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海河流域典型区域重金属沉积物生态风险研究

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摘要:针对水库重金属污染及其生态效应问题,分析海河流域北部4座典型水库沉积物中6种重金属(As、Cr、Cu、Ni、Pb和Zn)的分布情况,并评价污染物类型的相关性。采用地累积指数法、潜在生态风险指数法和物种敏感性分布法分析4个水库沉积物中重金属的生态风险。结果表明:沙河水库、密云水库和于桥水库的重金属沉积物生态风险等级为优,但官厅水库重金属沉积物生态风险等级为良。不同重金属对5%的底栖生物物种的危害质量分数(HC_5)不同,由高到低依次为As(0.210 mg/kg)>Ni(0.071 mg/kg)>Cr(0.052 mg/kg)>Zn(0.050 mg/kg)>Cu(0.006 mg/kg)>Pb(0.005 mg/kg)。研究成果有助于了解水库沉积物中重金属的生态风险,为水库生态管理提供依据。

关键词:水库;重金属;沉积物;生态风险;物种敏感性分布

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随着工业化和城市化进程的推进,流域生态系统也发生了巨大变化,水库作为人类社会发展的产物,在流域生态系统中起着重要作用[1-3]。据报道,我国现有9万余座水库,主要用于农业灌溉、防洪和发电,在我国社会中发挥着重要作用[4]。然而,水库正面临着生态风险问题。Zhang等[5]调查了海河流域山区城市带河流沉积物中的3种重金属,发现近30年矿山开采,城镇化水平会导致城市河流沉积物中因采矿造成的Cr和Zn污染加剧。海河北部水库作为流域上重要的汇水与储水工程,需要高度关注重金属污染,同时迫切需要对水库重金属污染可能造成的生态风险问题进行评价。

沉积物既是重金属的接收端,又是重金属的释放端,被认为是一种判别水体污染现状的重要指标[6-7]。一般情况下,重金属通过河流输送进入水库,并通过絮凝或沉淀的方式进入沉积物中[8-9]。研究[10]显示,进入水生态系统的85%以上的重金属以不同形式储存在沉积物中。Fu等[11]发现长江流域沉积物中的重金属污染物具有较高的生态风险,对水生态系统存在不利影响。因此,充分分析重金属沉积物在不同区域环境中的生态风险现状,精确描述重金属沉积物可能产生的风险水平,是当下生态安全管理的重要需求。

物种敏感性分布法于20世纪70年代被提出,是用于描述环境中不同生物对污染物敏感性的方法。结合环境暴露的分布情况,建立联合概率曲线,以更好地描述暴露概率和效应超越概率,用于整体风险评估[12-13]。与以往的确定性生态风险评估方法不同,物种敏感性分析在基于概率描述环境暴露与生态系统风险的关系方面更加科学[14]。利用物种敏感性分布法将污染物的污染现状与水环境中的生物联系起来,能得出更精确的评价结果,在水库生态

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安全管理中发挥重要作用。目前,基于物种敏感性的生态风险评价主要是在淡水河流中进行,而在水库环境系统中很少进行。

因此,本研究的主要目的是:估算海河流域北部水库沉积物中微量金属的质量分数特征;通过地累积指数法、潜在生态风险指数法和物种敏感性分布,对沉积物中的微量金属生态风险以及重金属沉积物可能危害生物比例进行定量分析。

1　材料与方法

1.1　研究区域与数据资料

海河流域北部是中国人口最密集、用水需求最大的区域之一。位于北纬 41°35 ′N～38°52 ′N 和东经118°44E～112°10E,区域总面积83 900 km²。属东亚季风气候温带,年平均气温 19 ℃,年平均降雨量 490 mm 左右,最高气温 33 ℃出现在 7 月,最低－6 ℃出现在 1 月[15]。为保证区域生产生活用水,海河流域北部有 4 座大(1)型水库、2 座大(2)型水库和 5 座中型水库。密云水库、于桥水库、官厅水库和沙河水库是海河流域北部 4 座典型水库。

密云水库、于桥水库、官厅水库和沙河水库沉积物重金属数据来自三大网络文献数据库(Web of Science、Science Direct 和中国知网)2002 年和 2019 年的文献。文献中重金属的测定方法为国家推荐的标准方法或按标准修订的方法。物种毒理学数据于 2020 年 10 月获取自美国环保局 ECOTOX 数据库。该数据库包含全球范围内化学品的急性和慢性毒性数据,包含了不同生态系统下不同物种,并不断更新,为物种敏感性分布模型构建提供数据基础。由于不同国家相似物种对相同污染物的耐受性不同,同一物种试验环境和自然环境中的耐受性也不同[16]。所以在筛选数据时,同一物种选择相同的环境、相同暴露时间和处理方法获得的数据。选取 As、Cr、Cu、Ni、Pb、Zn 在淡水介质中暴露 10 d 以内的半致死浓度(LC_{50})或半效应浓度(EC_{50})的毒理学数据。选择无脊椎生物、软体生物、蠕虫、底栖生物、甲壳类、节肢生物作为主要评价对象。当同一物种拥有多个毒理学数据值时,使用数据的几何平均值作为物种的毒理学数据[17]。

1.2　研究方法

1.2.1　地累积指数法

地累积指数法是一种广泛用于评价水体沉积物重金属生态风险的方法[18-19],该方法有效避免了自然沉积的对生态风险评价的影响,能更好地反映重金属污染现状。

$$I_{\text{geo}}=\log_2\left(\frac{C_n}{1.5\times B_n}\right) \tag{1}$$

式中:I_{geo}为地累积指数;C_n 为沉积物中重金属实测浓度;B_n 为沉积物背景参考值;1.5 为背景矩阵校正系数。$I_{\text{geo}}<1$ 为优;$1\leqslant I_{\text{geo}}<3$ 为良;$3\leqslant I_{\text{geo}}<5$ 为较差;$5\leqslant I_{\text{geo}}$为差。

1.2.2　潜在生态风险指数法

潜在生态风险指数法是 1989 被提出的一种简易快速的水体沉积物生态风险评价方法。该方法通过分析水体沉积物污染现状,反映沉积物中的重金属对环境的影响[20-21]。

$$C_{f,i}=\frac{C_{D,i}}{C_{R,i}} \tag{2}$$

$$E_{r,i}=T_{r,i}\times C_{f,i} \tag{3}$$

$$R_{\text{I}}=\sum_{i=1}^{n}E_{r,i} \tag{4}$$

式中:$C_{f,i}$ 为给定重金属的污染指数;$C_{R,i}$ 为沉积物中重金属的背景值;$C_{D,i}$ 为重金属的实测质量分数;$E_{r,i}$ 为重金属的潜在生态风险因子;$T_{r,i}$ 为单一重金属污染的毒性因子;R_{I} 为重金属总潜在生态风险指数。沉积物背景值的参考值为中国土壤背景值。Cd、Cu、Pb、Cr、Zn、Hg 和 Ni 的背景值分别为 0.07、20.00、23.60、53.90、67.70、0.04 和 24.90 mg/kg[22]。$R_{\text{I}}<150$ 时,风险水平较低;$150\leqslant R_{\text{I}}<300$,风险水平中等;$300\leqslant R_{\text{I}}<600$,风险等级高;$R_{\text{I}}\geqslant 600$,风险水平非常高。

1.2.3　物种敏感性分布法

选用 Burr Ⅲ 分布对累积暴露浓度曲线拟合,Burr Ⅲ 分布的偏度和峰度覆盖范围更大,可以使其更灵活地拟合参数。HC_5 是物种敏感性分布曲线上对应于 5% 影响物种的累积浓度。HC_5 越小,其对应重金属的毒性越强[23-25]。Burr Ⅲ 分布参数的函数方程为

$$\text{HC}(q)=\frac{b}{\left[\left(\frac{1}{q}\right)^{\frac{1}{k}}-1\right]^{1/c}} \tag{5}$$

$$\text{PAF}(x)=\frac{1}{\left[1+\left(\frac{b}{x}\right)^{c}\right]^{k}} \tag{6}$$

$$\text{msPAF}=1-\prod_{i=1}^{n}(1-\text{PAF}_i) \tag{7}$$

式中:q 是相应的保护级别;PAF 是对应于物种敏感性分布曲线上测量质量分数的有害物种的

比例；x 是实测的污染物质量分数；b、c、k 为函数的 3 个不同参数；msPAF 是多种污染物引起的危害物种的比例，进而反映水中多种污染物引起的综合污染水平。

3　结果与讨论

3.1　重金属的分布特征

密云水库、于桥水库、官厅水库和沙河水库沉积物中重金属含量现状见表 1。从表 1 可以看出，各重金属的含量变化较大，Zn 和 Cr 的平均质量分数分别为 158.66 mg/kg 和 118.65 mg/kg，是水库沉积物中主要的重金属。水库沉积物中 Ni 的平均质量分数为 39.32 mg/kg，在 6 种重金属中最低。4 座典型水库沉积物中重金属的分布有一定的相似性，重金属质量分数相近。Zhang 等[5]在调查海河流域沉积物时发现，沉积物中 Zn、Cu 的质量比受人类活动影响较大。分析结果表明，海河流域北部 4 座典型水库沉积物重金属质量比已经超出区域背景值，水库沉积物重金属质量比已受到当地工业化发展的影响。

表 1　海河北部 4 座典型水库沉积物重金属质量分数

Tab. 1　Heavy metal mass fraction in sediments of typical reservoirs in Haihe River basin and typical reservoirs in China

单位：mg/kg

水库名称	As	Cr	Cu	Ni	Pb	Zn
沙河水库[26-25]	35.75	65.41	54.36	52.65	31.72	291.17
密云水库[28-29]	38.00	119.30	37.33	38.78	55.32	106.82
官厅水库[29-30]	160.72	151.57	55.07	39.70	70.74	133.50
于桥水库[31-32]	10.08	138.33	49.28	26.16	21.34	103.16

由于 4 座典型水库具有相似的地理特征，通过相关性分析方法对 4 座水库沉积物中重金属的来源进行初步分析。分析发现，Ni-Cr（相关系数为 −0.778）、Zn-Cr（相关系数为 −0.887）和 Zn-Ni（相关系数为 0.867）之间存在显著相关关系，Pb-As（相关系数为 0.852）显著相关，见图 1。通过对比分析，Zn、Ni、Cr 存在明显的相关关系，Pb 和 As 也存在一定的相关关系。官厅水库上游为工业聚集区、有色金属冶炼和原料制造企业众多，年工业污水排放量达到 12.07 亿 m^3[33]。程麟钧等[34]对官厅水库入库重金属研究显示官厅水库的 As 在枯水期和丰水期含量差异较大，丰水期质量分数约为枯水期的 6 倍。沙河水库上游温榆河共有污水出水口 793 个，日污水排放量可达 90 万 t。温榆河重金属富集明显，As 积累较严重[35]。密云水库上游有丰富的矿产资源，矿石采选业和废弃尾矿库已经对上游水质产生了影响。潘丽波等[36]研究发现，密云水库上游矿区重金属富集严重，沉积物 Cu、Pb 和 Cd 超标，重金属和固体悬浮物存在向下游迁移的现象。重金属的开采也是水库上游的主要污染源，侯迎迎等[37]发现，Cd 主要受人为源的影响，As 和 Pb 以自然源为主，也受人为源的影响。采动产生的重金属也是于桥水库上游的主要污染来源。

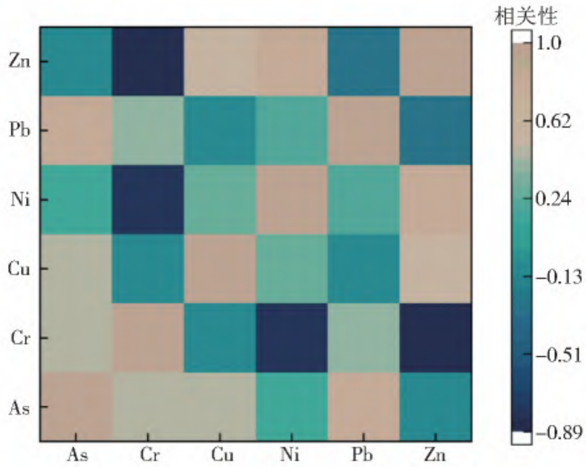

图 1　沉积物重金属相关性

Fig. 1　Correlation of heavy metals in reservoir sediments

3.2　重金属生态风险分析

3.2.1　重金属的分布特征

4 座水库沉积物重金属地累积指数见图 2（a）。对于沉积物中的 As，除官厅水库外，其余水库的地累积指数均小于 1，未受污染，范围为 0.02 ～1.18。其他重金属的地累积指数均小于 1，表明水库沉积物未受到重金属的严重污染。4 座典型水库沉积物重金属潜在生态风险指数见图 2(b)。沙河水库、密云水库、官厅水库和于桥水库的潜在生态风险指数分别为 90.68、91.92、275.69 和 47.69。官厅水库重金属沉积物潜在生态风险为良，其他 3 个水库的潜在生态风险为优，这与李捷等[38]的结果相似。通过地累积指数和潜在生态风险指数法的分析可以发现，As 是 4 座水库的主要污染物。As 在水生态系统和土壤生态系统中具有迁移、转化和沉积的能力。As 也容易被植物吸收，进入食物链和生物累积。沉积物中的重金属主要来自水库周围工矿企业的生产和大量未经处理废水的排放[26-32]。总体而言，As 是 4 座水库沉积物中污染最严重的重金属，对官厅水库重金属沉积物生态风险为良。As 应列为水库生态管理的重点污染物。

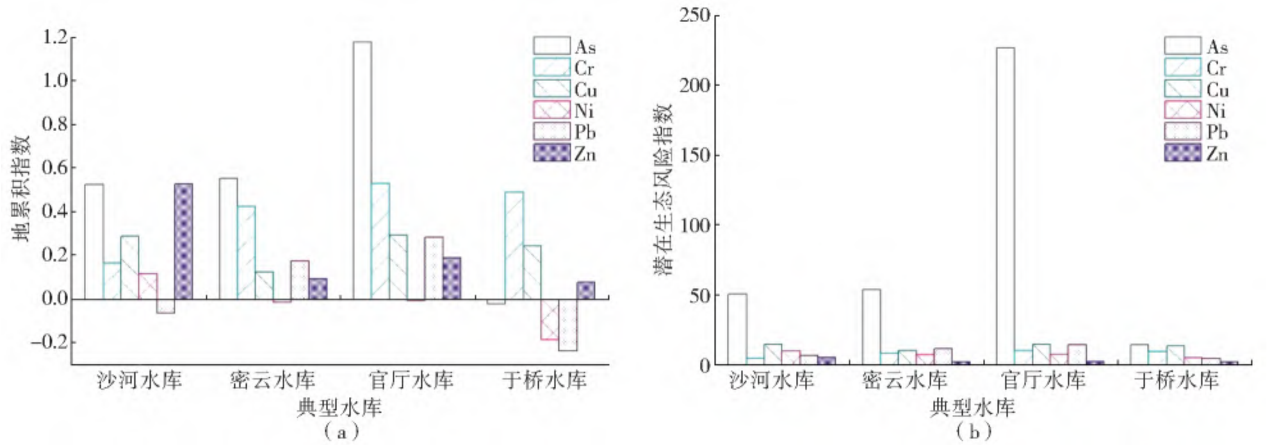

图 2　地累积指数和潜在生态风险指数评估结果

Fig. 2　Geoaccumulation index and potential ecological risk index of heavy metal in sediment

3.2.2　基于物种敏感性分析的生态风险

Burr Ⅲ和 Weibull 是最常见的最优物种敏感性分布曲线。考虑到物种敏感性分布的通用性、便捷性和可比性，大多数研究者倾向于使用对数正态分布和对数逻辑分布。然而，这些模型在本研究中的表现并不优于 Burr Ⅲ和 Weibull 模型。如图 3 所示，6 种重金属对淡水底栖生物有不同的影响。6 种重金属 HC_5 值的降序排列为 As(0.210 mg/kg)＞Ni(0.071 mg/kg)＞Cr(0.052 mg/kg)＞Zn(0.050 mg/kg)＞Cu(0.006 mg/kg)＞Pb(0.005 mg/kg)，说明在相同质量分数状态下，Pb 对水生态环境的影响最为显著。

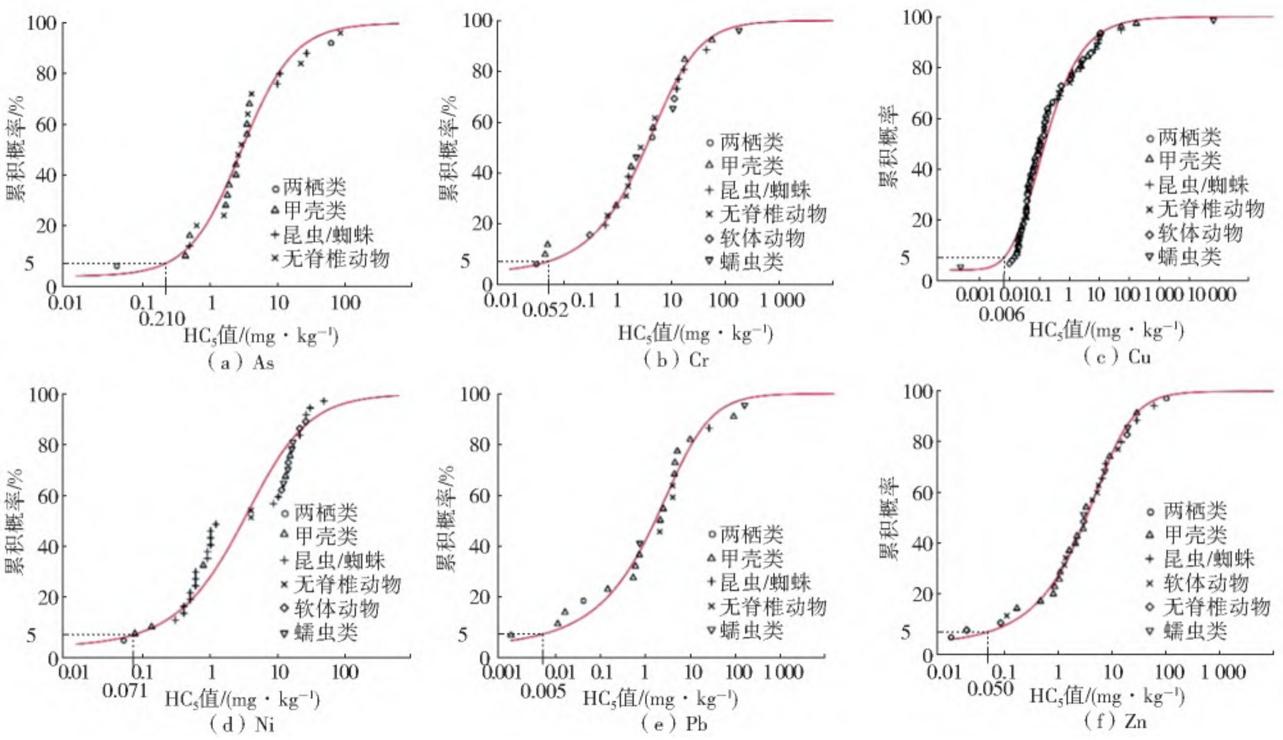

图 3　6 种重金属敏感性分布曲线

Fig. 3　Distribution curve of species sensitivity of heavy metals to all species

4 座典型水库沉积物中重金属的平均 PAF 由高到低依次为 Zn(97.5%)＞Cu(97.1%)＞Cr(96.6%)＞Zn(92.2%)＞Pb(91.8%)＞Ni(90.8%)，见图 4。4 座水库中 6 种重金属的平均 PAF 均在 90%以上。虽然物种敏感性分布曲线受到物种代表性、数据数量等因素的影响，但从结果来看沉积物对底栖生物的影响应受到高度关注。不同物种对 6 种重金属的耐受能力各不相相同，高质量分数的重金属沉积物可能会对物种丰度造成影响，江文渊等[31]发现于桥水库底栖动物的分布与沉积物重金属质量分数呈负相关。沉积物中铅的高质量分数对底栖动物的多样性和丰度有一定的影响，容易导致底栖动物的单一性。水库沉积物中有丰富的底栖生物，底栖生物独特的进食模式和生物调节机

制在使其体内积累了微量金属。沉积物中的重金属在底栖生物中积累,并通过食物链影响水生环境中的其他生物。与此同时,底栖生物的生命活动会对沉积物造成干扰,增加重金属的暴露风险。

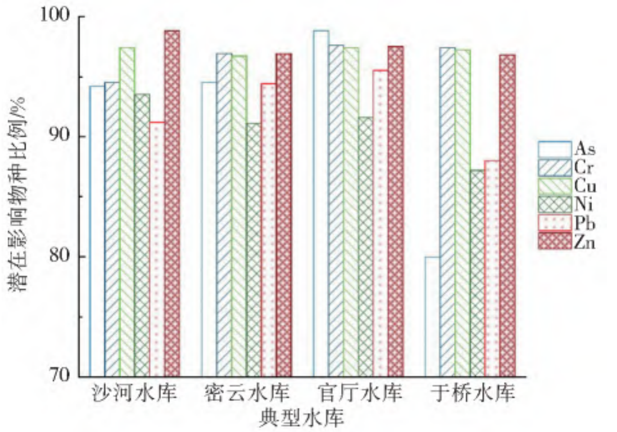

图 4　4 座典型水库重金属潜在影响的物种比例

Fig. 4　Potential affected fraction of four typical reservoirs

4　结　论

本研究从地累积指数、潜在生态风险指数和物种敏感性分布 3 个指标评价了水库沉积物中重金属的危害。地累积指数和潜在生态风险指数显示 4 座典型水库重金属沉积物生态风险处于优良水平。物种敏感性分布结果显示 6 种重金属的平均 PAF 均在 90%以上,重金属沉积物对底栖生物的影响应引起高度重视。运用 3 种生态风险评价方法从水生生物的角度,分析了水库重金属沉积物与水库生态环境的关系,评价了水库重金属沉积物的生态风险等级。与此同时不难发现,现阶段水库沉积物中重金属质量分数相对较低,生态风险水平较好,但沉积物中重金属对水库底栖生物的影响不可忽视。本研究的评价数据表明,为降低水库生态风险水平,重金属沉积物应是生态风险管理关注的重要指标。

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Ecological risk assessment of heavy metals in reservoir sediments of Haihe River basin based on species sensitivity distribution

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Abstract:With the development of industrialization and urbanization,the water environment problems in Haihe River basin are becoming increasingly prominent,and the ecological security of reservoirs is facing threats in Haihe River basin. Sediment is an important index to distinguish water pollution status. The reservoir ecological risk level can be effectively understood through sediment ecological risk assessment. Shahe Reservoir, Miyun Reservoir, Guanting Reservoir and Yuqiao Reservoir are selected as the main research objects because of heavy metal pollution and ecological effects in reservoirs. The data on the mass fraction and toxicology of heavy metals in reservoir sediments were obtained from published articles and journals. Through the analysis of distribution characteristics and correlation analysis, the distribution characteristics and pollution sources of heavy metal sediments were judged. The geological accumulation index and potential ecological risk index were used to evaluate the ecological risk level of heavy metal sediments. Finally, the species sensitivity index was used to evaluate the proportion of potentially harmful species in heavy metal sediments. The distribution characteristics and correlation analysis results show that the distribution of heavy metals in the sediments of the four typical reservoirs are similar to some extent, and the mass fraction of heavy metals are comparable. The distribution of heavy metal deposits in reservoirs of Haihe River basin is similar to some extent, and the mass fraction of heavy metal in sediments may be affected by industrialization. The results of ecological risk analysis showed that As was the most polluted heavy metal in the sediments of the four reservoirs. The ecological risk grade of Shahe Reservoir, Miyun Reservoir and Yuqiao Reservoir is low, but for Guanting Reservoir is medium. Species sensitivity distribution showed that different heavy metals had different mass fraction of harmful mass (HC_5) to 5% of benthic species. The average harmful species proportion (PAF) of heavy metals in the sediments of four typical reservoirs from high to low is Zn(97.5%)>Cu(97.1%)>Cr(96.6%)>Zn(92.2%)>Pb (91.8%)>Ni(90.8%). These results indicate that the six heavy metals in sediment may have certain effects on the survival of more than 90% of the benthic organisms in the reservoir. The overall results show that the mass fraction of heavy metals in the sediment a reservoir is relatively low, and the ecological risk level is good, but the impact of heavy metals in the sediment on the benthos of the reservoir cannot be ignored. The research results are helpful to understand the ecological risk of heavy metals in reservoir sediments and provide the basis for reservoir ecological management.

Key words: reservoir; heavy metals; sediment; ecological risk; species sensitivity distribution

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