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豫西金矿集区矿业活动对周边农田土壤重金属影响研究

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摘要: 矿业活动会促进重金属向生态系统扩散,并在周边农田土壤中累积而引发潜在生态风险。豫西金矿集区矿业生产历史悠久,但在长期的矿产资源开采、选冶、加工生产过程中,缺乏对矿区周边农田土壤重金属元素的累积、空间分布和生态风险的关注,矿业活动对环境的影响程度尚不清楚。为掌握该矿集区矿业活动对周边农田土壤重金属的影响程度,支撑服务矿集区生态修复和周边农业安全生产,本文在全矿集区周边农田采集 375 件土壤样品,采用冷蒸气原子荧光光谱法(CV-AFS)、氢化物发生原子荧光光谱法(HG-AFS)、电感耦合等离子体发射光谱/质谱法(ICP-OES/MS)检测了样品中 Cu、Pb、Zn、Ni、As、Hg、Cd、Cr 重金属元素含量。用地累积指数法和潜在生态风险指数法研究了矿集区周边农田土壤中重金属元素的累积特征、空间分布和生态风险,分析评价了矿集区矿业活动对周边农田土壤重金属的影响。研究结果表明:①矿集区周边农田土壤中 Cu、Pb、Zn、Ni、As、Hg、Cd、Cr 含量平均值都低于国家农田土壤重金属污染风险筛选值,但均高于背景值,分别是背景值的 1.47、3.24、2.06、1.05、1.03、1.52、2.77、1.07 倍,但都低于农田土壤重金属污染风险筛选值。②区内重金属元素空间变异系数(CV)顺序为:Pb(90.72%)>Hg(85.25%) >Cd(65.65%) >Zn(44.0%)>Cu(33.66%)>As(31.72%)>Ni(24.23%)>Cr(13.61%)。Pb、Hg、Cd 具有相对较高的变异系数,且分布位置均在矿业活动场所周边,显示矿业活动等外缘因素是引起重金属元素累积的主导因素。③ 8 种重金属地累积指数分别为-0.1、0.74、0.33、-0.56、-0.60、-0.29、0.62、-0.49,其中 Cu、Ni、As、Hg、Cr 元素未累积,Cd、Pb、Zn 元素为中等累积。④ 8 种重金属单因子潜在生态危害指数平均值介于 2.06~83.62,综合潜在生态风险指数平均值为 192.07,整体表现为中等潜在生态风险。本研究揭示:①长期的矿产资源开发是造成 Cd、Pb、Zn 局部累积的主要因素,Ni、Cr、Cu、As、Hg 以自然背景因素为主。②虽然研究区农田土壤重金属污染程度目前尚不严重,但仍需加强源头防控,避免重金属元素在土壤中进一步累积。

关键词: 矿集区; 农田土壤; 重金属元素; 电感耦合等离子体发射光谱/质谱法; 地累积指数; 生态风险指数

要点:

(1) 研究区 Cd 累积程度最高,其次为 Pb 和 Hg,而 Cu、Zn、Ni、As、Cr 不存在累积。

(2) 重金属元素空间变异性分析表明,矿业活动是研究区农田土壤产生潜在生态风险的重要因素。

(3) 研究区南部矿冶炼厂周边人口和农田分布集中区的综合潜在生态风险最高,应予以重点关注。

中图分类号: O657.63; X522 **文献标识码:** A

矿业活动是引发周边农田土壤重金属富集的重要因素,矿山开采、运输、选冶加工等各环节均会使重金属元素通过径流、大气沉降等途径扩散到环境中,并最终汇集到土壤中,造成周边农田土壤重金属污染[1-5]。20 世纪 50 年代,欧美、日本等一些发达国家已经发现严重的土壤重金属污染并开展了修复

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治理[6],荷兰从 1985 年每年用于治理土地污染的费用折合人民币达 31 亿元[7]。据自然资源部调查显示,中国重金属污染耕地达 1000hm^2,约占国土耕地面积的 10%[8]。重金属元素进入土壤后以不同的形态被植物吸收,在植物籽实中累积,通过食物链进入人体引发肌体病变[9-10]。因此,土壤重金属污染已成为环境污染领域的热点问题之一[11-12]。

矿区周边土壤的重金属污染问题,特别是农田重金属污染尤其受到关注。目前,众多学者针对重要矿集区、重点矿山周边的农田土壤重金属污染问题开展了大量研究。张江华等[13]分析了小秦岭金矿区土壤-小麦重金属累积效应,发现土壤中 Hg、Pb、Cd、Cu 的明显累积和污染,累积倍数分别为 18.97、8 67、4.50、4.03 倍,污染倍数分别为 4.48、3.50、3.46、3.13 倍,小麦中 Hg、Cu、Cd 也出现了累积现象,受到明显的人为影响;林荩等[14]研究了陕西潼关县金矿区周边农田重金属生态健康风险,发现该矿区农田土壤中 Cd、Hg、Ni、Zn、Pb、Cu 等重金属元素均高于潼关县土壤背景值,部分点位 Cd、Hg、Pb 超过土壤污染风险筛选值,Cd 和 Pb 分别有 47% 和 87.8%的点位达到重-极重污染;曹见飞等[15]研究了山东焦家金矿周边农田土壤的重金属含量特征,发现该矿区周边农田土壤中 As、Cr、Cu、Hg、Pb、Zn 等 6 种重金属元素,相对于当地背景值的超标率分别为 89%、69%、72%、94%、77% 和 61%,以金矿冶炼为主的大气沉降源,以及与金矿开采、尾矿堆放相关的人类活动源,贡献率分别达到了 25.1%、7.5%。上述专家学者对重要金矿集区、重点金矿区周边的农田土壤重金属污染研究,均揭示了金矿区矿业活动对周边农田土壤已经造成不同程度的重金属污染。而对于具有长期金矿开发历史的豫西金矿集区,开展土壤重金属污染研究,掌握矿业活动对周边农田土壤重金属的影响情况,为农田土壤重金属污染防控提供科学依据就显得尤为必要。

豫西金矿集区是中国极为重要的金矿化集中区,燕山晚期酸性岩浆活动强烈,成矿地质条件极为有利,已发现大、中、小型金矿床 40 余个,找矿潜力巨大。在黄河流域生态保护和高质量发展机遇下,河南省制定了筑牢“三屏四带”生态安全格局的时间表和路线图。在此背景下,为探索矿业活动对周边农田土壤重金属的影响,本文选择豫西金矿集区周边农田土壤为研究对象,采集耕作层(0~20cm)土壤样品,采用原子荧光光谱(AFS)、电感耦合等离子体发射光谱/质谱(ICP-OES/MS)等方法测定 Cu、Pb、Zn、Ni、As、Hg、Cd、Cr 八种重金属含量,并应用最为广泛的地累积指数法[16]和潜在生态风险评价指数法[17],开展了矿业活动对周边农田土壤重金属影响研究,通过两种方法对比分析,验证了评价结果的客观性,为矿区农田土壤重金属污染防治和监测预警提供科学依据。

1　实验部分

1.1　研究区概况

研究区位于河南省西部的洛阳市栾川县潭头盆地,地理位置属熊耳山低山与丘陵过渡区。水系主要为大坪河,为季节性河流,从研究区中央穿过,向南汇入伊河。农产品主要有小麦、花生、玉米、红薯、豆类、烟叶等。研究区是栾川县最为集中的农业生产区,土地利用类型有耕地、林地等农业用地和工矿用地。大地构造位置处于华北板块南缘和秦岭造山带接壤地带。燕山运动后期演化为断陷盆地。潭头盆地南部受马超营断裂控制,北部不整合于熊耳群地层上部。地层岩性主要为熊耳群坡前街组灰绿色安山岩夹紫灰色粗安山岩、紫红色凝灰岩。

研究区矿产资源丰富,有大型金矿和中型金矿各一个,金矿床集中分布,已有近 30 年的矿业活动历史。矿石类型为构造蚀变岩型金矿石和石英脉型金矿石,剩余可采储量 154 万余吨,开采方式为露天+地下开采。

1.2　样品采集

参照《土壤地球化学测量规程》(DZ/T 0145—2017),按照 8~16 点/km^2 均匀布点,样品采集时间为 2020 年 5—7 月,采集矿区周边农田耕作层土壤样品 375 件(图 1)。采样深度 0~20cm,根据采样区面积较小、地势相对平坦、土壤相对均匀的环境特征,采用梅花形多点混合取样,每件样品按 5 点取样均匀混合组成,保障了每件样品具有较好的代表性。样品质量大于 5kg,满足分析测试和留取副样的要求。

1.3　样品制备与测试

样品采集后置于阴凉通风处晾干,清除土壤以外的杂质,按照《土壤地球化学测量规程》(DZ/T 0145—2017)样品加工技术要求,用橡皮锤初步敲碎,过 10 目尼龙筛,装入塑料瓶中送实验室,经行星式玛瑙球磨机细碎至 200 目进行检测。用 iCAP-6300 型电感耦合等离子体发射光谱仪(ICP-OES)测试 Cu、Zn、Ni、Cr 含量;用 X-Series Ⅱ型电感耦合等离子体质谱仪(ICP-MS)测试 Pb、Cd 含量;用 AFS-230E 型氢化物发生原子荧光光谱仪(HG-AFS)测试 As 含量;用 XGY-1011A 型原子荧光光度

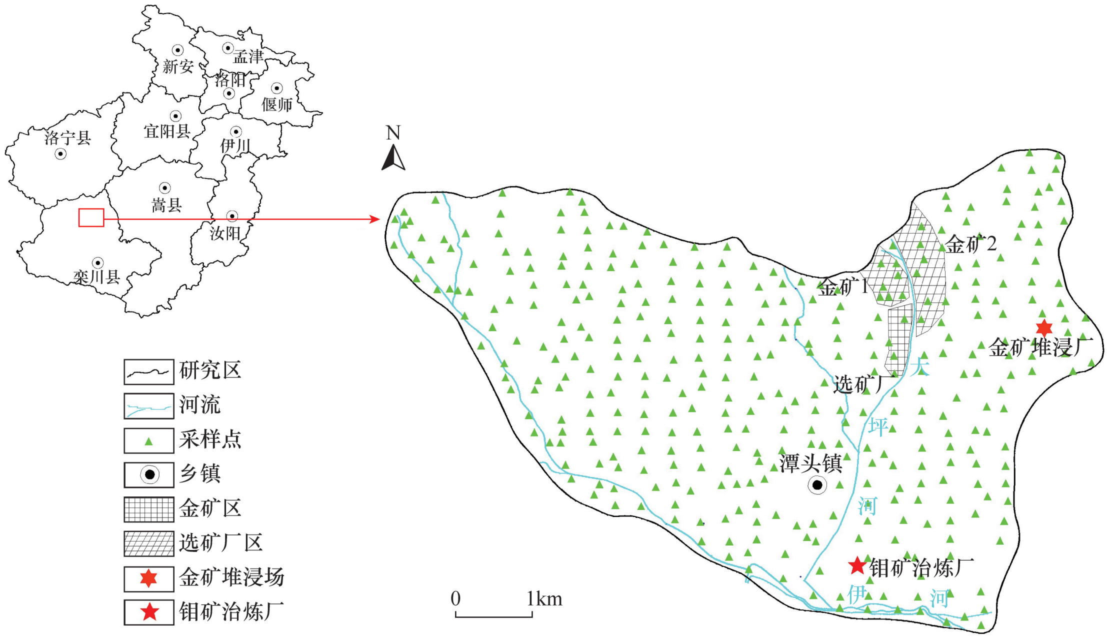

图 1　豫西金矿集区采样点位

Fig. 1　Sampling points of gold ore concentration area in western Henan.

计(CV-AFS)测试 Hg 含量。采用分析国家一级标准物质进行准确度、精密度控制,每 15 件样品中,随机插入国家一级标准物质 1 件和重复样 1 件,与试样同步测定。

样品分析测试工作由中国地质调查局西安矿产资源调查中心实验室完成,具体分析方法和执行的规范标准见表 1。

表 1　各指标分析测试检出限

Table 1　Detection limit of analyzed indicators

元素	检出限(μg/g)	元素	检出限(μg/g)
Hg	0.005	Ni	0.2
As	0.2	Zn	0.03
Cr	0.2	Cd	0.021
Cu	0.5	Pb	0.5

1.4　数据处理

数据处理采用 SPSS17.0 和 Execl 2010 软件,采样点分布图与克里格插值分析,利用 MapGis6.7 和 GeoIPAS3.0 软件完成。样品中出现的异常值,按 3σ 原则进行筛选,用背景值进行迭代替换。

2　评价方法

本次研究,用地累积指数法,分析矿区周边土壤中重金属累积特征;用潜在生态风险指数法,开展农田土壤重金属单项潜在生态风险评价和综合潜在生态风险评价。

2.1　地累积指数法

地累积指数法(I_{geo})是二十世纪中后期国外发展起来的,广泛应用于土壤重金属累积程度和污染分析的定量评价方法[18]。

本文研究区位于河南省西部,流域上处于黄河流域中游地区,因此,选择黄河中游地区土壤地球化学参数作为背景值,计算所研究元素的地累积指数[19]。按重金属污染程度,地累积指数目前有 Forstner 的 7 级分级标准和 Anon 的 5 级分级标准[20-21](表 2)。相较 5 级分级标准而言,7 级分级标准在 5 级标准中的中度影响~强影响(1~3)、强影响(3~5)增设指数 2 和 4 两个分档界限,分级更为精确。为更精细地刻画研究区重金属元素累积程度及其污染程度,本文选择 7 级分级标准来分析评价研究区重金属累积特征。

表 2　地累积指数(I_{geo})评价指标体系

Table 2　Index of geo-accumulation and classification of the influence effect degree

I_{geo} (Forstner)	级别	污染程度	I_{geo} (Anon)	级别	污染程度
<0	1	无影响	<0	1	无影响~轻度影响
0~1	2	无影响~中度影响	0~1	2	中度影响
1~2	3	中度影响	1~3	3	中度影响~强影响
2~3	4	中度影响~强影响	3~5	4	强影响
3~4	5	强影响	>5	5	极强影响
4~5	6	强影响~极强影响			
>5	7	极强影响			

2.2 潜在生态风险指数法

潜在生态风险指数法(potential ecological risk index,RI)是欧洲地球化学家 Hakanson 在 20 世纪 80 年代发展起来的,一种计算过程简洁、结果反映客观、评价指标体系成熟的定量评价方法[22-23]。该方法以土壤重金属含量为基础,结合重金属元素毒理性质,分析其产生的生态环境影响,以明确的数值指标,设定重金属潜在生态风险级别。

参考 Hakanson 制定的标准,生态风险指数分级见表 3。8 种重金属元素毒性响应系数分别为:Cu(5),Pb(5),Zn(1),Ni(5),As(10),Hg(40),Cd(30),Cr(2)。

表 3　风险因子、潜在生态危害系数及生态风险程度等级

Table 3　Risk factor (E_r^i), potential ecological risk index (RI) and the ecological risk degree

E_r^i	RI	生态危害程度
<40	<150	轻微
40~80	150~300	中等
80~160	300~600	强
160~320	≥600	很强
≥320	-	极强

3 结果与讨论

3.1 研究区农田表层土壤重金属含量特征

研究区农田土壤重金属含量(表 4)存在明显差异,Cu、Pb、Zn、Ni、As、Hg、Cd、Cr 含量(mg/kg)变化范围分别为:1.00~71.72、2.00~524.79、8.00~320.37、2.00~52.77、2.29~24.64、0.0067~0.268、0.04~1.30、28.20~107.93;平均含量(mg/kg)分别为 35.33、74.43、137.69、31.60、12.39、0.064、0.43、76.27。与研究区所处的黄河中游土壤背景值对比,Cu、Pb、Zn、Ni、As、Hg、Cd、Cr 含量平均值,分别是黄河中游土壤背景值的 1.47、3.24、2.06、1.05、1.03、1.52、2.77、1.07 倍,说明 8 种重金属元素在土壤中已存在不同程度的累积。但对照《土壤环境质量 农用地土壤污染风险管控标准(试行)》(GB 15618—2018),土壤中 8 种重金属元素含量均低于风险筛选值。

本次研究中,土壤样品 pH 平均值为 7.74,典型重金属污染元素为 Hg、Cd、Pb,与张江华等[13]和林苨等[14]对小秦岭金矿区和潼关金矿区的研究结果相似。说明金矿区矿业活动造成周边农田土壤重金属污染具有普遍性,特征污染元素具有相似性,矿业活动是引起周边农田土壤重金属污染的主要因素,区别之处仅在于不同的区域污染程度有所差异。

变异系数反映了重金属[24-27]在空间上的离散程度。研究区重金属元素空间变异系数(CV)顺序为:Pb(90.72%)>Hg(85.25%)>Cd(66.65%)>Zn(44.0%)>Cu(33.66%)>As(31.72%)>Ni(24.23%)>Cr(13.61%)。Pb、Hg、Cd 相对较高的变异系数,说明不同的采样点存在明显差异,离散性相对较大,重金属元素在空间分布上不均匀程度高,以及矿业活动、农业生产等外缘因素,是引起重金属累积的主导因素[28];Cu、Zn、Ni、As、Cr 相对较低的变异系数,表明这 5 种元素空间分布相对较为均匀,遭受外缘因素影响较小,成土母质等自然因素是重金属累积的主导因素[29-30]。根据研究区矿业活动造成周边农田土壤重金属污染的途径,金矿 1 和金矿 2(图 1)分别为蚀变岩型矿床和重晶石-石英脉含碲化物型金钼矿床,主要成矿元素为 Au、Mo,伴生元素有 Cu、Pb、Zn、Ni、As、Hg、Cd,伴生元素在矿石运输、废石渣堆沿河堆存、选冶、堆浸过程中,均可能扩散到周边环境中。从矿业活动的场地分布看,两个金矿区和选矿厂均分布在农田上游大坪河两侧山坡,东侧金矿堆浸场地位于山坡丘陵顶部,矿业活动产生的重金属可以通过飘尘、雨水淋虑、河流

表 4　研究区农田土壤重金属含量特征

Table 4　Heavy metal content characteristics of farmland soils in the study area

参数	pH	Cu	Pb	Zn	Ni	As	Hg	Cd	Cr
样品数量(件)	87	375	373	375	375	375	375	375	375
最小值(mg/kg)	5.11	1.00	2.00	8.00	2.00	2.29	0.0067	0.04	28.20
最大值(mg/kg)	8.75	71.72	524.79	320.37	52.77	24.64	0.268	1.30	107.93
平均值(mg/kg)	7.74	35.33	74.43	137.69	31.60	12.39	0.064	0.43	76.27
标准差(mg/kg)	0.74	11.89	67.52	60.58	7.66	3.90	0.055	0.29	10.38
变异系数(CV,%)	9.52	33.66	90.72	44.00	24.23	31.72	85.25	66.65	13.61
黄河中游土壤背景值(mg/kg)	-	24	23	67	30	12.0	0.042	0.155	71
表层土壤筛选值(mg/kg)	-	100	170	300	190	25	3.4	0.6	250

水系等向下游农田区域扩散,在周边农田土壤中累积,造成矿区周边农田土壤重金属污染。同时,Pb、Hg、Cd 等 3 种重金属在空间上变异程度相对较高,在地累积指数和潜在生态风险指数高值区,与矿业活动强烈区高度吻合,也进一步佐证了矿业活动是重金属累积的重要因素[31]。此外,牛真茹等[32]通过对云南某有色金属矿产冶炼场地浅层土壤重金属空间变异规律和分布特征的研究,也同样发现了有色金属矿产冶炼场地周边土壤重金属污染较为严重,重金属渗滤液沿地形优势通道迁移,在土壤中局部有利地段累积造成潜在生态风险。这一结论也同样显示,矿业活动是土壤中重金属累积和造成重金属潜在生态风险的重要因素。

3.2 土壤重金属累积特征

从研究区重金属地累积指数大小看(表 5),8 种重金属元素地累积指数排序为:Pb>Cd>Zn>Cu>Hg>Cr>Ni>As,其中 Cu、Hg、Cr、Ni、As 等 5 种重金属元素地累积指数平均值<0,说明对研究区农田土壤质量无影响;Pb、Cd、Zn 地累积指数平均值分别为 0.74、0.62、0.33,均介于 0~1,影响程度介于无影响~中度影响级别。整体而言,研究区重金属对农田土壤质量的影响程度在无影响~中度影响等级($-0.56<I_{geo}<0.74$)。但不可忽视的是,部分元素在局部点位显示出较高的累积程度,其中 Cd 元素在中度以上影响等级的样品数比例为 20.27%,在中~强影响等级的样品数比例为 7.73%,在影响等级的样品数比例 1.07%。Pb 元素在中度以上影响等级的样品数比例为 18.93%,在中度~强影响等级的样品数比例为 10.40%。Hg 和 Zn 也分别有 7.46%和 13.33%的样品达到中度影响等级,表明在局部采样点位,Hg、Cd 和 Pb 对农田土壤质量存在不同程度的影响。

3.3 土壤重金属潜在生态风险特征

以研究区所在的黄河流域中游土壤元素含量平均值为背景值,8 种重金属单因子潜在生态危害指数平均值介于 2.06~83.62(表 6), 其中 As、Cr、Ni、Cu、Zn 单因子潜在生态风险指数为轻微潜在生态风险。Pb 以轻微潜在生态风险为主,该程度的样品比例为 92%,有 7.47%样品达到中度潜在生态风险,0.53%样品达到强潜在生态风险。Cd 以中度潜在

表 5 研究区农田土壤重金属元素地累积指数(I_{geo})及影响程度分级比例

Table 5 Ground accumulation index of heavy metals in farmland soils and the ratio of different influence degree in the study area

元素	重金属元素地累积指数(I_{geo})			各级样品数所占比例(%)						
	最小值	最大值	平均值	0 级	1 级	2 级	3 级	4 级	5 级	6 级
Cu	-5.17	2.45	-0.10	65.33	31.47	2.93	0.27	0	0	0
Pb	-4.11	10.29	0.74	28.00	40.00	18.93	10.40	1.87	0.27	0.53
Zn	-3.65	2.33	0.33	33.87	51.73	13.33	1.07	0	0	0
Ni	-4.49	0.93	-0.56	97.07	2.93	0	0	0	0	0
As	-2.97	2.92	-0.60	96.27	2.93	0.27	0.53	0	0	0
Hg	-3.23	6.31	-0.29	71.47	16.80	7.46	2.66	0.80	0.53	0.27
Cd	-2.54	3.53	0.62	28.00	42.93	20.27	7.73	1.07	0	0
Cr	-1.92	2.02	-0.49	98.93	0.80	0	0.27	0	0	0

表 6 研究区农田土壤重金属潜在生态风险指数及危害程度等级比例

Table 6 Potential ecological risk index of heavy metals in farmland soils and the ratio of different hazard degree in the study area

评价指标	元素	毒性系数	最小值	最大值	平均值	各级样品数所占比例(%)				
						轻微	中度	强	很强	极强
E_r^i	Cu	5	0.21	15.85	7.37	100	0	0	0	0
	Pb	5	0.43	114.08	16.18	92	7.47	0.53	0	0
	Zn	1	0.12	4.88	2.06	100	0	0	0	0
	Ni	5	0.33	8.79	5.27	100	0	0	0	0
	As	10	1.91	23.38	10.35	100	0	0	0	0
	Hg	40	6.38	476.81	65.09	45.60	35.47	11.46	4.27	3.20
	Cd	30	7.74	260.86	83.62	17.6	46.14	25.33	10.93	0
	Cr	2	0.79	2.15	3.25	100	0	0	0	0
RI	-	-	51.66	689.64	192.07	46.40	41.07	11.20	1.33	0

生态为主,该程度的样品比例为 46.14%,另有 25.33%、10.93%的样品分别达到强和很强潜在生态风险。Hg 分别有 35.47%、11.46%、4.27%、3.20%的样品达到中度、强、很强、极强潜在生态风险。由此可见,研究区农田土壤中潜在生态风险影响主要由 Cd、Pb、Hg 三种元素引起。Cd、Pb、Hg 都是具有毒性的重金属元素,在人体内累积到一定程度会引发肌体病理反映[33],需进一步引起重视。综合潜在生态风险指数(*RI*)显示,综合潜在生态风险以轻微和中度影响为主,轻微影响程度的样品比例为 46.40%,中度影响程度的样品比例为 41.07%,但也有 11.20%和 1.33%的样品分别达到强和极强潜在生态风险影响程度。

单因子潜在生态风险指数空间分布图(图 2)表明,在研究区东部和南部农田区,Cd 的潜在生态风险指数相对较高。该区分布有金矿采场、金矿堆浸

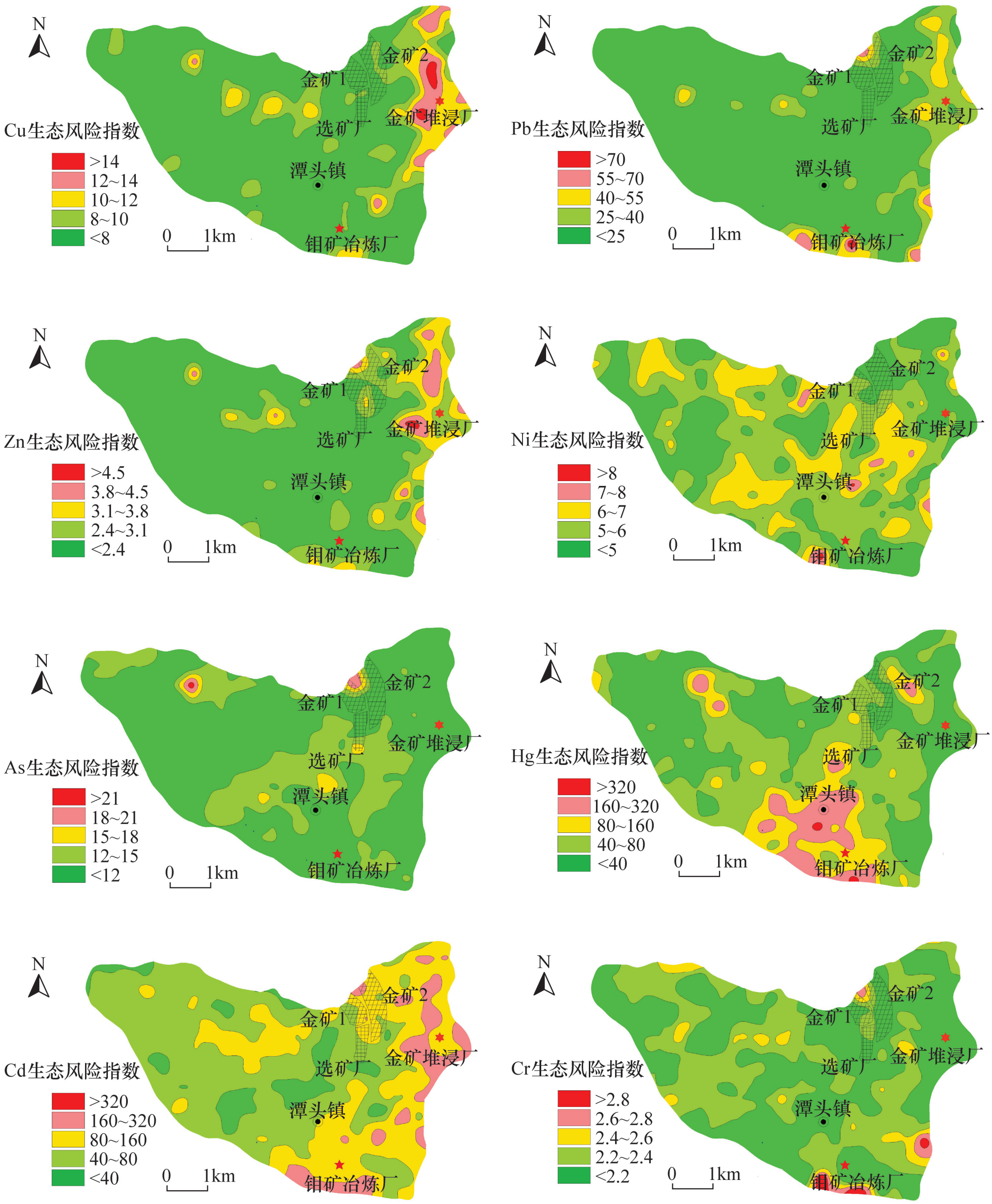

图 2　研究区农田土壤重金属单项潜在生态风险指数空间分布

Fig. 2　Spatial distribution of ecological risk coefficients of heavy metals in farmland soils of the study area.

场,是导致土壤中 Cd 潜在生态风险指数高的重要因素。南部靠近乡镇人类生活区,且分布有矿产品冶炼厂,两种外缘因素共同导致 Cd 的潜在生态风险指数增高。在研究区南部的乡镇生活区和冶炼厂周边区域,Hg 潜在生态风险指数相对较高,矿业活动和人类活动也是主导因素。

综合潜在生态风险指数(*RI*)分布图(图 3)显示,研究区综合潜在生态风险影响以中等为主,呈面状分布于研究区东半部,重金属对这些区域农田土壤质量存在中等潜在生态风险影响。在强及以上综合潜在生态风险区呈斑块分布于研究区南部,以镇区及冶炼厂周边区域为主。其中,强和极强综合潜在生态风险的农田面积分别为 349.4 公顷和 11.71 公顷。对比重金属元素单项潜在生态风险指数分布特征,Cd 与 Hg 指数异常在空间上呈现一定程度的重叠性,综合认为 Cd、Hg 是研究区土壤重金属潜在生态风险影响的主要贡献元素。

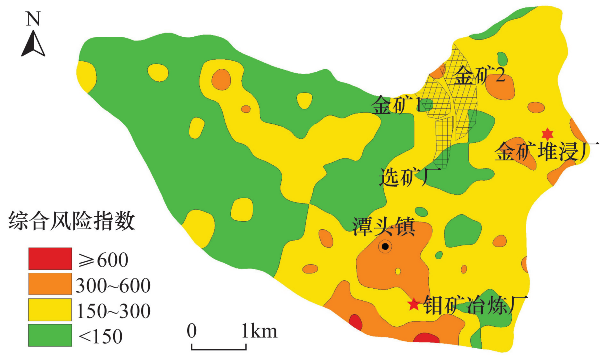

图 3 研究区农田土壤重金属综合潜在生态风险空间分布

Fig. 3 Spatial distribution of potential ecological risk of heavy metals in farmland soils of the study area.

研究区综合潜在生态风险指数(*RI*)介于 51.66 ~689.64,平均值为 192.07。各级潜在生态风险影响程度的样品比例为轻微 46.40%、中等 41.07%、强 11.20%、很强 1.33%,综合潜在生态风险影响以中等为主。镇区和南部农田,是重金属强及很强潜在生态风险影响相对集中的分布区。整体而言,Cd、Hg 具有很高的毒性系数,是引起研究区重金属潜在生态风险的主要贡献因子,且分布范围较广。因此,在加强对矿产资源开发监管、采取防治措施的同时,还需对土壤环境质量和农产品开展协同监测。

4 结论

本文对豫西金矿集区周边农田土壤中 8 种重金属的累积程度和潜在生态风险进行了分析研究得出:该金矿集区农田土壤中 8 种重金属含量未达到《土壤环境质量 农用地土壤污染风险管控标准》(GB15618—2018)中的农用地土壤污染风险筛选值,对土壤生态环境的风险低;Cd、Pb、Zn 在矿业活动强烈区存在不同程度的累积,Cu、Ni、As、Hg、Cr 五种元素不存在累积,地累积指数由大到小顺序为:Pb>Cd>Zn>Cu>Hg>Cr>Ni>As;重金属 Cd 和 Hg 存在很强的潜在生态风险,综合生态风险(*RI*)达到强(300~600)、极强(≥600),存在强和很强综合潜在生态风险的农田面积分别为 349.4 公顷和 11.71 公顷,Cd 和 Hg 是主要贡献元素,对土壤生态危害十分显著,应作为金矿集区土壤重金属污染防治的重点监控对象。

通过本次研究,较为客观地得出豫西金矿集区矿业活动周边农田重金属元素的累积和潜在生态风险状况,以及矿业活动对周边农田重金属的影响程度,能够为研究区重金属污染防范提供科学支撑。基于本文研究成果,建议继续开展土壤中重金属元素形态、有效态和重金属在农作物累积方面的研究,更系统地揭示矿业活动对生态环境的影响[34]。

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Influence of Mining Activities in the Gold Ore Concentration Area in Western Henan on the Heavy Metals in Surrounding Farmland Soil

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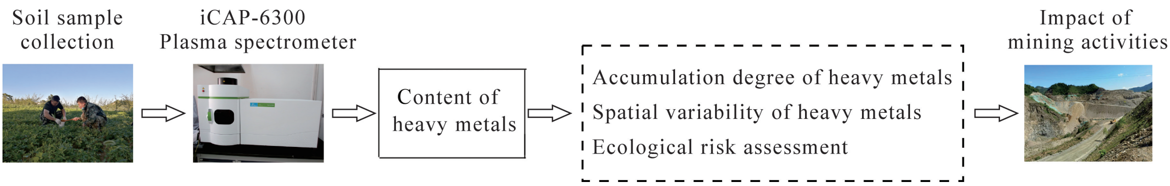
HIGHLIGHTS

(1) The Geo-accumulation index revealed that Cd showed the highest accumulation degree, followed by Pb and Hg, and Cu, Zn, Ni, As and Cr showed no accumulation.

(2) The spatial variability analysis of heavy metal elements showed that mining activity was the important factor of potential ecological risk in farmland soil of the study area.

(3) The comprehensive potential ecological risk showed the highest in the population and farmland concentration areas around the molybdenum mine smelter south of the study area, which should be paid special attention.



ABSTRACT

BACKGROUND: As the significant factor of the accumulation of heavy metals in farmland soils, mineral activities such as mining, traffic and mineral processing and smelting allow heavy metals to spread into the surrounding environment by water or atmospheric deposition, and finally collected into the soil, causing heavy metal pollution in the surrounding farmland soil. Heavy metals pollution in soils especially in farmland soils around the mining area thus has received great attention in the field of environmental pollution. Located in the middle reaches of the Yellow River watershed, the gold mining area in western Henan is an extremely important gold deposit area with great prospecting potential in China for the strong late Yanshan acidic magmatic activity and the extremely favorable metallogenic geological conditions, in which more than 40 large, medium or small gold deposits have been discovered. Under the background of ecological protection and high-quality development in the Yellow River watershed, the western Henan gold mining area, with a long history of gold mining development, lacks more attention to the accumulation, spatial distribution and ecological risk of heavy metals in farmland soil around the mining area during the years of mining, beneficiation and processing. It is particularly necessary to study the heavy metal pollution in soil, find out the impact of mining activities on heavy metals in surrounding farmland soil, and provide a scientific basis for prevention and control of heavy metal pollution in farmland soil.

OBJECTIVES: To clearly understand the impact of mining activities in the western Henan mining area on heavy metals in the surrounding farmland soil, provide necessary basic data for supporting the safe production of key mineral resources, the surrounding agricultural safety, and prevent and control heavy metal pollution in farmland soil.

METHODS: 375 topsoil samples from the farmland around the western Henan gold mining area at a depth of 0-20cm were systematically investigated and analyzed with reference to *Code of Practice for Soil Geochemical Survey* (DZ/T 0145—2017). The contents and spatial distribution characteristics of Cd, Cu, Zn, Pb, Hg, As, Cr, Ni were analyzed. The heavy metal pollution and ecological risk were evaluated by the geo-accumulation index method and potential ecological risk index method.

RESULTS: (1) The contents variation range of Cu, Pb, Zn, Ni, As, Hg, Cd, Cr are 1.00-71.72, 2.00-524.79, 8.00-320.37, 2.00-52.77, 2.29-24.64, 0.0067-0.268, 0.04-1.30, 28.20-107.93, respectively, and the average are 35.33, 74.43, 137.69, 31.60, 12.39, 0.064, 0.43, 76.27, respectively, showing significant differences between the 8 heavy metals. Compared with the soil background value in the middle reaches of the Yellow River, the average contents of Cu, Pb, Zn, Ni, As, Hg, Cd, Cr are 1.47, 3.24, 2.06, 1.05, 1.03, 1.52, 2.77 and 1.07 times of them, respectively, but lower than the value of risk screening values for soil contamination of agricultural land.

(2) The characteristics of coefficients of variation show that Pb(90.72%)>Hg(85.25%)>Cd(65.65%)>Zn(44.0%)>Cu(33.66%)>As(31.72%)>Ni(24.23%)>Cr(13.61%), the Pb, Hg, Cd are the primary factors causing the soil pollution as the external input by mineral activities for the high coefficients of variation and special relation with mining. The main ore-forming elements in the gold deposit area are Au and Mo, and the associated elements are Cu, Pb, Zn, Ni, As, Hg, Cd, which may diffuse into the surrounding environment during ore transportation, waste rock and slag piling along the river, and processing. Alongside the Daping River, the two gold mining areas and concentrators are distributed around the farmland, and the gold ore heap leaching site on the east side is located at the top of the hillside and hill. The heavy metals produced by mining activities can diffuse in the downstream agricultural areas through atmospheric deposition, rainwater leaching, river drainage, and can accumulate in the surrounding agricultural soil, causing heavy metal pollution in the agricultural soil around the mining area.

(3) The geo-accumulation index of 8 heavy metals is -0.1, 0.74, 0.33, -0.56, -0.60, -0.29, 0.62, -0.49 with the order Pb>Cd>Zn>Cu>Hg>Cr>Ni>As, in which Cu, Hg, Cr, Ni, As show no influence to the quality of soils for the average geo-accumulation index lower than 0, and Pb, Cd, Zn show moderate pollution for the average geo-accumulation index between 0-1. Among them, the proportion of samples with a Cd element of medium or higher impact grade is 20.27%, the proportion of samples with medium to strong impact grade is 7.73%, and the proportion of samples with strong impact grade is 1.07%. The proportion of samples with a Pb element above the moderate impact level is 18.93%, and the proportion of samples with moderate to strong impact level is 10.40%. Hg and Zn also have 7.46% and 13.33% of the samples reaching the moderate impact level, indicating that Hg, Cd and Pb in the soil at local sampling sites have different degrees of impact on farmland soil quality.

(4) The average value of the single-factor potential ecological risk index of eight heavy metals is between 2.06 and 83.62, among which the single-factor potential ecological risk index of As, Cr, Ni, Cu and Zn is a slight potential ecological risk. Pb is mainly subject to slight potential ecological risks for 92% of samples, moderate potential ecological risks for 7.47% of samples and strong potential ecological risks for 0.53% of samples. Cd is dominated by moderate potential ecological risks, with 46.14% of samples, and there are 25.33% and 10.93% of samples reaching strong and very strong potential ecological risks respectively. For the ecological risk index of Hg, there are 35.47%, 11.46%, 4.27% and 3.20% of the samples that reach moderate, strong, very strong and very strong degree. The comprehensive potential ecological risk index (*RI*) ranges from 51.66 to 689.64, with an average of 192.07. The proportion of samples with slight, moderate, strong and very strong impact degree is 46.40%, 41.07%, 11.20% and 1.33%, respectively. The overall comprehensive potential ecological risk index shows moderate potential ecological risks.

CONCLUSIONS: Compared with the risk screening values for soil contamination of agricultural land, the contents of Cd, Cu, Zn, Pb, Cr, Ni, As, Hg are all lower than the standard, indicating low risk for the soil environment. There were different degrees of accumulation surrounding the intense mining area of Cd, Pb, and Zn by longtime mineral development. Cu, Ni, As, Hg, and Cr were influenced by the natural factor. The farmland area with strong and very strong comprehensive potential ecological risks is 349.4 hectares and 11.71 hectares, respectively. Cd and Hg are the main contributing elements, with higher risk to the soil ecology, which should be monitored and controlled from source to avoid the further accumulation of heavy metal elements in the soil.

KEY WORDS: ore concentration area; farmland soil; heavy metal elements; inductively coupled plasma-optical emission spectrometry/mass spectrometry; cumulative index; ecological risk index