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基于 GIS 和受体模型的枸杞地土壤重金属空间分布特征及来源解析

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摘要:通过测定"万亩枸杞示范园"119 个表层(0~20 cm) 土壤样品中重金属铅(Pb)、镍(Ni)、锌(Zn)、锰(Mn)、铜(Cu)、铬(Cr)和镉(Cd)含量,以宁夏土壤背景值为评价标准,利用单因子指数、内梅罗综合指数和潜在生态危险指数评价土壤重金属污染状况,借助绝对因子分析/多元线性回归受体模型(APCS-MLR)与地统计相结合的方法,对土壤重金属空间分布及来源进行分析.结果表明,Pb、Ni、Zn、Mn、Cu、Cr和Cd含量分别为34.78、52.376、83.692、641.114、38.130、87.257和0.149 mg·kg⁻¹,均低于国家土壤污染风险筛选值但超过了宁夏土壤背景值.内梅罗综合指数显示枸杞地81.51%样点的土壤重金属呈现轻度污染,16.81%样点呈现中度污染,1.68%未受重金属污染.潜在生态危险复合指数表明,13.45%样点表现为轻微生态风险,86.55%样点表现为中等生态风险.枸杞地土壤重金属有4种主要来源:自然源、工业活动源、交通源和农业活动源,其中Ni和Cr的来源以自然源为主,贡献率分别为55.49%和64.66%,Pb和Mn的来源以工业活动源为主,贡献率分别为46.93%和42.53%,Zn和Cu的来源以交通源为主,贡献率分别为43.51%和53.71%,Cd的来源以农业活动源为主,贡献率为76.79%.枸杞地土壤重金属含量明显受人类活动影响且来源复杂,应根据其贡献率加强控制,确保中宁枸杞土壤资源的可持续利用.

关键词:宁夏; 重金属; 源解析; APCS 受体模型; 枸杞

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Spatial Distribution Characteristics and Source Apportionment of Soil Heavy Metals in Chinese Wolfberry Land Based on GIS and the Receptor Model

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Abstract: A total of 119 surface soil samples (depth of 0-20 cm) were collected from a Chinese wolfberry demonstration garden in Zhongning of Ningxia, and samples were analyzed for seven heavy metals (Pb, Ni, Zn, Mn, Cu, Cr, and Cd). The single factor index, comprehensive index, and potential ecological risk were used to assess the soil heavy metal contamination with the soil background values of Ningxia as the evaluation standards. The absolute principal component scores and multivariate linear regression (APCS-MLR) model as well as geostatistic analysis were combined to identify and apportion the pollution sources of soil heavy metals. The results showed that the average concentrations of Pb, Ni, Zn, Mn, Cu, Cr, and Cd in soils were 34.78, 52.376, 83.692, 641.114, 38.130, 87.257, and 0.149 mg·kg⁻¹, respectively. The mean concentrations of heavy metals were higher than the local soil background values but lower than the risk screening values for soil contamination of agricultural land. The comprehensive index results showed that the pollution degree of soil heavy metals was at the slightly polluted level in 81.51% of the samples, at the moderately polluted level in 16.81% of the samples, and at the unpolluted level in 1.68% of the samples. The comprehensive index values for potential ecological hazards were less than 60 in 13.45% of the samples, and these values were associated with a slight potential for ecological risks. The comprehensive index values for potential ecological hazards were less than 120 and more than 60 in 86.55% of the samples, and these values were associated with a moderate potential for ecological risks. The four main pollution sources of soil heavy metals in the study area included natural sources, industrial activity, traffic, and agricultural activity. Natural sources were the main source of Ni and Cr with average contribution rates of 55.49% and 64.66%, respectively. Industrial activity was the main source of Pb and Mn with average contribution rates of 46.93% and 42.53%, respectively. Traffic was the main source of Zn and Cu with average contribution rates of 43.51% and 53.71%, respectively. Agricultural activity was the main source of Cd with an average contribution rate of 76.79%. The study results indicated that soil heavy metals have tended to concentrate in the Chinese wolfberry demonstration garden, and the sources of heavy metals were complex and obviously influenced by human activities. Controls should be strengthened for sources that contribute to soil heavy metals to ensure the sustainable utilization of soil resources in the Chinese wolfberry land.

Key words: Ningxia; heavy metal; source apportionment; APCS model; Chinese wolfberry

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伴随着"一带一路"经济带建设快速推进,包括宁夏在内的西北内陆地区经济社会进入到快速发展期. 在承接东部地区产业转移同时,部分工业企业会对西北脆弱的生态环境产生负面影响[1]. 随着工业快速发展和农药化肥长期施用,西北内陆地区农田土壤出现重金属元素富集的现象,进而导致土壤质量下降和农副产品污染[2].同时《全国土壤污染状况调查公告》显示全国耕地点位的超标率达到19.4%,且以重金属污染为主[3].因此准确了解农业土壤重金属污染状况与重金属来源对防治农业土壤重金属污染、保障土壤环境质量及农产品安全具有重要意义[4.5].

近年来关于土壤重金属污染研究日益增多,研 究领域多集中在土壤重金属富集特征[6,7]、空间分 布^[8~10]、污染评价^[11,12]和污染源识别^[13,14]等. 其 中确定土壤重金属来源,特别是搞清土壤重金属是 人为活动污染所致还是来源土壤母质是一些学者所 关心的问题. 由于土壤污染源成分谱的未知性与难 确定性,目前以污染区域为研究对象的未知源成分 谱受体模型被一些学者用于土壤重金属污染源的定 量解析. 未知源成分谱受体模型有主成分分析/绝 对主成分分数法(PCA/APCS)[14]、正定矩阵因子分 析模型(PMF)[15]和化学质量平衡(CMB)[16]等, 其 中 PCA/APCS 可计算出每个污染源对每个样本的 浓度贡献量, 因此被一些学者应用于土壤重金属源 解析研究. 如瞿明凯等[14]在武汉市、陈秀端等[17] 在西安市、陈丹青等[18]在广州市均利用 PCA/APCS 方法定量解析出土壤重金属各污染源平均贡献量及 各样点各污染源对每种重金属的贡献量. 目前土壤 重金属污染源解析大多集中在经济发展迅速的城 市、污染严重的矿区或工业园区[17~19]. 然而不同 重金属在不同环境体系中会受到多种因素的影响, 进而会导致其污染和分布特征具有一定差异性[7], 且农业重金属污染问题也逐渐显现[11,12],因此研 究农业土壤重金属污染特征及来源解析对了解土壤 重金属富集规律和防治土壤重金属污染有重要 作用.

宁夏属西北干旱半干旱区域、生态环境脆弱,该区域主导风向明显、风力强、降水量少、蒸发强烈及植被覆盖率低等环境因素严重影响重金属污染的分布、特征和来源^[14].虽然已有学者对宁夏地区重金属污染进行了相关研究^[8,20],但关于枸杞地土壤重金属分布特征及源解析研究较少.土壤环境质量直接影响枸杞生产安全及其可持续发展^[21],"中宁枸杞"对区域经济发展和全国枸杞行业健康成长有至关重要的作用.随着中宁县工农业快速发展,

枸杞地土壤重金属含量是否能保证当地生态环境质量和农产品安全,是当前必须重视的问题^[2].本研究在评价枸杞地土壤重金属状况的基础上,将绝对主成分分数(APCS)与多元线性回归(MLR)以及克里金插值的方法相结合,定量解析中宁枸杞农田土壤重金属的主要来源及各自的贡献量,同时分析其空间分布特征,以期为评价枸杞地生态环境质量和保障农产品安全提供数据支持.

1 材料与方法

1.1 研究区概况

采样点位于宁夏中宁县"万亩枸杞示范园" (105°36′32″E,37°26′55″N),该区域海拔1258~1261 m,属典型的温带大陆性气候。年平均温度8.4℃,年均降水量184 mm,年均蒸发量1100 mm,年均日照时数3099 h,年均无霜期168 d. 土壤质地为黏质沙土,土壤类型为淡灰钙土。植被类型为枸杞(*Lycium chinensis*)。通过测定研究区土壤基本理化性质如下:pH 为8.57,电导率为220 μ S·cm⁻¹, CEC为13.12 cmol·kg⁻¹,有机质含量为17.39 g·kg⁻¹,黏粒含量为14.78%。

1.2 样点布设及土样采集测定

为避免土壤质地、地形和土地利用等对土壤重 金属含量的影响, 充分探讨工业、交通、施肥灌溉 等人类活动对土壤重金属含量的影响, 在野外调研 和分析的基础上选取土壤性质、植被和地形等较为 单一的中宁县"万亩枸杞示范园"作为研究区. 在 2016年10月中旬枸杞收获后,以100m×100m网 格采集土壤样品,采样点共119个,面积约1.6 km². 采样时利用 GPS 记录采样点的空间信息, 采 样点位置分布详见图 1. 采样时去掉土壤表层覆盖 的枯落物,每个样点利用木铲在采样点1 m 半径内 采集0~20 cm 土壤样品4个, 混合均匀后利用四 分法保留约1 kg 土样. 土样经风干、剔除杂质后研 磨过 100 目尼龙筛备用. 利用 HNO3-HCl-HF-HClO4 消解对土壤样品进行处理^[2], 然后采用 ICP-AES (HK-8100)测定土样中重金属 Cu、Zn、Mn、Ni、 Cr、Cd 和 Pb 含量, 检测限依次为 0.003、0.003、 0.003、0.005、0.005、0.003 和 0.03 mg·kg⁻¹. 试 验及测试过程采用3组平行试验,取其均值作为土 样重金属浓度,准确度和精密度利用国家标准土壤 物质(GSS-8)进行质量控制并计算加标回收率, Cu、Zn、Mn、Ni、Cr、Cd 和 Pb 的平均回收率分别 为:101.6%、100.5%、102.1%、100.1%、99.8%、 89.9%和102.3%,并进行随机检查和异常点检查, 结果符合质量监控要求.

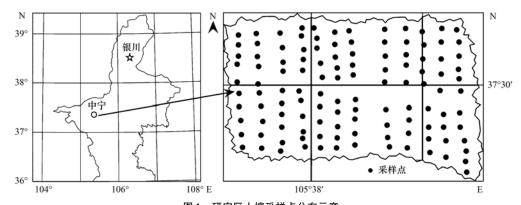


图 1 研究区土壤采样点分布示意

Fig. 1 Distribution of sampling sites

1.3 污染指数法

单因子指数和内梅罗综合污染指数可以全面反映出各污染物的污染状况,同时突出较高浓度污染物对土壤环境质量的影响,其计算公式为:

$$P_i = C_i / S_i \tag{1}$$

$$P_{\frac{6\pi}{3}} = \sqrt{\frac{(\overline{P}_{i})^{2} + (P_{i \max})^{2}}{2}}$$
 (2)

式中, P_i 为土壤中重金属元素 i 污染指数; P_{\S} 为土壤重金属元素的综合污染指数; \overline{P}_i 为单因子污染指数的平均数; $P_{i,max}$ 为最大单因子污染指数; C_i 为重金属元素 i 的含量($mg \cdot kg^{-1}$), S_i 为重金属元素 i 的土壤元素背景值,本文选择宁夏土壤元素背景值(Pb:20.6 $mg \cdot kg^{-1}$ 、Ni:36.6 $mg \cdot kg^{-1}$ 、Zn:58.8 $mg \cdot kg^{-1}$ 、Mn:524 $mg \cdot kg^{-1}$ 、Cu:22.1 $mg \cdot kg^{-1}$ 、Cr:60.6 $mg \cdot kg^{-1}$ 、Cd:0.11 $mg \cdot kg^{-1}$)。当 P_{\S} ≤ 1 为无污染, $1 < P_{\S} \leq 2$ 为轻污染, $2 < P_{\S} \leq 3$ 为中污染, $P_{\S} > 3$ 为重污染.

1.4 潜在生态危险指数法

潜在生态危险指数法不仅可以评价单个重金属 元素的生态危险,又可综合了解多种重金属对土壤 的潜在生态危险程度.其计算公式如下:

$$RI = \sum_{i=1}^{n} E_{r}^{i}$$
 (3)

$$E_{\rm r}^i = T_{\rm r}^i \times C_{\rm r}^i \tag{4}$$

$$C_{\rm r}^i = C_i / C_0^i \tag{5}$$

式中,RI 为综合潜在生态危险指数; E_r^i 为重金属单项潜在生态危险指数; T_r^i 为重金属毒性参数,Pb、Ni、Zn、Mn、Cu、Cr 和 Cd 的毒性参数分别取值 5、5、1、1、5、2 和 $30^{[23-25]}$. C_r^i 为重金属污染指数; C_i 为重金属实测值; C_0^i 为重金属参照值,本文选择宁夏土壤元素背景值[22]. E_r 值分级标准的第一级上限值是根据非污染的污染指数($E_r=1$)与所分析污染物中最大的毒性参数相乘得到,因此本文中 $E_r \leq 30$ 为轻微生态风险, $30 < E_r \leq 60$ 为中等生态

风险, $60 < E_r \le 120$ 为强生态风险, $120 < E_r$ 为很强生态风险. 考虑到 Hakanson 潜在生态危险指数的适用性, 结合相关学者的研究成果 [26], 本文根据所分析污染物的毒性和数量对 RI 分级标准进行了如下调整:

$$L_{1} = \sum_{i=1}^{7} T_{r}^{i} \times \frac{l_{1}}{T_{c}}$$
 (6)

式中, l_1 是 Hakanson 的第一级分级上限值, T_0 是 Hakanson 公式的 8 种污染物毒性参数总值. L_1 取十位整数后即为调整后的第一级分级上限值,其它级分级值为上一级分级值的 2 倍,因此得到调整后的 RI 的分级标准为: RI \leq 60 为轻微生态风险,60 < RI \leq 120 为中等生态风险,120 < RI \leq 240 为强生态风险。240 < RI 为很强生态风险。

1.5 绝对因子分析/多元线性回归受体模型 (APCS-MLR)

利用 APCS-MLR 模型对土壤重金属污染源进行定量解析. 首先,将因子分析的因子得分转化为绝对主成分因子得分,再分别对受体含量进行多元线性回归,利用回归系数计算各因子对应污染源对受体中该物质的贡献量[14]. 计算步骤见式(7)~(9).

(1)对所有重金属元素含量进行标准化,从主成分分析得到归一化的因子分数.

$$Z_{ij} = \frac{C_{ij} - \overline{C_i}}{\sigma_i} \tag{7}$$

式中, Z_{ij} 为标准化后的因子分数(无纲量); C_{ij} 为重金属元素含量实测值; $\overline{C_i}$ 和 σ_i 分别为元素 i 的平均含量和标准偏差.

(2)对所有元素引入1个含量为0的人为样本,计算得到该0含量样本的因子分数.

$$Z_{0i} = \frac{0 - \overline{C_i}}{\sigma_i} = -\frac{C_i}{\sigma_i} \tag{8}$$

(3)每个样本的因子分数减去 0 含量样本的因子分数得到每个重金属元素的 APCS;

(4)用重金属含量数据对 APCS 做多元线性回归,得到的回归系数可将 APCS 转化为每个污染源对每个样本的含量贡献.

$$C_i = b_{0i} + \sum_{p=1}^{n} (APCS_p \cdot b_{pi})$$
 (9)

式中, b_{0i} 为对金属元素 i 做多元线性回归所得常数项; b_{pi} 是源 p 对重金属元素 i 的回归系数; $APCS_p$ 为调整后因子 p 的分数; $APCS_p \cdot b_{pi}$ 表示源 p 对 C_i 的含量贡献;所有样本 $APCS_p \cdot b_{pi}$ 平均值表示源平均绝对贡献量.

1.6 数据分析

土壤重金属含量统计分析、主成分分析和多元 线性回归采用 SPSS 18.0 和 Excel 2007 软件, 地统 计学分析和空间分布图的制作通过 ArcGIS 10.0 完成.

2 结果与分析

2.1 中宁枸杞地土壤重金属含量描述

研究区 119 个采样点土壤重金属含量统计结果见表 1. Pb、Ni、Zn、Mn、Cu、Cr和Cd的平均含量分别为34.78、52.376、83.692、641.114、38.130、87.257和0.149 mg·kg⁻¹,除 Mn 没有国家标准值外,其它重金属含量均低于《土壤环境质量 农用地土壤污染风险管控标准(试行)》中的土壤污染风险筛选

值. 同时 Pb、Ni、Zn、Mn、Cu、Cr 和 Cd 这 7 种重金属元素平均值均超过宁夏土壤背景值,超标率分别为 98.32%、97.48%、83.19%、95.80%、99.16%、93.28%和 98.32%,说明随着城市化和工农业发展,枸杞地土壤重金属元素已受到人类活动的影响而出现富集趋势。根据 Wilding [27] 对变异程度的分类,枸杞地土壤中 Mn 和 Cd 变异系数小于 0.15,属于弱空间变异,空间差异不显著,其它 5 种重金属变异系数均大于 0.15 而小于 0.36,属于中等空间变异。利用 SPSS 进行 KS 正态分布检验,结果表明 Pb、Ni、Mn和 Cr 的 $P \ge 0.05$ 时,符合正态分布,而 Zn、Cu 和 Cd 的 P < 0.05 时,呈现非正态分布.

2.2 中宁枸杞地土壤重金属污染评价

根据 P_i 和 P_{\S} 评价标准,对各采样点土壤重金属不同污染级别所占比例进行分析(表 2). 通过 P_i 可以看出,7 种重金属在大部分样点处属于轻度污染,Ni、Mn 和 Cd 无中度和重度污染样点,Pb、Zn、Cu 和 Cr 中度污染样点数分别占总样点 17.65%、0.84%、25.21% 和 2.52%,其中 Cu 元素污染最严重,并出现了重度污染样点. 通过 P_{\S} 可以看出,中宁枸杞地 81.51% 样点呈现轻度污染,16.81% 样点呈现中度污染,只有 1.68% 未受重金属污染,说明经济发展带来的环境污染问题已威胁到枸杞地土壤质量和农产品安全.

表 1 枸杞地土壤重金属描述性统计特征1

Table 1	Descriptive statistical	characteristics for seve	en heavy metals in the stud	v area
Tubic 1	Descriptive statistical	Characteristics for Seve	en neavy metals in the stad	y area

-	1 1 1 1 1 1	1.00	1	-04			,	,	
重金属	最小值	最大值	平均值	标准差	变异系数	KS 检验	背景值	GB 15618-2018 II	NY/T 391-2013
里並馮	/mg•kg ⁻¹	/mg·kg ⁻¹	/mg·kg ⁻¹	/mg·kg ⁻¹	又开尔奴	KS 4M 3M	/mg·kg ⁻¹	$(pH > 7.5)/mg \cdot kg^{-1}$	$(pH > 7.5)/mg \cdot kg^{-1}$
Pb	16. 82	53. 21	34. 78	6. 98	0. 20	0. 889	20. 6	170	50
Ni	28. 794	72. 673	52. 376	9. 191	0.18	0.756	36. 6	190	_
Zn	24. 914	123. 380	83.692	20. 483	0.24	0	58. 8	300	_
Mn	435. 215	791. 310	641.114	65. 920	0.10	0.888	524	_	_
Cu	19. 605	74. 759	38. 130	10.895	0.29	0.013	22. 1	100	60
Cr	40. 592	125. 219	87. 257	17. 151	0.20	0. 944	60.6	250	120
Cd	0.081	0. 169	0. 149	0.014	0.09	0	0.11	0. 6	0. 4

1) GB 15618-2018 II:《土壤环境质量 农用地土壤污染风险管控标准》土壤污染风险筛选值; NY/T 391-2013;绿色食品产地环境质量标准

为进一步评价研究区土壤环境生态风险,根据 Hakanson [23] 制定的标准化重金属毒性响应系数,并 参考李春芳等 [26] 的研究: Pb(5)、Cd(30)、Cu(5)、 Zn(1)、Ni(5)、Cr(2)和 Mn(1),以宁夏土壤重金 属环境背景值为评价标准计算 E_r 和 RI 值 [24~26]. 结果表明 Pb、Ni、Zn、Mn、Cu 和 Cr 的 E_r 均小于 30,为轻微的生态风险等级水平,而 98. 32% 样点 出现 Cd 的 E_r 大于 30 且小于 60,为中等的生态风险等级水平。13. 45% 样点的 RI 小于 60,表现为轻微的生态风险,86. 55% 样点大于 60 而小于 120,表现为中等生态风险,表明研究区枸杞地土壤重金

属生态安全急需引起重视.

2.3 中宁枸杞地土壤重金属来源解析

环境学领域中常将多元统计分析中的聚类分析与因子分析相结合研究土壤重金属来源 $^{[17]}$.本研究中先将去除异常值之后的数据进行标准化,采用层次聚类法对各元素进行聚类分析,并绘制出 7 种元素的树状图(图 2). 聚类分析结果将研究区 7 种土壤重金属归为三类,其中 Ni、Cr、Mn、Pb 是 I类,Cu 和 Zn 是 \mathbb{I} 类,Cd 是 \mathbb{I} 类,I类可以分为 3个小类,Ni 和 Cr 是 \mathbb{I} 1类,Mn 和 Pb 分别是 \mathbb{I} 2类和 \mathbb{I} 3类.

表 2	土壤重金属污染指数和生态危险指数

Table 2. Percentages of sites at different pollution levels and potential ecological	ricks for seven heavy metals

			不同运动和日	月样点比例/%		11. 1. 17.11/	7	日本大豆吃菜	加兴上山庙	1 /0/
元素	污染指数	*	小 門 / 分 采 级 力	1件从比例/%		生态危险	1	同生态风险等	"级件点几例]/%
儿尔	17米油奴	无污染	轻度	中度	重度	指数	轻微	中等	强	很强
Pb	P_{i}	1.68	80.67	17.65	0	$E_{ m r}$	100	0	0	0
Ni	P_{i}	1.68	98.32	0	0	$E_{_{ m r}}$	100	0	0	0
Zn	\boldsymbol{P}_i	16.81	82.35	0.84	0	$E_{ m r}$	100	0	0	0
Mn	\boldsymbol{P}_i	4.20	95.80	0	0	$oldsymbol{E}_{\mathrm{r}}$	100	0	0	0
Cu	\boldsymbol{P}_i	0.84	72.27	25.21	1.68	$oldsymbol{E}_{\mathrm{r}}$	100	0	0	0
Cr	\boldsymbol{P}_i	6.72	90.76	2.52	0	$E_{ m r}$	100	0	0	0
Cd	\boldsymbol{P}_i	1.68	98.32	0	0	$E_{ m r}$	1.68	98.32	0	0
	$P_{ ext{ iny $ec s$}}$	1.68	81.51	16.81	0	RI	13.45	86.55	0	0

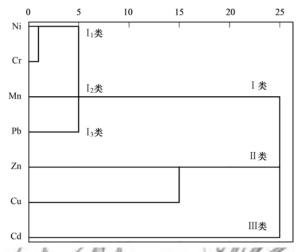


图 2 研究区 7 种重金属聚类分析树状图

Fig. 2 Dendrogram results of the hierarchical cluster analysis for seven heavy metals in the study area

KMO 检验和巴特利特球度检验(KMO 为 0.602, P < 0.05)说明变量之间相关性较强,适合做因子分析.基于主成分方法,采用 Kaiser 标准化的正交旋转法提取因子,采用最大方差法对因子载荷矩阵进行正交旋转(表 3),主成分分析提取了 4 个因子,共解释了 83.39%的方差,各元素的变量共同度较高,介于 0.768 ~ 0.992 之间,说明所提取的 4 个主成分因子能够较好地代表源数据所包涵的信息.

因子 1 解释了 24.099% 的总信息,是主要因子,组成第一因子的元素主要有 Ni 和 Cr,因子载荷为 0.789 和 0.887.一般认为 Ni 和 Cr 的含量与成土母岩的矿物成分相关,常作为污染程度最低的元素来判断其它元素的来源情况^[28,29].在江苏滨海^[28]、欧洲地中海地区^[30]和山东工业区^[31]土壤重金属 Ni 和 Cr 均主要受控于成土母质,同时王美娥等^[2]也发现宁夏中宁枸杞地重金属 Ni 和 Cr 具有很强的同源性,主要来源于成土母质即自然源.结合聚类分析结果,Ni、Cr、Mn 和 Pb 同为 I 类,说明研究区 Ni 和 Cr 的来源主要是成土母质,但同时也受到周边工业污染的影响.

因子2解释了23.494%的总信息,组成第二因

子的元素主要有 Pb 和 Mn, 因子载荷为 0.829 和 0.769. 随着无铅汽油的普遍使用, Pb 已不能作为交通污染源的标识元素, 而燃煤可以产生 Pb, 同时枸杞园周边 10 km 范围内有许多工业园区, 以南有瀛海工业区、宁新工业园区、中宁赛马水泥公司、宁夏新世纪冶炼有限公司等, 以北有中宁工业园、石空工业园区、天元锰业等, 以水泥生产和金属冶炼为主的工业带来大量 Pb 和 Mn 等污染元素的排放, 因此因子 2 确定为工业活动源.

因子 3 解释了 21. 198% 的总信息,组成第二因子的元素主要是 Cu 和 Zn,因子载荷为 0. 864 和 0. 774. Zn 是汽车轮胎生产过程中重要的添加剂,具有润滑改良、抗氧化和清洁的作用^[15]; Cu 具有高耐腐蚀性与高导热性,常用于制备车辆制动系统与汽车散热器.因此 Cu 和 Zn 可以作为交通污染源的标识元素^[19],研究区作为枸杞示范园区,近年来其观光旅游业发展造成该区车辆往来和停放数量明显增加,因子 3 确定为交通源.

因子4解释了14.598%的总信息,组成第四因子的元素主要是Cd. 枸杞园周边农业环绕,复合肥和农药的大量使用、禽畜粪便和农村生活垃圾随意堆放等原因导致枸杞园土壤Cd含量增加,由于磷肥复合肥中含有大量Cd,其一般可作为使用农药和化肥等农业活动的标识元素^[32],苏州水稻土^[33]和九龙江沉积物^[34]中重金属Cd均主要来源于农业活动,因此因子4确定为农业活动源.

2.4 APCS-MLR 模型分析

主成分分析方法只能定性地推测各个重金属的潜在主要污染源而不能直接用于源解析^[18]. APCS-MLR 模型不但可以定量确定每个变量对每个源的载荷,还可以定量确定源对其重金属的平均贡献量和在每个采样点的贡献量^[14]. 进行 APCS-MLR 模型分析时,先将因子分析的 4 个因子分数转换为绝对因子分数,再将各绝对因子分数与各重金属元素含量做多元线性回归,分别得到每个重金属元素与4 个绝对因子的多元线性回归方程, Pb、Ni、Zn、

Mn、Cu、Cr 和 Cd 回归方程的复相关系数 R² 分别为 0.768、0.771、0.851、0.801、0.849、0.806 和

0.992, 较高的 R^2 值说明多元线性回归方程的拟合效果较好.

表 3 土壤重金属含量因子分析的旋转成分矩阵1)

Table 3	Rotated	component	matrix fo	or data	on soil	heavy	metals in	the study	area
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元素 -		因	子		- 变量共同度
九系 —	1	2	3	4	文里六円反
Pb	0. 090	0. 829	-0.227	-0.148	0.768
Ni	0. 789	0. 371	-0.088	0.047	0.771
Zn	- 0. 347	0. 361	0.774	-0.034	0.851
Mn	0. 382	0.769	0. 252	-0.021	0.801
Cu	0.040	-0.290	0.864	0. 129	0.849
Cr	0.887	0.048	-0.098	-0.082	0.806
Cd	-0.036	-0.110	0.073	0. 986	0. 992
特征值	2. 370	1. 515	1. 169	0. 783	
解释总方差/%	24. 099	23. 494	21. 198	14. 598	
累积解释总方差/%	24. 099	47. 593	68. 492	83. 390	

1) 黑体字表示主成分分析提取的 4 个因子中最高的因子载荷

根据多元线性回归方程的回归系数分别计算得 出各重金属元素不同来源的贡献率(图3). 枸杞地 土壤重金属 Ni 和 Cr 的来源以自然源为主, 其对 Ni 和 Cr 贡献率分别为 55. 49% 和 64. 66%, 其次是工 业活动源对 Ni 的贡献率为 26. 35%, 交通源、农业 活动源和其它源对 Ni 的贡献率均小于 10%. Cr 除 自然源外,还有18.33%的贡献率来自其它源,工 业活动源、交通源和农业活动源对 Cr 贡献率较低. Pb 和 Mn 的来源以工业活动源为主, 其对 Pb 和 Mn 的贡献率分别为 46.93% 和 42.53%, 同时其它源 对 Pb 和 Mn 的贡献率分别为 26.36% 和 21.17%. Zn 和 Cu 的来源以交通源为主, 其对 Zn 和 Cu 的贡 献率分别为 43.51% 和 53.71%, 其次是工业活动 源的贡献率分别为 20.57% 和 18.56%. Cd 的来源 以农业活动源为主, 其贡献率为76.79%, 其它几 种来源的贡献率均较小.

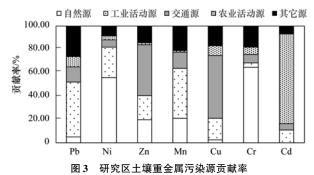


Fig. 3 Source contribution ratios of soil heavy metals from study area

2.5 中宁枸杞地土壤重金属空间分布特征

利用 SPSS 软件对研究区土壤重金属元素含量及其主要来源进行 KS 正态分布检验, Pb、Ni、Mn和 Cr 含量的显著性水平 Sig. 值大于 0.05, Ni、Cr 的自然源贡献率和 Cu 的交通源贡献率显著性水平 Sig. 值大于 0.05, 而其它重金属含量及来源贡献率

均小于 0.05, 对其进行对数数据转换后,显著性水平 Sig. 值均大于 0.05, 说明可以采用普通克里金插值法绘制土壤重金属元素含量及其主要来源的空间分布. 图 4 可以看出, Ni 和 Cr 的分布格局相似,其高值主要分布于中部偏西位置,低值主要分布于东部区域. Zn 和 Cu 含量的高值主要分布于研究区东西两侧,而中部区域含量较低. Pb 和 Mn 呈现斑块状分布格局,在区域中部和南部边缘有高值分布. Cd 元素含量的低值主要分布于东南区域和西侧边缘.

根据土壤重金属来源贡献率空间分布可以看出(图5),区域内相同来源的贡献率具有相似的空间分布特征. Ni 和 Cr 的自然源贡献率在中西部有明显的高值分布区. Zn 和 Cu 的交通源贡献率主要受到南北向道路影响,呈现出自东西侧向内递减的趋势. Pb 和 Mn 的工业源贡献率主要受到周边工业的影响,中部和南部有高值分布. Cd 的农业源贡献率的空间差异最小,主要由于研究区内农业耕作方式、土地利用等较一致.

3 讨论

宁夏枸杞作为我国地理标志保护产品,其品质和产量对于区域经济和产业发展具有重要作用.同时枸杞作为药食同源产品,其质量和安全性成为人们关注的焦点^[21].枸杞的药用价值与其果实中含有多种对人体健康有益的微量元素密切相关,但也可能存在重金属元素超标的问题^[35,36].与绿色食品产地环境质量标准相比,研究区土壤 Pb、Cu和Cr的超标率分别为 1.68%、5.04% 和 3.36%,其它重金属均没有超标,枸杞土壤重金属元素基本达到绿色食品环境质量标准,但 7 种重金属元素平均值均超过宁夏土壤背景值.可以看出目前中宁土壤

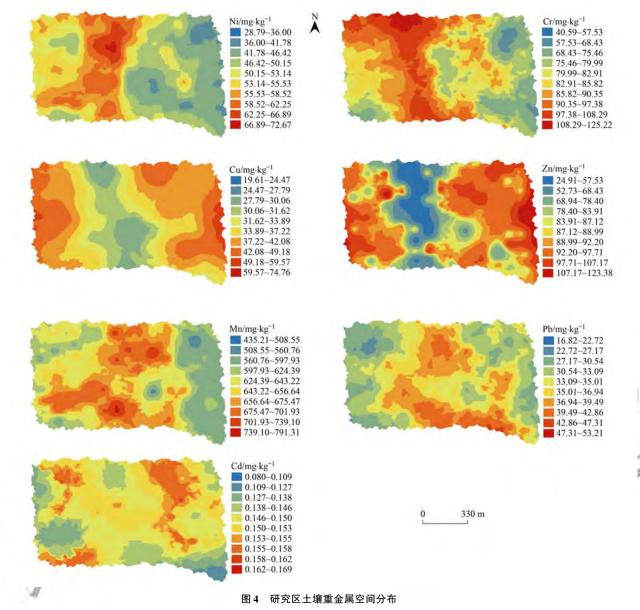


Fig. 4 Spatial distribution of soil heavy metals in the study area

可放心种植枸杞,然而研究区土壤亦明显受到工农业等活动的影响,存在重金属元素富集的趋势,因此有必要加强枸杞土壤外源污染物综合防控措施.

土壤重金属来源解析对于防治土壤污染、制定环境管理政策和维护区域生态环境安全有重要作用.不同区域不同重金属输入输出途径、经济社会发展和工农业分布等因素导致重金属来源复杂多样^[37].利用 PCA/APCS 方法得出研究区土壤重金属有 4 种主要来源,即自然源、工业活动源、交通源和农业活动源.其中 Ni 和 Cr 以自然源为主,贡献率分别为 55.49% 和 64.66%,Pb 和 Mn 以工业活动源为主,贡献率分别为 46.93%和 42.53%,Zn和 Cu 以交通源为主,贡献率分别为 43.51% 和 53.71%,Cd 以农业活动源为主,贡献率为 31.71%,Cd 以农业活动源为主,贡献率为 76.79%.陈秀端等^[17]和陈丹青等^[18]也利用 PCA/APCS 方法定量解析出西安城市居民区和广州市土

壤重金属污染源性质、各污染源平均贡献量及各样 点各污染源对每种重金属的贡献量. 说明利用 PCA/APCS 方法定量解析枸杞土壤重金属污染来源 是可行的.

结合空间插值图可以看出,Ni和Cr的自然源贡献率空间格局相似,在中西部有高值集中分布区域.该区域中西部边缘有地势低洼区域,重金属含量受到水流冲积的影响.陈丹青等[18]在广州市、吕建树等[28]在江苏海岸带、于元赫等[29]在黄河下游、都研究得出,Ni和Cr等主要受到成土母质影响的重金属元素在河流冲积处、湖积处含量高、易富集.Pb和Mn的工业活动源贡献率在中部和南部边缘较高,Zn和Cu的交通源贡献率显著在区域东西边缘最高,而中部区域较低.工业活动源贡献率受到污染源空间分布的影响,研究区南有瀛海工业区、宁新工业园区等,以北有中宁工业园、石空工

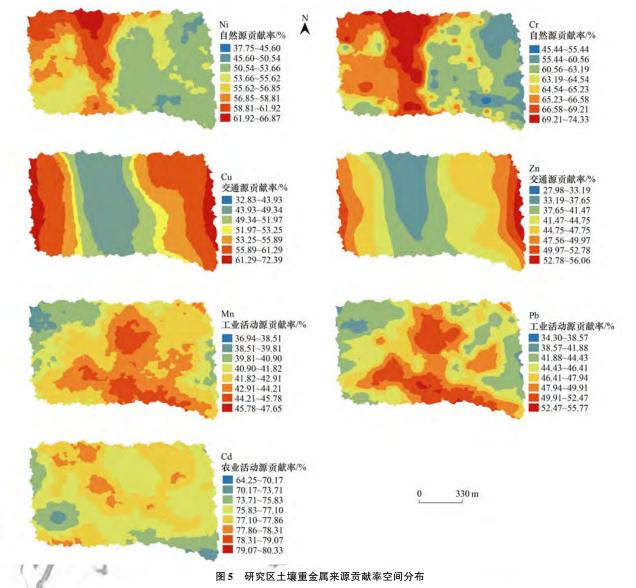


Fig. 5 Spatial distribution of source contribution for soil heavy metals in the study area

业园区和天元锰业,同时该区域主导风向为西北 风,导致来自工业源的重金属 Pb 和 Mn 向东南方向 扩散. 交通源贡献率的空间分布明显受到区域两侧 道路分布的影响, 研究区域东侧为中宁县城, 道路 密集, 车辆较多, 而西侧临近银西铁路中宁段, 因 此呈现出自东西两侧向中心的阶梯式递减的特征. Cd 的农业活动源贡献率高低值分布零散,没有明 显集中分布区域. 农业活动源贡献率空间分布较均 匀, 空间异质性不明显. 宋志廷等[38]的研究得出, 土壤重金属 Cd 的变异性主要受到化肥、农药等农 业投入的面源污染影响,局部存在点源污染. 农业 投入的空间无差别性导致 Cd 农业活动源贡献率在 空间分布上差异较小. 可以看出, 结合地统计分析 污染源空间分布特征的研究, 能进一步明确各类污 染源的空间分布状况、验证土壤污染来源, 这表明 APCS/MLR 与地统计相结合的方法可以很好地应用 于土壤重金属污染来源解析. 有助于解析土壤重金

属富集的行为机制和规律,从而有针对性地提出土壤环境治理的策略.

4 结论

- (1)枸杞地土壤重金属平均含量普遍高于宁夏土壤背景值,但低于农用地土壤污染风险筛选值和绿色食品环境质量标准.以宁夏土壤背景值为标准,P_综值表明81.51%样点的土壤重金属呈现轻度污染,16.81%样点呈现中度污染,1.68%未受重金属污染.RI值表明13.45%样点表现为轻微生态风险,86.55%样点表现为中等生态风险.
- (2)聚类分析和主成分分析结果表明,研究区土壤 Ni 和 Cr 来源以自然源为主,贡献率分别为55.49%和64.66%, Pb 和 Mn 来源以工业活动源为主,贡献率分别为46.93%和42.53%, Zn 和 Cu 来源以交通源为主,贡献率分别为43.51%和53.71%, Cd 来源以农业活动源为主,贡献率为

76.79%.

(3)Ni和 Cr 的自然源贡献率在西部区域较高,特别是在中西部有高值集中分布区域. Pb 和 Mn 的工业活动源贡献率在中部和南部边缘较高, Zn 和 Cu 的交通源贡献率明显在区域东西边缘较高,而中部区域较低, Cd 的农业活动源贡献率高低值分布零散,没有明显集中分布区域.

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