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拒马河流域河流沉积物与土壤重金属含量及风险评价

韩双宝1,2,3, 袁磊2*, 张秋霞2, 郑焰3, 李甫成2

(1. 哈尔滨工业大学环境学院,哈尔滨 150090; 2. 中国地质调查局水文地质环境地质调查中心,保定 071051; 3. 南方科技大学环境科学与工程学院,深圳 518055)

摘要: 拒马河流域河流沉积物与土壤存在污染下游北京市和雄安新区生态环境的风险,为此,沿源头至张坊出山口采集河流沉积物与土壤样品,将样品进一步分为干流底泥(29件)、河岸土壤(27件)和农田土壤(26件)这3种类型,采用富集因子法和潜在生态风险指数法开展了重金属富集特征与生态风险评价研究.结果表明,研究区河流沉积物与土壤Cd、Hg、Pb、Zn和Cu含量均值高于白洋淀底泥与河北省表层土壤含量均值,As、Cr和Ni含量则偏低.各重金属污染程度由高到低为:Cd>Hg>Pb>Zn>Cu>Cr>Ni>As,生态风险综合指数显示农田土壤和河岸土壤以轻微风险为主,其次为中度;干流底泥潜在生态风险则以中度、重度和严重为主,分别占比为35.5%、24.1%和24.1%,主要贡献因子为Cd和Hg.多元统计分析结果表明Cd、Pb、Zn和Cu主要污染源为工矿活动;Cr、Ni和As则主要由成土母岩风化控制,As还受农业活动等的影响;Hg则由工矿活动、母岩风化和大气降尘等复合污染源控制.总体上,研究区土壤重金属风险整体处于轻微等级,但台峪一司各庄-蓬头河段干流底泥中存在Cd等重金属明显富集的现象,环境监测、河道清淤与治理应以该河段为重点.

关键词: 拒马河流域;河流沉积物与土壤;重金属;来源解析;生态风险

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Heavy Metal Content and Risk Assessment of Sediments and Soils in the Juma River Basin

HAN Shuang-bao^{1,2,3}, YUAN Lei^{2*}, ZHANG Qiu-xia², ZHENG Yan³, LI Fu-cheng²

(1. College of Environment, Harbin Institute of Technology, Harbin 150090, China; 2. Center for Hydrogeology and Environmental Geology Survey, China Geological Survey, Baoding 071051, China; 3. School of Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China)

Abstract: The sediment and soil in the Juma River channel pose a risk of pollution to the downstream ecological environment of Beijing and Xiong'an New Area. To address this issue, sediments and soil samples were collected along the river from the source to the Zhangfang outlet. The samples were further divided into three types; main stream sediment (29 samples), riverbank soil (27 samples), and farmland soil (26 samples). Enrichment factor analysis and the potential ecological risk index were employed to investigate the ecological risk. The results showed that the average concentrations of Cd. Hg, Pb, Zn, and Cu in the river sediment and soil in the study area were higher than those in the Baiyangdian Lake sediment and the surface soil of Hebei Province, whereas the concentrations of As, Cr. and Ni were relatively lower. The ranking of heavy metal pollution levels from high to low were Cd > Hg > Pb > Zn > Cu > Cr > Ni > As. The comprehensive ecological risk index showed that farmland soil and riverbank soil were mainly at a slight risk, followed by a moderate risk. The potential ecological risk of the main stream sediment was mainly moderate, severe, and extremely severe, accounting for 35. 5%, 24. 1%, and 24. 1%, respectively, and the main contributing factors of the risk were Cd and Hg. The results of multivariate statistical analysis indicated that the main pollution sources of Cd., Pb, Zn, and Cu were industrial and mining activities. Cr, Ni, and As were mainly controlled by the weathering of the parent rock, and As was also influenced by agricultural activities. Hg was controlled by composite pollution sources such as industrial and mining activities, parent rock weathering, and atmospheric dust fall. Overall, the risk of heavy metal in the soil of the research area was generally at a slight level. However, there was a significant enrichment of Cd and other heavy metal in the sediment of the Taiyu-Sigezhuang-Pengtou River. This river section should be the focus of environmental monitoring, river dredging,

Key words: Juma River Basin; river sediments and soil; heavy metals; source apportionment; ecological risk

表层土壤是地球系统圈层的重要物质层,与大气、水、岩石和生物有着密切联系,是人类赖以生存的基础. 而重金属则直接影响破坏表层土壤环境质量,进而影响水环境质量与生物健康[1-3]. 近年来白洋淀和海河流域河流沉积物与土壤重金属污染状况引起高度关注,尹德超等[4]通过在白洋淀高密度取样发现白洋淀沉积物环境质量总体较好,河流入淀口所在淀区重金属潜在生态风险高于其他淀区,局部淀区存在重金属污染潜在生态风险;许梦雅等[5]通过取样分析证实白洋淀沉积物中Cd、Cu和Zn超过土壤背景值,不同类型水体中以水道区域生态

风险最高;陈兴宏等^[6]对府河影响区沉积物重金属污染特征及风险进行了分析,结果表明重金属污染的主要元素为Cd、Cu、Zn、Hg和Pb,特别是府河人淀区属于重金属重度生态风险等级.已有研究证实白洋淀以Cd、Cu、Zn、Hg和Pb元素污染较为突出,而入淀河流是白洋淀重金属的主要来源之一.

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作者简介: 韩双宝(1983~),男,高级工程师,主要研究方向为流域 水土环境污染风险评价,E-mail: hanshuangbao@mail. cgs.

* 通信作者,E-mail: yuanlei@mail.cgs.gov.cn

太行山北段是雄安新区的主要物源区^[7],拒马河发源于太行山北段腹地,是白洋淀重要的天然入淀水源,同时拒马河为南水北调中线工程生态补水河道,对于下游北京市、雄安新区和河北省保定市生态环境质量有着直接影响^[8-10].

太行山北段是华北地区重要的多金属成矿带, 区内分布的涞源杂岩体是铜、铅和锌矿等有色金属 的主要集聚区[11],柳峰等[12]通过对流域内某铅锌矿 区周边土壤取样分析,发现矿区周边土壤受到 Cd、 Pb、Hg和Zn等多金属复合污染, Cd、Pb和Zn主要 受上游铅锌矿开采后重金属迁移污染, As 和 Cr 主 要由成土母质和农业活动控制.前人研究多集中在 白洋淀淀区和周边平原区[13~16],在上游物源区开展 工作甚少, 而近几十年来上游山区河流底泥和土壤 环境质量受人类活动影响程度较大, 因此亟需在太 行山北段开展河流沉积物与土壤调查取样研究,查 明重金属分布特征、生态风险及来源.综合上述已 有研究成果,本次研究选取Cd、Pb、Hg、Zn、Cu、 As、Cr和Ni为重金属测试元素,选择白洋淀上游人 类活动强度较高的拒马河流域为研究区部署采样与 测试工作(图1).

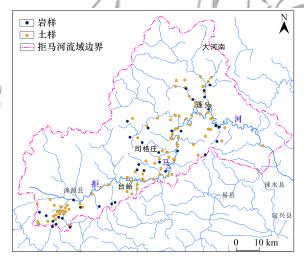


图1 拒马河流域取样点分布示意

Fig. 1 Distribution of samples in Juma River Basin

1 材料与方法

1.1 研究区概况

拒马河是海河流域大清河水系的主要河道之一,地处河北省中部,为温带大陆性季风气候,发源于太行山腹地涞源县盆地,向东流经河北省易县、涞水县和北京市房山区等地,水量少时流入白洋淀,水量大时则入海.拒马河是河北省内唯一常年不断流的河流,是白洋淀重要的天然入淀水源.研究区内涞源县、易县和涞水县农业及工矿业均较为发达,有铁、铅、锌、钼和铜等矿产.

1.2 沉积物样品采集及测试

2018~2021年,沿拒马河源头至张坊出山口水 文站调查采集基岩、河流沉积物与土壤共134组, 包括基岩39组,土壤与底泥95组,另包括平行样7 组(图1).剥离表土后,土壤取样深度范围为表层5~ 15 cm,采样方法为双对角五点采样法.测试工作由 河北省地质实验测试中心完成,测试项目为 Cd、 Pb、Hg、Zn、Cu、As、Cr和Ni共8项.其中As元素 测定采用氢化物发生-原子荧光光谱法,Cd元素测定 采用电感耦合等离子体质谱法,Hg元素测定采用蒸 气发生-冷原子荧光光谱法,Cr、Cu、Pb、Ni和 Zn 元素测定均采用波长色散 X射线荧光光谱法.测试分 析方法参照国家土壤一级标准物质进行质量控制, 所有元素回收率、准确度和精密度符合相关要求.

1.3 重金属污染评价方法

相关学者对不同地区土壤进行了各类评价,已 形成以单因子指数法、多因子指数法和统计学法相 配合为主流的综合评价方法^[17-22]. 本文拟采用富集 因子法、潜在生态风险评价法和多元统计法来综合 分析评判.

1.3.1 富集因子法

富集因子法常用来评价人为因素对表层土壤中 重金属富集程度,计算公式为:

$$EF = (C_i/C_n)_S / (C_i/C_n)_B$$
 (1)

式中,EF为富集因子系数, C_i 为元素i的含量 $(mg \cdot kg^{-1})$; C_n 为标准化元素Al的含量 $(mg \cdot kg^{-1})$. S和B分别表示样品和背景,本文参考 Sutherland 将元素的富集程度分为6个级别(表1)^[23,24],背景值参考河北省土壤A层重金属背景值^[25].

1.3.2 潜在生态风险评价

潜在生态风险指数法是由 Håkanson^[26]于 1980年 创立的从沉积学原理评价重金属生态风险的方法. 该方法将重金属的含量、生态效应、环境效应以及 毒理学效应联系起来,是目前生态风险评价中广泛 应用的方法^[27,28].其计算公式如下:

$$E_{\rm r}^i = T_{\rm r}^i \cdot C_i / B_i \tag{2}$$

$$RI = \sum_{i=1}^{n} E_r^i \tag{3}$$

式中, T_i 为重金属i的毒性系数,Zn、Cr、Cu、Ni、Pb、As、Cd和 Hg毒性系数分别为 1、2、5、5、5、10、30 和 $40^{[28,29]}$; C_i 为重金属i的实际测量值 $(mg \cdot kg^{-1})$; B_i 为重金属i的参比值 $(mg \cdot kg^{-1})$,文中采用河北省土壤 A 层重金属背景值[25]; E_i 为第i种重金属的潜在生态风险系数;RI为多种重金属元素综合潜在生态风险指数.潜在生态风险等级划分标准见表 1.

表1 重金属污染评价方法和分级标准划分

Table 1 Evaluation methods and classification standards

for heavy metal pollution

EF	分级	$E_{ m r}^i$	RI	生态风险等级
EF ≤ 1	无富集	$E_{\rm r}^i < 40$	RI < 150	轻微
$1 < \mathrm{EF} \leq 2$	轻微富集	$40 \leqslant E_{\rm r}^i < 80$	$150 \leq \mathrm{RI} < 300$	中度
$2 < EF \le 5$	中度富集	$80 \le E_{\rm r}^i < 160$	$300 \le \mathrm{RI} < 600$	重度
$5 < \mathrm{EF} \leq 20$	显著富集	$160 \le E_{\rm r}^i < 320$	RI ≥ 600	严重
$20 < EF \le 40$	强烈富集	$E_{\rm r}^i \geqslant 320$		极严重
EF > 40	极强富集			

1.4 数据处理

本文采用 Excel 及 SPSS 20 软件进行数据统计处理、相关性分析及主成分分析,采用 Excel制作数据分析图表,采用 AreGIS 10.2 和 MapGIS 软件进行空间数据分析及图件绘制.

2 结果与讨论

2.1 重金属元素含量与分布特征

2.1.1 描述性统计分析

拒马河流域土壤、底泥及基岩重金属含量如表 2 所示,河流沉积物与土壤 $\omega(As)$ 、 $\omega(Hg)$ 、 $\omega(Cr)$ 、 $\omega(Ni)$ 、 $\omega(Cu)$ 、 $\omega(Zn)$ 、 $\omega(Cd)$ 和 $\omega(Pb)$ 平均值分别 为 7.20、0.10、54.39、22.97、45.39、146.21、0.62 和 37.54 $mg\cdot kg^1$. Hg、Cu、Zn、Cd 和 Pb 含量均值高于白洋淀底泥均值和河北省背景值,其中 Cd 含量均

值分别为白洋淀底泥均值和河北省背景值的 1.9 倍和 6.6 倍,As、Cr和 Ni 含量均值低于白洋淀底泥均值和河北省背景值.由表2变异系数可知,As、Cr和 Ni 变异系数小于 60%,反映出样本离散程度较小;而 Cd、Pb、Hg、Cu和 Zn变异系数均大于 100%,反映出其离散程度大,面状分布差异性强.

基岩样本涵盖了碳酸盐岩、变质岩、火山岩等研究区全部成土母岩类型,其重金属含量均值明显小于白洋淀底泥均值与河北省背景值.但个别样本的 Cr、Ni、Cu、Zn、Cd和Pb含量高于白洋淀底泥均值和研究区样品均值,对比拒马河流域某铅锌矿区土壤重金属均值^[9]可知,矿区土壤 Zn、Cd和Pb含量明显高于研究区,说明高重金属含量矿石和采矿活动是研究区土壤 Zn、Cd和 Pb等元素的潜在污染源.

表 2 研究区重金属描述性统计

Table 2 Descriptive statistics of heavy metal in the study area

统计区	样本数	统计值	As	Hg	Cr	Ni	Cu	Zn	Cd	Pb
(0)	3	最大值	30.50	1.20	109.00	44.30	904.00	1 811.00	3.52	326.00
S		最小值	0.96	0.01	10.21	4.92	6.35	29.20	0.10	13.70
研究区土壤	95	均值	7.20	0.10	54.39	22.97	45.39	146.21	0.62	37.54
或底泥	93	中位数	6.83	0.04	56.10	23.35	25.70	86.20	0.21	25.20
		标准差	4.30	0.17	17.15	7.56	96.61	226.62	1.65	44.67
		变异系数	59.8	174.5	31.5	33.0	212.9	155.0	165.3	119.1
研究区基岩	39	均值	0.83	0.01	31.59	19.70	14.03	46.39	0.08	14.97
矿区土壤[9]	150	均值	10.83	0.12	61.13	_	39.15	412.94	1.02	106.10
白洋淀底泥[4]	484	均值	9.91	0.05	75.46	37.22	37.43	102.43	0.33	27.78
河北省[25]	_	均值	13.60	0.04	68.30	30.80	21.80	78.40	0.094	21.50

1)变异系数单位为%,其余重金属的统计值单位均为 $mg \cdot kg^{-1}$;"—"表示文献中没有相关数据

2.1.2 重金属含量分布特征

将研究区样品按土地利用类型进一步分为河流底泥、河岸土壤和农田土壤,样本数量分别为29、27和26组,不同土地利用类型土壤重金属含量统计如表3所示.可看出Hg、Cu、Zn、Cd和Pb含量及标准差均表现出干流底泥>河岸土壤>农田土壤的特征,推测该组重金属元素多依靠水动力迁移,由于近几十年来研究区采矿活动强度明显增强,重金属通过烟尘、废水和矿渣等形式暴露在空气中,在降

水淋滤与产汇流过程中汇集到拒马河干流底泥中,因此干流底泥中 Cd和Pb等重金属含量最高,空间分布最不均匀,其次为河岸土壤,农田土壤含量最低.而不同土壤分区中As、Cr和Ni含量较为相近,空间分布差别较小,仅以农田土壤含量略高,推测其主要受母岩风化控制,此外由于耕地多分布在村镇和道路两侧的山坡或河谷阶地中,相较于河岸土壤与底泥更容易受到农药和化肥使用、燃煤和汽车尾气排放等轻微影响.

表 3	不同土地利	用类型重金属含	a量统计/mg·kg ⁻¹
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Table 3	Statistics of	hoovy motol	content in	different	land use	twnee	/m a • k a -1

统计区	参数	$\omega(As)$	$\omega({\rm Hg})$	$\omega(\mathrm{Cr})$	$\omega({ m Ni})$	$\omega(Cu)$	$\omega(Zn)$	$\omega(\mathrm{Cd})$	$\omega(\mathrm{Pb})$
T 14 P 17 MI	范围	0.96 ~ 13.6	0.01 ~ 0.95	12.50 ~ 89	4.92 ~ 44.3	6.35 ~ 190	29.20 ~ 916	0.12 ~ 3.52	13.70 ~ 192
干流底泥 (n=29)	平均值	5.92	0.13	51.34	21.28	42.79	168.43	0.89	52.95
(n-29)	标准差	3.35	0.23	18.88	9.44	40.99	185.59	0.95	71.82
>	范围	2.82 ~ 26.2	0.02 ~ 0.4	27.50 ~ 88	12.00 ~ 39.4	13.7 ~ 155	44.50 ~ 376	0.09 ~ 1.34	14.40 ~ 87
河岸土壤 (n=27)	平均值	7.66	0.07	53.90	23.43	35.82	101.92	0.36	28.40
(11-21)	标准差	4.27	0.09	13.27	6.38	31.73	69.58	0.32	16.84
	范围	1.20 ~ 12.2	0.02 ~ 0.5	31.80 ~ 109	11.90 ~ 33.7	9.47 ~ 69	42.80 ~ 162	0.10 ~ 0.65	15.70 ~ 116
农田土壤 (n=26)	平均值	7.71	0.08	62.34	25.80	25.26	82.21	0.24	28.30
(n-20)	标准差	3.21	0.13	17.17	5.92	10.95	23.03	0.14	19.34

沿拒马河水流方向,Hg、Pb、Cu、Zn和Cd含量在距离河源45~80 km处出现第一个高值区[图 2(b)和 2(c)中 I区],在距离河源110~145 km出现第二个高值区[图 2(b)和 2(c)中 II区],在重金属富集区河段,拒马河接受多个流经矿区的支流,Pb和Cd等重金属可能受到局部矿区污染.参照《农用地土壤污染

风险管控标准(试行)》(GB 15618-2018)^[30]中其他类土壤污染风险筛选值,干流底泥中 Cd、Hg和 Pb 含量最高值(3.52、0.95和192 mg·kg⁻¹)均超过了土壤污染风险筛选值(3.4、0.6和170 mg·kg⁻¹). Ni、Cr和 As这 3类重金属沿拒马河流向呈现出波动缓慢下降的趋势,未出现明显的富集区.

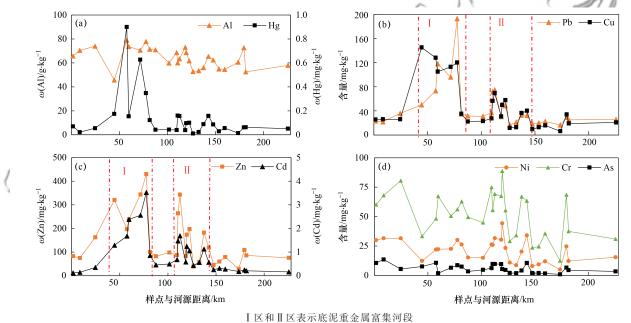


图 2 拒马河干流底泥重金属含量变化 Fig. 2 Heavy metal content in the main stream sediment of the Juma River

2.2 重金属富集状况

由图 2(a)可知 Al元素在研究区分布无明显空间变化趋势,基本不受人为活动影响且抗风化能力较强,因此将 Al作为富集因子法的标准化元素.如表 4 所示,研究区干流底泥、河岸土壤和农田土壤这 3 类土的 As、Cr和 Ni 富集系数基本处于 0.1~1.5,平均值均小于 1,标准差多处于 0.2~0.3间,3类元素无富集状态;Cu、Zn和 Pb为轻微富集状态,Hg为中度富集状态;河岸土壤和农田土壤中 Cd 为中度富集状态,干流底泥中 Cd 为显著富集状态.各重金属按富集程度均值由高到低排序为:Cd > Hg > Pb >

Zn > Cu > Cr > Ni > As. 干流底泥中重金属 Cd、Hg和Pb最为富集,其中Cd、Hg和Pb元素 EF最大值分别达 44.5、28.2和18.0,显著高于河岸土壤与农田土壤. 标准差结果也指示干流底泥 Cd和Hg等重金属分布不均,存在局部污染源造成的富集区.

2.3 潜在生态风险评价

样品 As、Cr、Ni 和 Zn 单因子潜在生态风险指数评价均为轻微生态风险; Cu 和 Pb 除干流底泥样品中分别有1组和2组为中度风险外,其他均为轻微风险; Hg和 Cd潜在生态风险指数较高(表5),其中 Hg元素潜在生态风险分级以轻度和中度为主,二

表 4 不同土地利田米刑 重 全 屋 今 量 宣	住田フは田

Table 4 Results of enrichment factors for heavy metal content in different land use types

统计区	参数	As	Hg	Cr	Ni	Cu	Zn	Cd	Pb
工体产用	范围	0.08 ~ 1.0	0.37 ~ 28.2	0.20 ~ 1.3	0.18 ~ 1.4	0.32 ~ 10.4	0.41 ~ 13.9	1.30 ~ 44.5	0.58 ~ 18.0
干流底泥 (n=29)	平均值	0.45	3.59	0.79	0.71	1.85	1.90	9.61	2.04
(11-29)	标准差	0.24	5.59	0.24	0.27	2.35	2.68	10.25	3.54
	范围	0.18 ~ 2.0	0.49 ~ 10.1	0.49 ~ 1.1	0.44 ~ 1.3	0.73 ~ 7.9	0.45 ~ 5.3	1.77 ~ 15.6	0.63 ~ 4.4
河岸土壤 (n=27)	平均值	0.60	2.02	0.81	0.78	1.70	1.36	3.89	1.38
(11-21)	标准差	0.33	2.44	0.16	0.19	1.55	0.98	3.61	0.85
4016	范围	0.08 ~ 0.9	0.54 ~ 13.6	0.43 ~ 1.6	0.36 ~ 1.1	0.42 ~ 3.2	0.62 ~ 2.1	1.08 ~ 6.1	0.67 ~ 5.3
农田土壤 (n=26)	平均值	0.54	2.18	0.90	0.83	1.15	1.03	2.53	1.30
(n-20)	标准差	0.24	3.29	0.24	0.18	0.51	0.28	1.39	0.88

者合计约占总样品的75%, Cd元素潜在生态风险指数范围为31.9~1123.4, 以中度风险及以上为主.这与白洋淀沉积物Cd是生态风险最高的重金属结果一致[31].

整体上拒马河流域河流沉积物与土壤各重金属指标潜在生态风险以轻微和中度为主,单指标潜在生态风险由高到低排序为: Cd>Hg>Pb>Cu>As>

Ni>Zn>Cr. 从不同类型沉积物来看,As、Cr和Ni潜在生态风险排序为:农田土壤>河岸土壤>干流底泥,而Hg、Cu、Zn、Cd和Pb潜在生态风险排序为:干流底泥>河岸土壤>农田土壤,特别是干流底泥Cd元素潜在生态风险以重度到极严重为主,其中极严重占比为37.9%,河岸土壤和农田土壤Cd元素潜在生态风险则以中度为主.

表 5 研究区 Hg、Cd 元素潜在生态风险分级占比统计/%

Table 5 Statistics of potential ecological risk of Hg and Cd in the study area /%

重金属	土地类型	轻微	中度 重度	严重	极严重
	干流底泥	24.1	34.5 20.7	10.3	10.3
Hg	河岸土壤	39.3	42.9 7.1	3.57	7.1
616	农田土壤	44.0	32.0 16.0	0	-8.0
	干流底泥	3.0	17.2 24.1	17.2	37.9
Cd	河岸土壤	14.3	50.0 10.7	17.9	7.1
Ca 8/1	次田土壤	12.0	68.0 12.0	8.0	0

拒马河流域样品潜在生态风险综合指数 RL分布范围为 72.3~1913.2, Cd和 Hg 为主要贡献因子.样本潜在生态风险以轻微到中度风险水平为主(图 3),农田土壤和河岸土壤潜在生态风险以轻微为主,其次为中度,合计占总样本的 85%;干流底泥潜在生态风险则以中度、重度和严重为主,占比分别为 35.5%、24.1%和 24.1%.由图 3 可知重度和严重生态风险样本主要分布在台峪-司各庄-蓬头一带的干支流底泥和河岸土壤中,这与前文中沿河流流向干流底泥样品重金属富集与分布规律一致.

2.4 重金属来源解析

采用多元统计分析是识别多种变量之间复杂关系的有效手段^[32, 33],拒马河流域内村镇人口众多,工矿业与农业均较为发达,河流沉积物与土壤重金属潜在污染源包括母岩风化、工矿业污染、农业污染、汽车尾气及混合污染.为更有效地分析母岩风化对重金属含量的影响,引入Al与8类重金属进行Pearson相关性分析(表6),结果表明Cu、Zn、Cd和Pb等4种元素两两之间均为极显著相关(P<0.01),

说明这 4种元素含量空间变化相似,可能存在共同的污染源. As、Cr和 Ni 等 3 种元素两两之间均为极显著相关(P < 0.01),说明三者空间含量变化相似,同时 Cr、Ni 与 Al 为极显著相关(P < 0.01),指示 Cr和 Ni 富集与分布受母岩风化控制. Hg与 Cd 为极显著相关(P < 0.01),同时 Hg与 Al、Pb 为显著相关(P < 0.05),指示其受混合来源影响,不同样本主控污染源不同.

基于主成分分析(图 4)与污染模式(图 5)对拒马河流域河流沉积物与土壤 8种重金属富集成因进行分析,主成分分析中前 4个主成分累计解释了 92.2% 的重金属成因信息.

第一主成分(PC1)方差贡献率 43.7%, 其特征表现为 Cu、Zn、Cd和Pb元素具有较高的正载荷, As、Cr和Ni载荷较低.通过富集因子法与重金属分布特征分析, Cd、Pb和 Zn等重金属含量在干流底泥中分布极为不均, 主要富集在台峪-司各庄-蓬头的干支流底泥中, 部分河段样本 Cd、Hg和Pb含量超过农用地土壤污染风险筛选值^[30], 河道治理时应优先

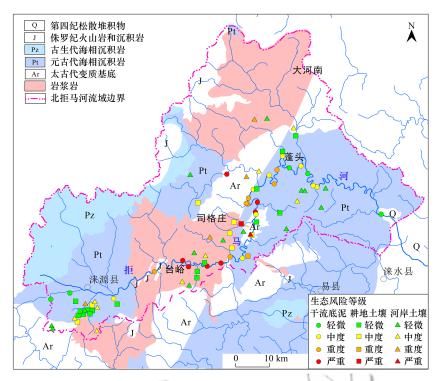


图 3 研究区样品生态风险等级分布(RI)

Fig. 3 Ecological risk level of samples in the study area(RI)
表 6 研究区河流沉积物与土壤重金属相关性 1)

Table 6 Correlation of heavy metal in river sediments and soils of the study area

	/Al	As	Hg	Cr	Ni	Cu	Zn	Cd	Pb
Al) "]["	Ka		/. ()	, 1	(-
$\mathbf{A}\mathbf{s}$	0.153	1	7 116			/ B \	1 Por	~	9 /
Hg	0.215*	0.099	1 1/1/	011		18/1			8
Cr /	0.521**	0.328**	0.036	(I)	\	No 10	7.1		-
Ni	0.497**	0.631**	0.067	0.872**	4 1		**		
Cu /	-0.059	0.122	0.134	-0.013	0.078	1			
Zn	-0.049	0.102	0.195	-0.041	0.062	0.88^{**}	1		
Cd	0.033	0.042	0.391**	-0.006	0.062	0.685^{**}	0.804^{**}	1	
Pb	0.028	0.144	0.223*	-0.06	0.087	0.68**	0.898**	0.765**	1

1)*表示P<0.05,为显著相关;**表示P<0.01,为极显著相关

对该河段进行清淤等无害化处理.而Cd、Pb和Zn在河岸土壤与农田土壤中多为轻微富集状态,仅部分样本Cd富集状态和生态风险为中度.

台峪-司各庄-蓬头河段流经岩浆岩成矿区(图3),区内蕴含铅锌矿和铜钼矿等矿体,几十年来大规模的矿山活动显著影响了区域水土环境. 区内某铅锌矿区土壤 $\omega(Zn)$ 、 $\omega(Cd)$ 和 $\omega(Pb)$ 均值达412.9、1.0 和 106.1 mg·kg⁻¹,均高于干流底泥含量均值(168.43、0.89 和 52.95 mg·kg⁻¹);矿区土壤 $\omega(Zn)$ 、 $\omega(Cd)$ 和 $\omega(Pb)$ 最大值为6 240.8、13.4、1 037.3 mg·kg⁻¹,是干流底泥样品均值的10~37倍,废弃矿山成为重金属污染的重要来源.前人研究已证实铅锌矿等矿石采冶过程中产生的废水、粉尘和尾矿渣是Cd、Pb、Zn、Cu和Hg等重金属元素的重要污染

源^[34-37]. 研究区内多为露天采矿场,采选工艺较为粗放,采矿剥离的围岩、尾矿和冶炼后的废渣形成的尾矿库等堆积在沟谷中,重金属经过雨水淋滤迁移至环境土壤,矿石冶炼过程中产生大量含有重金属的废气和粉尘,也会通过大气沉降进入矿区周边土壤^[38],重金属再经过降水-产流-汇流聚集在拒马河干支流底泥中,导致该河段 Cd、Pb、Zn和 Cu等重金属元素富集,此外携带大量重金属的选矿废水也是重金属的来源之一. 在更大区域尺度的研究中也证实海河流域河流沉积物中 Cd、Pb和 Zn 有相似的污染来源^[39,40],综合分析第一主成分主要反映工矿业活动.

第二主成分(PC2)方差贡献率27.9%, 其特征表现为As、Cr和Ni这3种元素具有较高的正载荷, Cu、Zn、Cd和Pb载荷较低.As、Cr和Ni这3种元素

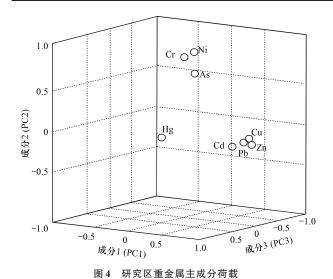


Fig. 4 Principal component load of heavy metals in the study area

在流域空间分布中为低变异性、无富集特征、轻微生态风险,说明其基本不受人类活动影响.3类重金属均值略低于白洋淀底泥与河北省背景值,高于研究区基岩均值,同时与Al含量有较强的相关性,符合物源区土壤重金属含量特征,表明第二主成分主要反映母岩风化影响^[41,42].

第三主成分(PC3)方差贡献率12.0%,主要反映Hg的信息,Hg与Cd、Pb和Al均有较强相关性,反映出Hg的来源具有多源性.在低强度人类活动区Hg含量低,主要受控于母岩风化,因此表现出与Al显著相关(P<0.05);在矿区影响范围内Hg富集主要受控于工矿活动,在矿石破碎和燃煤过程中Hg会大量通过烟尘、废气逸散,再通过大气干湿沉降、径流进入土壤和河道,矿区周边受到污染最为明显,因此Hg与Cd、Pb有较好的相关性[43].第三主成分可认为是金属冶炼废气和大气干湿沉降来源.

第四主成分(PC4)方差贡献率 8.6%, 主要反映 As 的部分信息, As 与 Al 呈不显著相关, 河岸土壤 和农田土壤中 As 的含量和富集程度略高于干流底泥, 说明 As 受到一定程度非工矿业人类活动影响. 拒马河上游涞源盆地多分散性居民区, 农田多沿河谷分布, 耕地面积超过 260 km², 并发展有猪和鸡牲畜养殖基地,已有研究证实 As、Cr和 Hg等重金属易受到化肥与农药的使用、牲畜粪便和生活垃圾影响, As 等重金属随着养殖废水和堆肥等方式再进入河岸土壤环境中[44.45], 第四主成分主要反映农业活动和生活垃圾等来源.



图 5 研究区重金属污染模式

Fig. 5 Heavy metal pollution pattern of the research area

3 结论

(1)拒马河流域河流沉积物与土壤 Cd、Hg、Pb、Zn和 Cu 重金属含量均值高于白洋淀底泥与河北省表层土壤重金属含量均值,As、Cr和 Ni含量则与之相反.区内农田土壤、河岸土壤重金属含量处于偏低无风险状态,台峪-司各庄-蓬头河段干流底泥中存在重金属含量超标的现象,主要超标元素为 Cd.干流底泥中 Cd、Hg、Pb、Zn和 Cu等重金属在距离河源 45~80 km 处和 110~145 km 处出现 2个富集

区,河道清淤与治理应以该河段为重点.

(2)据重金属富集状况与污染程度评价,各重金属污染程度由高到低为: Cd>Hg>Pb>Zn>Cu>Cr>Ni>As. 生态风险综合评价结果显示农田土壤和河岸土壤以轻微风险为主,其次为中度;干流底泥潜在生态风险则以中度、重度和严重为主,分别占比为35.5%、24.1%和24.1%. RI主要贡献因子为 Cd和 Hg.

(3)多元统计分析结果表明,重金属主要受工矿活动、母岩风化、农业活动、大气沉降和生活垃圾

等因素影响.其中污染严重的 Cd、Pb和Zn 主要为上游矿山采冶活动产生的废水、粉尘和尾矿等工矿污染源; Cr、Ni和As则主要由成土母岩风化控制, As还受农业活动和生活垃圾的影响; Hg为工矿活动、母岩风化和大气降尘等多种因素的复合污染源.

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