang, Z., 2015a. Probabilistic ecological risk assessment of copper in Chinese offshore marine environments from 2005 to 2012. Mar. Pollut. Bull. 94, 96–102.
Jin, X., Wang, Z., Wang, Y., Lv, Y., Rao, K., Jin, W., Giesy, J.P., Leung, K.M., 2015b. Do water quality criteria based on nonnative species provide appropriate protection for native species? Environ. Toxicol. Chem. 34, 1793–1798.
Johnson, I., Sorokin, N., Atkinson, C., Rule, K., Hope, S.J., 2007. Proposed EQS for Water Framework Directive Annex VIII Substances Ammonia (Un-ionised). Science Report.
Kallqvist, T., Svenson, A., 2003. Assessment of ammonia toxicity in tests with the microalga, Nephroselmis pyriformis, Chlorophyta. Water Res. 37, 477–484.
Lang, T., Peters, G., Hoffmann, R., Meyer, E., 1987. Experimental investigations on the toxicity of ammonia - effects on ventilation frequency, growth, epidermal mucous cells, and gill structure of rainbow-trout Salmo-Gairdneri. Dis. Aquat. Organ 3, 159–165.
Li, Y., Xu, E.G., Liu, W., Chen, Y., Liu, H., Li, D., Liu, Z., Giesy, J.P., Yu, H., 2017. Spatial and temporal ecological risk assessment of unionized ammonia nitrogen in Tai Lake, China (2004–2015). Ecotoxicol. Environ. Saf. 140, 249–255.
Liu, N., Wang, Y., Yang, Q., Lv, Y., Jin, X., Giesy, J.P., Johnson, A.C., 2016. Probabilistic assessment of risks of diethylhexyl phthalate (DEHP) in surface waters of China on reproduction of fish. Environ. Pollut. 213, 482–488.
Luo, S., Wu, B., Xiong, X., Wang, J., 2016. Short-term toxicity of ammonia, nitrite, and nitrate to early life stages of the rare minnow (Gobiocypris rarus). Environ. Toxicol. Chem. 35, 1422–1427.
Malaj, E., von der Ohe, P.C., Grote, M., Kuhne, R., Mondy, C.P., Usseglio-Polatera, P., Brack, W., Schafer, R.B., 2014. Organic chemicals jeopardize the health of freshwater ecosystems on the continental scale. Proc. Natl. Acad. Sci. U. S. A 111, 9549–9554.

Maltby, L., 1995. Sensitivity of the crustaceans Gammarus pulex (L.) and Asellus aquaticus (L.) to short-term exposure to hypoxia and unionized ammonia: observations and possible mechanisms. Water Res. 29, 781–787.

Mayes, M.A., Alexander, H.C., Hopkins, D.L., 1986. Acute and chronic toxicity of ammonia to freshwater fish: a site-specific study. Environ. Toxicol. Chem. 5, 437–442.

MEP, 2009. Ministry of Environmental Protection. Annual Statistic Report on Environment in China 2009 (in Chinese). China Environmental Science Press, Beijing.

MEP, 2010. Ministry of Environmental Protection. Why We Should Control Ammonia Nitrogen in 12th Five-year Plan? http://www.mep.gov.cn/xxgk/hjyw/201003/t20100315_186841.shtml (in Chinese).

MEP, 2013. Ministry of Environmental Protection. Annual Statistic Report on Environment in China 2013 (in Chinese). China Environmental Science Press Beijing.

Milne, I., Seager, J., Mallett, M., Sims, I., 2000. Effects of short-term pulsed ammonia exposure on fish. Environ. Toxicol. Chem. 19, 2929–2936.

Mitz, S.V., Giesy, J.P., 1985. Sewage effluent biomonitoring. II. Biochemical indicators of ammonia exposure in channel catfish. Ecotoxicol. Environ. Saf. 10, 40–52.

Mohseni, O., Stefan, H.G., 1999. Stream temperature air temperature relationship: a physical interpretation. J. Hydrol. 218, 128–141.

Mummert, A.K., Neves, R.J., Newcomb, T.J., Cherry, D.S., 2003. Sensitivity of juvenile freshwater mussels (*Lampsilis fasciola, Villosa iris*) to total and un-ionized ammonia. Environ. Toxicol. Chem. 22, 2545–2553.

Passell, H.D., Dahm, C.N., Bedrick, E.J., 2007. Ammonia modeling for assessing potential toxicity to fish species in the Rio Grande. Ecol. Appl. 17, 2087–2099.

Peng, S.T., Wang, A., Wang, X.L., Zhou, R., Zhang, J.F., Liu, Z.Y., 2015. The long-term variations of water quality in the haihe river, China. Fresenius Environ. Bull. 24, 873–880.

Qu, J.H., Fan, M.H., 2010. The current state of water quality and technology development for water pollution control in China. Crit. Rev. Environ. Sci. Technol. 40, 519–560.

Randall, D.J., Tsui, T.K.N., 2002. Ammonia toxicity in fish. Mar. Pollut. Bull. 45, 17–23.

Rattan, K.J., Corriveau, J.C., Brua, R.B., Culp, J.M., Yates, A.G., Chambers, P.A., 2017. Quantifying seasonal variation in total phosphorus and nitrogen from prairie streams in the Red River Basin. Manitoba Canada. Sci. Total Environ 575, 649–659.

SEPA, 1989. State Environmental Protection Administration. Water Quality Standard for Fisheries (GB11607-89).

SEPA, 1998. State Environmental Protection Administration. Integrated Wastewater Discharge Standard (GB 8978–1996).

Siripong, S., Rittmann, B.E., 2007. Diversity study of nitrifying bacteria in full-scale municipal wastewater treatment plants. Water Res. 41, 1110–1120.

Solomon, K., Giesy, J., Jones, P., 2000. Probabilistic risk assessment of agrochemicals in the environment. Crop Protect. 19, 649–655.

State Council, 2011. How to Start the Reduction of Ammonia Nitrogen Emissions? Focus on Four Reduction Emission Targets. http://www.mep.gov.cn/xxgk/hjyw/201105/t20110523_210998.shtml (in Chinese).

State Council, 2012. Comprehensive Work Program for Energy Conserva-tion and Emission Reduction in 12th Five-year Period. http://www.gov.cn/zwgk/2011-09/07/content 1941731.htm (in Chinese).

Stephan, C., Mount, D., Hansen, D., Gantile, J., Chapman, G., Brungs, W., 1985. Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses[M]. US Environmental Protection Agency, Duluth, MN.

USEPA, 1999. Update of Ambient Water Quality Criteria for Ammonia[R]. EPA/822/R-99/014. Final/Technical Report. US Environmental Protection Agency, Washington, DC.

USEPA, 2013. Aquatic Life Ambient Water Quality Criteria for Ammonia – Freshwater.EPA/822/R-13/001. Technical Report. US Environmental Protection Agency, Washington, DC.

Wang, B., Yu, G., Huang, J., Yu, Y., Hu, H., Wang, L., 2009. Tiered aquatic ecological risk assessment of organochlorine pesticides and their mixture in Jiangsu reach of Huaihe River. China. Environ. Monit. Assess 157, 29–42.

Wang, C., Shan, B., Zhang, H., Zhao, Y., 2014. Limitation of spatial distribution of ammonia-oxidizing microorganisms in the Haihe River, China, by heavy metals. J. Environ. Sci. 26, 502–511.

Wang, P., Shang, H., Li, H., Wang, Y., Li, Y., Zhang, H., Zhang, Q., Liang, Y., Jiang, G., 2016a. PBDEs, PCBs and PCDD/Fs in the sediments from seven major river basins in China: occurrence, congener profile and spatial tendency. Chemosphere 144, 13–20.

Wang, S.J., Lu, A.G., Dang, S.H., Chen, F.L., 2016b. Ammonium nitrogen concentration in the weihe river, central China during 2005-2015. Environ Earth Sci 75.

Wang, Y., Yan, Z., Zhang, Y., Yang, N., Zheng, X., Liu, Z., 2016c. Preliminary aquatic life criteria development and ecological Risk assessment of ammonia in seven major basins in China. Mar. Sci. Bull. 29, 77–83.

Wheelera, J.R., Grista, E.P.M., Leung, K.M.Y., Morritta, D., Cranea, M., 2002. Species sensitivity distributions:data and model choice. Mar. Pollut. Bull. 45, 192–202.

Wu, F., Meng, W., Zhao, X., Li, H., Zhang, R., Cao, Y., Liao, H., 2010. China embarking on development of its own national water quality criteria system. Environ. Sci. Technol. 44, 7992–7993.

Xia, X., Zhou, J., Yang, Z., 2001. Nitrogen contamination in the Yellow river basin of China. J. Environ. Qual. 31, 917–925.

Yan, Z., Meng, W., Liu, Z., Yu, R., 2011. Development of freshwater aquatic life criteria for ammonia in China (in Chinese). Environ. Sci. 32, 1564–1570.

Yang, X., Liu, Q., Fu, G., He, Y., Luo, X., Zheng, Z., 2016. Spatiotemporal patterns and source attribution of nitrogen load in a river basin with complex pollution sources. Water Res. 94, 187–199.

Yang, J., Zhang, X., Xie, Y., Song, C., Sun, J., Zhang, Y., Giesy, J.P., Yu, H., 2017. Ecogenomics of zooplankton community reveals ecological threshold of ammonia nitrogen. Environ. Sci. Technol. 51, 3057–3064.

Zhang, W., Wang, J., Zhang, B., Bi, J., Jiang, H., 2015. Can China comply with its 12th five-year plan on industrial emissions control: a structural decomposition analysis. Environ. Sci. Technol. 49, 4816–4824.

Ecological risks posed by ammonia nitrogen (AN) and un-ionized ammonia (NH_3) in seven major river systems of China

Li Zhang[1], Elvis Genbo Xu[2], Yabing Li[1], Hongling Liu[1*], Doris E. Vidal-Dorsch[3], John P. Giesy[1,4,5]

[1] State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, Jiangsu 210023, China
[2] Department of Chemical Engineering, McGill University, Montreal, Quebec, H3A 0G4, Canada
[3] VDA LCS Consulting Services, Costa Mesa, CA 92626, USA
[4]Toxicology Center and Department of Veterinary Biomedical Sciences, University of Saskatchewan, Saskatoon, SK S7N 5B3, Canada
[5] School of Biological Sciences, University of Hong Kong, SAR, China

Correspondence to: School of the Environment, Nanjing University, Nanjing, Jiangsu 210023, China.

SUPPLEMENTAL INFORMATION

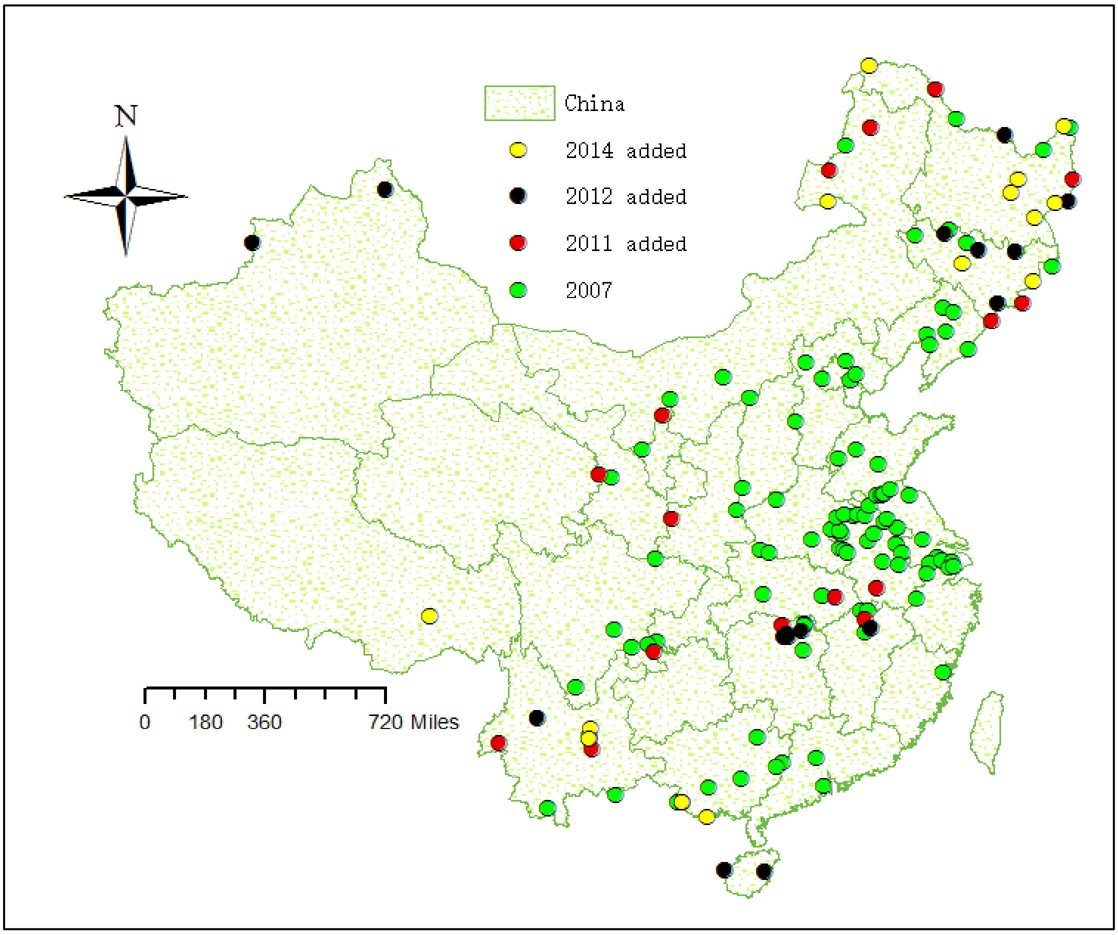


Fig. S1 Geographical location of Chinese sites where the data for this study were collected. Data were generated between the years 2007 to 2014.

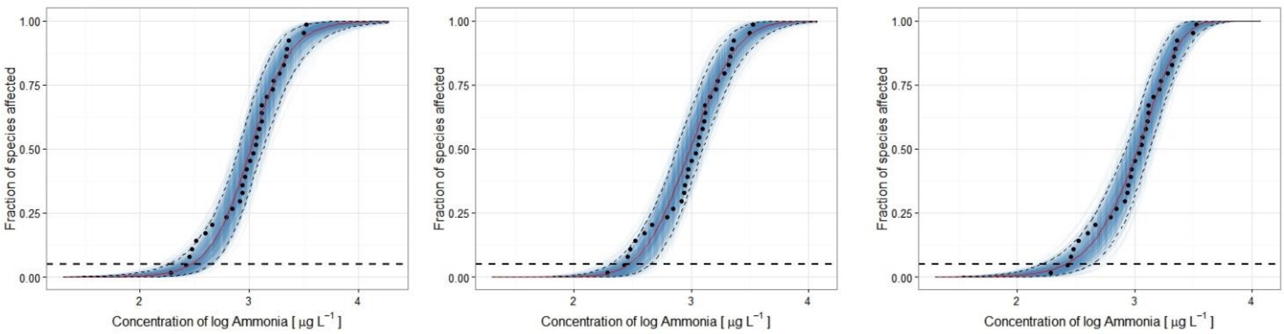


Fig. S2. Parametric distribution curves of acute toxicity. From left to right: Log-logistic, Log-normal, and Weibull.

Table S1. Seasonal AN variation in the seven major river systems of China from the years 2007-2014. Values represent average±standard deviation. The units are mg/L.

Season	2007	2008	2009	2010	2011	2012	2013	2014
Spring	1.31±2.91	1.34±3.45	1.23±2.92	1.10±3.47	0.89±2.13	0.60±1.35	0.58±1.56	0.46±1.19
Summer	0.72±1.82	0.78±2.15	0.71±1.65	0.57±1.42	0.56±1.34	0.44±1.07	0.39±0.97	0.36±0.83
Autumn	1.13±2.90	0.91±2.08	0.84±2.27	0.70±1.95	0.72±1.66	0.52±1.47	0.52±1.27	0.53±1.55
Winter	1.91±3.78	2.76±4.21	1.53±2.97	1.32±3.64	1.14±3.31	0.89±2.18	0.87±2.04	0.82±2.25

Table S2. Seasonal NH_3 variation in seven major river systems of China from the years 2007-2014. Values represent average±standard deviation. The units are μg/L.

Season	2007	2008	2009	2010	2011	2012	2013	2014
Spring	61.86± 133.28	92.84± 169.5	80.30± 37.39	42.32± 42.79	45.78± 52.37	21.46± 60.70	21.10± 25.44	15.13± 76.73
Summer	38.90± 157.89	40.35± 511.11	39.46± 142.01	29.64± 113.88	32.13± 119.08	33.72± 97.81	20.80± 109.17	18.64± 69.90
Autumn	37.49± 271.89	25.19± 134.53	15.73± 434.71	16.37± 184.03	17.42± 158.56	10.55± 230.41	8.85± 79.57	12.11± 42.27
Winter	39.90± 182.54	45.43± 90.74	44.08± 240.53	17.07± 42.54	22.82± 81.43	14.23± 31.87	16.90± 47.42	10.53± 20.59

Table S3. Statistics of AN concentrations in the seven major river systems of China from the years 2007 to 2014 (mg/L).

Values	2007	2008	2009	2010	2011	2012	2013	2014
Minimum	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Median	0.32	0.35	0.33	0.29	0.29	0.24	0.23	0.22
Mean	1.24	1.22	1.08	0.92	0.82	0.60	0.59	0.55
Maximum	30.40	31.70	38.80	45.70	60.70	30.10	22.10	22.30

Table S4. Statistics of NH_3 concentrations in seven major river systems of China from the years 2007 to 2014 (μg/L).

Values	2007	2008	2009	2010	2011	2012	2013	2014
Minimum	0.02	0.01	0.01	0.04	0.02	0.01	0.01	0.00
Median	6.53	7.31	6.54	5.8	6.52	3.95	3.55	3.34
Mean	44.4	50.65	44.68	26.34	29.34	20.12	16.89	14.13
Maximum	5851.94	7111.43	7417.04	2823.37	1844.65	3688.52	2127	2391.81

Table S5. Acute NH_3 toxicity for freshwater organisms native to China.

GMAV(mg/L)	Genus	family	order	class	phylum
0.19	*Siniperca*	*Percichthyidae*	*Perciformes*	*Actinopterygii*	*Chordata*
0.27	*Carassius*	*Cyprinidae*	*Cypriniformes*	*Actinopterygii*	*Chordata*
0.29	*Acipenser*	*Acipenseridae*	*Acipenseriformes*	*Actinopterygii*	*Chordata*
0.30	*Corbicula*	*Cyrenidae*	*Veneroida*	*Bivalvia*	*Mollusca*
0.33	*Hypophthalmichthys*	*Cyprinidae*	*Cypriniformes*	*Actinopterygii*	*Chordata*
0.40	*Oncorhynchus*	*Salmonidae*	*Salmoniformes*	*Actinopterygii*	*Chordata*
0.46	*Tetraodon*	*Tetraodontidae*	*Tetraodontiforms*	*Actinopterygii*	*Chordata*
0.62	*Pelteobagrus*	*Bagridae*	*Siluriformes*	*Actinopterygii*	*Chordata*
0.70	*Poecilia*	*Poeciliidae*	*Cyprinodontiformes*	*Actinopterygii*	*Chordata*
0.82	*Lymnaea*	*Lymnaeidae*	*Basommatophora*	*Gastropoda*	*Mollusca*
0.86	*Salvelinus*	*Salmonidae*	*Salmoniformes*	*Actinopterygii*	*Chordata*
0.88	*Lepomis*	*Centrarchidae*	*Perciformes*	*Actinopterygii*	*Chordata*
0.92	*Macrobrachium*	*Palaemonidae*	*Decapoda*	*Malacostraca*	*Arthropoda*
0.95	*Simocephalus*	*Daphniidae*	*Diplostraca*	*Branchiopoda*	*Arthropoda*
1.01	*Penaeus*	*Penaeidae*	*Decapoda*	*Malacostraca*	*Arthropoda*
1.09	*Ceriodaphnia*	*Daphniidae*	*Diplostraca*	*Branchiopoda*	*Arthropoda*
1.14	*Cottus*	*Cottidae*	*Scorpaeniformes*	*Actinopterygii*	*Chordata*
1.18	*Cyprinus*	*Cyprinidae*	*Cypriniformes*	*Actinopterygii*	*Chordata*
1.25	*Lumbriculus*	*Lumbriculidae*	*Lumbriculida*	*Clitellata*	*Annelida*
1.30	*Ictalurus*	*Lctaluridae*	*Siluriformes*	*Actinopterygii*	*Chordata*
1.30	*Daphnia*	*Daphniidae*	*Cladocera*	*Branchiopoda*	*Arthropoda*
1.31	*Eriocheir*	*Varunidae*	*Decapoda*	*Malacostraca*	*Arthropoda*
1.45	*Chydorus*	*Chydoridae*	*Diplodtraca*	*Branchiopoda*	*Arthropoda*
1.63	*Gasterosteus*	*Gasterosteidae*	*Gasterosteiformes*	*Actinopterygii*	*Chordata*
1.67	*Oreochromis*	*Cichildae*	*Perciformes*	*Actinopterygii*	*Chordata*
1.90	*Silurue*	*Silurudae*	*Siluriformes*	*Actinopterygii*	*Chordata*
2.08	*Chironomus*	*Chironomidae*	*Diptera*	*Insecta*	*Arthropoda*
2.17	*Gambusia*	*Poeciliidae*	*Cyprinodontiformes*	*Actinopterygii*	*Chordata*
2.22	*Tubifex*	*Naididae*	*Oligochaeta*	*Clitellata*	*Annelida*
2.29	*Misgurnus*	*Cobitidae*	*Cypriniformes*	*Actinopterygii*	*Chordata*
3.16	*Procambarus*	*Cambaridae*	*Decapoda*	*Malacostraca*	*Arthropoda*
3.36	*Gobiocypris*	*Cyprinidae*	*Cypriniformes*	*Actinopterygii*	*Chordata*

Table S6. Acute-chronic NH_3 ratio for species native to China.

Species	Acute value (mg/L)	Chronic value (mg/L)	ACR	ACRs	Chronic criterion (μg/L)
Daphnia magna	1.3	0.72	1.82		
Cyprinus carpio	1.18	0.28	4.16	3.79	13. 6
Lepomis macrochirus	0.88	0.12	7.19		