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Ecological Risk Assessment of Cadmium in Karst Lake Sediments Based on *Daphnia pulex* Ecotoxicology

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Abstract: The background value of cadmium (Cd) in soil and water sediments in the karst area is 0.31 mg kg^{-1}, with a typical high background of cadmium geochemistry. It is well-known that Cd is classified as a highly toxic metal. Therefore, at the Yelang reservoir in Guizhou province, eco-toxicological tests were carried out using *Daphnia pulex.* The Geo-Accumulation Index and Potential Ecological Risk Index were used to assess the environmental risk of Cd in sediments. The Cd contents in the sediments of Yelang reservoir ranged from 2.51 to 5.23 mg kg^{-1}, while the LC$_{50}$ values of the acute toxicity test of *Daphnia pulex* and Cd at 24, 48, 72, and 96 h were 1.17, 0.50, 0.24, and 0.12 mg L^{-1}, respectively, giving a Safe Concentration threshold of Cd of 1.20×10^{-3} mg L^{-1} in the water body. Based on curve fitting the solid–liquid two-phase distribution model of cadmium in Yelang reservoir was Y = $7.59 \times 10^{-9} \times X^{2.58}$ (R^2 = 0.9995). The safety threshold sediment Cd concentration was 103 mg kg^{-1}, and was much higher than the Cd content in the sediment of the Yelang reservoir. The Geo-Accumulation Index (I_{geo} 2.432–3.491) results show that the sediments had reached medium-strong or strong risk levels. The Potential Ecological Risk Index (E_r^i 242.8–505.9) reached a very high or extremely high-risk level. However, due to high concentrations of Ca^{2+} and Mg^{2+}, and the pH being in the neutral–alkaline range of water body in karst areas, the Daphnia ecotoxicology evaluation method showed slight ecological risk, quite different from other assessment results, thus this method could be considered to use in such areas.

Keywords: cadmium; sediment; *Daphnia pulex*; ecotoxicology; LC$_{50}$; ecological risk assessment; karst areas

1. Introduction

Sediment is an important accumulation site for many natural and anthropogenic heavy metals (HMs) [1,2]. The HMs' concentration within the sediment is perhaps higher in degree than the overlying water [3]. Sediments create very demanding environments for aquatic organisms, as a results harboring pollutants that can directly influence the water quality [2].

A group of freshwater zooplankton commonly referred to as Cladocera's are broadly spread in the aquatic environment, which are available in an extensive range of habitats and are significant links in various food chains [4]. For instance, Daphnia sp. are widely utilized to explore the acute and chronic toxicity of industrial and agricultural chemicals in aquatic ecosystems [5]. This is evident by their relatively short life cycle, less space requirement, adaptability to laboratory conditions, and sensitivity to a wide range of aquatic contaminants [6] and trace quantities of toxic heavy metals in aquatic systems. The trace elements of Cadmium are present in the aquatic environment, which usually leads to significant negative consequences if concentrations are sufficiently raised [7]. Consequently,

affecting the growth rate of the population of Cladocerans [8]. Moreover, acute experiments have shown that cadmium is more toxic to daphniids in high temperature compared to low temperature [9]. Interestingly, toxicity may decline if a greater amount of energy can be directed to endure the toxic stress within higher food levels [10].

Numerous indexes have been put forward to assess the environmental risk of HMs in lake sediments based on the total content, bioavailability, and toxicity. These indexes include the enrichment factor, geo-accumulation index, pollution index, potential ecological risk index (RI), and so on [11–13]. However, the different evaluation indexes have varying limitations [1,14]. For instance, the Geo-Accumulation Index (Igeo) method of Müller is the current classical method of assessing the ecological risk of metals in sediments [15]. The Potential Ecological Risk Index (RI) method proposed by Hakanson [16], which is based on the research theory of sedimentology, has also been widely used by researchers both nationally and internationally to assess ecological risks of metals in sediments and soils [11–13]. Both methods are based on the assessment of the entire amount of metals without considering the biological effects of metals in sediments or the interaction between water ions.

Besides the mentioned indexes above, other approaches have been suggested, such as the development of theoretical and empirical single guidelines, evaluations of populations and communities, interstitial water quality, tissue residue, and spiked sediment toxicity, including laboratory and field toxicity testing of single species [1,3]. For instance, the calculation of toxic units is one way to estimate both the concentration and potential toxicity of multiple chemicals in sediments. The concentrations of toxicant in pore-water are divided by the LC_{50} for a reference organism [1,3,17]. These laboratory toxicity tests are of great importance, because they provide information for determining and managing decisions and the consequences of these decisions. Moreover, these tests are critical to the establishment of effective prediction of genuine benthic effect in the environment and the development of appropriate guidance for their application within a regulatory framework [1,3,17,18]. However, very few studies have attempted to compare and combine indexes, including the geo-accumulation index, and potential ecological risk with the LC_{50} *Daphnia Pulex* toxicity test to assess the environmental risk of HMs and detect the specific effects of chemicals on living organisms in lake sediments. These methods will provide adequate information to analyze and understand the ecotoxicology and biotoxic effects of HMs on zooplankton. Thus, an inclusive risk assessment should be given consideration based on a comparison among these indexes.

Guizhou province, located in the southwest of China, is an abnormal geochemical region with respect to cadmium (Cd), representing high background levels of metals [19,20]. For instance, Ling [21] has shown statistically that the geochemical background value of Cd in soils and sediments in Guizhou Province is 0.31 mg kg^{-1}. This is higher than in non-karst regions and is 2.46 times higher than the average value of water sediments in China 0.126 mg kg-1 [22]. Several studies have found that Cd is the leading metal pollutant in various karst lakes, with very high ecological risks [20,22]. The primary objective of this study is to assess the ecological risk of Cd in sediments of Yelang reservoir located in the Guizhou Province based on the *D. pulex* acute toxicity test. A comparative analysis of Geo-Accumulation Index (Igeo) and Potential Ecological Risk Index methods were conducted to provide additional references for environmental and ecological risk assessment.

2. Materials and Methods

2.1. Study Area

Yelang reservoir is located 35 km North of Anshun City, Guizhou Province, in the middle of Sancha Lake, north of Puding County. The reservoir area is about 20 square kilometers, and the water storage is about 420 million cubic meters. Its upstream tributaries into the lake are mainly Sancha Lake and Boyu Lake. The main structures at Yelang reservoir are the middle and upstream comprising Permian and Triassic carbonates, whilst the downstream is generally Cambrian, Ordovician and Silurian carbonate. Moreover, it

displays a highly developed karst topography that accounted for 71.5 of the area, rich in mineral resources, mainly coal, iron, ore, copper, and aluminum-zinc. The principal landform is agricultural land, which is practically used for sewage irrigation owing to karst rock desertification [20]. The reservoir has been used for power generation, flood control, tourism, and water supply. Its basic parameters are shown in Table 1.

Table 1. Basic parameters at Yelang reservoir.

Total Reservoir Capacity/km^3	Normal Reservoir Capacity/km^3	Normal Catchment Area/km^2	Flow/km^3	Distance/km	Age/a	Evolution Stage
4.2	2.48	19.25	33.8	238.4	24	Middle level

The above data are from [23].

2.2. Sample Collection

Sediment sampling was done from 15 randomly selected sampling points at the Yelang reservoir in June 2016 (Figure 1). Sediment samples were collected at depths of 0–8 cm from the sites. The collection site was divided into three areas, namely the upstream Sancha lake area, midstream Dachuanbian and Shachong area and downstream Tianfen and Shawan area of the reservoir. The samples were placed in bags, sealed, and taken to the laboratory within 24 h after sampling. Prior to the collection of the sediment samples, surface water samples were collected at the 15 sites for water characterization, major ions, and metal analysis.

Figure 1. Distribution of sampling sites at Yelang reservoir in Guizhou province.

2.3. Sample Determination

The samples were air-dried to remove impurities followed by grinding and later put in a 100-mesh nylon sieve for subsequent analysis. Total cadmium in the sediment was extracted by the HNO_3–HF-$HClO_4$ triacid digestion method and determined by inductively coupled plasma mass spectrometer (X2 ICP-MS, Thermo Fisher Scientific, Waltham, MA). A parallel sample was set up in the experiment to ensure the accuracy of the measured data. The standard reference material GBW07405 (GSS5) was used for quality control.

For each water sample, the water temperature (t), conductivity (EC), pH, and other parameters for the overlying water were measured using a portable multiparametric water quality analyzer (DZB-718, Shanghai Leici Instrument Inc., Shanghai, China). The water samples for calcium and magnesium ions analysis were acidified with high purity nitric acid (HNO_3) to a pH < 2. Moreover, the results were determined by ICP-AES (ACTIVA-M, Horiba, Kyoto, Japan). The final results are shown in Table 2.

Table 2. Water quality parameters and main ionic composition at Yelang reservoir.

pH	EC/μs cm^{-1}	T/°C	DO/mg L^{-1}	Ca^{2+}/mg L^{-1}	Mg^{2+}/mg L^{-1}	HCO$_3{}^-$/mg L^{-1}
7.92	535	24.6	8.35	56.44	15.15	151.87

The definitions for the abbreviations within the table are as follows; pH, Water Temperature (t), Electrical Conductivity (EC), Dissolved Oxygen (DO), Calcium Ions (Ca^{2+}), Magnesium Ion (Mg^{2+}), and Bicarbonate Ion (HCO$_3{}^-$).

2.4. Biotoxicity Experimental Design

2.4.1. Test Organism and Culture Conditions

Organism experiment and culture conditions followed the procedures of Wu [24]. *D. pulex* were obtained from the Chinese Environmental Science Academy and monocultured in the laboratory of Guizhou University. The culture was maintained at 20.0 ± 0.5 °C with a photoperiod of 14 h light:10 h dark, and light intensity was around 1200 lux. The fresh *Scenedesmus* obliquus (2.0×10^5 cells/mL) was used as a daily feed. Throughout the experiment, half the water in the culture containers was replaced three times weekly. *D. pulex* neonates at 48 h of age were collected for subsequent test.

2.4.2. Test Material and Water Dilution

The culture medium was prepared following [25] with slight modifications. Basically, tap water was oxygenated with an oxygen action machine for more than three days until it reached DO > 8 mg L^{-1}. The Cd^{2+} toxin was prepared by dissolving CdCl$_2$ 2H$_2$O in deionized water, and the final concentration was 100 mg L^{-1}, and kept at 4 °C. The simulated lake water was prepared following the prescribed diluent water formula for Daphnia—China National Standard Formula GB/T13266-1991 [26]: A total of 1 mol L^{-1} high purity hydrochloric acid and 1 mol L^{-1} high purity sodium hydroxide were used and regulated in 7.8 ± 0.2 of pH.

2.4.3. Simulation of Sediment Samples with Different Concentration Gradients

The labeling method of sediment samples of different pollution gradients was simulated based on [27] with slight modification. Eight beakers of capacity 1 L, each numbered 1 to 8, were used to fill the simulated sediment samples. Two hundred grams of dried and sieved sediment was put into each beaker and filled with 800 mL of simulated lake water at room temperature. All beakers' contents were mixed well with a stir bar and then kept for 3 days. After, the overlying water was poured. The 8 beakers were spiked with varying quantities of CdCl$_2$ 0, 50, 100, 200, 600, 800, 1000, and 2000 μg mL^{-1}, respectively. The samples were thoroughly mixed and kept for 7 days. Next, sediments were "washed" with clean simulated lake water every 5 days. The total Cd was measured before each washing. The washing involved draining most of the overlying water, refilling and stirring. The water renewal was repeated until it stabilizes and the process was completed after 40 days. At this point, it was observed that Cd had reached an equilibrium state between the column water and the sediment. Sediment samples were then dried naturally for analysis.

The overlying water samples were filtered through a 0.45 μm filtration membrane before the analysis. Simultaneously, the sediment samples were digested with a mixture of high purity HNO$_3$, HF, and HClO$_4$ in digested vessels. Lastly, Cd concentrations were

analyzed by inductively coupled plasma mass spectrometry (ICP-MS, ACTIVA-M, Horiba, Kyoto, Japan). The conditional distribution coefficient was calculated as follows:

$$Kp = Cs/Cw$$

where Cs is the Cd content in the sediment ($\mu g \ g^{-1}$), and Cw is the Cd concentration in the overlying water ($\mu g \ mL^{-1}$).

2.4.4. Acute Toxicity Test of Cd to *Daphnia pulex* in Water Bodies

Acute toxicity tests were conducted with *Daphnia pulex*. The test solution preparation followed standard guidelines ISO [28]. All steps and details concerned with these tests are reported [25]. Preliminary test was performed to determine the range of the maximum concentration that inhibited the movement of 100% of the *D. pulex.* Based on the set in equal logarithmic spacing, the toxic concentration intervals were determined, setting the Cd^{2+} concentration gradient to 0, 0.1, 0.18, 0.32, 0.56, 1.01, 1.82, and 3.27 mg L^{-1}. The determination of LC_{50} was based on ISO [28], and Zhou and Zhang [29]. *D. pulex* was first rinsed in the simulated lake water 3 times, 5 min each time. Ten neonates were transferred to new test solutions with different concentrations of toxin solution (100 mL). The conditions were the same as the culture conditions except for no feeding during the test. The test was conducted at a constant temperature of 20.0 ± 0.5 °C. The mortality were defined based on sinking to the bottom of the water or does not display movement in the container.

The Safe Concentration (SC) of cadmium was calculated based on the equation given below:

$$SC = 96 \ h - LC_{50} \times AF$$

AF is the application factor, which takes a value of 0.1 or 0.01 [30]. According to the acute toxicity of the different chemical substances, cadmium is a toxic substance with a low decomposition and high accumulation rate, hence the value 0.01 [31,32].

2.4.5. Acute Toxicity Test of Cd to *Daphnia pulex* in Sediments

Before the exposure experiment, two duplications of the simulated sediment, each weighing 45 g. were mixed with 180 mL of the simulated clean lake water. After being placed for 7 days, 40 Daphniids were put in one of the duplications exposing *D. pulex* to the water–sediment system. The other duplication filled with overlying water was drained and 40 Daphniids were added for the overlying water system experiment. *D. pulex* were extracted after 72 h of exposure, and the mortality rate was recorded, according to [27] with slight modification.

2.4.6. Measurement of the Accumulation of *Daphnia pulex* Body

After exposure, 10–15 *D. pulex* from each concentration group were taken and placed into simulated clean lake water for 1–2 h to let the *D. pulex* remove the metal from the internal organs. The *D. pulex* were subsequently removed and washed with distilled water twice. The samples were dried at 80 °C and then digested with concentrated HNO_3 (Superior purity, 68%) at 110 °C till the solution was transparent. After cooling, 2% HNO_3 (high purity) was used to dilute the volume to a measurable range. The Cd concentrations in digested organisms were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS).

2.5. Risk Assessment Method for Heavy Metals in Sediments
2.5.1. Geo-Accumulation Index Method

The Geo-Accumulation Index (I_{geo}) is one of the most widely used methods for the quantitative evaluation of metals in sediments. It reveals the changing characteristics of the distribution of metals and identifies the environmental impact of human activities. It

has been used by researchers to evaluate the risk of metals in sediments from rivers [13] and lakes and reservoirs [12]. The calculation formula was based on [13,15] as follows:

$$I_{geo} = \log_2 \frac{C_i}{k \times B_i}$$

where C_i is the measured concentration of the element in the sample, k is the background value change that may be caused by the action of natural rock formation, the overall value is 1.5, and B_i is the geochemical background value of the element in the soil. The classification standards of Müller [15] are shown in Table 3.

Table 3. Geo-Accumulation Index (I_{geo}) and classification of pollution level.

Geoaccumulation Index (I_{geo})	Rank	Pollution Level
$I_{geo} \leq 0$	0	Unpolluted
$0 < I_{geo} \leq 1$	1	Unpolluted to moderately polluted
$1 < I_{geo} \leq 2$	2	Moderately polluted
$2 < I_{geo} \leq 3$	3	Moderately to strongly polluted
$3 < I_{geo} \leq 4$	4	Strongly polluted
$4 < I_{geo} \leq 5$	5	Strongly to extremely polluted
$5 < I_{geo} \leq 10$	6	Extremely polluted

2.5.2. Potential Ecological Risk Index Method

The method is relatively fast, convenient, and straightforward. It not only reveals the impact of various pollutants in sediment environments of a particular area, but it also reveals the combined comprehensive effects of multiple contaminants in the environment. A single metal's Potential Ecological Risk Index were determined by following the formula below [16] and developed by Qi et al. [33]:

$$E_r^i = T_r^i \times C_f^i,$$

$$C_f^i = \frac{C^i}{C_n^i}$$

where E_r^i the is potential ecological risk factors for each heavy metal; T_r^i The toxicity response factor for the given element of "i", the toxicity response factor of Cd is 30 and C_f^i the pollution coefficient of a single element of "i"; C^i is the measured concentration of heavy metal in sediment; C_n^i which is the background value of heavy metal in sediment. The superscript "i" indicates the specific pollutant. The classification standards are shown in Table 4.

Table 4. Criteria for individual potential ecological risk coefficient indices (E_r^i).

| Rank	Individual Potential Ecological Risk Index (E_r^i)	Individual Potential Ecological Risk Level
1	<40	Slight
2	40–80	Medium
3	80–160	High
4	160–320	Very High
5	≥320	Extremely High

2.6. Data and Statistical Analysis

The Data Processing System (DPS 2000) was used to carry out statistical analysis of experimental data. The probability value method was applied to obtain the corresponding four times under the LC_{50} [34]. The toxicological concentration and toxic regression equation for Daphnia mortality rate in overlying water was established, and chi-square was tested on regression equations formula [35] using Origin 2019b. Each value signifies

the mean of four replicates $\pm$ standard deviation (SD). Levels of statistical significance are shown as * $p < 0.05$ and ** $p < 0.01$.

3. Results and Discussion

3.1. Distribution Coefficient and Fitted Model of Cd in Simulated Sediment and Overlying Water Systems

This crucial stage was carried out by mixing concentrated Cd and sediments. The Cd contamination of the simulated sediment samples were obtained after simulated lake water treatment with varying contents of Cd^{2+}. After repeated washing, Cd reached an equilibrium state between column water and sediment. The concentration of Cd in the simulated sediment and the overlying water system are shown in Figure 2. When the concentration of exogenous Cd increases, the Cd concentration in sediments and overlying water also increase. The ranges of Cd concentration in the sediment was between 2.7 and 3530.0 mg kg^{-1}, while the Cd concentration in the overlying water system was 0.00–10.40 mg kg^{-1}. The distribution coefficients were between 339.42 and 28,787 L kg^{-1}.
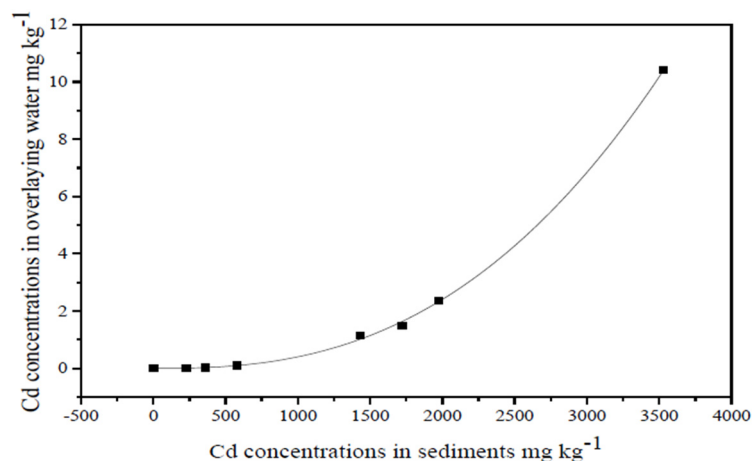
Figure 2. Cadmium concentrations in simulated sediments and overlying water systems (curve fitted by the power function).

The distribution coefficient showed a tendency to decrease because the adsorption sites on the sediment gradually became saturated. When the Cd concentration of the marker increases, the adsorption capacity of the sediment decreases. The Cd concentration relationship between the two systems was fitted by the model $Y = 7.59 \times 10^{-9} \times X^{2.58}$ ($R^2 = 0.9995$). Additionally, based on curve fitting, the solid–liquid two-phase distribution model of cadmium in the Yelang reservoir was $Y = 7.59 \times 10^{-9} \times X^{2.58}$ ($R^2 = 0.9995$). The safety threshold of total cadmium concentration in the sediment was 103 mg kg^{-1}, which was used as a reference value to evaluate the ecological risk of the sediment. The cadmium content in the sediments of Yelang reservoir was at a low level, and the environmental and ecological risks equally low. This was similar to the prior study conducted by Luo et al. [20], in which their finds claimed that the deposition rate of heavy metals in the Yelang Lake sediment is higher than the release rate, and the ecological risk from heavy metals is relatively low. When the release of heavy metals in sediments occurs, it can speedily affect the overlying water in a short time and, consequently, affect the water quality significantly [36].

3.2. Ecological Risk Assessment Based on Daphnia pulex Bio Toxicity Test

In this study, *Daphnia pulex* was selected as test organisms. The choice of *D. pulex* is owed to its sensitivity to toxins and the ability of obtaining precise information. In addition, it is recommended as a standard "Test for Acute Inhibition of Chemical Tritium GB/T 21830-2008" [37] in carrying out such investigations.

3.2.1. Lethal Effect of Cd^{2+} on *Daphnia pulex*

The sublethal concentration LC_{50} and lethal effect of Cd^{2+} in *D. pulex* at different times are shown in Table 5. Based on the lethal effect of Cd^{2+} on *D. pulex*, the sublethal concentration values and toxicological regression equations were obtained at 24, 48, 72, and 96 h. The results show that, along with time, the sublethal concentration indicated a tendency to decrease gradually. In addition, the chi-square value of the toxicological equation fitted in each period was less than the critical value ($\chi^2 = 9.49$). This illustrates that the toxicological regression equation describing the bio-toxicity of Cd^{2+} on *D. pulex* was feasible. The correlation coefficients for different times were >0.90. According to the Safe Concentration formula, SC = 96 h – $LC_{50} \times$ AF, where AF took the value of 0.01 and gives the Safety Concentration SC = 1.20×10^{-3} mg L^{-1}. This value is similar to previously reported values [32], with the sample possessing a limit of second-class water standard of 5×10^{-3} mg L^{-1}. These results are generally less than the recommended ranges of the surface water environmental quality standard GB3838—2002 [38].

Table 5. The lethal effects of Cd2+ on *D. pulex*.

Exposure time/h	LC_{50}/mg L^{-1}	95% Confidence Ìnterval	Toxicology Regression Equation	Coefficient of Correlation R^2	Chi-Square
24	1.17	0.85~1.60	y = 4.89 + 1.66x	0.98	0.01
48	0.50	0.23~1.03	y = 6.38 + 4.47x	0.92	0.68
72	0.24	0.15~0.38	y = 7.16 + 3.46x	0.97	0.23
96	0.12	0.04~0.29	y = 7.70 + 2.80x	0.93	0.3

The fundamental concept in toxicology is the concentration–response relationship. For instance, toxicological evaluation naturally uses estimation points such as LC_{50} to compare species sensitivities [17,39]. Therefore, in this study, the 96 h LC_{50} values of several other aquatic organisms collected from previous reports and summarized in Table 6. (Due to different experimental designs in the literature, if a species has multiple data, then only the lowest values were collected).

Table 6. The 96 h-LC_{50} values of some common aquatic organisms in other studies.

Species	96 h-LC_{50}/mg L^{-1}	Author(s)	Safe Concentration /mg L^{-1}
Sipunculus nudus	24.328	[40]	0.24
Misgurnus anguillicaudatus	1753.8	[41]	17.54
Argopecten irradiams	3.45	[31]	0.03
Mytilus coruscus	3.1	[42]	0.03
Eriocheir sinensis	40.279	[43]	0.40
Megalobrama terminalis	3.2	[44]	0.03
Carassius auratus gibelio	26.51	[45]	0.27
Gambusia affinis	22.55	[46]	0.23
Tanichthys albonubes	4.447	[47]	0.04
Ctenopharyngodon idella	23.51	[48]	0.24
Tigriopus japonicus	6.31	[32]	0.06
Chironomus javanus	0.06	[49]	6×10^{-4}
Cyathura carinata	37	[50]	0.37
Rasbora sumatrana	0.1	[17]	0.001
Poecilia reticulata	1.06		0.0106
Kryptolebias marmoratus	6.43×10^{-3}	[51]	6.43×10^{-5}
Fundulus heteroclitus	2.94×10^{-3}		2.94×10^{-5}

Table 6. *Cont.*

| Species	96 h-LC$_{50}$/mg L^{-1}	Author(s)	Safe Concentration /mg L^{-1}
Macrobrachium lanchesteri	0.007		7×10^{-5}
Stenocypris major	0.013		1.3×10^{-4}
Nais elinguis	0.027		2.7×10^{-4}
Chironomus javanus	0.06	[52]	6×10^{-4}
Rasbora sumatrana	0.1		1×10^{-3}
Poecilia reticulata	0.17		1.7×10^{-3}
Duttaphrynus melanostictus	0.32		3.2×10^{-3}
Melanoides tuberculata	1.49		1.49×10^{-2}
Eurytemora affinis	Male 127.8	[39]	1.28
	Female 90.0		0.09
Orconectes juvenilis	0.06		6×10^{-4}
Orconectes placidus	0.037		3.7×10^{-4}
Orconectes virilis	3.3		0.03
Procambarus acutus	0.368	[53]	3.68×10^{-3}
Procambarus alleni	3.07		0.03
Procambarus clarkii	0.624		6.24×10^{-3}

The 96 h LC$_{50}$ value is found to be 6.43×10^{-3}–1753.8 mg L^{-1}, and its Safe Concentration was evaluated based on the formula SC = 96 h − LC$_{50}$ × AF (value of 0.01), calculated as 6.43×10^{-5}–17.54, or 0.05–14,615 times the *D. pulex* 96 h LC$_{50}$ (0.12 mg L^{-1}) and the Safe Concentration (1.20×10^{-3} mg L^{-1}). In comparison to the collected aquatic organisms mentioned above, the *D. pulex* is one of the most sensitive aquatic species models in particular for cadmium toxicity [54,55]. Moreover, the 96 h LC$_{50}$ of some organisms can only be obtained in harsh environments, as highlighted in the literature [51], with the lowest value of 6.43×10^{-3} mg L^{-1}. Such a low 96 h LC$_{50}$ requires the ionic concentration in the water body to be extremely low. After adding a certain amount of calcium and magnesium ions, its value is increased significantly. In this study, it was increased from 0.23 to 23.2 mg L^{-1}, which is higher than the 96 h LC$_{50}$ of *D. pulex*. In addition, compared to the results of other freshwater Daphnia studies, Yang [56] measured the 48 h sublethal concentration of Cd^{2+} 0.62 mg L^{-1} in *Daphnia carinata* King (Cladocera—Daphnidae). This is relatively close to this study with a Cd^{2+} concentration of 48 h LC$_{50}$ = 0.50 mg L^{-1}.

Cadmium (Cd) is not an essential element for either plant or animal survival and yet one of the most toxic metals [54,55]. However, similar to a previous report [57], this study also found that the less toxicity for the tested daphniids may very likely be due to the Cd competing with calcium (Ca^{2+}) at enzymatic locations in organisms. The acute toxicity of Cd *D. pulex* is significantly minimized by increasing calcium and magnesium concentrations. The findings of this study is also supported by Clifford et al. [7], who explained that the acute toxicity of CdT to *D. pulex* is significantly influenced by Ca and Mg, which lower the potential risk of cadmium. Additionally, the less toxicity of the cadmium is evident by the dominance of mobile species in well-aerated water bodies with a pH closer to 8 [58,59]. Another possible explanation can be given using the results of researches that focused on mRNA expression as an indicator of the response to metals. For instance, Chen et al. [60] reported that miRNAs and metallothionein (MT) play critical roles in *D. pulex* tolerance to Cd, and confirmed that, when exposed to Cd-polluted environments, aquatic organisms can raise their tolerance to Cd in order to survive. In *Daphnia pulex*, different gene expression and high gene duplication rates have been identified, which enhances its adaptation in adverse environmental conditions [55,61].

3.2.2. Mortality Rate and Cd Accumulation of *Daphnia pulex* after Cd Exposure in Both Systems

Mortality is generally the primary parameter to consider when assessing the impact of contaminants in the environment. Trace metals are predictable by their toxic effects on

aquatic organisms [39]. This study investigated the toxic effects of Cd on *Daphnia pulex* in overlaying water and water–sediment systems. It is generally assumed that absorption by organisms will reduce the concentration of metals in water and thus predicted that *D. pulex* only absorbs Cd from overlying water. However, because the change in the value of Cd concentration was small, $\leq 5\%$, the concentration of Cd in the overlying water system is negligible. It was assumed that the concentrations of Cd in the water during the exposure process were constant. The mortality rate of *D. pulex* after exposure to pollutants with different levels of Cd pollution is shown in Figure 3. The mortality rate of *D. pulex* increases with the increase of Cd concentration in sediments. When the Cd concentration in the sediment exceeded 1500 mg kg^{-1}, the mortality rate of *D. pulex* reached 100%. This suggests that Cd in the solid phase (sediment) could also intoxicate the *Daphnia pulex* by sediment mud feeding and other particles. It is supported by Caumette [14], who reported that part of the assessed arsenic signal comes from the sediments ingested by *Daphnia pulex* when the residues were analyzed with soluble arsenic after extraction. Li et al. [3] argued that *D. magna* or daphniids could absorb some heavy metals, and accumulate more Cd by assimilating solid particles. Moreover, Barton et al. [1] defended that benthic organisms exposed to metal-contaminated sediments can accumulate metals by ingesting contaminated sediments and other suspended particles, and by exposure to dissolved metals in the overlying water. The overlying water systems and water–sediment systems showed no significant difference (*t*-test, $p > 0.05$) in the mortality rate of *D. pulex*. The Cd content in the *D. pulex* body after exposure with different levels of Cd pollution is shown in Figure 4. The Cd content in the *D. pulex* body increases with the increasing Cd content in the sediments with significant linear correlation (Overlying water system: $R^2 = 0.936$, $p < 0.01$; water–sediment systems: $R^2 = 0.973$, $p < 0.01$). It is interesting to note that the amount of Cd in the overlying water increased along with Cd concentration in sediment. Notably, when the Cd concentrations in sediment were 2.7 and 3530.0 mg kg^{-1}, the concentrations in the overlying water were 0.00 and 10.40 mg kg^{-1}, respectively. This scenario was also observed in a previous study [3]. Their study hence revealed that when the Cd concentrations in sediment were 344.2 and 742 µg/g, the concentrations in the overlying water were 0.531 and 1.76 mg/L, respectively. The findings of this study are supported by the conclusions of previous researches [3,62]. The increase in mortality and Cd accumulation in the two systems was principally owing to the rise in Cd concentration in the overlying water (see Figure 5).
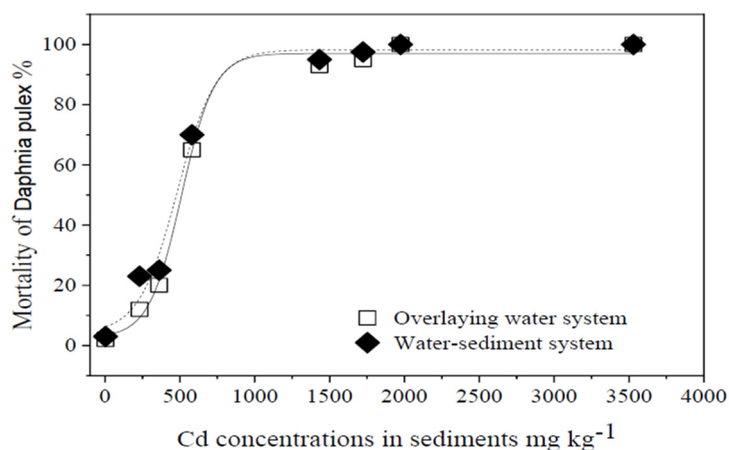
Figure 3. The mortality rate of *Daphnia pulex* under different Cd pollution levels in sediments (curves fitted by the Boltzmann function).
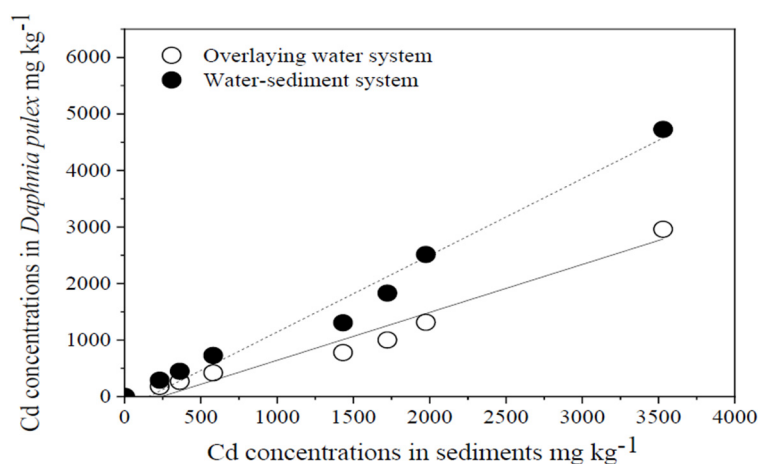
Figure 4. Cadmium concentrations in *Daphnia pulex* under different Cd pollution levels in sediments.
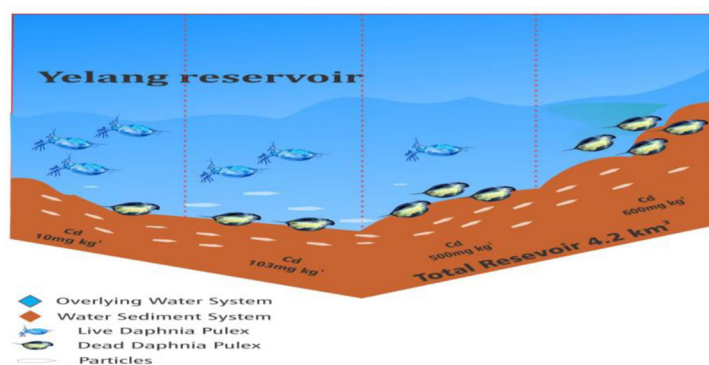
Figure 5. Highlighting the mortality rate of *Daphnia pulex* under different Cd pollution levels in sediments.

3.3. Cadmium Content in Sediments of Yelang Reservoir

The Cd content in the sediments is shown in Table 7. The content ranges from 2.51 to 5.23 mg kg^{-1} and the average value was 3.95 mg kg^{-1}. The obtained values clearly indicated that the samples exceeded the screening value of soil pollution risk on agricultural land and partly greater than the environmental quality control value of 0.6 mg kg^{-1} (GB15618-2018, China) [63]. The Cd content in the middle stream and downstream was smaller than the upstream, which could very likely be due to the larger storage area in the middle stream compared to the upstream and downstream. After an absolute reduction, the risk rates of the downstream and midstream were low. The source of cadmium concentration at the Yelang reservoir is mainly from anthropogenic activities, including domestic, agricultural and mining wastes, sewage discharge, and natural factors such as the influence of carbonate rocks of the karst terrain and its high geological background.

3.4. Ecological Risk Assessment Based on Sedimentology

The evaluation results of Cd content in the sediments of the Yelang reservoir by the Geo-Accumulation Index method are shown in Table 7. The index ranges from 2.432 to 3.491 and the contamination levels reached classes III and IV, suggesting medium–strong and strong risk levels. The degree of Cd pollution in the middle stream is lower than in the upstream and downstream due to the large volume of water which tends to lower potential risk of the Cd contents.

The Potential Ecological Risk Index method evaluation of the Cd content of the sediments of the Yelang reservoir are shown in Table 7. The risk index ranges from 242.8 to 505.9 with an average value of 381.8, suggesting that the risks were between

very strong and extremely strong. The results were identical to the evaluation results of the geo-accumulation index method. There were differences in pollution levels at the upstream, middle, and downstream, such that the hazard index was in the order midstream < downstream < upstream.

Table 7. Concentration and evaluation results of Cd in sediments at the Yelang reservoir.

Sampling Site	Concentration of Cd/mg kg^{-1}	I_{geo}	Classification of Geoaccumulation Index	E_r^i	Potential Ecological Risk Level
1	4.13	3.15	4	399.3	Extremely strong
2	3.9	3.068	4	377.4	Extremely strong
3	4.19	3.17	4	405.1	Extremely strong
4	4.18	3.168	4	404.5	Extremely strong
5	4.25	3.191	4	410.9	Extremely strong
6	4.45	3.259	4	430.6	Extremely strong
7	3.69	2.989	3	357.2	Very strong
8	4.43	3.253	4	429.1	Extremely strong
9	2.74	2.557	3	264.8	Very strong
10	4.22	3.18	4	407.9	Extremely strong
11	2.51	2.432	3	242.8	Very strong
12	5.23	3.491	4	505.9	Extremely strong
13	2.8	2.592	3	271.3	Very strong
14	5.04	3.439	4	488.1	Extremely strong
15	3.43	2.884	3	332.1	Extremely strong

The results obtained from the Geo-Accumulation Index method and the Potential Ecological Risk Index method showed that the Cd risk of the Yelang reservoir has reached a high-risk level. The Geo-Accumulation Index method pays more attention to the total amount of metals [64]. The Potential Ecological Risk index method combines metal toxicity, the local metal background value, the general migration and transformation law in the sediments, and evaluation of the regional sensitivity to metal pollution [11,65]. Both evaluation methods were based on the total amount of metals.

A large quantity of Ca, Mg, and other alkaline soil metal ions in carbonate rocks in karst areas enter the water body through erosion, weathering, and transportation, thereby increasing the contents of Ca^{2+} and Mg^{2+}. Furthermore, a significant amount of calcite and dolomite, among others, consume some H^+ in the aqueous solution during the dissolution process, causing the pH of the water body to become weakly alkaline, thereby inhibiting the effectiveness of Cd [51,57]. Many studies [32,51] have confirmed that the bio-toxicity of metals will decrease with increasing pH and hardness of water bodies. Shi [66] and other authors who studied karst areas have found that Ca^{2+} and Mg^{2+} contained in water bodies can antagonize the biological toxicity of metals, increasing the 96 h LC_{50} of the *Daphnia*. Xiong [67] confirmed that, along with the increase in the water body's hardness, the sublethal concentration (96 h LC_{50}) and Safe Concentration of Cd on *Gobiocypris rarus* both increased significantly, showing that the hardness of a water body can effectively reduce the acute toxicity of cadmium in organisms.

3.5. Analysis of the Application of Ecological Risk Assessment Methods for Cadmium in Karst Lake Reservoir Sediments

The sediment quality evaluations were mainly focused on specific chemical analysis (Cd) results, and the results obtained are an accurate reflection of its effects on the aquatic animals at the Yelang reservoir. The sediment metal risk assessment system is a large-scale system that integrates a variety of uncertainties, such as randomness, greyness, uncertainty, and ambiguity [11,68,69]. The application of conventional assessment methods without analysis cannot accurately reveal the real situation of the metal pollution level of sediments [12]. In recent years, some researchers have improved these methods [12,33,70] to make them favorable and adequately applicable. During the assessment of ecological risks in karst areas, the particularity of the region should be taken into account for the evaluation results to be more accurate. However, the biological toxicity test method directly

revealed the toxic effect of Cd on *D. pulex*, and did not require considering the particularity of the regional environment. This study only conducted preliminary toxicity tests and did not consider the effects of biomicroscopy. Further studies are required to assess whether further ranks of consumers in the food chain will produce any ecological risk.

Although karst areas are an abnormal geochemical region with respect to cadmium (Cd), due to the high concentration of Ca^{2+} and Mg^{2+} and the pH remains in the neutral–alkaline range of water body, the *Daphnia pulex* ecotoxicology evaluation method showed slight ecological risk, which is quite different from other methods used for environmental risk assessment, thus the method could be considered to use in such areas.

4. Conclusions

The sediment quality evaluations were mainly focused on specific chemical analysis (Cd) results, and the results obtained are an accurate reflection of its effects on the aquatic animals at the Yelang reservoir. The sediment toxicity experiment was carried out by mixing concentrated Cd and sediments. Based on the bio-toxicity experiment, it was deduced that the Safe Concentration threshold of Cd in the sediment was 103 mg kg^{-1}. The cadmium contents in the sediment of the Yelang reservoir ranged from 2.51 to 5.23 mg kg^{-1}. The Geo-Accumulation Index and the Potential Ecological Risk Index showed that the water environment of the Yelang reservoir had strong to extremely strong ecological risks. However, due to the high concentration of Ca^{2+} and Mg^{2+} and that the pH remains in the neutral–alkaline range, the *Daphnia pulex* ecotoxicology evaluation method showed slight ecological risk, which is quite different from the current available for environmental risk assessment, thus the method can be considered for use in the karst area. This study only conducted preliminary toxicity tests and did not consider the effects of biomicroscopy, further studies are required to assess whether further ranks of consumers in the food chain will produce any ecological risk.

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