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铜冶炼场地周边土壤重金属污染特征与风险评价

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摘要: 铜冶炼生产活动会造成周边土壤重金属污染, 威胁公众健康. 通过收集整理已发表文献数据, 从整体上研究了国内外40个铜冶炼场地周边不同土地利用类型土壤重金属的累积特征、分布规律以及健康风险. 结果表明, 铜冶炼场地周边土壤重金属 $\omega(\text{As})$ 、 $\omega(\text{Cd})$ 、 $\omega(\text{Cu})$ 、 $\omega(\text{Pb})$ 和 $\omega(\text{Zn})$ 平均值分别为 196、10.5、1 948、604 和 853 $\text{mg}\cdot\text{kg}^{-1}$, 地累积指数 (I_{geo}) 依次为: $\text{Cd}(5.63) > \text{Cu}(3.88) > \text{As}(2.96) > \text{Pb}(2.30) > \text{Zn}(1.27)$, Cd 和 Cu 累积最严重. 土壤重金属内梅罗指数 (NPI) 高值主要出现在冶炼历史长、工艺落后和环保措施不足的场地. 土壤重金属含量之间呈现显著相关性, 随着采样半径增加而降低, 主要累积在冶炼场地周边 2~3 km 内. 相对于冶炼历史、规模和工艺, 土地利用类型对土壤重金属含量影响较小. 铜冶炼场地周边土壤重金属普遍存在致癌风险与非致癌风险, 其中冶炼生产区 As 和 Pb, 林地 Pb 的健康风险较高. 研究结果可以指导冶炼场地周边土壤重金属污染风险防控工作.

关键词: 冶炼场地; 土地利用类型; 风险评价; 全球尺度; 数据整合分析

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Characteristics and Risk Assessment of Heavy Metals in the Soil Around Copper Smelting Sites

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Abstract: Copper smelting can cause heavy metal pollution in surrounding soil and threaten human health. This study examined the characteristics, distribution, and health risk of heavy metals in soil with different land uses around 40 copper smelting sites at home and abroad by collecting published literature data. The results showed that the mean values of $\omega(\text{As})$, $\omega(\text{Cd})$, $\omega(\text{Cu})$, $\omega(\text{Pb})$, and $\omega(\text{Zn})$ in the soil around the copper smelting sites were 196, 10.5, 1 948, 604, and 853 $\text{mg}\cdot\text{kg}^{-1}$, respectively. The order of I_{geo} was $\text{Cd}(5.63) > \text{Cu}(3.88) > \text{As}(2.96) > \text{Pb}(2.30) > \text{Zn}(1.27)$, and the accumulation of Cd and Cu was the most serious. High Nemer index (NPI) values were found in the soil around smelting sites with a long history of smelting, outdated process, and insufficient environmental protection measures. Significant correlations were found between the concentrations of heavy metals in the soil, which decreased with the sampling distance. The heavy metals mainly accumulated within 2-3 km from the smelting sites. Compared with the smelting history, scale, and process, land use type had a lower effect on soil heavy metal concentrations. The heavy metals in the soil around copper smelters may pose carcinogenic and non-carcinogenic risks on residents. The high health risks were mainly caused by As and Pb in smelting production areas, and Pb in woodland. These results may guide the risk prevention of heavy metal pollution in the soil around smelting sites.

Key words: smelting site; land use type; risk assessment; global scale; data integration and analysis

有色金属冶炼是造成土壤重金属污染的主要原因之一^[1]. 铜冶炼是对铜矿石的精炼和提纯过程, 涉及焙烧和电解等工艺, 因此生产过程中会排放大量的废水、废气和废渣^[2]. 冶炼废气和废水中重金属在经由大气扩散和径流迁移后, 会在冶炼场地周边土壤中累积^[3]. 冶炼废渣如被不合理堆放, 其中重金属会随降雨产生的地表径流迁移, 污染周边土壤^[4]. 土壤重金属具有易积累、难降解、隐蔽性强和残留时间长等特点, 难以彻底去除^[5,6]. 同时土壤重金属可以通过多途径进入人体, 威胁居民健康^[7]. 许多铜冶炼企业位于城市郊区, 随着城市扩张和环保要求升级, 冶炼企业普遍迁移和关停, 但其遗留的土壤污染问题不容忽视^[8,9].

目前, 对于冶炼场地周边土壤污染研究主要集中在重金属分布规律、源解析和风险评价等方面^[10~12]. 土地利用类型会影响到重金属的迁移和归趋, 进而影响土壤重金属累积量^[13]. 但现有研究大

多针对单个冶炼场地与单种土地利用类型^[14,15], 对不同冶炼场地以及不同土地利用类型下土壤重金属整体累积特征的研究较少. 通过分析公开发表的文献数据, 可以更为系统地分析土壤污染物整体分布和形成规律^[16,17]. 例如, Jiang 等^[18] 和 Lei 等^[19] 通过研究已发表文献数据, 阐明了我国冶炼场地周边土壤重金属的累积特征与主要污染元素. 但全球铜冶炼场地周边土壤重金属的分布规律和风险特征尚不明确. 因此本研究在全球范围收集了已发表的铜冶炼场地周边土壤重金属数据, 通过整合分析: ①阐明铜冶炼场地周边土壤重金属累积和分布特征; ②揭示土地利用类型对铜冶炼场地周边土壤重金属含量及其健康风险的影响, 以期对铜冶炼场地周边土壤重金属污染治理与风险防控提供建议与支持.

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1 材料与方法

1.1 数据收集与处理

本研究整理收集了近 20 年发表的铜冶炼场地及周边土壤重金属相关研究论文,其主要来源为 Web of Science (www. webofknowledge. com)、Science Direct(www. sciencedirect. com)和中国知网(www. cnki. net). 检索关键词包括“土壤重金属”“铜冶炼”“重金属”以及各个国家的名称等. 文献筛选要求为公开发表且经过同行评议,并且报道了定量分析和质控方法的研究性论文. 此外,为保证数据代表性,每个研究采样点数需大于 3 个,同时给出相关采样点位布设信息. 文献中土壤重金属含量的定量方法主要为原子吸收光谱法(AAS)、电感耦合等离子体质谱法(ICP-MS)和电感耦合等离子体发射光谱法(ICP-OES)等. 因筛选后文献大多针对 As、Cd、Pb、Cu 和 Zn 进行研究,且这 5 种元素是铜冶炼的主要污染物^[20,21],因此本研究选用这 5 种元素作为对象. 最终筛选出 19 个国家的 40 个铜冶炼场地及周边区域的 35 篇文献,共计 1 296 个表层土样(0~20 cm)的重金属含量数据. 本研究对文献中冶炼场地位置、采样半径、土地利用类型和重金属含量统计值进行了整理汇总和二次统计分析.

1.2 内梅罗综合指数(NIPI)

使用内梅罗综合指数法研究土壤重金属的污染程度,既能全面评价土壤中不同污染物的综合污染水平,还能反映高含量污染物对环境的危害^[22]. 计算公式为:

$$PI = C_i/B_i \quad (1)$$

$$NIPI = \sqrt{(PI_{ave}^2 + PI_{imax}^2)/2} \quad (2)$$

式中,PI 表示污染物的单因子污染指数,PI_{ave} 表示土壤中各重金属的污染指数平均值,PI_{imax} 表示土壤中各重金属的污染指数最大值, C_i 表示土壤中重金属的含量 (mg·kg⁻¹), B_i 表示其参考背景含量 (mg·kg⁻¹),根据已有研究,使用上地壳含量^[23~25]. 内梅罗综合指数法将土壤重金属污染程度划分为 5 个等级:NIPI ≤ 0.7 为清洁,0.7 < NIPI ≤ 1 为尚清洁,1 < NIPI ≤ 2 为轻度污染,2 < NIPI ≤ 3 为中污染,NIPI > 3 为重度污染.

1.3 地积累指数(I_{geo})

I_{geo} 被广泛应用于评估土壤重金属的累积程度^[26,27]. 计算公式为:

$$I_{geo} = \log_2(C_i/1.5B_i) \quad (3)$$

式中,C_i 和 B_i 含义同公式(1). 按 I_{geo} 大小可以将土壤重金属累积程度分为 7 个等级:I_{geo} ≤ 0 为未累积,

0 < I_{geo} ≤ 1 为未累积至中度累积,1 < I_{geo} ≤ 2 为中度累积,2 < I_{geo} ≤ 3 为中度累积至重度累积,3 < I_{geo} ≤ 4 为重度累积,4 < I_{geo} ≤ 5 为重度累积至严重累积, I_{geo} > 5 为严重累积.

1.4 健康风险评价

美国环保署基于土壤污染物的暴露水平和毒性效应评估其致癌和非致癌风险,并制定了土壤污染物风险筛选值 SL^[28],可以用来快速评估土壤污染物的健康风险. 根据 USEPA 建议,对 As 进行致癌风险分析,其它元素进行非致癌风险分析. 基于筛选值的健康风险计算公式如下^[29].

致癌风险:

$$T_{riskc} = \sum_i^n (C_i/SL_i^c) \times 10^{-6} \quad (4)$$

非致癌风险:

$$T_{riskn} = \sum_i^n (C_i/SL_i^N) \quad (5)$$

式中,SL^c 表示致癌物的筛选值 (mg·kg⁻¹), T_{riskc} 表示总致癌风险,SL^N 表示非致癌物的筛选水平 (mg·kg⁻¹), T_{riskn} 表示总非致癌风险. 根据筛选水平通用表,As、Cd、Cu、Pb 和 Zn 的筛选水平标准分别为 0.68、71、3 100、400 和 23 000 (mg·kg⁻¹). 对于致癌风险,风险值低于 10⁻⁶ 代表安全水平,介于 10⁻⁶ 和 10⁻⁴ 之间的代表潜在致癌风险,大于 10⁻⁴ 则代表存在致癌风险,非致癌物的风险界定阈值为 1.

1.5 数据处理

本研究中 I_{geo} 和 NIPI 的计算通过 Excel 2019 (Microsoft Corp., USA) 完成. 相关性分析通过 SPSS 22.0 (IBM, USA) 完成. 在相关分析之前,将重金属含量进行对数转换以获得近似正态分布. 土壤重金属含量的空间分布图使用 ArcGIS 10.2 (ESRI, Inc., USA) 绘制. 其它统计图通过 Sigmaplot 14.0 (Systat Software, USA) 绘制.

2 结果与讨论

2.1 铜冶炼场地周边土壤重金属累积特征

如表 1 所示,铜冶炼场地周边土壤重金属 ω(As)、ω(Cd)、ω(Cu)、ω(Pb) 和 ω(Zn) 平均值分别为 196、10.5、1 948、604 和 853 mg·kg⁻¹,分别超过了背景值的 34.4、175、72.1、24.2 和 11.1 倍. 场地间重金属含量差异很大,多数场地重金属含量远高于背景值. ω(As) 和 ω(Cd) 最高值出现在墨西哥,分别为 1 816 mg·kg⁻¹ 和 86.3 mg·kg⁻¹. ω(Cu)、ω(Pb) 和 ω(Zn) 最高值分别出现在伊朗、波兰和加拿大,为 31 240、3 533 和 7 001 mg·kg⁻¹. 场地间土壤重金属含量差异与冶炼矿石品质、冶炼历

史、冶炼工艺和环保措施等差异有关^[30~32]. 重金属平均 I_{geo} 大小依次为: $Cd(5.63) > Cu(3.88) > As(2.96) > Pb(2.30) > Zn(1.27)$, 见表 2. 铜冶炼场地周边土壤均受到不同程度 Cu 和 Cd 累积, Cd 和 Cu 的 $I_{geo} > 3$ 的场地占比超过 90% 和 55%, 说明大部分铜冶炼场地周边土壤 Cd 和 Cu 在重度至严重

累积水平. 土壤中 As、Pb 和 Zn 的 I_{geo} 值从未累积到严重累积均有分布. As 和 Pb 处于重度及以上污染的场地分别占 43.5% 和 35.3%. 土壤 Zn 累积程度最低, 有 41.9% 的场地不存在 Zn 累积. 总之, 铜冶炼活动会造成周边土壤重金属明显累积, 尤其是 Cd 和 Cu 元素.

表 1 铜冶炼场地周边土壤重金属含量平均值汇总¹⁾

Table 1 Summary of average concentrations of heavy metals in soil around copper smelting sites										
国家	城市	土地利用类型	采样 点数	采样半径 /km	$\omega(As)$ /mg·kg ⁻¹	$\omega(Cd)$ /mg·kg ⁻¹	$\omega(Cu)$ /mg·kg ⁻¹	$\omega(Pb)$ /mg·kg ⁻¹	$\omega(Zn)$ /mg·kg ⁻¹	文献
澳大利亚	Kembla	居住用地	25	24	4.10	—	76.0	29.0	63.0	[33]
波兰	Rudawy Janowickie	林地	4	0.2	63.3	—	196	115	91.5	[34]
波兰	Lower Silesia	林地	3	2.1	—	—	5 169	3 533	1610	[35]
波兰	Glogow	农用地	3	2	—	—	297	111	47.5	[36]
俄罗斯	Karabash	林地	3	6	285	7.75	2 669	620	1216	[37]
法国	Limoges	冶炼生产区	3	0.2	—	4.10	396	170	86.0	[38]
芬兰	Harjavalta	林地	3	4	—	—	97.5	—	—	[39]
刚果(布)	Lubumbashi	冶炼生产区	30	2	—	7.73	4 562	182	338	[40]
加拿大	Rouyn-Noranda	林地	75	9	—	—	—	869	—	[41]
加拿大	Flin Flon	林地	3	5.1	251	36.7	2 073	1 205	7 001	[42]
加拿大	Coniston	居住用地	5	36	17.7	—	237	39.8	58.6	[43]
加拿大	Sudbury	居住用地	10	6.2	—	2.80	557	33.0	63.0	[44]
加拿大	Sudbury	居住用地	6	3.2	—	2.70	207	24.0	50.0	[45]
加拿大	Sudbury	居住用地	4	5	—	2.70	464	34.0	54.0	[45]
罗马尼亚	Zlatna	农用地	55	2	204	5.20	1 683	1 303	1 933	[45]
罗马尼亚	Baia Mare	居住用地	121	8	87.9	—	248	864	394	[46]
美国	Anaconda	林地	3	1	—	8.50	884	215.7	615	[47]
美国	Tucson	居住用地	3	1	96.7	5.33	—	145	—	[48]
墨西哥	San Luis Potosi	冶炼生产区	22	1	1 816	86.3	2 003	3224	1192	[49]
墨西哥	Morales	居住用地	71	1.5	791	—	—	1 450	—	[50]
瑞典	Rönnskär	冶炼生产区	10	3	—	—	—	3 326	—	[51]
塞尔维亚	Bor	冶炼生产区	242	8	48.2	—	—	—	—	[52]
斯洛伐克	Krompachy	林地	3	5.3	—	—	2 957	—	1 108	[53]
西班牙	Huelva	林地	155	20	14.0	—	110	45.0	100	[54]
伊朗	Kerman	农用地	24	12	23.8	0.30	92.0	13.7	55.0	[55]
伊朗	Sarchehmeh	冶炼生产区	3	1	413	11.6	31 240	345.4	781	[56]
英国	Prescot	林地	3	1.5	77.3	22.0	661	565	144	[57]
赞比亚	Kitwe	冶炼生产区	55	1.7	9.52	—	4 010	35.6	62.7	[58]
智利	La Greda	农用地	10	1.9	65.3	1.30	1 394	96.3	307	[59]
智利	Los Maitenes	农用地	10	2.5	73.0	1.10	1 078	137	232	[60]
智利	Valle Alegre	农用地	10	6.4	23.0	0.50	286	45.0	165	[60]
智利	Puchuncaví	农用地	10	8.6	45.1	1.00	571	84.4	165	[60]
中国	安徽芜湖	农用地	6	3	—	—	83.8	33.1	55.1	[60]
中国	江西鹰潭	农用地	12	1	33.9	—	505	90.4	83.4	[61]
中国	浙江嘉兴	农用地	99	2.4	—	—	317	—	—	[62]
中国	浙江杭州	农用地	4	0.18	—	3.98	344	—	4 311	[63]
中国	浙江绍兴	农用地	7	0.6	—	—	308	—	2 238	[64]
中国	湖北大冶	农用地	71	5.8	36.6	5.28	193	93.8	—	[65]
中国	湖北大冶	农用地	102	5.3	35.8	4.90	195	92.7	—	[66]
中国	辽宁沈阳	冶炼生产区	38	厂内	—	9.35	2 022	1 359	1 281	[67]
土地含水量	—	—	—	—	5.70	0.06	27.0	25.0	75.0	[23]
平均值	—	—	—	—	196	10.5	1 948	604	835	
最小值	—	—	—	—	4.1	0.30	76.0	13.7	47.5	
最大值	—	—	—	—	1 816	86.3	31 240	3 533	7 001	

1) 采样半径表示冶炼场地为中心的最大采样距离; “—”表示文献中没有相关数据

表 2 铜冶炼场地周边土壤 I_{geo} 平均值与等级分布

Table 2 Mean I_{geo} value and grade distribution of heavy metals in soil around copper smelting sites

元素	I_{geo} 平均值	占比/%					
		$I_{geo} \leq 0$	$0 < I_{geo} \leq 1$	$1 < I_{geo} \leq 2$	$2 < I_{geo} \leq 3$	$3 < I_{geo} \leq 4$	$I_{geo} > 5$
As	2.96	4.35	8.70	17.39	26.09	17.39	17.39
Cd	5.63	0.00	0.00	4.55	4.55	13.64	63.64
Cu	3.88	0.00	2.86	11.43	28.57	17.14	31.43
Pb	2.30	20.59	8.82	26.47	8.82	5.88	20.59
Zn	1.27	41.94	9.68	12.90	6.45	16.13	6.45

2.2 全球范围铜冶炼场地周边土壤重金属分布特征

如图 1 所示,已有研究中铜冶炼场地主要分布在欧洲(30%)、亚洲(27.5%)和北美洲(25%),其次是南美洲(10%)和非洲(5%),大洋洲仅占 2.5%。其中研究较多的国家有中国、加拿大、智利和波兰等。以上国家铜矿资源丰富,属于全球主要产铜国,因此利用本国丰富的铜资源建立了较多的铜冶炼厂^[68]。重金属的 NIPI 指数可以反映出土壤重金属的整体污染水平。大多数场地的 NIPI > 3,说明大部分场地土壤属于重度污染。NIPI 超过 300 的场地分别位于墨西哥 San Luis Potosi(1 054.7)、伊朗 Sarchehmeh(843.4)和加拿大 Flin Flon(449.8)。100 < NIPI < 300 的场地主要分布在英国 Prescott、波兰 Lower Silesia、瑞典 Rönnskär、刚果(布) Lubumbashi、墨西哥 Morales、中国辽宁省沈阳市、赞比亚 Kitwe、

美国 Anaconda 和俄罗斯 Karabash。这些高污染场地多为当地规模较大的工业场地,建立时间早,工艺落后,因而周边土壤重金属累积程度高。如英国 Prescott 和瑞典 Rönnskär 的场地建厂生产分别超过了 100 a 和 70 a^[54,60]。墨西哥 Morales、伊朗 Sarchehmeh 和波兰 Lower Silesia 等场地,将未经处理的冶炼渣随意堆放,经风力侵蚀和雨水冲刷后,可能向周边土壤释放重金属^[38,54,59]。虽然一些冶炼厂在经过长期生产后改进了工艺、增设了过滤设备,但是土壤中重金属历史累积量大,污染仍然严重^[37,53]。相比之下,西班牙 Huelva 和中国安徽省芜湖市的场地 NIPI 相对较低(NIPI 分别为 3.35 和 2.51),这与冶炼厂生产历史较短、工艺较为先进有关^[54,60]。因此,冶炼历史、生产工艺和环保措施是影响铜冶炼场地周边土壤重金属污染程度的主要因素。

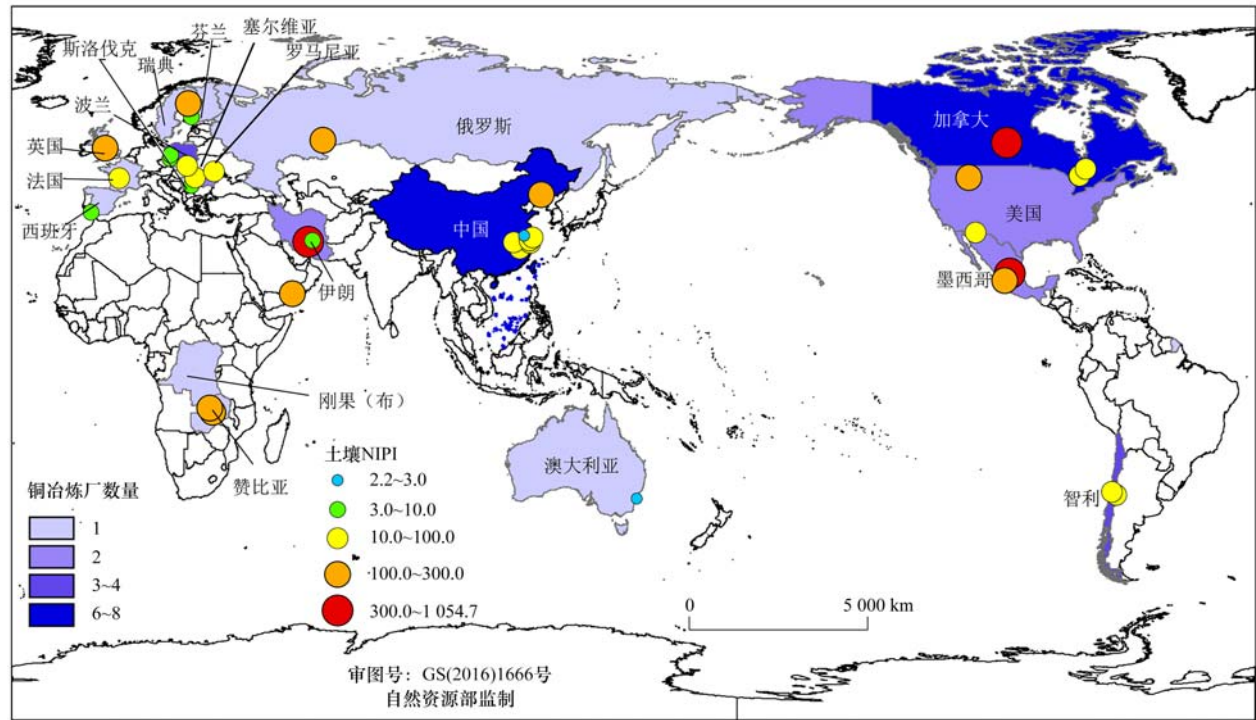


图 1 铜冶炼场地周边土壤重金属 NIPI 空间分布

Fig. 1 Distribution of NIPI values of heavy metals in soil around copper smelting sites

2.3 铜冶炼场地周边土壤重金属相关性分析

铜冶炼场地周边土壤重金属间相关性分析结果见表 3, As 与 Cd、Cu、Pb 和 Zn 间显著相

关($P < 0.01$), Cd 与 Pb 和 Zn 之间显著相关($P < 0.05$),说明这些重金属都有相似的来源。铜矿石中含有多种重金属元素,As、Cd、Pb

和 Zn 都是其中的伴生元素^[20,58]。铜矿石在冶炼生产中会经历焙烧、浸出、电解和萃取等一系列工序，导致多种重金属元素从铜矿石中释放出来，以三废的形式进入冶炼场地周边环境中。因此冶炼场地周边土壤往往呈现出多重金属元素复合污染。

表 3 铜冶炼场地周边土壤重金属含量与采样半径间相关性分析结果¹⁾

Table 3 Correlations between soil heavy metal concentrations and sampling radius near copper smelting sites						
	采样半径	As	Cd	Cu	Pb	Zn
采样半径	1					
As	-0.551 **	1				
Cd	-0.496 *	0.798 **	1			
Cu	-0.393 *	0.644 **	0.402	1		
Pb	-0.378 *	0.891 **	0.779 **	0.607 **	1	
Zn	-0.345	0.815 **	0.564 *	0.547 **	0.866 **	1

1) * 表示 $P < 0.05$, ** 表示 $P < 0.01$

采样半径代表各研究中土壤采样点与冶炼场地的最大采样距离,其与土壤 As、Cd、Cu 和 Pb 均呈显著负相关($P < 0.05$)。这说明随着采样范围增大,As、Cd、Cu 和 Pb 含量逐渐降低。由于土壤 Zn 累积程度较低,含量与采样距离无显著相关。大气沉降和地表径流迁移是重金属进入土壤的主要途径,因而随着到污染源的距离增加,土壤重金属的含量逐渐降低^[69~71]。各研究采样半径分布不均,其中 3 km 和 2 km 两个采样半径的场地分别占到研究总数的 55% 和 42.5%,因此本研究选取了这两个采样半径进行对比(图 2),结果表明采样半径 < 3 km 的研究中土壤 As、Pb 和 Cu 含量显著高于采样半径 > 3 km 的研究结果($P < 0.05$)。此外,采样半径 < 2 km 的

土壤 Cd 和 Cu 含量显著高于采样半径 > 2 km 的研究($P < 0.05$)。可见场地周边 2 ~ 3 km 内土壤重金属累积更为严重,需重点关注。但是部分场地 3 km 外土壤重金属依然存在严重累积,如斯洛伐克 Krompachy 的场地土壤样品采集在下风向,重金属迁移范围更大^[53]。俄罗斯 Karabash 的场地冶炼区域植被退化,重金属随地表径流迁移更远^[37]。另外,部分研究由于采样点不足、采样范围较小,可能会低估污染范围。

2.4 不同土地利用类型下土壤重金属累积特征

冶炼场地周边不同土地利用下土壤重金属含量存在差异,土壤 $\omega(\text{As})$ 、 $\omega(\text{Cu})$ 、 $\omega(\text{Pb})$ 和 $\omega(\text{Cd})$ 平均值在冶炼生产区中最高,其次为林地土壤(图 3)。冶炼生产区与污染源距离最近,因此重金属含量平均值最高。而林地通常分布在冶炼厂周边,且林地中树冠会拦截大气环境重金属,植物凋落物分解后的有机质会增加土壤对重金属的吸附能力^[72,73],因此林地土壤重金属含量仅次于冶炼生产区。农用地中重金属来源除了大气沉降和污水灌溉,农药和化肥施用也会向农用地输入重金属^[74],因此在农用地中 Cu 和 Zn 含量也较高。居住用地通常距离冶炼生产区更远,因此重金属含量相对较低。方差分析表

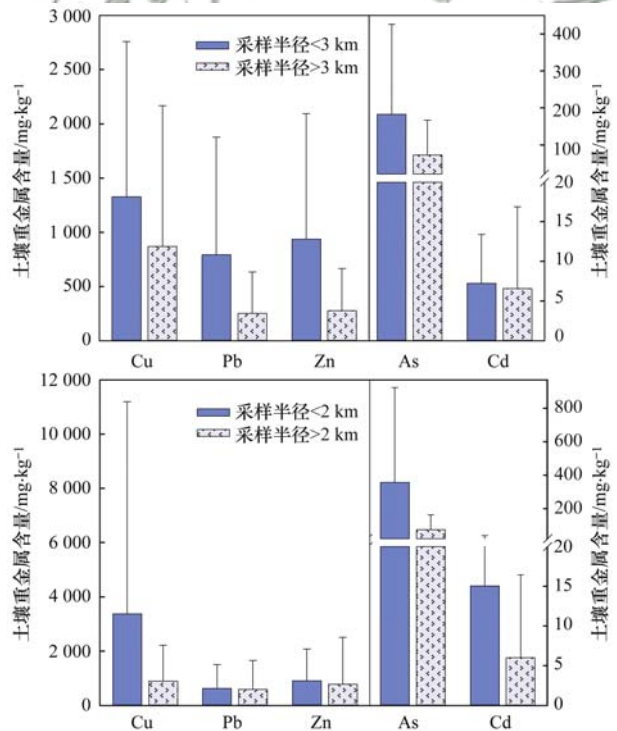


图 2 铜冶炼场地周边不同采样半径下土壤重金属含量特征

Fig. 2 Concentrations of heavy metals in soil around copper smelting sites under different sampling radiuses

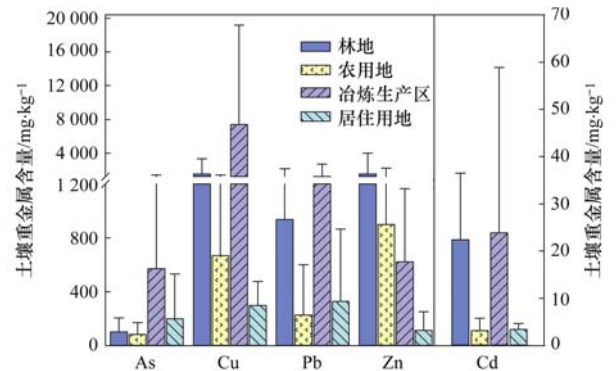


图 3 铜冶炼场地周边不同土地利用类型下土壤重金属含量特征

Fig. 3 Concentrations of heavy metals in soil with different land uses around copper smelting sites

明不同土地利用类型中土壤重金属含量差异不显著,这可能是因为各个研究针对的土地利用类型不一致,如在加拿大 Flin Flon 的 Cu-Zn 冶炼厂周边仅研究了林地土壤,而其 $\omega(\text{Zn})$ ($7\,001\text{ mg}\cdot\text{kg}^{-1}$) 显著提高了林地土壤 Zn 平均值. 罗马尼亚 Zlatna 场地仅采集了农田土壤,其 Cu、Pb 和 Zn 含量显著高于其它研究结果. 因此,冶炼历史、规模和工艺等因素在场地间的差异可能覆盖了土地利用类型对于土壤重金属累积的影响.

2.5 铜冶炼场地及周边土壤重金属健康风险评价

铜冶炼场地周边土壤重金属健康风险评价结果见表 4. 铜冶炼场地周边土壤总体致癌风险 T_{riskc} 平均值为 (2.77×10^{-4}) $> 10^{-4}$, 说明铜冶炼场地周边土壤 As 普遍存在致癌风险. 从空间分布上看,存在致癌风险场地主要分布在北美洲、亚洲和欧洲,风险较高的位于墨西哥 San Luis Potosi 和 Morales、伊朗 Sarchehmeh 和罗马尼亚 Zlatna 等场地,主要是因为这些场地土壤 As 含量较高. 除了受冶炼影响外,高风险也与周边工业分布情况有关,如 San Luis Potosi 场地附近的 As_2O_3 工厂增加了 As 污染排放与

风险^[52]. 不同土地利用类型中, T_{riskc} 平均值依次为冶炼生产区 (6.73×10^{-4}) $>$ 居住用地 (2.93×10^{-4}) $>$ 林地 (1.49×10^{-4}) $>$ 农用地 (1.21×10^{-4}), 冶炼生产区中土壤致癌风险最高. 总体非致癌风险 T_{riskn} 平均值为 2.31, 说明整体上存在非致癌风险. 各元素的 T_{riskn} 平均值依次为: Pb (1.51) $>$ Cu (0.63) $>$ Cd (0.14) $>$ Zn (0.04), 可知 Pb 是主要非致癌风险元素. 存在非致癌风险的场地主要分布在欧洲、北美洲、亚洲,风险较高的场地有波兰 Lower Silesia、墨西哥 San Luis Potosi、中国辽宁省沈阳市等,主要是因为土壤 Pb 含量过高而产生的风险. 不同土地利用类型中, T_{riskn} 平均值依次为: 冶炼生产区 (4.29) $>$ 林地 (3.13) $>$ 居住用地 (0.96) $>$ 农用地 (0.87), 说明冶炼生产区和林地土壤非致癌风险较高. 需注意的是,农田土壤中 Cd 过量累积会通过食物链造成健康风险^[75,76], 然而本研究中健康风险评价没有考虑到农作物吸收重金属经食物链对人体的健康风险,因此会低估农用地 Cd 的风险. 总之,冶炼生产区土壤 As 和 Pb, 以及林地土壤 Pb 的健康风险需要重点关注.

表 4 铜冶炼场地周边不同土地利用类型土壤重金属健康风险评价结果

Table 4 Health risks of heavy metals in soil with different land uses around copper smelting sites

土地利用类型	致癌风险 (T_{riskc})	非致癌风险				
		Cd	Cu	Pb	Zn	T_{riskn}
总体	2.77×10^{-4}	0.14	0.63	1.51	0.04	2.31
林地	1.49×10^{-4}	0.24	0.49	2.34	0.07	3.13
农用地	1.21×10^{-4}	0.04	0.22	0.57	0.04	0.87
冶炼生产区	6.73×10^{-4}	0.34	0.84	3.09	0.03	4.29
居住用地	2.93×10^{-4}	0.04	0.10	0.82	0.00	0.96

3 结论

通过收集整理已发表的研究数据,表明铜冶炼场地及周边土壤中 $\omega(\text{As})$ 、 $\omega(\text{Cd})$ 、 $\omega(\text{Cu})$ 、 $\omega(\text{Pb})$ 和 $\omega(\text{Zn})$ 平均值分别为 196、10.5、1 948、604 和 $853\text{ mg}\cdot\text{kg}^{-1}$, I_{geo} 平均值依次为: Cd (5.63) $>$ Cu (3.88) $>$ As (2.96) $>$ Pb (2.30) $>$ Zn (1.27), 土壤 Cd 和 Cu 累积最严重. NIPI 值较高的场地位于英国 Prescot、瑞典 Rönnskär、墨西哥 Morales、伊朗 Sarchehmeh 和波兰 Lower Silesia 等. 冶炼历史较长、生产工艺落后且缺乏有效的环保措施是这些场地周边土壤污染程度高的主要原因. 冶炼场地周边土壤重金属之间相关性显著,都随着采样距离的增加而下降,场地周边 2~3 km 内土壤重金属累积更严重. 相对于冶炼历史、规模和工艺等因素来说,土地利用类型对土壤重金属含量的影响较小. 冶炼场地及周边土壤重金属存在不同程度健康风险,其中冶炼生产区 As 和 Pb, 以及林地土壤 Pb 健康风险较高.

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