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The Taxon-Specific Species Sensitivity and Aquatic Ecological Risk Assessment of Three Heavy Metals in Songhua River Water, China

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Abstract: Copper (Cu), zinc (Zn), and nickel (Ni) are essential micronutrients for aquatic life, but they produce adverse effects on aquatic organisms when environmental concentrations exceed a certain threshold. The objective of this study was to analyze the taxon-specific sensitivities of aquatic life to the three metals and assess ecological risks at exposure levels prevalent in the Songhua River, China. The results showed that sensitivities to these metals varied among different taxonomic groups, with intra-taxon sensitivities being lower than inter-taxa sensitivities, and the consistency of intra-taxon sensitivity increased from phylum to order. The maximum detected concentrations of Cu, Zn, and Ni in the Songhua River were 52.7, 166.0, and 65.3 μg/L, respectively, which met the water quality standards set by China but exceeded the chronic criteria established by the USA. A probabilistic risk assessment based on chronic toxicity data revealed that these three metals posed an intermediate to high risk to aquatic animals, with maximum risk products of 36.4% for Cu, 14.3% for Ni, and 6.2% for Zn, respectively. These results indicate that the ecological damage of heavy metals in the Songhua River cannot be ignored.

Keywords: taxon-specific; risk assessment; species sensitivity distribution; copper; zinc; nickel; Asia

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1. Introduction

Aquatic ecosystems have been affected by various types of contamination around the globe in recent years. Metals are one of the most common pollutants that have severely deteriorated aquatic ecosystems [1]. Heavy metal contamination in the aquatic environment has attracted global attention because of its environmental toxicity, abundance, and persistence [2–6]. In recent years, greater amounts of metals have been released into rivers worldwide due to rapid global population growth and intensive domestic activities, urban development, and expanding industrial and agricultural activities [7–9]. The major sources of metals include industrial outfalls, domestic wastes, urban sewage, and agricultural and stormwater runoff [10,11]. It was reported that metal mines affect 479,200 km of river channels and 164,000 square kilometers of floodplains worldwide. China, with 9.742 million people living in floodplains contaminated by active and inactive mines, is the most vulnerable region, which may pose a serious risk to ecosystems and human health [12]. Copper (Cu), zinc (Zn), and nickel (Ni) are transition metals that serve as essential micronutrients for aquatic life [13,14]. However, if the exposure concentrations surpass the thresholds associated with adverse effects, they can induce acute and/or chronic toxic effects on aquatic organisms [15]. This may cause losses of habitat and biodiversity, as well as potentially being a direct or indirect (via diet) threat to human health [16,17]. Copper generally poses a higher level of toxicity to aquatic organisms compared to humans and other terrestrial organisms, particularly water fleas [18]. Zn^{2+} significantly enhanced the growth of chlorella at a concentration of 0.01 mg/L, while the biomass of algal cells was inhibited at a concentration of 0.5 mg/L [19].

In China and other developing countries, there are limited toxicity data available for native species. This scarcity of information has emerged as a significant constraint in conducting ecological risk assessments in these countries [20,21]. Theoretically, species that feed on similar foods and have similar physiologies will likely have similar exposures and responses to toxicants. In the classification system known as "biotaxy", aquatic organisms are divided into taxa according to similarities among physiologies. Researchers have developed relationships between the sensitivity of a species to a toxicant and its natural history such as feeding guild, morphology, and physiological traits that could be used to predict the sensitivities of species for which no information on sensitivity to a particular toxicant exists [22–27]. Jin et al. [28] analyzed the effect of 2,4-dichlorophenol in the aquatic environment and found there were no significant differences between native species and non-native species. Based on the analysis, non-native species of the same taxon, such as class or genus, as native biota can be used as an alternative when native species toxicity data are lacking. This can reduce uncertainty in assessments, especially when the lacking toxicity data are tested with sensitive taxa. Therefore, it is necessary to conduct a taxon-specific species sensitivity analysis using as much toxicity data as possible.

In China, rapid economic development in recent decades has resulted in severe metal pollution in aquatic environments, and therefore, the deleterious effects and ecological risks of metals in Chinese aquatic ecosystems have raised concerns [29,30]. According to the same analysis method, the risk from metals in Chinese rivers can be several times higher than that experienced in UK rivers [31]. The Songhua River (SHR) is a river in Northeast China, flowing approximately 1,434 km from the Changbai Mountains through the Jilin and Heilongjiang provinces. The river covers an area of 557,180 km^2 and has a mean annual discharge of 2463 m^3/s. An enormous amount of aquatic life lives in the big river, and it supplies a lot of aquatic products to humans. With economic development and the increasing pace of urbanization, significant quantities of industrial wastewater and domestic sewage are continuously being released into the Songhua River. The mining operations in the upper section of the Songhua River, the presence of petrochemical plants in the middle section, and petroleum extraction in the lower section have caused a significant escalation in heavy metal contamination within the river [32]. Several large cities situated along the riverbanks of the Songhua River basin play a significant role in the introduction of metals via surface runoff and the discharge of wastewater originating from agricultural and industrial operations. In order to balance anthropogenic activities and ecosystem health and environmental protection, a comprehensive management scheme is urgently required.

Until now, the taxon-specific species sensitivities of Cu, Zn, and Ni have rarely been reported. Moreover, the pollution levels and ecological risks associated with heavy metals in the Songhua River basin remain unclear. So, this paper presents the preliminary results of a research program aimed at documenting: (1) species sensitivities towards Cu^{2+}, Zn^{2+}, and Ni^{2+} on three taxon-specific levels; (2) the spatial and temporal changes of Cu, Zn, and Ni in the water of Songhua River; and (3) the potential risks that these metals pose to aquatic animals.

2. Materials and Methods

2.1. Exposure Concentration of Three Metals

In this study, concentrations of Cu^{2+}, Zn^{2+}, and Ni^{2+} were measured in water collected from 2019 to 2021 during three seasons, wet, normal, and dry, from 21 sites along the *Songhua* River (Ch: *Songhua*) (Figure 1). Samples of water were filtered through 0.45 μm membranes and the concentrations of metals were quantified by the use of a Shimadzu model AA6300 atomic absorption spectrophotometer [33] and flame atomic absorption spectrometric method [34]. In statistical analyses, the samples whose concentrations were less than the method detection limits (MDLs) were replaced with a surrogate value equal to half the MDL. The detected concentration represented soluble metals.

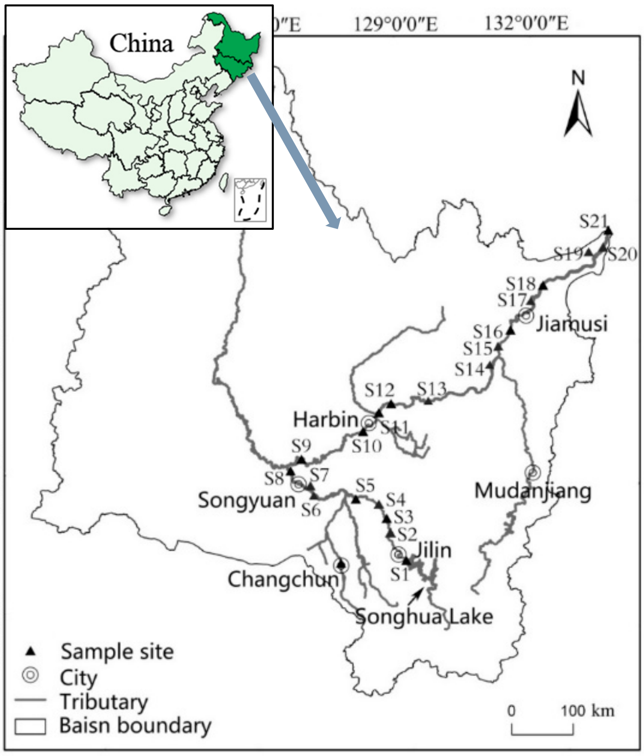


Figure 1. Profile of sample sites along the Songhua River.

2.2. Toxicity Data Collection and Species Sensitivity Analysis

Toxic potencies of Cu^{2+}, Zn^{2+}, and Ni^{2+} towards freshwater organisms were collected from existing toxicity databases, such as the ECOTOX Knowledgebase developed by the US EPA (https://cfpub.epa.gov/ecotox/search.cfm, 10 March 2023), published in the open, peer-reviewed literature and government documents. For better comparison and consistency, toxicity data were further selected based on the following standards:

(1) Test protocols should follow ASTM or other standardized methods; (2) the same test endpoints should be used. For acute toxicity data, the selected measurement endpoints were the median lethal concentration (LC_{50}) or median effect concentration (EC_{50}). For chronic toxicity data, the endpoint should be no observed effect concentration (NOEC). (3) If more than one toxicity study is performed with the same species and different toxicological standards, the lowest toxicity value is used. If several toxicity tests are performed with the same species and the same toxicological standard, the geometric mean of these values is used.

Due to the limited availability of chronic toxicity data, the analysis of species sensitivity primarily concentrated on acute toxicity data. The comparison of inter-taxa sensitivity was conducted by employing the species sensitivity distribution (SSD) concept. Toxicity data were ranked in ascending order, and centiles were assigned (Equation (1)).

$$P_i = i/(N + 1) \quad (1)$$

where i is the rank of the datum in ascending order and N is the total number of data points [35].

Various environmental physical and chemical factors can influence the bioavailability of copper in a specific water system. These factors, such as pH, dissolved organic carbon (DOC), and the presence of other ions like Ca^{2+} and H^+, can affect metal speciation, complex free metal ions, or compete with metals at the site of uptake by organisms. Among these factors, hardness, pH, and DOC have been identified as crucial parameters [36]. Because the three key parameters of Songhua River are similar to those of Lake Tai (Ch: *Taihu*), the water effect ratio (WER) of 2.55 determined in Lake Tai [37] was utilized to modify the chronic toxicity data of Cu when constructing the joint probability curve (JPC).

2.3. Ecological Risk Assessment of Three Metals

Probabilistic ecological risk assessment (PERA) is the most widely used method, which qualifies and quantifies ecological risks by combining probability distributions describing exposures and effects. PERA can better describe the likelihood of exceeding effect thresholds and the risks of adverse effects [38]. This approach has been adopted by a number of researchers [39–42]. In PERA, the estimation of risk is described as being proportional to the degree of the overlap of distributions, and one method of displaying risk visually is through the use of joint probability curves (JPCs), which describe the probability of a particular set of exposure conditions occurring relative to the number of taxa that would be affected [43]. The y-axis of the JPC represents the magnitude of effects, while the x-axis represents their probability of occurring. Each point on the curve represents both the probability that the chosen proportion of species will be affected and the frequency with which that magnitude of effect would be exceeded. The closer the JPC is to the axes, the lower the probability of adverse effects.

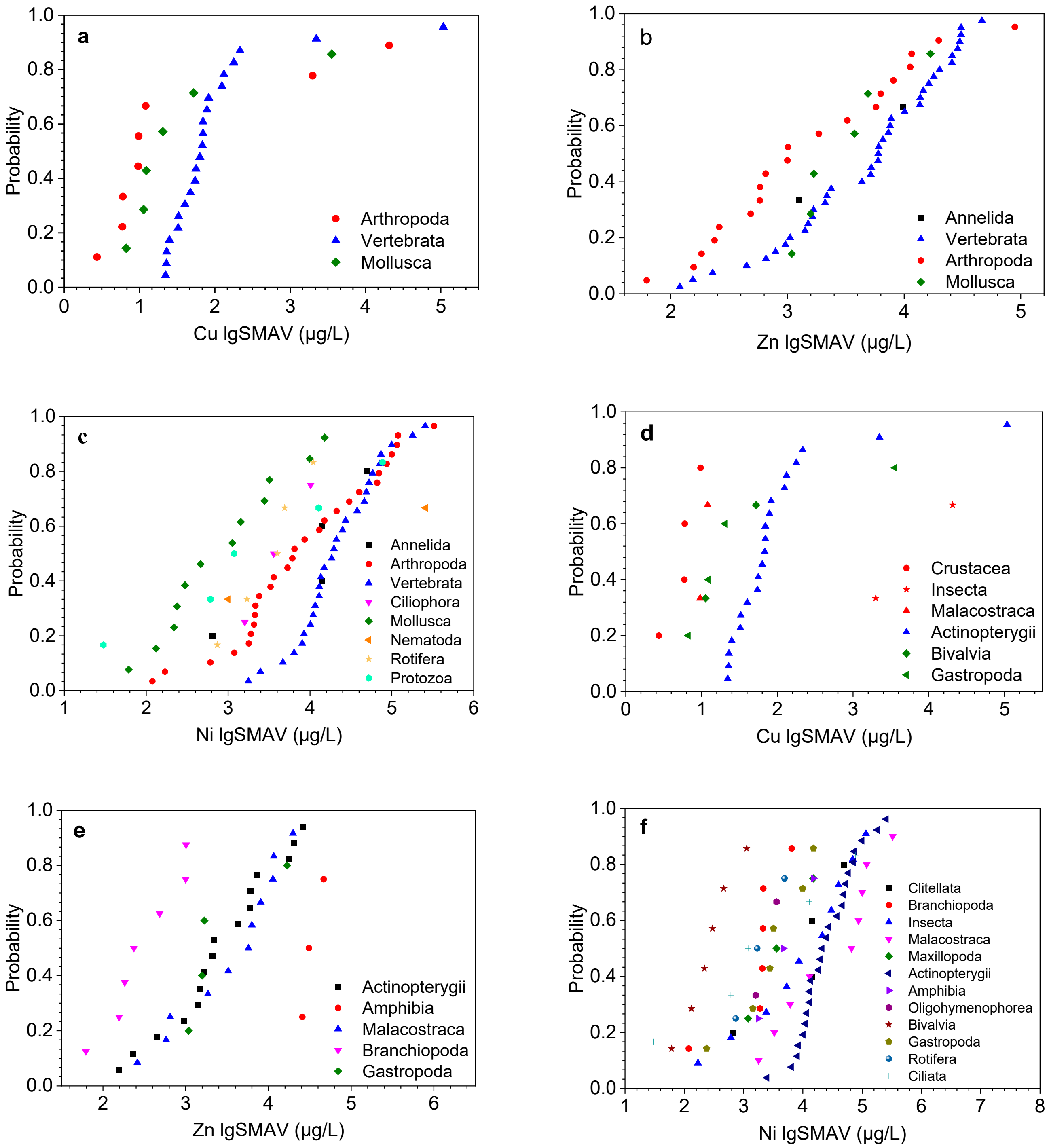
In this study, positively detected concentrations of three metals in Songhua River and chronic toxicity data for responses of various species of aquatic animals were tested for normality as raw or log-transformed data by use of the Kolmogorov–Smirnov test and then were compiled and transformed to *probits* by fitting appropriate distributions. The maximum risk product (MRP) was calculated (risk product = exceedance probability $\times$ magnitude of effect) and was then used to categorize risk as de minimis (MRP $<$ 0.25%), low (0.25 $\leq$ MRP $<$ 2%), intermediate (2 $\leq$ MRP $<$ 10%), or high (MRP $\geq$ 10%) based on the criteria described in Moore et al. [44].

3. Results and Discussion

3.1. Species Sensitivity Analysis and Effect Assessment

Various species have developed a variety of elaborate mechanisms to maintain internal concentrations of micronutrients within narrow limits, while external concentrations fluctuate over several orders of magnitude or resist the toxicity of non-essential chemicals [45]. These mechanisms for maintaining homeostasis are based on particular physiological structures. Therefore, species that have similar physiologies will likely experience similar exposures and also exhibit similar responses to toxicants. Here, we describe differences in taxon-specific sensitivities based on both native and non-native species so that they can be used to predict the sensitivities of species for which no information on sensitivity to a particular toxicant exists.

After retrieving and screening, there were a total of 36 values for the acute toxicity and 23 values for the chronic toxicity of Cu; 40 values for the acute toxicity and 21 values for the chronic toxicity of Zn; and 98 values for the acute toxicity and 21 the chronic toxicity data of Ni. The species include Arthropoda, Chordata, Mollusca, Annelida, Cnidaria, et al. For acute toxicity, the main species taxa in aquatic ecosystems were covered, but for chronic toxicity, fewer taxa were covered. Thus, only acute toxicities were used to analyze taxon-specific species sensitivity distribution (Figure 2).



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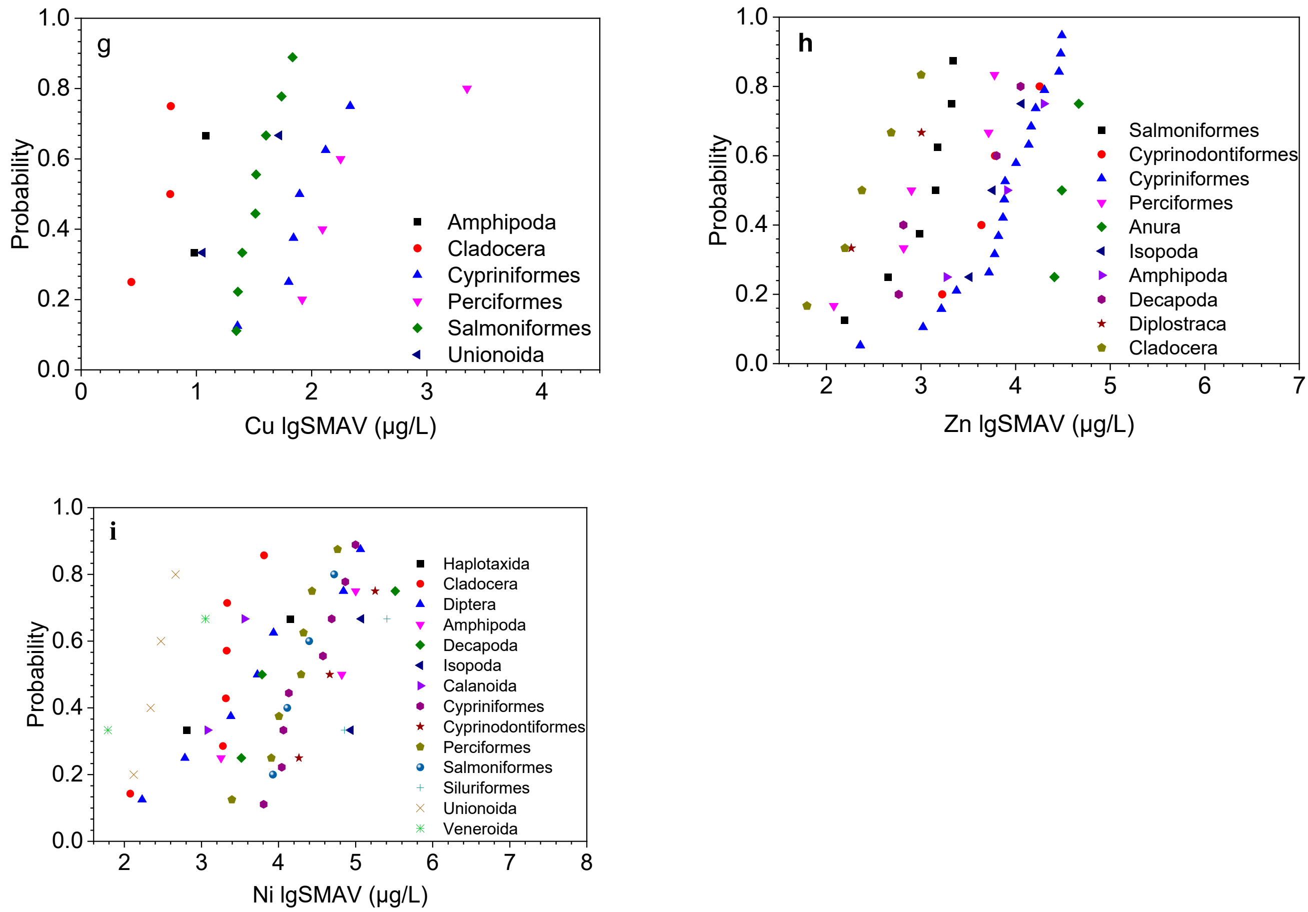

Figure 2. Specific species sensitivity for three metals ((**a**–**c**): phylum level, (**d**–**f**): class level, (**g**–**i**): order level).

At the phylum level (Figure 2a–c), different taxa demonstrate varying degrees of sensitivity to metals, resulting in their classification as either more sensitive or less sensitive/tolerant taxa. For instance, Arthropoda are the most sensitive species for Cu and Zn (SSD curve on the far left), whereas Mollusca exhibit relatively less sensitivity, and Vertebrata demonstrate the most tolerance (SSD curve on the far right). For Ni, Mollusca are more sensitive than Arthropoda, and Vertebrata are relatively more tolerant compared to other taxa. Moreover, species within the same phylum may demonstrate divergent sensitivities to metals. For instance, Vertebrata exhibit more consistent sensitivity for all three metals compared to Arthropoda. This discrepancy may be attributed to substantial disparities in life histories, physiologies, morphologies, and behaviors among these taxa.

At the level of class (Figure 2d–f), Crustacea are the most sensitive group to Cu, followed by Gastropoda and Malacostraca, while Insecta are relatively tolerant. For Zn, Branchiopoda are considered the most sensitive while Amphibia exhibit the most tolerance. For Ni, Bivalvia are the most sensitive, and Actinopterygii and Malacostraca are the most tolerant. At the level of order (Figure 2g–i), the number of available toxicity data was lower. For Cu, Cladocera are the most sensitive. Cypriniforms and Perciformes are the most tolerant, and Salmoniformes are moderately sensitive. Compared to results when grouping taxa at the level of the phylum, the consistency of sensitivity to Cu when aggregating taxa at the level of the order was greater. For Zn, Cladocera are most sensitive, and Anura are most tolerant. Cypriniforms are also more tolerant, while Salmoniformes, which belong to the same class (Actinopterygii), are more sensitive. For Ni, Unionoida and Veneroida are the most sensitive, and Isopoda and Siluriformes are the most tolerant. In ecotoxicology, the range of sensitivities among various species means that different species respond differently to a chemical at a given concentration. While, traditionally, species have been classified according to morphology, for biosystematics, they can also be classified by physiology. The results of the taxon-specific species sensitivity analysis demonstrated that intra-taxon variability is relatively less than inter-taxa variation in sensitivities to the three metals studied.

Various species from different taxa make up the complex aquatic ecosystem through the food chain, symbiosis, competition, and other relationships [46]. Each species has its own specific functions within the ecosystem. The presence of pollutants can disrupt the balance of the entire aquatic ecosystem when it affects any of these species. The tolerance of aquatic ecosystems to pollutants is influenced, to a certain degree, by the sensitivity of the most vulnerable taxa, particularly the keystone species that are highly sensitive. Consequently, comprehending the susceptibility of species to metallic contaminants is of utmost importance for making informed decisions and mitigating the adverse effects on aquatic ecosystems. Furthermore, when employing the SSD approach to evaluate the adverse effect posed by metals, the inclusion of a greater number of taxa would enhance the capacity of the SSD curve to accurately depict the ecosystem that requires safeguarding. In order to address the limitations arising from inadequate toxicity data, it is imperative to conduct supplementary toxicity tests on unexplored taxa. This endeavor will enhance the probability of identifying species that are more sensitive to contaminants. At the same time, it will diminish uncertainties in ecological risk evaluations and enhance the capacity to safeguard the valued services provided by ecosystems. Overall, intra-taxon and inter-taxa variation in sensitivity to environmental pollutants is apparently not only a core problem but also a basis for finding solutions to increase the ecological significance of SSD.

3.2. Exposure Assessment in Songhua River Water

The concentrations of Cu, Ni, and Zn in the waters of the Songhua River varied between non-detectable (ND) and 52.7 µg/L, ND and 65.3 µg/L, and ND and 166.0 µg/L, respectively. The detection rates for Cu, Ni, and Zn were 95%, 98%, and 77%, respectively, while the corresponding mean concentrations were determined to be 28.43 µg/L, 29.31 µg/L, and 33.3 µg/L. The distribution of the three metals in various periods is shown in Figure 3 and Table S1. The ranges of the concentrations of Cu (mean) in the Songhua River water were 5.8~40.7 (22.9) µg/L, 27.1~52.7 (36.4) µg/L, and 10.8~37.6 (25.6) µg/L in the wet, normal, and dry period, respectively. On average, the concentration of Cu was highest in the normal period, and this value was 1.8 and 1.4 times higher than those in the wet and dry periods. This may be attributed to the greater diluting effect on concentrations of Cu during the wet period, whereas the release of pollutants from sediment was comparatively lower during the dry period due to the presence of icebound conditions. Previous studies have reported the highest concentration of Cu in the sediment of the Songhua River during the freezing period [47]. The environmental water quality standard (EQS) for Cu for class III freshwater in China [48], which is designated for surface drinking water sources and fish, shrimp overwintering, migration, or aquaculture water, as well as swimming for humans, is 1000 µg/L. The concentrations of Cu were lower than the standard. When the USEPA revised its water quality standards for Cu [49], the criterion maximum concentration (CMC) and criterion continuous concentration (CCC) for Cu were set at 60 and 18.6 µg/L (at hardness = 50 mg/L $CaCO_3$, DOC = 10 µg/L), respectively. None (0.0%) of the concentrations of Cu in the Songhua River exceeded the CMC, while 74.6% exceeded the CCC. In comparison to findings from previous studies, the background values of Cu in the surface water of the Heilongjiang Province have been reported to be 1.46 µg/L [50]. In the downstream of Songhua River, the concentration of Cu was found to range from 0.75 to 7.55 µg/L in July (the wet period) 2015 [51]. These results suggest a significant increase in Cu concentrations, potentially influenced by human activities.

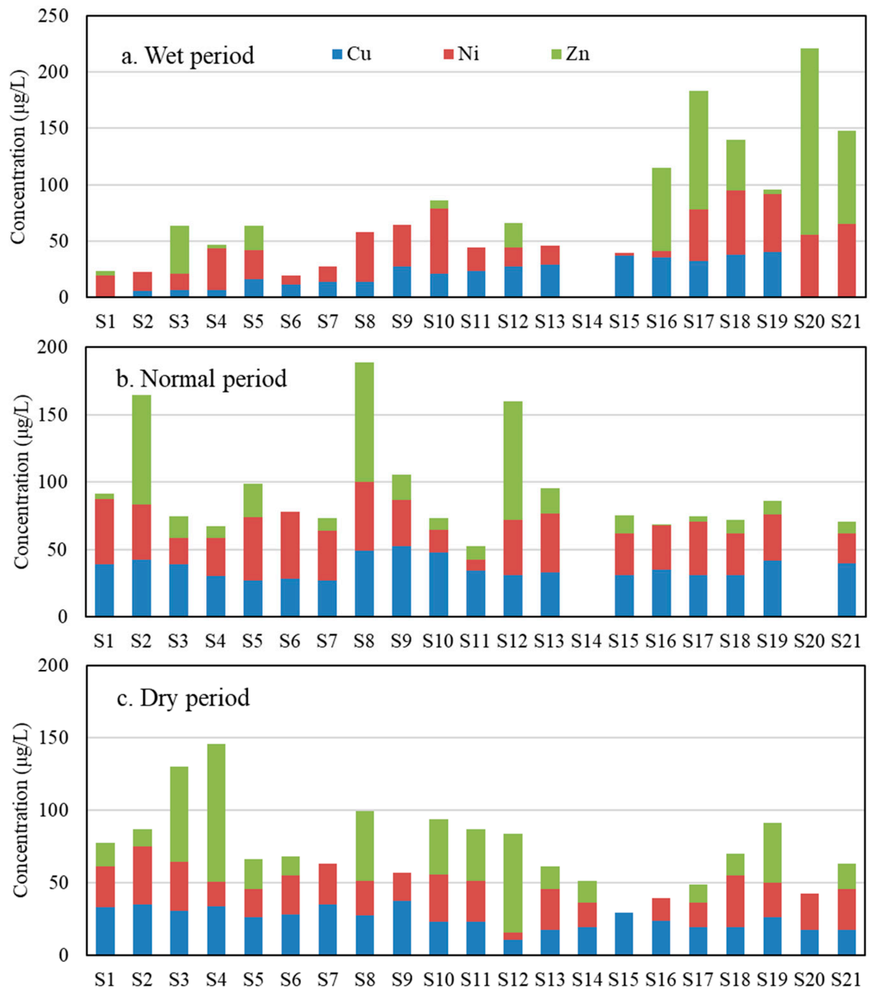

Figure 3. Concentrations of three metals in Songhua River waters.

The range of concentrations (mean) of Ni in Songhua River water was 2.5~65.3 (30.5) μg/L, 8.2~52.0 (34.5) μg/L, and 0.7~39.6 (23.5) μg/L in the wet, normal, and dry period, respectively. Ni is not set as a necessary factor in the Chinese water quality standard for surface water [48], so the concentration of Ni cannot be compared with the standard. The CMC and CCC water quality criteria for Ni given by the USEPA are 480 and 52 μg/L. Compared to the criteria, about 0% of concentrations of Ni in Songhua River waters exceeded the CMC and approximately 6.7% of concentrations exceeded CCC.

The range of concentrations (mean) of Zn in Songhua River water was ND~166 (29.6) μg/L, ND~88.2 (22.4) μg/L, and ND~94.4 (26.0) μg/L in the wet, normal, and dry periods, respectively. In China, the EQS of Zn for classes II and III are 1000 μg/L [48]. Class I, which refers to national nature reserves, is 50 μg/L. Concentrations of Zn were less than the class II standard, and 15% of the sites exceeded the class I standard. Both the CMC and CCC water quality criteria for Zn in USEPA were 120 μg/L. Only 1.7% of the concentrations of Zn in the Songhua River exceeded the CMC and CCC. Lu et al. [52] investigated the middle and lower reaches of the Second Songhua River (the section of S1 to S9 in this study) and found concentrations ranging from 0.92 to 70.81 μg/L, with a mean concentration of 25.41 μg/L. Compared to the results of a previous study, concentrations of Zn in the Songhua River increased slightly.

Comparisons of the maximum values of heavy metal concentrations with those in other regions are listed in Table 1. The maximum concentration of Cu (52.7 μg/L) and Zn (166 μg/L) from the Songhua River was far lower than other regions. However, the maximum concentration of Ni (65.3 μg/L) in the Songhua River was greater than the Yangtze River (18 μg/L) in China.

Table 1. Heavy metal concentrations in water samples from the Songhua River and other selected rivers from the references (unit: μg/L).

Location	Metal	Number of Points	Minimum	Median	Maximum	References
Bohai Region Rivers	Copper	816	0.00071	4.7	2755	[31]
	Nickel	118	0.8	9.3	571	[31]
	Zinc	838	0.035	35	25,370	[31]
Pearl River	Copper	187	n.d	8	2169	[31]
	Nickel	125	n.d	12	128	[31]
	Zinc	156	n.d	27	37,500	[31]
Yangtze River	Copper	1314	n.d	2.44	343	[31]
	Nickel	44	0.4	2.7	18	[31]
	Zinc	1307	n.d	10.8	500	[31]
UK	Copper	89,604	0.1	1.66	5320	[31]
	Nickel	14,981	0.25	1.69	270	[31]
	Zinc	11,679	0.702	6.5	6900	[31]
Songhua River	Copper	57	5.8	29.1	52.7	Present study
	Nickel	59	2.5	28.2	65.3	Present study
	Zinc	46	0.8	16.85	166	Present study

3.3. Probabilistic Ecological Risk Assessment

Data sets for each metal were tested for normality by the use of the Shapiro–Wilk test prior to the application of parametric statistics (Table 2). Joint probability curves for each metal in each period were derived by integrating the distribution for surface water concentrations with chronic toxicity effects on various species to indicate the probability of exceeding effects of differing magnitudes (Figure 4). According to the JPC results, the three metals posed intermediate to high risks to aquatic animals at the river scale, with a relative rank of risks as follows: Cu > Ni > Zn. Chronic risks for Cu in the three periods and Ni in the normal and dry periods were categorized as high, with a maximum risk product (MRP) ranging from 10.0% to 36.4%. An intermediate risk of chronic effects on aquatic animals was identified for Zn in three periods and Ni in the wet period, with maximum risk products ranging from 3.7% to 8.9%.

Table 2. Parameters of joint probability curves (JPCs) for the 3 metals.

Metal	N	Mean (μg/L)	SD	Coefficients of Variation	Shapiro–Wilk Test for Log-Normal Distribution
			Exposure data set		
Cu—normal	19	36.4	7.8	0.21	0.207
Cu—wet	17	22.9	11.9	0.52	0.060
Cu—dry	21	25.7	7.3	0.28	0.179
Ni—normal	17	35.1	9.7	0.28	0.011
Ni—wet	20	30.5	19.8	0.65	0.068
Ni—dry	19	24.6	6.9	0.28	0.225
Zn—normal	18	23.6	29.2	1.24	0.098
Zn—wet	12	48.1	50.5	1.05	0.270
Zn—dry	15	34.5	25.1	0.73	0.069
			Toxicity data set		
Cu	23	124	201	1.62	0.071
Ni	21	10,630	32,092	3.02	0.621
Zn	21	511	906	1.77	0.011

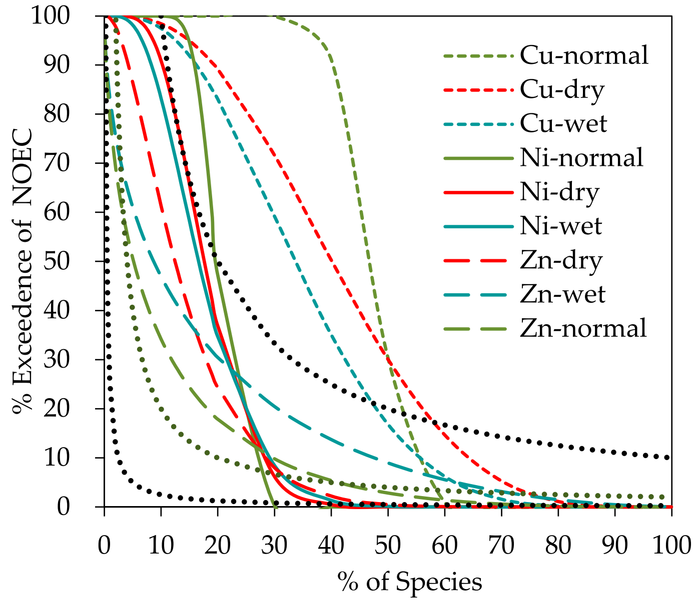

Figure 4. Joint probabilistic curve of 3 metals of Songhua River water in different water periods. Three black dotted lines organize ecological risk into 4 sections, from the lower left corner to the upper right direction: de minimis, low, intermediate, and high risk.

The risks posed by the three metals varied among the three periods due to their different distributions of exposure concentrations. Cu and Ni represented the greatest risk during the normal period, followed by the dry and wet periods, while the risks posed by Zn were greatest during the wet and dry periods. The cumulative probabilities of surpassing the threshold for detrimental impacts on 5% of the species were found to be 100% for Cu throughout all three periods, as well as 100% for Ni during the normal period and 98.2% and 99.7% during the wet and dry periods, respectively. In the case of Zn, the likelihood of 5% of the species being affected was determined to be 61.1%, 50.7%, and 86.5% during the wet, normal, and dry periods, respectively.

Results from the estimated risk curves can also be used to describe the probability of exceeding the percentages of taxa that would be affected. The probability of exceeding a 5% adverse effect depended on the most sensitive species, while the shape of the risk curve was related to the ranges and variability of datasets that could be described by coefficients of variation (CV) [53]. For example, the JPCs for Ni in the normal period were classified as high risk to 10–19% of species, an intermediate risk to 20–28% of species, and a low to de minimis risk to more than 28% of species. This is because this metal was predicted to exhibit toxicity to a small subgroup, with a large CV for effect data and a small value of exposure (Figure 5). Alternatively, the JPCs for Zn in the wet period decreased more slowly and represented an intermediate risk to a wider range of species (from 3% to 70%). That was because the CV for estimates of exposure were much larger and the detected concentrations were greater than many species. Because the exposure data of Cu in the normal period fell within a small range (27.1~52.7 μg/L) that was higher than some toxicity data, with a low CV of exposure and a relatively higher CV of effect, Cu in the normal period presented high risks to 53% of species but insignificant risks to 60% of species at the river scale.

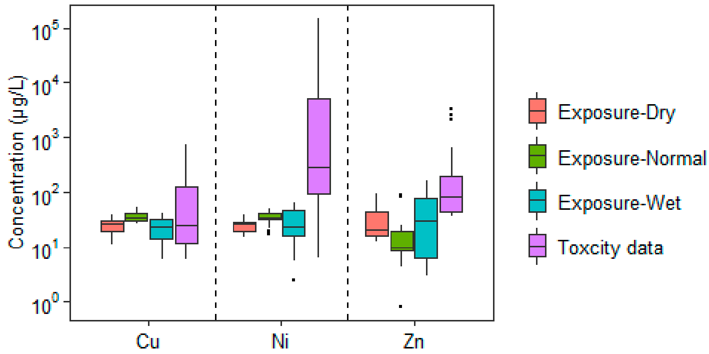

Figure 5. Comparisons among point estimates of exposure and effects for three metals. The horizontal lines represent the 10th and 90th percentiles, and the boxes represent the 25th and 75th percentiles. Median concentrations are shown as solid lines. Outliers are shown as black dots.

3.4. Limitations

Uncertainty in ERA is inevitable. Sources of uncertainty in the ERA include the variability of concentrations within a single body of water, the ecological relevance of the toxicity data, the bioavailability of metals, and the risk characterization model, et al. For the first, in this study, information on spatial and temporal variation in three metal concentrations was limited, especially for basin-wide monitoring. To describe exposures more completely, further information needs to be collected to describe the concentrations of pollutants at various spatial and temporal scales. Furthermore, the ecological relevance of the toxicity data is an important scientific issue for ecosystem risk assessment researchers. Chronic toxicities are preferable to derive the toxicity threshold in ERA to better mimic real-world scenarios of long-term exposure. The more species were used in the assessment, the more representative results were obtained. But, until now, numerous species have had insufficient toxicity data, and the existing data may not represent the most sensitive endpoints. In addition, the chemistry of metals affects their distribution, availability, and ultimately their potential toxicity to aquatic biota. In aquatic systems, metal speciation was dominated by naturally occurring organic ligands (e.g., humic acid), the major component of dissolved organic carbon responsible for binding metal ions. So, in order to obtain more accurate results, the bioavailability of metals must be considered when predicting the ecological risk of metals in the environment based on dissolved concentrations. In the present study, the effects of factors that influence the bioavailability of Zn and Ni were not considered, because of a deficiency of associated data and an unsound risk characterization model. The mechanism of speciation and changes in chemistry should be further studied.

In addition, this study was based solely on the adverse effects of metals on aquatic animals but did not take into account the potential risks posed to producers and decomposers. Copper and zinc are indispensable elements for the proliferation of algae. The impact of copper (Cu) and zinc (Zn) on algae has been observed to enhance growth at low concentrations while inhibiting growth at high concentrations [19]. Algal and plant growth can provide enhanced nutrition for aquatic animals. However, when the growth becomes excessive, it can result in harmful algal blooms, which disrupt the ecosystem.

Also, microorganisms play a critical role in the release, transfer, and precipitation of heavy metals. The interaction between microorganisms and heavy metals should not be ignored. Firstly, microorganisms can promote the dissolution of heavy metals by chelating the metal elements with amino acids, proteins, and peptides created during microbial growth. Secondly, microorganisms can reduce the toxicity of heavy metals by changing the species of heavy metals through redox reactions, biomineralization, and methylation [54]. On the other hand, high concentrations of heavy metals can damage the structure of cell membranes, alter enzyme specificity, modify protein structure, disrupt DNA, induce cell death, and, finally, impact the biomass and diversity of microorganisms. The present study showed that luminescent bacteria and activated sludge bacteria are very sensitive to industry wastewater [55]. For example, the transformation of ammonia and nitrite was seriously inhibited when Cu^{2+} or Zn^{2+} was added to the activated sludge [56]. In order to evaluate the ecological risk from metals, a comprehensive analysis of their impact on ecosystems is imperative.

4. Conclusions

Species belonging to the same taxonomic group may exhibit different levels of sensitivity to diverse types of metals. Arthropods were identified as the taxa most sensitive to both Cu and Zn, whereas Mollusks exhibited the highest sensitivity to Ni. Vertebrata exhibit more consistent sensitivity than Arthropoda for all three metals. Furthermore, the consistency of sensitivity at the order level was higher compared to the phylum level. This heterogeneity implies that the dataset used to derive the criteria should encompass a wide range of species from diverse taxa. Concentrations of Cu, Ni, and Zn in Songhua River waters ranged from ND-52.7, ND-65.3, and ND-166.0 μg/L, with a detected rate of 95%, 98%, and 77%, respectively. The greatest concentration of Cu and Ni was found in the normal period, while Zn was found in the wet period. The maximum values of metals from the Songhua River were lower than rivers in the UK and other rivers in China, except for Ni in the Yangtze River. Neither Cu nor Zn surpassed the class III water quality standards established by China. However, all three metals exceeded the CCC values set by the US EPA to protect aquatic organisms, with percentages of 79% for Cu, 6.7% for Ni, and 1.7% for Zn. The overall probabilities of ecological risks based on chronic adverse effects on aquatic animals were categorized as high for Cu, intermediate to high for Zn, and intermediate for Ni in the three periods.

In conclusion, with the development of the social economy, stringent control has been implemented on the exogenous input of heavy metals. Although the content of heavy metals in water is often below current standards, prolonged exposure can still adversely impact aquatic animals. This indicates that the existing water quality standards do not provide sufficient protection for freshwater ecosystems. It is crucial to improve the quality of the water environment and pay attention to water ecological safety at a national scale. Therefore, comprehensive revision and augmentation of the current environmental water quality standards are imperative, encompassing the consideration of sensitive species and addressing potential chronic adverse effects. The results of this study indicate that researchers should attempt to investigate the chronic toxic effects of metals on a wider range of species and explore the most sensitive endpoint for a given species. The methodology and process might provide a reference for other research on metal evaluation and management for river, lake, and sea waters worldwide.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15203694/s1, Table S1 Concentrations of three metals in Songhua River waters. Table S2 Chronic toxicity data of three metals to freshwater species.

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