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开封市主要河道沉积物重金属时空分布特征及生态风 险评价

丁亚鹏¹, 卢希昊¹, 王晓婧^{1,2}, 武锟鹏¹, 张浩杰¹, 李欢³, 付贤志^{4*}, 王洪涛¹

(1.河南大学地理与环境学院,开封 475004; 2.河南大学黄河中下游数字地理技术教育部重点实验室,开封 475004; 3.中国环境科学研究院环境基准与风险评估国家重点实验室,北京 100012; 4.河南大学生命科学学院,开封 475004) 摘要:城市河流沉积物重金属污染是影响河流生态系统健康的重要威胁.为探究开封市河流沉积物重金属时空分布特征,分别于2015年和2021年对河流表层沉积物进行采样,对比不同时期沉积物中Cd、Cr、Cu、Ni、Pb和Zn的含量,使用地累积指

别于 2015 年和 2021 年对河流表层沉积物进行采样,对比不同时期沉积物中 Cd、Cr、Cu、Ni、Pb 和 Zn 的含量,使用地累积指数、生物毒性风险评价和潜在生态风险指数法对两个时期重金属污染进行了评价. 结果表明,2021 年开封市河流沉积物重金属含量相较于 2015 年出现较大幅度的下降,Cd、Cr、Cu、Ni、Pb 和 Zn 分别下降 94.42%、18.4%、85.7%、45.19%、75.61% 和 92.28%,化肥河和惠济河两个时期重金属含量均高于其他河流. 相关分析和主成分分析表明开封市河流沉积物重金属污染源具有高度的相似性,产业布局、道路交通和土地利用等人类活动是其主要污染源. 不同时期主要污染物存在一定差异性,2015 年 Cd、Cr、Pb 和 Zn 是主要污染物,2021 年 Cd、Cu、Pb 和 Zn 是主要污染物. 地累积指数、生物毒性风险评价和潜在生态风险指数评价结果表明,开封市河流沉积物重金属污染时空差异大,惠济河和化肥河污染状况依然严重,仍属于中、高污染等级,特别是Cd 污染严重. 开封市河流重金属治理任重道远,特别需要加强对重点河段的工程治理和对重点污染元素的有效监测.

关键词:开封市;城市河流;沉积物;重金属;风险评价

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Spatial and Temporal Distribution Characteristics of Heavy Metals in Main Rivers Sediments and Ecological Risk Assessment in Kaifeng City

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Abstract: Heavy metal pollution in urban river sediments is an important threat to river ecosystem health. To explore the temporal and spatial distribution characteristics of heavy metals in river sediments of Kaifeng City, the surface sediments of rivers were sampled in 2015 and 2021, respectively, and the contents of Cd, Cr, Cu, Ni, Pb, and Zn in sediments at different periods were compared. The heavy metal pollution in the two periods was evaluated using the indices of geo-accumulation, bio-toxicity risk assessment, and potential ecological risk. The results showed that the content of heavy metals in river sediments of Kaifeng City in 2021 were decreased significantly compared with that in 2015. Cd, Cr, Cu, Ni, Pb, and Zn decreased by 94.42%, 18.4%, 85.7%, 45.19%, 75.61%, and 92.28%, respectively. The heavy metal content in the Huafei River and Huiji River was higher than that in other rivers in both periods. Correlation and principal component analyses showed that the heavy metal pollution sources of river sediments in Kaifeng City were highly similar, and human activities such as industrial layout, road traffic, and land use were the main pollutants were different between the two sampling times. In 2015, Cd, Cr, Pb, and Zn were the main pollutants, and in 2021, Cd, Cu, Pb, and Zn were the main pollutants. The results of the geo-accumulation, bio-toxicity risk assessment, and potential ecological risk indices showed that the temporal and spatial differences in heavy metal pollution in river sediments in Kaifeng City were large. However, the heavy metal pollution of the Huiji River and Huafei River was still serious, with contents in the medium and high pollution levels, especially to Cd. The heavy metal treatment of rivers in Kaifeng City has a long way to go, and it is particularly necessary to strengthen the engineering treatment for key river sections and effectively monitor key pollution elements.

Key words: Kaifeng City; urban rivers; sediment; heavy metals; risk evaluation

城市河流作为城市生态系统的重要组成部分, 在调蓄洪涝、景观娱乐、气候调节和生物多样性维 持等方面发挥着重要的作用,对维持城市生态系统 功能、提供生态系统服务十分重要^[1,2].但随着城市 化和工业化的快速发展,城市河流污染问题日益凸 显^[2,3],尤其是河流中的重金属污染^[4],因其具有较 强的生物毒性成为备受关注的水体污染物之 一^[5,6].河流沉积物重金属污染对河流生态系统影 响较大,尤其是对河流底栖生物的影响远高于水体 重金属污染^[7].进入河流后的重金属被水体中悬浮 物吸附,最终蓄积在沉积物中^[8],而当水环境条件改变,重金属则会重新进入水体,形成二次污染源^[9,10].因此,河流沉积物不仅是重金属主要储存库,也是其潜在释放源^[11].即使河流水体污染消除,但受重金属污染的沉积物也可长期释放重金属等污

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染物,一旦通过食物链进入人体,可能会对人体健康造成巨大危害^[12].

当前国内外学者围绕城市河流沉积物重金属污 染开展了大量研究[3,13~15],主要关注河流沉积物重 金属的富集特征[16]、生态风险评价[17,18]及来源解 析[19,20]等多个方面[21,22],取得了丰富的研究成果. 关于城市河流沉积物重金属富集特征的研究大多集 中在单一时间点不同河段沉积物重金属的差异 性[23]及不同水文时期沉积物重金属的差异性方 面[24],对长时间序列城市河流沉积物重金属的变化 研究较少. 在河流沉积物重金属的生态风险评价方 面,由于评价方法多样,如地累积指数法[25,26]、沉积 物富集系数法[27,28]、潜在生态风险指数[29,30]和内 梅罗综合污染指数[31,32]等,尚未形成统一的认知, 常会根据研究目的不同而选择相应的方法. 河流沉 积物重金属来源方面探究多采用相关分析[13]、主 成分分析[20,32]和正定矩阵因子分解模型[33]等方法, 各种方法均能够在一定程度上解析沉积物重金属来 源,运用广泛.

城市作为人口-经济-产业高度集中的区域,因功能区的差异和生产生活要素的非均衡分布等,对河流沉积物重金属的时空分布会产生一定影响,不同河段沉积物重金属的生态风险也会存在差异^[34].因此,开展城市河流沉积物重金属时空分布特征和生态风险评价的研究,有利于进一步了解城市河流沉积物重金属污染特征及动态变化规律,对于城市

河流环境治理与沿岸居民健康具有重大意义.本文以开封城市河流沉积物为研究对象,分析沉积物中重金属含量的时空变化特征,并对其进行生态风险评价,通过探究城市河流沉积物重金属的动态变化及其生态风险,以期为开封市河流管理提供一定的科学依据.

1 材料与方法

1.1 研究区概况

开封市位于黄河下游地区(图1),属于温带大陆性季风气候,年均温14.52℃,年均降水量627.5 mm,降水多集中在7月和8月.该地区成土母质为黄河冲积物,主要土壤类型为黄潮土,境内河流众多,素有"北方水城"之称.市区内主要河流有黄汴河、护城河、马家河和化肥河等,均属于惠济河支流,河流主要水源是引黄水,同时城市生活污水、工业废水、大气降水和地下水共同补给河流.市区河流具有引黄灌溉、生物廊道和景观娱乐等重要功能,特别是2017年实施"一渠六河"综合治理工程以来,沿河区域被打造成滨河公园,是市民重要的休闲娱乐场所.在河流出市区范围后,化肥河、惠济河和马家河成为沿河农田灌溉的主要水源.

1.2 样品采集与处理

在城市河流水系图的基础上,结合实地调查,分别于2015年6月和2021年6月采用抓斗式采样器对黄汴河(HB)、护城河(HC)、马家河(MJ)、化肥

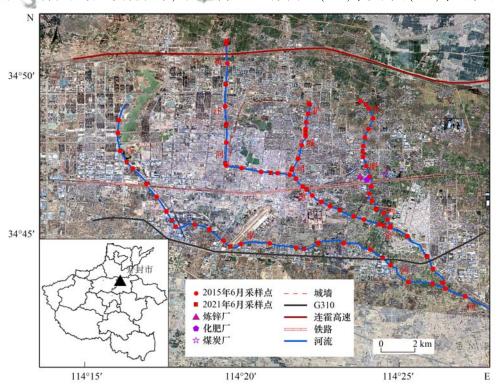


图 1 研究区位置及采样点分布示意

Fig. 1 Location of the investigation area and distribution of the sampling sites

河(HF)和惠济河(HJ)进行沉积物采样(图 1).每个采样点取 6 个样品,混合均匀后封存,并记录采样点坐标和周围信息. 2015 年 6 月在 HB 设置 11 个采样点,HC 8 个采样点,HF 16 个采样点,MJ 20 个采样点,HJ 17 个采样点,共计72 个采样点; 2021 年 6 月在 HB 设置 5 个采样点,HC 3 个采样点,HF 3 个采样点,MJ 5 个采样点,HJ 4 个采样点,共计20 个采样点.两次采样均采用统一的处理方式,将采集的样品带回实验室,至于阴凉通风处自然风干,挑出石粒、枯枝落叶、生活垃圾等杂物,研磨后过100 目筛备用.

实验采用盐酸-硝酸-氢氟酸-高氯酸消解法,在石墨全自动消解仪(ST-60)上进行消解,采用电感耦合等离子体质谱仪(ICP-MS,美国 Thermos Scientific)测量样品中Cd、Cr、Cu、Ni、Pb和Zn元素含量.为保证实验精确度并减少随机误差,利用国家标准土样(GSS-3)、平行样和空白样进行质量控制.每个样品检测3次取均值,样品加标回收率在92.5%~107.8%之间.

1.3 沉积物重金属污染评价

本文对河流沉积物重金属污染评价采用地累积 指数法、生物毒性风险分析和潜在生态风险指数法 这 3 种方法. 地累积指数法通过对比土壤或沉积物中重金属含量与其地球化学背景值的关系,直观地反映外源性重金属在区域土壤或沉积物中的富集程度^[25,26,35];生物毒性风险法能够反映河流沉积物重金属对河流生物的危害^[36~38];潜在生态风险指数法可以反映土壤或沉积物中单种污染物的影响和多种污染物的综合影响,定量划分潜在风险程度^[35,39]. 3 种方法分别从沉积物重金属含量与背景值的联系、沉积物重金属含量对河流生物的危害、沉积物重金属含量的综合影响和潜在生态风险角度全面评价开封市河流沉积物重金属污染状况.

1.3.1 地累积指数法

地累积指数法是由德国科学家 Muller^[26]提出的,在河流沉积物重金属评价中应用广泛^[25,35],计算公式如下.

$$I_{\text{geo}} = \log_2\left(\frac{C_i}{K \times B_i}\right)$$

式中, C_i 为重金属i的实测值; B_i 为重金属i的背景值,考虑到开封市以潮土为主的土壤类型,本研究采用潮土作为背景值 $[^{39]}$;K为修正系数,通常取 1.5; I_{geo} 为重金属i的地累积指数,分级标准见表 1.

表 1 沉积物重金属污染评价

C 30	Va.	Table 1	Assessment of heav	y metal pollution i	n sediments		4/
3/5 // 1/	れ指数 I _{geo})		i性风险 EC-Q)		生生态风险指数 $\mathbf{E}_{\mathbf{r}}^{i}$)		宗合潜在生态 数(RI)
指数	风险等级	指数	风险等级	指数	风险等级	指数	风险等级
<0	无污染	< 0. 1	低	< 40	低风险	< 150	低风险
0 ~ 1	轻污染	0.1 ~1	中	40 ~80	中风险	150 ~ 300	中风险
1 ~ 2	中污染	1 ~ 5	高	80 ~ 160	较高风险	300 ~600	较高风险
2 ~ 3	中-重污染	>5	极高	160 ~ 320	高风险	600 ~4 400	高风险
3 ~4	重污染	1)	_	> 320	极高风险	>4 400	极高风险
4 ~ 5	重-极重污染	_	_	_	_	_	_
> 5	极重污染	_	_	_	_	_	_

1)"一"表示无数据

1.3.2 生物毒性风险分析

生物毒性风险(mPEC-Q)可以评价河流沉积物 重金属对河流中生物的影响^[36~38],计算公式如下:

mPEC-Q =
$$\sum_{i=1}^{n} \frac{C_i}{n \cdot \text{PEC}_i}$$

式中,n为重金属种类; C_i 为重金属i的实测值;

PEC_i 为第 i 种重金属的可能效应浓度. 根据 mPEC-Q 值的大小,判定生物毒性风险等级(表 1), mPEC-Q 包括可能效应浓度(PEC)和阈值效应浓度(TEC),通过对比单一重金属含量与 PEC(TEC)的大小来判断单一沉积物重金属的生物毒性(表 2), 当 C_i 小于 TEC 时,重金属 i 对河流底栖生物不产生

表 2 沉积物重金属污染评价参数/mg·kg⁻¹

Table 2 Assessment parameters of heavy metal pollution in sediments/mg·kg⁻¹

				0 0		
项目	Cd	Cr	Cu	Ni	Pb	Zn
中国潮土背景值	0.064	63. 3	20	27. 3	21. 8	62. 5
土壤环境质量标准(试行)1)	0.8	350	200	190	240	300
可能效应含量(PEC)	4. 98	111	149	48. 6	128	459
阈值效应含量(TEC)	0. 99	43. 3	31.6	22. 7	35. 8	121

^{1)《}土壤环境质量 农用地土壤污染风险管控标准(试行)》(GB 15618-2018)

危害, C_i 小于 PEC 时但大于 TEC 时,重金属 i 对河流底栖生物可能产生危害, C_i 大于 PEC 时,重金属 对河流底栖生物产生一定危害.

1.3.3 潜在生态风险指数法

本文采用 Hakanson 潜在生态风险指数法^[29]对 开封市河流沉积物重金属污染进行评价,计算公 式如下:

$$C_{r}^{i} = \frac{C_{i}}{C_{n}^{i}}$$

$$E_{r}^{i} = T_{r}^{i} \times C_{r}^{i}$$

$$RI = \sum_{i=1}^{n} E_{r}^{i} = \sum_{i=1}^{n} T_{r}^{i} \times C_{r}^{i}$$

式中, C_r^i 为重金属的污染指数; C_i 为重金属的实测值; C_n^i 为重金属i的参比值,本研究采用潮土背景值为参比值; E_r^i 为单一重金属潜在生态风险指数; T_r^i 为重金属i的生物毒性因子,Cd、Cr、Cu、Ni、Pb 和 Zn 的生物毒性因子分别为 30、2、5、5、5 和 1; RI 为多种重金属潜在风险指数. 潜在生态风险指数分级标准见表 1,重金属的参比值见表 2.

1.4 数据处理

实验数据在 Excel 中记录整理;空间图在 ArcGIS 10.7 中完成;进行数据分析之前,首先对数据的正态分布进行检验,对不符合正态分布的数据进行对数转换;使用 R 语言进行相关分析和主成分分析并绘制图,相关分析采用皮尔逊(Pearson)相关法(*P*<0.05).

2 结果与分析

2.1 开封市河流沉积物重金属时空分布特征

不同时期开封市河流沉积物重金属含量差异较大,2021年开封市河流沉积物重金属含量相较于2015年出现较大幅度的下降(表3).其中,Cd和Zn的下降幅度最大,均降低了90%以上;Cu和Pb的下降幅度次之,降低了80%左右;Ni降低了45%,Cr降低了18%.此外,开封市河流沉积物重金属的变异系数差异较大,2015年Cd、Cu和Zn的变异系数均较高,Pb次之,Cr和Ni的变异系数较小.除Pb以外,其余重金属2021年的变异系数均出现不同程度的下降,其中Cr和Ni的变异系数较小,分别为18.16%和37.89%.

表 3 开封市河流沉积物重金属含量特征

Heavy metal content of the river sediments in Kaifeng City Table 3 平均值 最大值 最小值 变异系数 年份 1% /mg•kg⁻ /mg•kg /mg·kg-256. 85 337. 15 2015 0.86 25. 46 Cd 9. 29 2021 0.25 1.42 170.91 2015 206.7 19.9 69.81 64.36 2021 80.71 56.96 18.16 43.33 2015 3 919.8 13.7 299.81 216.83 Cu 2021 184.84 15.83 42.87 108.64 49. 23 2015 136.6 16.1 28.89 Ni 29.87 9. 13 15.84 37.89 2021 2015 545.6 13.6 106.73 142.92 Pb 3.59 2021 168.09 26.03 170.29 31.6 2 011. 69 195. 48 2015 13 696. 4 Zn 2021 35.45 133.92 881.93 155.27

开封市不同河流沉积物重金属的时空分布差异较大(图 2). 其中 Cd、Cu、Pb 和 Zn 的变化较大, 2015 年 HF 的 ω (Cd) 为 104. 59 mg·kg⁻¹, HB、HC、HJ 和 MJ 的 ω (Cd) 均较低, 分别为 2. 25、1. 70、5. 75 和 1. 176 mg·kg⁻¹; 2021 年 Cd 含量大幅降低, 但 HF 的 ω (Cd) 依然最高, 为 3. 76 mg·kg⁻¹, HJ 次之, HB、HC 和 MJ 的 Cd 含量较低. 2015 年 MJ 的 ω (Cu) 高达 561. 3 mg·kg⁻¹; HF 和 HJ 次之, 分别为 253. 88 mg·kg⁻¹和 321. 89 mg·kg⁻¹, HB 和 HC 的 Cu 含量均较低; 2021 年 Cu 含量大幅降低, HF 和 HJ 的 Cu 含量较高, 分别为 99. 78 mg·kg⁻¹和 70. 62 mg·kg⁻¹, 其他河流含量较低. 2015 年 HF 的 ω (Pb)

为 316. 61 $\,\mathrm{mg \cdot kg^{-1}}$,其他河流含量较低;2021 年 Pb 含量大幅降低,但 HF 和 HJ 的 Pb 含量较高,分别为 60. 83 $\,\mathrm{mg \cdot kg^{-1}}$ 和 56. 83 $\,\mathrm{mg \cdot kg^{-1}}$,其他河流的 Pb 含量较低. 2015 年 HF 和 HJ 的 $\omega(\mathrm{Zn})$ 较高,分别为 7 881. 44 $\,\mathrm{mg \cdot kg^{-1}}$ 和 840. 29 $\,\mathrm{mg \cdot kg^{-1}}$,到 2021 年大幅下降,但依旧分别为 290. 83 $\,\mathrm{mg \cdot kg^{-1}}$ 和 340. 01 $\,\mathrm{mg \cdot kg^{-1}}$. 两个时期 Pb 和 Zn 的空间分布具有高度一致性,均是 HF 和 HJ 的 Pb 和 Zn 含量较高;Ni 和 Cr 含量在两个时期变化均较小,具有较强的均匀性.

2.2 开封市河流沉积物重金属来源分析 为探究开封市河流沉积物重金属来源的差异,

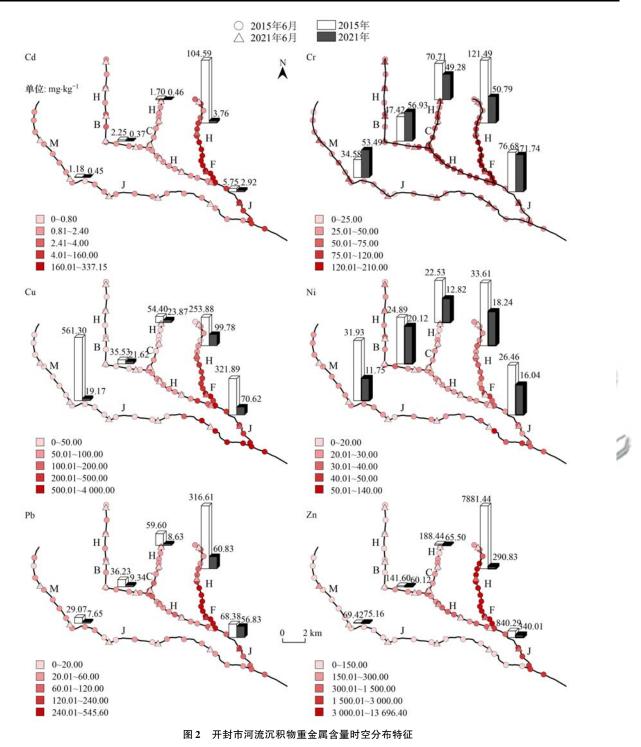
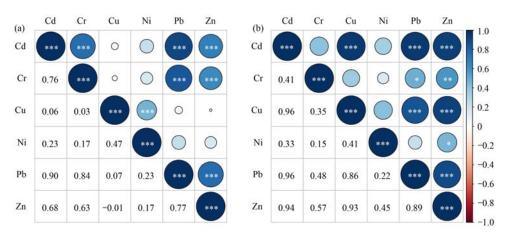


Fig. 2 Temporal and spatial distribution characteristics of heavy metal content in river sediments of Kaifeng City

将不同时期开封市河流沉积物重金属进行相关分析 (图 3). 不同时期开封市河流沉积物重金属进行相关分析 (图 3). 不同时期开封市河流沉积物重金属相关性 存在差异,2015 年 Cd、Cr、Pb 和 Zn 之间相互呈显著正相关(P<0.001),这 4 种重金属与 Cu 和 Ni 之间相关性不显著;Cu 和 Ni 之间呈显著正相关(P<0.001). 2021 年 Cd、Cu、Pb 和 Zn 之间相互呈显著正相关(P<0.01);Cr 分别与 Pb 和 Zn 呈显著正相关(P<0.05);Ni 和 Zn 之间呈显著正相关(P<0.05),与其他重金属之间相关性不显著.

为进一步探究开封市河流沉积物重金属的来

源,对其进行主成分分析(表4).主成分分析结果显示,2015年前3个主成分累计解释比例分别为88.44%,表明其可以代表6种元素的大部分信息.2015年第一主成分解释比例为56.31%,因子载荷较高的是Cd、Cr、Pb和Zn,分别为0.50、0.48、0.53和0.45,表明这4种重金属来源可能具有一致性;第二主成分解释比例23.49%,因子载荷较高的是Cu和Ni,分别为0.73和0.66;第三主成分解释比例8.63%,因子载荷较高的还是Cu和Ni,分别为0.67和-0.72,由于负值的出现,因此不能判断Cu



(a)2015 年,(b)2021 年;色柱颜色表示相关系数大小,颜色越深,相关系数越大;*表示 0.05 水平显著, **表示 0.01 水平显著,***表示 0.001 水平显著

图 3 不同时期开封市河流沉积物重金属相关分析

Fig. 3 Correlation analysis of heavy metals in river sediments of Kaifeng City in different periods

和 Ni 的来源是否具有一致性. 2021 前 2 个主成分累计解释比例分别为 84. 91%,表明其可以代表 6 种元素的大部分信息. 2021 年第一主成分解释比例为 69. 98%,因子载荷较高的是 Cd、Cu、Pb 和 Zn,分别为 0. 47、0. 46、0. 46 和 0. 48,表明这 4 种重金属来源可能具有一致性;第二主成分解释比例 14. 93%,因子载荷较高的是 Ni,为 0. 88,因此 Ni 的来源可能跟其他重金属元素存在差异.

表 4 不同时期开封市河流沉积物重金属的主成分分析结果

Table 4 Results of principal component analysis of heavy metals in river sediments in Kaifeng City under different periods

年份	项目		PC1	PC2	PC3	PC4
31	特征	值	1.84	1. 19	0.72	0. 62
2015	解释比例	列/%	56. 31	23.49	8.63	6. 37
	累计解释比	上例/%	56.31	79.81	88.44	94.81
	特征	值	2. 05	0. 95	0.86	0. 33
2021	解释比例	列/%	69. 98	14. 93	12.47	1.86
	累计解释比	比例/%	69. 98	84. 91	97. 38	99. 24
年份	重金属			因子载荷	苛	
	里並周	PC1	PC	2	PC3	PC4
	Cd	0.50	-0.	06	0. 05	0. 21
	Cr	0.48	-0.	10	0. 12	0.47
2015	Cu	0.07	0.	73	0. 67	-0.12
2013	Ni	0.18	0.	66 -	0.72	0.07
	Pb	0. 53	-0.	07	0.07	0.09
	Zn	0.45	-0.	12 -	0.07	-0.84
	Cd	0.47	-0.	05 -	0. 26	-0.09
	Cr	0. 28	-0.	41	0.84	0.07
2021	Cu	0.46	0.	08 -	0. 26	0.61
2021	Ni	0. 22	0.	88	0.35	-0.20
	Pb	0.46	-0.	21 -	0. 19	-0.72
	Zn	0.48	0.	01	0.03	0. 23

2.3 开封市河流沉积物重金属污染评价

2.3.1 地累积指数法

以中国潮土作为背景值,计算开封市河流沉积

物重金属的地累积指数(图 4). 相较于 2015 年,开封市河流沉积物重金属污染下降明显. 总体来说,2015 年 Cd 属于极重污染,地累积指数为 5. 22; Cu和 Zn属于中度污染,地累积指数分别为 1. 58和1. 87; Pb属于轻污染,地累积指数为 0. 84; Cr和 Ni属于无污染,地累积指数分别为 - 0. 70和 - 0. 58. 2021年 Cd污染下降,但依然属于中-重度污染,地累积指数为 2. 85; Cu属于轻污染,地累积指数为 0. 03; Cr、Ni、Pb和 Zn 地累积指数均小于 0,属于无污染.

开封市不同河流沉积物重金属污染状况差异较大.其中 Cd 污染最为严重,2015 年 5 条河流 Cd 污染等级为: HF(极重污染)> HJ(极重污染)> HB(重-极重污染)> HC(重污染)> MJ(重污染); 2021 年 5 条河流 Cd 污染下降,污染等级为: HF(重-极重污染)> HJ(重污染)> HC(中-重污染)> MJ(中-重污染)> HB(中污染). 其次是 Cu 污染,2015年 5 条河流 Cu 污染等级为: HJ(中-重污染)> HF(中-重污染)> HF(中-重污染)> HB(中污染)> HC(轻污染)> HB(中污染); 2021年 Cu 污染降低,HB、HC和 MJ均属于无污染,HF属于中污染,HJ属于轻污染.两个时期 Pb和 Zn污染均出现降低,差异性减小; Cr和Ni污染程度较低.

2.3.2 生物毒性风险评价

结合图 2,通过对比单一重金属 PEC 和 TEC 的大小,对开封市河流沉积物单一重金属污染生物毒性风险进行评价(表 5).不同时期开封市河流沉积物单一重金属污染生物毒性风险发生变化:2015 年对河流底栖生物会产生一定危害主要是 Cd、Cu 和 Zn,其含量超过 PEC 的样点占比分别为 26.39%、26.39%和 27.78%; 2021年重金属含量超过 PEC

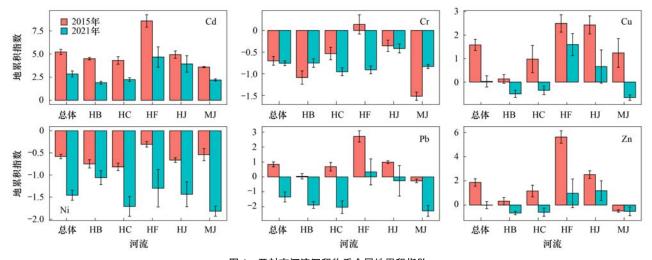


图 4 开封市河流沉积物重金属地累积指数

Fig. 4 Geo-accumulation index of heavy metals in river sediments of Kaifeng City

表 5 开封市河流沉积物重金属污染特征

Table 5 Heavy metal pollution characteristics of river sediments in Kaifeng City

			· ·				-	
元素	年份	中国潮土背景值	土壤环境质量标准值	超标率	平均超标	> PEC 样点	< TEC 样点	TEC 和 PEC 之间样点
儿系	十加	/mg⋅kg ⁻¹	/mg⋅kg ⁻¹	/%	倍数	占比/%	占比/%	占比/%
Cd	2015	0.064	0.8/	100	31. 82	26. 39	9. 72	63. 89
Cu	2021	0.004	110.00	20	1.78	10	85	Set (8
Cr	2015	63. 3	(350)	0	0. 2	16. 67	38. 89	44. 44
	2021	03.5	1 1/3/2/	0	0. 16	1018	0	100
Cu	2015	20	200	29. 17	1.5	26. 39	29. 17	44.44
Cu	2021	-/ / ZO	5 1 760	0	0. 21	Q 5	75	20
Ni	2015	27. 3	190	0	0. 15	1. 39	18. 06	80. 56
	2021	(A)	(V) */	0	0.08	0	80	20
Pb	2015	21. 8	240	12. 5	0. 44	15. 28	34.72	50
40)	2021	8 Miles	7 200	0	0.11	5	85	10
Zn	2015	62. 5	300	41.67	6.71	27. 78	38. 89	33. 33
Zil	2021	02. 3	300	15	0. 52	5	70	25

的样点占比大幅下降,其中 Cd 的占比最高,为 10%.从空间分布来看,两个时期均是 HF 和 HJ 沉积物单一重金属污染生物毒性风险较高.

不同时期开封市河流沉积物重金属生物毒性风险存在差异(图5).总体来说,两个时期开封市河流沉积物重金属生物毒性风险主要是属于中等级,2015~2021年生物毒性风险等级出现下降.2015年开封市河流沉积物重金属生物毒性风险指数为2.26,2021年为0.33,其中HF下降最大,2015~2021年从7.36下降到0.56.空间差异较大,2015年高和极高等级的污染主要集中在HF,HJ和MJ也有部分河段处于其中,2021年只有HJ部分河段属于高等级.

2.3.3 潜在生态风险指数法

不同时期开封市河流沉积物单一重金属潜在风险指数存在差异(表6),单一重金属潜在生态风险等级下降.2015年开封市河流沉积物单一重金属潜在生态风险等级总体状况是 Cd 属于极高风险

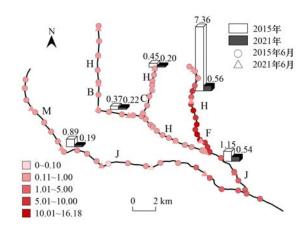


图 5 开封市河流沉积物重金属生物毒性风险指数

Fig. 5 Bio-toxicity risk index of heavy metals in river sediments of Kaifeng City

(≥320), Cu 属于中风险(40~80), Cr、Ni、Pb 和 Zn 潜在生态风险指数均低于 40, 属于低风险; 2021年 Cd 依然属于极高风险(≥320), 其他重金属均属于低风险. 空间差异较大, 2015年 HB 和 HC 的 Cu

属于低风险, HF属于中风险, HJ和MJ属于较高风险; HF的Pb属于中风险, Zn属于较高风险, 其他河流两种元素均属低风险. 2021年HF和HJ的Cd属于极高风险, 其他河流属于高风险; Cr、Cu、Ni、Pb和Zn在各河流均属于低风险.

与2015年相比,2021年开封市河流沉积物重

金属综合潜在风险指数出现下降. 2015 年开封市河流沉积物重金属综合潜在风险等级属于极高风险,到 2021 年属于高风险. 2015 年除 HF 河流沉积物重金属综合潜在风险等级属于极高风险,其他河流均属于高风险; 2021 年 HF 和 HJ 属于高风险,其他河流均属于中风险.

表 6 开封市河流沉积物重金属潜在风险指数

Table 6 Potential risk index of heavy metals in river sediments of Kaifeng City

							0 ,	
年八	項目		阜	色一重金属潜在生	上态风险指数 ((E_{r}^{i})		综合潜在生态风险
年份	项目	Cd	Cr	Cu	Ni	Pb	Zn	指数(RI)
	总体	11 933. 33	2. 21	74. 95	5. 29	24. 48	32. 19	12 072. 45
	HB	1 054. 69	1.5	8. 88	4. 56	8. 31	2. 27	1 080. 2
2015	HC	796. 29	2. 23	13.6	4. 13	13. 67	3.02	832. 93
2013	HF	49 026. 27	3.84	63.47	6. 15	72. 62	126. 10	49 298. 45
	HJ	2 693. 11	2.42	80. 47	4. 85	15. 68	13.44	2 809. 98
	MJ	551. 25	1.09	140. 33	5. 85	6. 67	1. 11	706. 29
	总体	665. 39	1.8	10. 72	2. 9	5. 97	2. 48	689. 26
	HB	171. 56	1.8	5. 41	3. 69	2. 14	-0.96	185. 56
2021	HC	215. 63	1. 56	5. 97	2. 35	1. 98	1. 05	228. 52
2021	HF	1 760. 94	1.6	24. 94	3.34	13. 95	4. 65	1 809. 43
	HJ	1 368. 75	2. 27	17. 65	2. 94	13. 03	5.44	1 410. 08
	MJ	209.06	1. 69	4. 79	2. 15	1.75	1. 2	220. 66
			7 2	7.1		7 3	C 10 1	1 3. 7.0

2.3.4 开封市河流沉积物重金属污染总体评价

开封市河流沉积物重金属污染存在时空差异, 2021 年相较于 2015 年污染状况大幅降低. 沉积物 重金属与中国潮土背景值和土壤环境质量标准值进 行对比(表5),除 Ni 以外,Cd、Cr、Cu、Pb 和 Zn 的 含量均超过潮土的背景值,其中 Cd 的污染状况最 严重,严重超出土壤环境质量标准. 2015 和 2021 年 Cd 样点超标率分别为 100% 和 20%,分别平均超出 土壤环境质量标准的 31.82 倍和 1.78 倍. 另外,从 地累积指数、单一重金属生物毒性风险和单一重金 属潜在生态风险指数来看,Cd 是开封河流沉积物重 金属的主要污染元素. 从空间分布来看, 各类重金属 污染最严重的是 HF,特别是 2021 年 HF 依旧属于 高污染河段. 从综合指标来看,2021 年相较于 2015 年生物毒性风险和综合潜在生态风险指数均出现降 低,但有所差异. 2015 年开封市河流沉积物重金属 生物毒性等级主要处于中风险,在 HF、HJ 和 MJ 部 分河段处于极高风险; 2021 年基本均属于中风险. 而两个时期综合潜在生态风险指数均属于高和极高 风险,2021年HB、HC和MJ河段属于中风险,HJ 和 MJ 依旧是高风险.

3 讨论

城市河流沉积物重金属空间分布与来源受人类活动影响较大,产业布局和土地利用类型等均会对沉积物重金属含量产生影响. 开封市河流沉积物重金属含量较高的区域主要集中在东南方向的化肥河

沿岸,为开封市的主要工业区,分布有化肥厂、炼锌厂、仪表厂、煤炭厂和联合收割机厂等^[40,41]大型工业企业,大量的生产废水排入其中,其生产废水虽经过处理,但其中各类重金属含量依然较高^[42],长期对河流排放废水导致沉积物重金属含量不断累积.惠济河重金属含量也较高,特别是化肥河注入以后,惠济河沉积物重金属含量高于之前河段,主要是各河流都属于惠济河支流,河流重金属随河水迁移,在下游河段沉积,导致惠济河下游河段河流沉积物重金属含量较高.加之开封市东南方向是开封市的老城区,生活配套设施相对落后,人口密度大,生活垃圾流入河流较多^[43],这也导致了河流沉积物的富集.

从相关分析结果来看,不同时期 Cd、Pb 和 Zn 之间相关性显著,表明其来源具有一致性,主成分分析中,2015 年第一主成分因子载荷较高的是 Cd、Cr、Pb 和 Zn,2021 年第一主成分因子载荷较高的是 Cd、Cu、Pb 和 Zn,这就表明两个时期 Cd、Pb 和 Zn 具有同源性.相关分析和主成分分析表明在 2015 年 Cd、Cr、Pb 和 Zn 来源可能具有一致性,本文结合样点信息,发现这些含量较高的样点集中在化肥河和惠济河下游河段.已有研究表明,Cd 主要来自于农业肥料和煤炭等能源燃烧^[44];Cr 和 Zn 主要来自机械制造和化工等产业污染排放^[45];橡胶轮胎、汽车润滑剂、汽车尾气等交通工具是 Pb 和 Cu 的重要来源^[46].化肥河附近分布有煤炭厂、炼锌厂、仪表厂和化肥厂等,再加之铁路经过,可能共同造成了该地

区的重金属污染. 2021 年相关分析和主成分分析表明 Cd、Cu、Pb 和 Zn 来源可能具有一致性,说明在不同时间段主要污染物会发生变化. 但就开封市来说,两个时期的主要污染物均与产业布局、道路交通、土地利用类型密切相关,因此可以认定对开封市河流沉积物重金属污染影响最重要的因子是人为复合因子. Ni 作为两个时期的第二主成分,来源跟第一主成分存在差异,加之沉积物中 Ni 含量并未超出潮土背景值较多,所有样点均在土壤环境质量标准值以内,因此不能够判断其来源,但 Ni 跟 Cu 具有一定的相关性,部分采样点 Ni 含量较高,不排除人为污染的可能性.

不同时期开封市河流沉积物重金属含量下降幅度较大,表明开封市河流重金属污染治理取得重大成功. 开封市政府于2018~2020年期间开展并完成"一渠六河"综合治理工程,该工程截污清淤,治理河底,目的是改善城市水生态环境. 本研究表明,开封市"一渠六河"综合治理工程对降低河流沉积物重金属含量有效,清除淤泥是治理河流沉积物重金属污染的有效手段^[47]. 此外,河流沉积物重金属含量解低也可能和人为污染强度降低有关,"一渠六河"征收沿河老旧建筑,截污控污,有效制止了外来污染物向河流水体及沉积物的输入,同时对两岸进行生态修复,如增加绿化面积,改善沟渠地形,从而防止因水土流失造成的废物进入水体.

对开封市河流沉积物重金属污染风险评价 3 种 方法结果进行对比分析可知,不同河流沉积物污染 风险存在差异,特别是在"一渠六河"治理后开封河 流沉积物污染风险降低,在今后治理过程中应采用 不同的治理方式,黄汴河、护城河、马家河重金属 污染程度较低,应以保持预防为主; 惠济河、化肥 河的3种评价方法结果其风险指数均高于其他河 流,表明惠济河和化肥河是今后开封市河流污染治 理的重点. 开封市河流沉积物重金属生物毒性处于 中等风险,生物环境质量有所提高,但潜在生态风险 等级较高,表明开封市河流沉积物重金属污染形势 依旧严重. 后期对于开封市城市河流沉积物重金属 仍需加强监管,应对其进行持续性监控以及进一步 治理. 从单一重金属污染来看, Cd 污染严重, 需要特 别加强对其关注. 清淤是治理河流沉积物重金属的 有效手段,同时要注重污染源头的控制,加强对主要 元素的监测和来源分析,尤其部分采样点 Cd 含量 依旧高于土壤环境质量标准值. 河流污染治理是一 项长期工作,随着时间推移,沉积物重金属含量可能 出现较大变化,因此需要持续监控以及进一步治理.

4 结论

- (1)2021 年开封市河流沉积物重金属含量相较于 2015 年出现较大幅度的下降,尤其是 Cu 和 Zn,均下降了 90%以上.同时,不同重金属元素含量空间差异性不同,Cd、Cr、Pb 和 Zn 的空间变异性高,化肥河和惠济河两个时期各类重金属含量均高于其他河流.
- (2) 开封市河流沉积物重金属污染源具有高度的相似性,污染物主要来源于产业布局、土地利用类型、道路交通等人类活动,特别是在化肥河和惠济河河段表现最为明显.
- (3)从地累积指数、生物毒性风险评价和潜在生态风险指数评价结果来看,2021年开封市河流沉积物重金属污染指数相较于2015年大幅降低,但惠济河和化肥河污染状况依然严重,仍属于中、高污染等级,其中特别是生物毒性风险评价,开封市各河流依然处于极高风险等级.

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