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重金属污染农田安全利用：进展与展望*

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摘 要: 我国耕地土壤污染面积广, 污染情况复杂, 农产品重金属超标问题已经关系到国计民生。常用的物理化学修复方法成本高, 不适用于大面积的中低污染农田。植物提取修复方法成本低, 环境友好, 但修复时间长, 推广困难。总的来讲, 基于重金属移除的诸技术在解决农田重金属污染方面还没有太大优势。相较而言, 农田安全利用在不移除或缓慢移除土壤重金属的条件下, 以生产安全农产品为目标, 具有更加坚实的现实意义和推广价值。种植低吸收农作物是安全利用的重要措施, 基因工程手段在低吸收农作物品种筛选中具有巨大的潜力, 但其可能带来的生态环境风险使得这些通过基因工程得到的低吸收作物的田间种植面临着巨大挑战。土壤添加剂可以改变土壤重金属形态, 降低重金属的生物有效性, 但会对土壤质量产生影响。微生物尤其是土著微生物的利用越发受到关注, 改变微生物的生存环境与基因工程手段能够强化微生物的钝化效果。施肥、水分管理、间作等农艺措施也能改变土壤重金属的形态, 抑制作物对重金属的吸收。未来以加强推广为目的, 多种技术手段的联合应用是重金属污染农田安全利用的重要发展方向, 其中以生物技术为核心的利用模式具有十分重要的意义。

关键词: 重金属污染农田; 安全利用; 农作物; 添加剂; 微生物; 农艺措施; 重金属钝化
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Safe utilization of farmland contaminated with heavy metals in China: Progress and outlook*

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Abstract: Farmland heavy metal pollution is now a serious problem in China. Food heavy metal contents in some agricultural regions exceed the national limits and threaten human health and the development of economy and society. Meanwhile, farmland resources are very limited in China. Therefore, farmland heavy metal pollution needs to be resolved urgently. Among available remediation tools, the physical or chemical ones are costly and are not suitable for the slightly / moderately

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contaminated farmland at a large scale. The phytoextraction method is cost-effective and environmentally friendly, but requires a long time. Overall, techniques aiming at heavy metal removal have limitations in solving heavy metal pollution in farmland. Safe utilization is to produce safe agricultural products, without removing the heavy metal content in soil purposefully. Safe utilization of heavy metal contaminated farmland is preferable for China at this stage. Cultivation of low-accumulation crops is an important option for the safe utilization scheme. A number of low-accumulation cultivars of grain crops and vegetables have been screened out in China. Genetic engineering has potential in breeding of low-metal-accumulation crops. Soil additives such as clay minerals, organic wastes and biochar can inhibit heavy metal uptake of crops by immobilization of heavy metals in soil, via ion-exchange, precipitation, etc. However, use of soil additives may impact soil qualities by changing soil structure, loss of nutrition and secondary pollution. Some microorganisms showing strongly resistant to heavy metals have already been used to inhibit the heavy metal uptake of crops. Genetically modified microbes possessing stronger immobilization ability should be paid more attention. Furthermore, agronomic strategies including fertilization, water management, and intercropping can transform the heavy metal forms in soil and influence the heavy metal uptake by crops. However, the crop yield and quality like nutrient content can also be influenced by the safe utilization measures. Efforts should be made to get a balance between low accumulation of heavy metals and crop yield and qualities. In the future, researches may focus on the integration of various remediation techniques for the large-scale field implementation.

Keywords: Heavy metal contamination; Farmland; Safe utilization; Crops; Soil amendments; Microorganism; Agronomic strategy; Heavy metal immobilization

我国耕地资源十分紧缺, 2016 年底耕地面积为 1.35 亿 hm^2(20.24 亿亩)[1], 人均占有量不及世界平均水平的 1/2, 且总体质量不高, 中低产田达到了 2/3[2]。此外, 由于建设占用、灾毁、生态退耕、农业结构调整等原因, 我国耕地面积保有量近年总体有所下降。与此同时, 土壤污染加剧了耕地资源的紧张。据 2014 年发布的《全国土壤污染调查公报》, 我国农田土壤受到了广泛的重金属污染, 其中轻微、轻度、中度和重度污染点位比例分别为 11.2%、2.3%、1.5%和 1.1%[3]。重金属污染不仅减少了可利用耕地面积, 而且降低了耕地质量。另有研究发现, 我国部分地区已经出现农产品重金属含量超标现象, 威胁到了人体健康[4-5]。由此可见, 我国重金属污染耕地土壤修复刻不容缓。

土壤重金属污染修复分为两种技术路线, 一是将重金属从土壤中提取出来, 减少其在土壤中的含量, 称为提取修复; 二是降低土壤重金属的生物有效性, 抑制其进入生物链, 称为固化修复。提取修复方法主要包括物理修复、化学修复与生物修复(主要为植物提取修复)[6]。

物理、化学修复方法(表 1)能够有效地去除土壤中的重金属, 且修复时间短, 但由于其对修复设备与技术的要求高, 修复成本高, 且会对土壤质量产生影响, 故其主要适用于污染严重、面积小的场地污染。

表 1　重金属污染土壤主要物理、化学修复方法的原理和不足

Table 1　Mechanisms and disadvantages of some main physical and chemical remediation methods of heavy metals polluted soil

修复方法 Remediation method		修复原理 Remediation mechanism	缺点 Disadvantage
物理修复 Physical remediation	客土、换土、深耕翻土 Soil dressing, deep tillage	用清洁土壤替换、混掺污染土壤或直接将污染土壤挖走[6] Polluted soil is replaced or mixed with clean soil or removed to other places[6]	所用清洁土壤要求土质好、肥力高、数量大, 工程量大, 费用高, 挖走的污染土壤可能产生二次污染[6-8] High soil quality and vast amount of clean soil and large work amount inducing high cost; secondary pollution by removed polluted soil[6-8]
化学或物理化学修复 Chemical/physical-chemical remediation	化学淋洗 Chemical leaching	利用淋洗剂通过解吸附、溶解等作用将土壤固相上的重金属转移到液相淋洗液中, 再对淋洗液进行处理[9] Heavy metals in soil solid phase are desorbed or dissolved by leaching agents, and treated safely later[9]	淋洗剂成本高, 可能造成二次污染, 造成土壤营养元素流失[10-11] Vast cost, secondary pollution, loss of soil nutrients[10-11]
	热解吸 Thermal desorption	对重金属污染土壤进行连续加热, 温度到达一定的临界温度时某些重金属(如 Hg、Se 和 As)挥发, 收集挥发产物集中处理[6] Soil is heated to volatilize Hg, Se and As, and volatile products are gathered and treated safely later	能耗高, 需要特定设备, 成本高, 影响土壤性质[12-13] Vast cost and consumption of energy, special equipment needed, attenuation of soil quality[12-13]
	电动修复 Electrokinetic remediation	向重金属污染土壤中插入电极, 施加直流电压导致重金属离子在电场作用下进行电迁移、电渗流、电泳等过程, 使其在电极附近富集进而从溶液中导出并进行适当的物理或化学处理[6] Direct current is applied by install electrodes in polluted soil to make heavy metals move and gather around the electrodes which are treated safely later[6]	引起土壤 pH 不平衡与水解反应, 产生二次污染[14], 设计复杂, 技术水平要求高, 目前主要处于实验室研究阶段[15] Soil pH unbalance and hydrolysis reaction, secondary pollution[14]; complicated design, at the stage of laboratory research[15]

植物提取利用超积累植物或累积能力较强的植物吸收富集污染土壤中的重金属并在地上部积累, 收割植物地上部分从而达到去除重金属的目的, 具有环境友好、修复成本低的特点。但其修复周期长(表 2)。用于修复的植物往往没有经济产出, 在没有政府补贴的情况下, 农民的参与度不高, 不利于推广应用。

表 2　部分植物提取修复重金属污染土壤所用时间
Table 2　Time required by phytoextraction of heavy metals polluted soil in some researches

重金属 Heavy metal	研究地 Research site	目标含量 Targeted content (mg·kg^{-1})	初始含量 Initial content (mg·kg^{-1})	最终含量 Final content (mg·kg^{-1})	修复年限 Remediation time (a)	修复植物 Remediation plant	参考文献 Reference
As	广西环江 Huanjiang, Guangxi	30^*	36.66±18.6	<30	2	蜈蚣草 *Pteris vittata* L.	[16]
As	North Carolina, US	40	82	40	8	蜈蚣草 *Pteris vittata* L.	[17]
Cd	辽宁沈阳 Shenyang, Liaoning	0.3^*	1.94~3.69	1.29~2.76	2	龙葵 *Solanum nigrum* L.	[18]
Cd	辽宁葫芦岛 Huludao, Liaoning	0.3^*	8.68	0.3	4.2	伴矿景天 *Sedum plumbizincicola* G. et Z. ex W.	[19]
Zn		200^*	476	200	3.9		
Cd	浙江 SLD Shuanglingdong, Zhejiang	1.0^*	16.9	1.0	21.2	伴矿景天 *Sedum plumbizincicola* G. et Z. ex W.	[19]
Zn		300^*	1 308	300	7.6		
Cd	浙江 ZJW Zhujiawu, Zhejiang	0.6^*	2.28	0.6	20.0	伴矿景天 *Sedum plumbizincicola* G. et Z. ex W.	[19]
Zn		250^*	1 201	250	4.4		

土壤环境质量标准(GB 15618—1995)。 indicates the Soil Environmental Quality Standard (GB 15618—1995).

综上, 农田土壤重金属污染修复是一个长期工程, 农田土壤将长期处于污染状态。考虑到我国耕地资源紧张与全面建设小康社会的要求, 在污染农田土壤上生产重金属含量不超标的安全农产品成为了适合我国当前实际情况的治理方法。相较于提取修复, 重金属污染农田安全利用通过降低土壤中重金属的生物有效性来减少重金属进入食物链的可能性, 从而保障农田的安全生产与人体的身体健康, 在我国现阶段具有十分重要的意义。进行重金属污染农田安全利用的措施主要包括低吸收作物种植、土壤添加剂与微生物调控以及农艺管理等。

1　低吸收作物种植

1.1　现有低吸收品种

对于重金属吸收富集能力的差异, 既存在于植物物种之间, 也存在于同一物种的不同品种之间, 即同时具有种间差异和种内差异。自低吸收品种的概念提出以来, 国内外已经开展了众多相关的试验筛选研究, 且大多数来自于亚洲尤其是中国(表 3)。已筛选的作物涵盖小麦(*Triticum astivum* L.)、水稻(*Oryza sativa* L.)、玉米(*Zea mays* L.)、大麦(*Hordeum vulgare* L.)等粮食作物, 白菜(*Brassica pekinensis* L.)、芹菜(*Apium graveliens* L.)、辣椒(*Capsicum annuum* L.)等蔬菜作物, 大豆(*Glycine max* L.)等油料作物以及烟草(*Nicotiana tabacum* L.), 针对的重金属包括 Cd、Pb、Zn、Cu、As、Cr、Hg 等。部分研究发现在污染农田种植低吸收品种使农产品重金属含量达到了国家安全标准[20]。

1.2　低吸收作物筛选

寻找新的低吸收作物品种一直是污染农田安全利用的主要发展方向。低吸收品种除了保障对重金属的低吸收外, 还应该具有如下特征:

1)当地适应性。由于农田土壤的类型、理化性质、污染程度、气候等存在差异, 同一作物品种在不同地区之间可能存在重金属吸收能力的差异。因此, 当在某地区种植低吸收作物时, 需要对已知的低吸收品种进行重新验证或重新筛选适合当地的低吸收品种。

2)多金属抗性。我国土壤多为重金属复合污染。若某 Pb-Cd 复合污染地区的小麦品种仅对 Pb 低吸收, 而 Cd 含量超标, 那此地出产的小麦仍不能进入食物链流通。此外, 我国部分地区土壤还存在着有机污染、干旱、盐碱、低温等胁迫, 寻找新的作物品种时还应考虑其对多种胁迫因素的耐受性。

3)产量不受太大影响。我国人口数量巨大, 耕地资源稀缺, 必须要保障农产品高产; 高产带来的高经济收益也有利于新的低吸收品种在农民中的推广应用。此外, 由于人们对生活质量的要求不断提高, 生产营养物质更加丰富的农产品也是寻找低吸收作物品种的目标之一。

当前, 我国低吸收作物品种的筛选主要集中在水稻、小麦等粮食作物上。除了粮食, 重点经济作物如烟草、油料、中草药等也是重金属进入人体的重要途径, 且我国拥有大面积种植这些农作物的产

区，因此对油料、中草药、棉麻等作物进行低吸收 品种的筛选也十分必要。

表 3　我国筛选出的部分用于重金属污染土壤修复的重金属低吸收作物及品种

Table 3　Low-heavy metal-accumulating crops and cultivars for remediation of heavy metals polluted soils in China

农作物 Crop	主要品种 Main cultivar	重金属 Heavy metal	参考文献 Reference
小麦 *Triticum aestivum* L.	尧麦 16、洛麦 9909 Yaomai 16, Luomai 9909	Cd	[21]
	洛麦 23 Luomai 23	Cd	[22]
	松蕊麦(四号)、云麦 34、石家庄 54 Songruimai (No.4), Yunmai 34, Shijiazhuang 54	Pb	[20]
	白条鱼、青春 28、半截芒 Baitiaoyu, Qingchun 28, Banjiemang	Cd	[20]
	红金包银、秃麦芒、日喀则 8 号 Hongjinbaoyin, Tumaimang, Rikaze No. 8	Zn	[20]
	济麦 22、中麦 175、良星 66 Jimai 22, Zhongmai 175, Liangxing 66	Pb, Cd	[23]
	临麦 2 号 Linmai No. 2	Cu, Cd	[24]
	花培 8 号、周麦 20 Huapei No. 8, Zhoumai 20	Pb	[25]
水稻 *Oryza sativa* L.	镇稻 5171 Zhendao 5171	Cd	[26]
	HGD70	Cu	[26]
	D62B, IRBN95-90, GRlu 17/ai TTP//lu 17_2	Cd	[27]
	辽星 1 号、沈农 15、沈农 315 Liaoxing No. 1, Shennong 15, Shennong 315	Cd	[28]
	铁 156、G227、TL213 Tie 156, G227, TL213	Cd	[29]
	秀水 128、秀水 09、秀水 134 Xiushui 128, Xiushui 09, Xiushui 134	As	[30]
玉米 *Zea mays* L.	成单 30 Chengdan 30	As	[31]
	川单 418 Chuandan 418	Cu	[31]
	寻单 7 号 Xundan No. 7	Pb	[32]
	新东单 16、东单 60、沈禾 118 Xindongdan 16, Dongdan 60, Shenhe 118	Cd	[33]
	雅玉 10、金玉 308、科玉 3 Yayu 10, Jinyu 308, Keyu 3	As	[34]
	川单 15、金玉 308、雅玉 10 Chuandan 15, Jinyu 308, Yayu 10	Hg	[34]
	雅玉 26、东单 60、科玉 3 Yayu 26, Dongdan 60, Keyu 3	Cu	[34]
	126115、2133、科玉 3 126115, 2133, Keyu 3	Zn	[34]
	川单 428、南 005、2133 Chuandan 428, Nan 005, 2133	Cd	[34]
	长玉 13、DT6327、南 005 Changyu 13, DT 6327, Nan 005	Cr	[34]
	雅玉 26、雅玉 10、川单 418 Yayu 26, Yayu 10, Chuandan 418	Pb	[34]
	云瑞 88、云瑞 220、云瑞 6 号 Yunduan 88, Yunduan 220, Yunduan No. 6	As, Pb, Cd	[35]
	先玉 335 Xianyu 335	Cd	[36]
蕹菜 *Ipomoea aquatica* F.	Sihainongwangliuyebaigu, Sihainongwangdabaigeng, Jianxiyuanzhongdaye	Cd	[37]
	Sihainongwangliuyebaigu, Sihainongwangdabaigeng,	Cr, Pb, Zn	[37]
	Sihainongwangdabaigeng	Cu	[37]
	Chunqingliuye, Zixinshuiweng	Cd	[38]
烟草 *Nicotiana tabacum* L.	Xiangyan 3, Yunyan 87, High potassium strain	Cr	[39]
	Yunyan 87	As, Pb, Cu	[39]
	Xiangyan 3	Hg	[39]
大麦 *Hordeum vulgare* L.	Beitalys, Shang 98-128	Cd	[40]
芹菜 *Apium graveliens* L.	Shuanggangkangbing	Cd, Pb	[41]
萝卜 *Raphanus sativus* L.	Baifentuan, Xiamen gF1, Xinbaiyuchun	Cd	[42]
大豆 *Glycine max* L.	Liaodou35	Cd	[43]
	垦丰 16 号、绥农 28 号、中黄 35 号 Kenfeng No.16, Suinong No.28, Zhonghuang No.35	Pb	[44]
小青菜 *Brassica chinensis* L.	Hualv 2, Huajun 2	Cd	[45]
辣椒 *Capsicum annuum* L.	Yeshengchaotianjiao, Heilameixiaojianjiao	Cd	[46]
菜薹 *Brassica parachinensis* L.	49-No.19, 49 caixin, Xianggang 49	Cd, Pb	[47]
食用苋菜 *Amaranthus mangostanus* L.	Quanhong, Huahongyuanye	Cd	[48]
白菜 *Brassica pekinensis* L.	28 tiansushengbaicai, Tiancuichunshuibai, Siyueman	Cd	[49]
甘薯 *Ipomoea batatas* L.	Nan 88 (No.10), Xiang 20 (No.12), Ji78-066 (No.15)	Cd	[50]

1.3　基因工程应用

基因工程改造是另一个获得具有优良性状的低吸收品种的途径。目前, 生物体内的部分与重金属抗性相关的基因已经被确认和验证(表 4)。这些基因表达产生植物螯合肽合成酶(phytochelatins, PCs)、转运蛋白、还原酶等, 通过螯合、转运、区隔化等作用降低重金属的毒性和调节对重金属的积累。通过基因工程技术改变这些基因在植物体内的表达量可以显著影响植物对重金属的抗性和吸收[51-54]。例如, 转入 *AKR4C9* 基因或 *MsALR* 提高了大麦对 Cd 和 As 的抗性[55]; 过表达 *TaGolS3* 基因提高了水稻对 Zn 的抗性[56]; 转入 *AtACR2* 基因提高了烟草对 As 的抗性并降低了地上部 As 的浓度[57]; 过表达 *OsHMA3* 基因或者敲除 *OsNramp5*、*OsHMA2* 或 *OsLCT1* 降低了水稻地上部或籽粒对 Cd 的积累量[58-61]。

通过基因工程技术可以使农作物对重金属的积累量显著降低, 但复杂的田间因素与转基因作物可能带来的生态环境风险以及公众对转基因作物安全性的争议, 使得这些通过基因工程得到的低吸收作物的田间种植面临着巨大挑战[62-64]。

值得注意的是, 有些作物品种地上部能够积累大量的重金属, 而可食用部分如籽粒中的含量不超过安全标准, 这样的农作物被称作 cropaccumulator[62]。种植 cropaccumulator 既可以减少土壤重金属的含量, 也能够保证农产品的产量与安全, 是一种很有前途的污染土壤的安全利用方式。通过基因工程技术将外源基因转入到作物中, 增强作物对重金属的抗性和积累能力被认为是一种获得 cropaccumulator 的方法[62]。Luo 等[65]鉴定出了影响水稻 Cd 积累量的数量性状基因位点(quantitative trait locus, QTL)*CAL1*。*CAL1* 能够调节叶片中 Cd 的积累, 而对 Fe、Zn、Cu 等其他营养元素和籽粒中的 Cd 无显著影响。这为 cropaccumulator 的寻找提供了有力的基础。

表 **4**　作物中部分与重金属抗性相关的基因(以 **Cd** 为例)

Table 4　Some heavy metal resistance genes (case of Cd) in crops

基因 Gene	来源 Resource	功能 Function	参考文献 Reference
OsPCS1	水稻 *Oryza sativa* L.	合成植物螯合肽[51-54] PCs synthesis[51-54]	[51]
TaPCS1	小麦 *Triticum aestivum* L.	合成植物螯合肽[51-54] PCs synthesis[51-54]	[66]
AtPCS1	拟南芥 *Arabidopsis thaliana* L.	合成植物螯合肽[51-54] PCs synthesis[51-54]	[67]
BjPCS1	印度芥菜 *Brassica juncea* L.	合成植物螯合肽[51-54] PCs synthesis[51-54]	[68]
AsPCS1	大蒜 *Allium sativum* L.	合成植物螯合肽[51-54] PCs synthesis[51-54]	[69]
OsNramp5	水稻 *Oryza sativa* L.	控制 Cd 由土壤向根部转运 Control Cd uptake from soil to root	[59,70]
OsHMA3	水稻 *Oryza sativa* L.	控制 Cd 由细胞质向液泡转运 Control Cd translocation from cytoplasm to vacuole	[71]
OsHMA2	水稻 *Oryza sativa* L.	控制 Cd 由地下部向地上部转运及向籽粒的转运 Control Cd translocation from root to shoot and grain	[72-73]
OsLCT1	水稻 *Oryza sativa* L.	控制 Cd 向籽粒的转运 Control grain Cd uptake	[58]
AKR4C9	拟南芥 *Arabidopsis thaliana* L.	降低脂类过氧化物的毒性 Lipid peroxidation detoxification	[74]
MsALR	苜蓿 *Medicago sativa* L.		
YCF1	酿酒酵母 *Saccharomyces cerevisiae* M.	控制 Cd 向液泡中的转运 Control Cd translocation from cytoplasm to vacuole	[75]
Cdae-1	Sponge-associated bacterial metagenome	控制 Cd 的胞内积累 Control cytoplasmic Cd accumulation	[76]
SpPCS	裂殖酵母 *Schizosaccharomyces pombe* L.	合成 PCs PCs synthesis	[77]

2　土壤添加剂应用

土壤添加剂可以改变重金属在土壤中的赋存形态与生物有效性, 进而影响植物对重金属的吸收。因此, 利用土壤添加剂钝化土壤重金属是污染农田安全利用的一种重要措施。常被用于土壤重金属钝化修复的添加剂如下。

2.1　石灰性材料

大量研究表明重金属在土壤中的生物有效性与土壤 pH 呈负相关关系[78-81], 提高土壤 pH 可以钝化土壤重金属。石灰的主要成分为 $CaCO_3$, 能够显著提高土壤 pH, 常被用来改善酸化土壤[82]。多种含有石灰的材料, 如煅烧的贝壳[83]、钢炉渣[84]、磷灰石[85-87]、海泡石[88]等已被用来进行土壤重金属钝化修复。但土壤 pH 升高也会导致营养元素的有效性和土壤酶活性的降低[89-91], 降低农作物生物量[88]。

2.2 磷酸盐材料

磷酸盐能够与重金属形成稳定的磷酸盐沉淀，降低重金属在土壤中的迁移性[92-93]。Chen 等[89]发现磷酸盐能够将土壤中的 Pb、Zn、Cd 由可交换态、有机结合态转化为磷氯铅矿等残渣态，进而降低油菜(*Brassica campestris* L.)中这些重金属的含量。

2.3 有机废弃物

农业有机废物如畜禽粪便、农作物秸秆等常常作为有机肥为植物提供营养元素[94]。研究表明向土壤中施加粪肥、作物秸秆等能够降低重金属的生物有效性，减少植物对重金属的吸收[95-98]。这主要有如下几个原因：首先，施加粪肥、秸秆等能使土壤有机质含量增加，这些有机物通过络合作用吸附重金属，降低重金属的生物有效性[99-100]；其次，施加有机废弃物能够提高土壤 pH[95,101]，进而降低重金属的生物有效性；此外，施加有机废弃物能够提高土壤有效磷的含量[97]，而磷能够有效钝化土壤重金属[92]。

2.4 生物炭

生物炭具有非常高的比表面积，可高达 65.85 $m^2 \cdot g^{-1}$[102]，且带有负电荷，有利于其吸附重金属离子[103-105]。此外，生物炭表面含有大量的—OH、—COOH 等官能团，可与重金属形成稳定的络合物[106]。生物炭多呈碱性[107-109]，施用生物炭能够提高土壤 pH，强化对重金属离子的钝化[110-111]。

2.5 黏土矿物

膨润土、蒙脱石、伊利石、高岭石等黏土矿物具有较高的阳离子交换量，能够通过离子交换作用将土壤重金属离子吸附于其表面上，进而降低重金属的迁移性[112-113]。重金属还能与矿物晶体通过共价键形成专性吸附，很难再从黏土矿物上解吸下来[113-114]。Sun 等[115]、徐奕等[116]在 Pb、Cd 污染土壤中施入膨润土后，土壤中 Pb、Cd 主要由可交换态转化为了残渣态，且水稻体内的 Pb、Cd 浓度显著降低。

土壤添加剂在土壤重金属污染修复中也存在着一些问题。(1)过量施用添加剂会改变土壤性质。长期施用石灰等碱性物质会破坏土壤团粒结构，造成土壤板结和养分流失，也会对土壤微生物的群落结构产生影响[117]。(2)添加剂可能会引入新的污染物质。有机废弃物可能会携带大量重金属、有机污染物、病原菌等有害物质，如果不经处理直接施用会对土壤造成二次污染，并降低土壤质量[118]。(3)添加剂对重金属的钝化效果会随土壤环境的改变而改变。有机添加剂容易被降解，被其固定的重金属会重新释放出来，因此，需要对其进行长期的环境风险评估[117]。(4)添加剂可能会降低农作物的产量。Sun 等[88]研究发现在碱性土壤中施加 0.5%~5%的海泡石会降低菠菜(*Spinacia oleracea* L.)地上部的生物量。

3 微生物调控

微生物能够改变土壤中重金属的赋存形态，影响其生物有效性，也能调节植物的养分供应，促进植物的生长发育。由于经济性与环境友好性，微生物越来越多地被应用于土壤重金属污染的钝化修复中。当前，多种具有重金属抗性或积累能力的微生物已经被筛选出来(表 5)，这些微生物能显著降低小

表 5 部分能够抑制农作物吸收重金属的微生物
Table 5 Some microbes which inhibit heavy metal uptake of crops

微生物 Microbe	域 Domain	农作物 Crop	重金属 Heavy metal	参考文献 Reference
Funneliformis geosporum C.	丛生菌根真菌	小麦 *Triticum aestivum* L.	Zn	[119]
Glomus intraradices S. et S. BEG 141	Arbuscular mycorrhizal fungi (AMF)	玉米 *Zea mays* L.	Cd	[120]
毛头鬼伞 *Coprinus comatus* M.	大型真菌 Marofungi (mushroom)	生菜 *Lactuca sativa* L.	Cu	[121]
固氮菌 *Azotobacter* spp.	细菌 Bacteria	小麦 *Triticum astivum* L.	Cd, Cr	[122]
巨大芽孢杆菌 H3 *Bacillus megaterium* B. H3	细菌 Bacteria	水稻 *Oryza sativa* L.	Cd	[123]
Neorhizobium huautlense W. T1-17	细菌 Bacteria	水稻 *Oryza sativa* L.	Cd	[123]
Alishewanella sp. WH16-1	细菌 Bacteria	水稻 *Oryza sativa* L.	Pb	[124]
Neorhizobium huautlense W. T1-17	细菌 Bacteria	白菜、萝卜 *Brassica pekinensis* L., *Raphanus sativus* L.	Cd, Pb	[125]
真氧产碱杆菌 Q2-8 *Ralstonia eutropha* M. et C. Q2-8	细菌 Bacteria	白菜 *Brassica pekinensis* L.	As	[126]
Rhizobium tropici M. Q2-13	细菌 Bacteria	白菜 *Brassica pekinensis* L.	As	[126]
Exiguobacterium aurantiacum C. Q3-11	细菌 Bacteria	白菜 *Brassica pekinensis* L.	As	[126]

麦、水稻、白菜、萝卜(*Raphanus sativus* L.)等农作物中 Cd、Pb、Cu、As、Cr 等重金属的含量。

3.1 微生物调控机理

微生物抑制植物吸收重金属的机制已经有大量研究，主要包括降低土壤重金属的有效性与影响植物吸收两个方面。

1)降低土壤重金属生物有效性。微生物可以通过分泌胞外聚合物(extracellular polymeric substances, EPS)来钝化重金属。EPS 富含羟基、羧基、氨基等官能团[127-128]，可通过静电吸附、络合等作用与重金属键合并钝化重金属。Li 等[129]发现白腐真菌(*Phanerochaete chrysosporium* B.)分泌的 EPS 对低浓度 Pb 的钝化起着十分重要的作用。Joshi 等[122]发现固氮菌(*Azotobacter* spp.)可以通过分泌 EPS 来钝化土壤中的 Cd、Cr 离子，进而降低小麦体内 Cd、Cr 的含量。

微生物可以将重金属矿化进而钝化重金属。Li 等[130]发现 *Sporosarcina pasteurii* M.、*Terrabacter tumescensi* L.等细菌能够产生脲酶将尿素水解，提高土壤 pH，使土壤溶液中的 Cd、Cu、Pb、Ni 等重金属在其表面沉淀形成碳酸盐结晶。Qian 等[131]发现，*Penicillium chrysogenum* T. CS1 可以将土壤中的 Pb、Cr 主要转化为方解石、钒钙、碳酸钙、氧化铬等碳酸盐矿物。除了碳酸盐矿物，微生物还能将重金属转化为磷氯铅矿、水白铅矿等[132-133]。

微生物可以通过影响土壤中有机质的转化来钝化重金属。微生物在有机质降解及腐殖质形成过程中起着重要的作用[134]。腐殖质富含羟基、羧基、氨基等官能团[135-136]，这些官能团能够与重金属形成稳定的络合物，进而钝化重金属[137]。Zhang 等[138]发现，在堆肥过程中加入白腐真菌(*Phanerochaete chrysosporium* B.)能够显著提高腐殖质的含量，降低 Zn、Pb、Cu 和 Ni 的生物有效性，且重金属的残渣态或氧化物结合态的含量与腐殖质或其某些成分(如胡敏酸)的含量具有良好的相关性。

部分微生物对重金属具有很强的积累能力[139-140]，可以将土壤中的重金属大量吸收到体内，进而减少可被植物吸收的重金属含量。Wu 等[121]通过盆栽试验发现，种植蘑菇(*Coprinus comatus* M.)显著降低了生菜(*Lactuca sativa* L.)体内 Cu 的积累量与土壤中 HOAc 提取态的含量，且土壤中可交换态 Cu 的含量变化与蘑菇体内 Cu 的积累量的变化趋势一致，这说明土壤中有效态的 Cu 主要被 *C. comatus* 吸收从而减少了生菜对 Cu 的吸收。

2)影响植物对重金属的耐性和吸收。重金属会引起植物体内活性氧(ROS)的过量产生，进而对植物产生毒害作用。通过提高体内的抗氧化酶如 SOD、POD 和 CAT 含量来清除 ROS 是植物应对重金属毒害的一种重要机制[141]。微生物可以影响植物体内抗氧化酶含量进而减轻重金属对作物的毒害作用。Devi 等[142]发现，向土壤中施加真菌 *Trichoderma* sp. (WT2)显著提高了向日葵(*Helianthus annus* L.)体内 SOD、POD 和 CAT 的含量，增强了向日葵对 Pb 的耐受性。

微生物可以增强植物对营养元素的吸收，提高植物的生物量，对体内的重金属起到稀释作用(growth dilution effects)，进而降低植物体内的重金属含量。Wu 等[143]发现接种丛枝菌根真菌(arbuscular mycorrhizal fungi, AMF)(*Rhizophagus irregularis* S.)能够加强蒲公英(*Taraxacum platypecidum* D.)对 P 的吸收，显著提高其生物量，降低其体内 Cr 的浓度。AMF 外生菌丝具有很高的表面积与阳离子交换量，能够将重金属离子结合在其表面[144-145]，在植物根系周围钝化大量重金属，减少植物对重金属的吸收。Nayuki 等[146]通过 X-ray fluorescence (XRF)成像技术发现，AMF 能够将 Cd 大量地固定在其外生菌丝的细胞壁和液泡中，且不会转运到宿主植物的根中。即使外生菌丝能够将 Cr、Zn 等转运到植物根系中，也会显著地抑制这些重金属由植物地下部向地上部的转移[146-147]。

3.2 钝化效果强化

强化微生物对重金属的钝化效果是今后的主要研究方向。添加剂可以影响微生物的活动，进而强化其对重金属的钝化效果。Wang 等[148]发现使用由畜粪制成的有机添加剂能够显著增加 AMF 对烟草根部的侵染率。添加硫酸盐和葡萄糖能够强化硫酸盐还原细菌(sulfate reducing bacteria)的活动，促进其将重金属转化为硫化物沉淀[149]。与单独添加微生物相比，微生物与生物炭、煤泥等钝化剂联合使用能显著降低 Cd、Pb 等重金属在土壤中的生物有效性以及在玉米、绿豆(*Vigna radiata* L.)、萝卜、生菜等农作物中的含量[120,125,149-152]。微生物的活动与群落结构容易受到诸多土壤性质的影响[153]，故也可以通过调节土壤的 pH[154]、C/N 比[155]、有机质含量与含水率等来控制微生物对重金属的钝化活动。此外，通过基因工程手段将与重金属抗性相关的外源基因转入微生物，可以强化微生物对重金属的钝化修复

效果。Elahian 等[156]将 *Mucor racemosus* B.的 *Cyb5R* 基因转入毕赤酵母(*Pichia pastoris* G.)后发现，毕赤酵母能够将 Ag^+转化成毒性更低的纳米银并将其大量吸附在细胞表面。Li 等[157]发现，转入来自豆梨(*Pyrus calleryana* D.)的 *PcPCS1* 基因能够增强大肠杆菌(*Escherichia coli* E.)对 Cd、Cu、Hg 离子的抗性和积累量。

3.3 土著微生物利用

在需要进行安全利用的地区土壤中寻找具有重金属钝化功能的土著微生物具有重要意义。严重污染地区(如矿区)土壤的重金属含量非常高，能够在这些土壤中存活下来的微生物往往对重金属具有很强的抗性，这种天然筛选使人们更容易寻找到能够应用于重金属污染土壤修复的目标微生物[158-163]。但由于土壤性质存在较大的差异以及与土著微生物的竞争作用，由污染严重的矿区分离筛选出来的微生物的活动或功能在污染程度较低的农田土壤中可能会发生改变[164-165]，进而影响这些微生物的修复效果。土著微生物能够更好地适应待修复农田的土壤环境，进而产生更好的修复效果。Oller 等[166]从当地农田土壤中筛选出的杆菌 *Enterobacter* sp.、假单胞菌 *Pseudomonas* sp.和红球菌 *Rhodococcus* sp.均对 As 具有很强的抗性和积累能力，且能够促进大豆的生长，具有很大的潜力应用于当地污染土壤的粮食安全生产。Abu-Elsaoud 等[119]在当地农田土壤中筛选出的 AMF(*Funneliformis geosporum* N. et G.)能够增强小麦对 Zn 的抗性并抑制 Zn 向地上部的转运。此外，随着宏基因组等技术的发展，土壤中微生物的种质资源能够被更加充分地发掘，这将助力人们筛选出更多的能够应用于污染土壤修复的土著微生物。

4 农艺管理

农艺措施能改变土壤的通气、水分、养分等条件，除了能够提高农作物产量，增加收益，防治病虫害，改善土壤外，还能影响土壤中重金属的生物有效性和植物对重金属的抗性。因此，农艺措施也是污染农田土壤安全利用的一种重要调控措施。当前，人们主要通过施肥、水分管理、间套作等农艺措施来控制农作物对重金属的吸收。

4.1 施肥

肥料能够为农作物提供必需的营养，增强作物对重金属的抗性，提高生物量，对体内的重金属起到稀释作用。此外，肥料中的 P 能够与 As、Cr 等重金属竞争植物根系表面吸附位点，故施加磷肥能够抑制作物对重金属的吸收[142,167-170]。肥料还能通过改变土壤 pH 及络合、沉淀等作用降低重金属的迁移性与生物有效性，进而减弱植物对重金属的吸收[92,95,97,99-101]。

一些学者研究了叶面施肥对农作物吸收转运重金属的影响。叶面喷施锌肥能够降低白菜[49]、油菜[171]、黄瓜(*Cucumis sativus* L.)[172]、小麦[173]体内的 Cd 含量，叶面喷施 Si 肥能够减少水稻地上部和籽粒中 Pb 的含量，抑制 Pb 由地下部向地上部的转运[174]。这可能是因为通过叶面进入植物体内的 Zn 与 Cd 竞争植物细胞表面的吸附位点，抑制植物对 Cd 的吸收[175-176]；而 Si 可能将 Pb 等重金属固定在植物细胞壁上，进而抑制了 Pb 在植物体内的运输[177-178]。此外，叶面肥比土施肥具有更低的修复成本。在达到减少农作物重金属含量的相同效果时，叶面肥的用量比土施肥的用量至少减少 5 倍[171,179]。

此外，改变肥料的用量也能影响作物对重金属的吸收。Tang 等[49]发现白菜体内 Cd 含量与土壤 K、Zn 的含量呈负相关关系，故认为增施钾肥或锌肥能够抑制白菜对 Cd 的吸收。

4.2 水分管理

氧化还原条件会影响重金属在土壤中的价态和赋存形态，而这决定了重金属的毒性与迁移性[180-182]，故通过水分条件管理控制土壤的氧化还原条件对土壤重金属污染修复具有重要意义。Hu 等[183]研究了不同淹水条件对水稻吸收 Cd 和 As 的影响。结果发现，从不淹水到定期淹水再到始终淹水，水稻籽粒中 Cd 含量从 0.21 $mg\cdot kg^{-1}$ 减少到 0.02 $mg\cdot kg^{-1}$，然而 As 的浓度却从 0.14 $mg\cdot kg^{-1}$ 增长到 0.21 $mg\cdot kg^{-1}$。土壤中有效态 Cd 与 As 的含量也呈现出了相反的变化趋势。还需注意的是，减少两种重金属含量的水分管理模式下的水稻产量均较传统模式减少。因此，需要进一步采取特定的措施来同时控制水稻 Cd 和 As 的含量，同时保证水稻的产量。

4.3 间作

植物间作是利用不同种植物之间的互补作用达到提高产量，控制病虫害等目的[184-185]的种植模式。将农作物与超富集植物间作，可以在保证农产品安全的前提下，利用超富集植物持续地减少土壤中的重金属含量，这是污染农田安全利用的主要发展方向。Wang 等[186]将 Cd 超富集植物龙葵(*Solanum nigrum* L.)与 Cd 低吸收品种大葱(*Allium fistulosum* L.)进行间作，发现间作模式下，大葱的Cd含量没有

变化，符合国家食品安全标准，且大葱的产量没有降低；另一个有利的结果是，经过 90 d 的种植，龙葵去除了表层土壤(0~20 cm)中 7%的 Cd。其他研究也获得了较好的结果。谭建波等[187]发现与 Cd 超级累植物断续菊(*Sonchus asper* L.)间作能够显著减少玉米 Cd 的含量，显著提高断续菊 Cd 的浓度，此外，间作均提高了两种植物的生物量。Zhan 等[188]将断续菊与茄子(*Solanum melongena* L.)进行间作，也得到了相似的结果。但间作模式也存在着不理想的情况。Yang 等[189]发现，将瞿麦(*Dianthus superbus* L.)与白车轴草(*Trifolium repens* L.)进行间作能够显著降低瞿麦体内 Pb 含量，但也降低瞿麦的药用成分大黄素的含量，这主要是由于白车轴草与瞿麦的竞争作用减少了瞿麦对营养元素的吸收。Yang 等[190]发现香根草(*Vetiveria zizanioides* L.)与豆科植物间作对两种植物的 Cd 含量与生物量均无显著影响。汤福义等[191]发现与龙葵间作甚至会提高白菜幼苗 Cd 的积累量。可见，利用间作模式进行污染土壤的安全利用需要对农作物、间作植物、目标污染物进行综合考虑。

5　农业资源研究中心相关研究与展望

截止到目前，国内外均进行过污染土壤的修复实践。国外最具代表性的污染土地的管理方法当属美国的“超级基金”，它是为了实现污染场地的再生产利用由美国国会批准设立的管理法案，对污染场地和责任者的确定，修复资金的筹备与使用，修复工程的设计和实施，后期运营与监测等环节均进行了规范，已经被多个国家借鉴[192]。超级基金规定由责任者或污染者对污染场地进行修复，对找不到责任者或责任者没有修复能力的，由超级基金支付修复费用[192]。但污染场地修复的经费投入巨大，责任者往往难以承担，而“超级基金”也面临着经费缺乏的问题[192]。根据“超级基金”的经验，我国污染农田面积大，且污染者难以确定，无论污染企业还是地方政府，在没有类似“超级基金”的经费支持下，均难以进行完整的污染农田土壤的修复进而实现再生产利用。而国内农田土壤的修复实践目前多以示范为主[6]，鲜有大面积的推广应用。

污染农田管控即禁止在污染农田上种植粮食也是一种保障食品安全的管理方法。但对粮食安全的坚定的要求决定了我国不能进行大面积的污染农田管控。此外，我国农田的所有与使用制度难以保障管控措施的实施，在被管控的农田上仍可能继续进行粮食种植，对我国的食品安全产生潜在的威胁。维持农田生产并保障粮食与食品安全是我国当前的形势所需。因此，在污染农田上生产出安全的农产品即污染农田的安全利用具有非常重大的意义。目前，污染农田的安全利用已经被学界和政府普遍接受。

将多种技术手段进行整合，实现优势互补，是当前污染农田安全利用的重要发展趋势。就目前来看，少数的技术集成取得了显著进展，但可重复性与经济成本还远不能满足推广需求。农民作为实施主体对技术手段的接受程度也是影响安全利用推广的重要因素，他们更容易接受操作简单、接近农艺措施的技术，比如种子与肥料。这要求这些技术手段具有更佳的抑制重金属吸收转运的效果。生物技术在改变植物以及土壤微生物等对重金属的吸收转运能力方面具有极大的潜力。故发展以生物技术为核心的污染农田安全利用模式是我国重要的研究方向。

中国科学院遗传与发育生物学研究所农业资源研究中心作为中国科学院主要农业类研究所之一，在农业环境包括农田重金属污染治理方面做了多年的布局和投入。在重金属污染农田安全利用研究方面，相关研究组按照机理与技术并重的发展理念，提出了以生物技术为核心的技术模式，并在中国科学院“百人计划”和河北省杰出青年基金等项目的资助下，系统开展了华北微生物 Cd 固定剂和 Cd 低吸收小麦品种的筛选，并且在生物快速提取方面取得了进展。过去 2 年中，研究组在微生物菌剂和修复方法方面提交并授权了多项核心专利(表 6)，正在成为我国污染农田安全利用技术发展的新力量，并提出了生物技术为核心的技术模式(图 1)，可尽可能地

表 6　部分农业资源研究中心微生物菌剂与土壤修复方法的专利

Table 6　Some patens of inoculants and soil remediation methods of Center for Agricultural Resources Research

序号 Number	名称 Name	申请号 Application number
1	双层植物培养装置 A double-layer device for plant cultivation	201720719277.9
2	一株镉钝化真菌 A cadmium immobilization fungi strain	201711100179.8
3	一株镉吸附真菌 A cadmium adsorption fungi strain	201710669924.4
4	微生物分离装置 A device to isolate microbes	201720722170.x

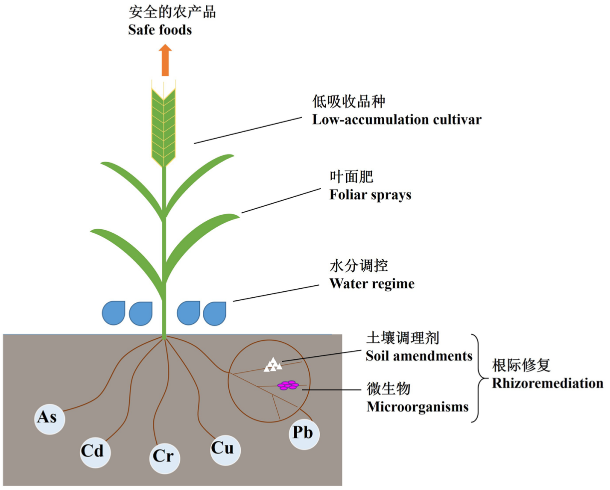

图 1 当前重金属污染农田安全利用的技术模式
Fig. 1 Technical patterns for safe utilization of heavy metal-contaminated farmland

减少化学固定剂如石灰和磷肥的使用，提高重金属污染农田利用的安全性。以治理理念的进步和技术积累为基础，农业资源研究中心重金属污染修复团队已经获得了与国内相关科研单位(包括南京土壤研究所、山东师范大学、河北地质职工大学等)和相关环保企业合作，在雄安和承德等地开展了修复示范工作。

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