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农田镉砷污染防控与作物安全种植技术探讨

周莉^{1,2,3}, 郑向群^{1,2}, 丁永祯^{1,2*}, 黄宏坤⁴, 郑顺安⁴, 师荣光^{1,2}, 李晓华⁴,
冯人伟^{1,2}, 王瑞刚^{1,2}

(1.农业部环境保护科研监测所, 天津 300191; 2.农业部产地环境污染防控重点实验室, 天津 300191; 3.沈阳农业大学土地与环境学院, 沈阳 110866; 4.农业部农业生态与资源保护总站, 北京 100125)

摘要: 文章综述了农田镉、砷污染现状、环境风险及其来源, 阻控作物镉、砷吸收的关键技术环节, 包括农业投入品控制、水分管理、土壤钝化调控、叶面调理、低吸收作物品种选择与替代种植、秸秆移除削减等。结合“土十条”, 提出镉、砷污染农田作物安全种植的几点思考: 一是建立基于耕地-农产品污染等级的安全种植技术体系; 二是采取集成农艺措施进行综合防控, 重点提出作物安全种植 VIRL (Variety-Input and Irrigation-Root zone and Removal of straw-Leaf blade) 技术模式。该模式将源头预防(农业投入)、过程阻控(作物本身镉、砷吸收特性, 影响作物地下部与地上部镉、砷吸收的各个环节)、末端治理(秸秆移除修复)高度统一起来, 然后根据耕地-农产品污染等级, 采取或紧或松的关键(联合)技术调控, 实现镉、砷污染农田的安全种植; 三是对镉、砷复合污染农田同步防控问题进行了探讨和展望。

关键词: 农田; 镉; 砷; 污染防治; 作物安全种植; VIP+n 技术模式; VIRL 技术模式

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Probes of prevention and control of farmland pollution by cadmium & arsenic and crop production safety

ZHOU Li^{1,2,3}, ZHENG Xiang-qun^{1,2}, DING Yong-zhen^{1,2*}, HUANG Hong-kun⁴, ZHENG Shun-an⁴, SHI Rong-guang^{1,2}, LI Xiao-hua⁴,
FENG Ren-wei^{1,2}, WANG Rui-gang^{1,2}

(1. Agro-Environmental Protection Institute, Ministry of Agriculture, Tianjin 300191, China; 2. Key Laboratory of Agro-Environmental Pollution Control and Prevention, Ministry of Agriculture, Tianjin 300191, China; 3. College of Land and Environment, Shenyang Agricultural University, Shenyang 110866, China; 4. Rural Energy & Environment Agency, Ministry of Agriculture, Beijing 100125, China)

Abstract: Farmland pollution by cadmium and arsenic, at present, is one of the major environmental problems confronting agricultural production. In this paper, the situation of farmland pollution by cadmium and arsenic and its risks to health are reviewed and the key technologies to obstruct and control cadmium and arsenic from being absorbed by crops are observed, such as agricultural input control, water management, soil passivant regulation, leaf surface conditioning, selection and substitute planting of low absorption crop varieties, and removal of straws. Combining the Soil Pollution Prevention Action Plan, the following ideas are proposed in this paper regarding the production safety on cadmium- and arsenic- polluted farmland: (1) determine an appropriate technology for safe production according to the farmland pollution index and (2) control and prevent pollution in comprehensive ways using integrated agronomic measures. In this paper, the control and prevention of farmland pollution by cadmium and arsenic is explained, and regarding crop production safety, a technical mode, VIRL (Variety-Input and Irrigation-Root zone and Removal of Straw-Leaf blade), is presented. This mode highly integrates source control (agricultural inputs), process control (crops' native characteristics of cadmium and arsenic absorption, various elements in both underground and

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作者简介: 周莉(1980—), 女, 湖北麻城人, 副研究员, 从事农业环境学研究。E-mail: zhouli@aeppi.org.cn

* 通信作者: 丁永祯 E-mail: dingyongzhen@caas.cn。

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aboveground parts affecting cadmium and arsenic absorption), and terminal control of farmland. Then, a key (joint) technical regulation, strict or loose, is carried out based on the farmland pollution level, thus securing safe production on cadmium- and arsenic- polluted farmland.

Keywords: farmland; cadmium; arsenic; pollution prevention and control; crops' production safety; VIP+n technical mode; VIRT technical mode

农田土壤重金属污染日益严重,特别是镉(Cd)和砷(As),全国点位超标率分别为7.0%和2.7%^[1],同时被国际癌症研究机构定为I类致癌物^[2]。鉴于二者农田污染的普遍性及对人体危害的突出性,本文围绕镉、砷,就其农田污染现状、污染防治以及污染农田作物安全种植技术展开综述和探讨,以期为我国农田镉、砷污染防治提供资料支持和参考。

1 农田镉、砷污染现状

1.1 我国农田镉、砷污染及其风险

我国农田镉、砷污染问题突出。沈阳张士灌区土壤镉超标严重,高达 $4.12 \text{ mg} \cdot \text{kg}^{-1}$ ^[3],北京农田砷超标率达1.8%^[4]。白银郊区农田土壤镉、砷污染严重,平均含量分别高达 $127.3 \text{ mg} \cdot \text{kg}^{-1}$ 和 $423.5 \text{ mg} \cdot \text{kg}^{-1}$ ^[5]。云南沘江流域农田土壤镉、砷超标率分别为100%和16.67%^[6]。湖北大冶农田土壤镉平均值高达 $1.41 \text{ mg} \cdot \text{kg}^{-1}$ ^[7]。湖南采矿区、冶炼区周边水稻土镉、砷污染严重且潜在风险高^[8]。珠三角350个农田土壤代表样品,镉超标率为18.28%^[9]。各地区镉、砷污染呈大面积、整体性污染态势,给农产品安全造成严重的威胁。

农田镉、砷通过作物吸收与转移,直接危害到农产品质量和人体健康。北京蔬菜砷对部分人群构成一定的健康风险^[10]。湖南稻米镉、砷是影响人体健康的主要因子^[11-12],湘江流域某县稻米镉超标60%,其中11%超过国标5倍^[13]。广东省蔬菜镉、砷超标率分别为21.2%和17.8%,其中韶关地区分别为58.9%和40%^[14]。针对华东、东北、华中、西南、华南和华北县级以上市场170份大米随机样品分析,发现大米镉超标率为10%^[15],污染农产品已成为国人镉、砷暴露的主要途径之一。

1.2 农田镉、砷污染主要来源

农田镉、砷来源主要包括采矿冶炼等工业活动、污水灌溉、大气沉降、农业投入品等。Li等^[16]综述了我国22省72矿区的土壤重金属污染状况,发现砷、镉平均值比我国II级土壤环境质量标准分别高6.5、36.5倍。采矿冶炼活动释放的砷、镉通过风力、水力扩散造成区域大面积农田污染,典型的如湘江流域^[17]、

刁江流域^[18]、沘江流域^[6]。污水灌溉也造成严重污染,全国55个污灌区1378个土壤点位中,26.4%超标,主要为镉、砷和多环芳烃^[1]。大气镉、砷主要源于化石燃料燃烧、金属冶炼以及交通废气排放等,大气镉、砷污染范围广泛^[19]。我国镉大气沉降农田年均输入量为 $4 \text{ g} \cdot \text{hm}^{-2}$ ^[20],远超欧洲平均输入量($0.35 \text{ g} \cdot \text{hm}^{-2}$)^[21]。我国耕地总砷的43%~85%来源于大气沉降^[20]。肥料与农药也是砷的重要来源,长期使用含砷农药、杀虫剂、除草剂的农田,残留砷达到 $2 \text{ g} \cdot \text{kg}^{-1}$ ^[22],有机肥、磷肥、污泥和畜禽粪便亦是造成耕地镉、砷污染的重要因素^[23-24]。

2 农田镉、砷污染防治

我国农田镉、砷污染主要属于大面积的轻中度污染,限于人多地少的国情,必须走耕地安全利用途径,主要遵循源头预防、过程阻控和末端治理的全过程综合防控理念。

2.1 水源与农业投入品源头预防

保障水源清洁是农田安全种植的重要环节。被动污灌带来的镉、砷污染越来越严重,洞庭湖水系所属湘江、耒水、资水、汨罗江等支流,水和悬浮物中砷和镉含量高^[25],给流域农田带来大面积的污染^[14,26]。应加强工业、农业、水利等部门协作,建立农田污水准入制度,加强灌溉水源管理,建立污水处理设施,或通过前置池(塘)等措施实现镉、砷的沉淀,或根据农作物对镉、砷吸收能力特点,合理地安排作物类型,将污染降到最低。

含重金属农业投入品的使用是造成农田镉、砷累积的主要原因之一。磷肥、有机-无机复混肥料等不同肥料均可导致土壤重金属累积^[24,27]。闫湘等^[28]检测了4027份水溶肥,发现砷、镉超标率分别为3.50%和1.27%,微量元素水溶肥超标最为严重,而大量元素水溶肥料中的砷超标率最高(11.0%)。有机肥料成分和来源复杂,普遍存在镉、砷等重金属含量较高的问题^[24,29],应该加强肥料监管,从源头上预防。

2.2 水分管理减少作物镉、砷吸收

水分管理影响土壤中镉、砷活性,对作物吸收影

响显著。土壤淹水可通过降低氧化还原电位加强镉与 S^{2-} 的共沉淀、促进有机质、 $CaCO_3$ 等物质对镉的吸持,增加还原态铁、锰等阳离子,这些阳离子与镉形成竞争吸附,增加的 Mn^{2+} 还可通过 $OsNRAMP_5$ 转移子抑制水稻根系镉吸收^[30]。长期淹水下土壤交换态、碳酸盐结合态镉显著低于常规处理^[31]。水稻在淹水条件下根表形成的氧化铁膜,在达到一定厚度时也能阻碍水稻根系镉吸收。水作空心菜地上部和根系镉含量较旱作处理分别降低52.2%和49.3%^[32]。

水分对砷的影响与镉几乎完全相反。土壤砷主要以无机态的 $As(III)$ 和 $As(V)$ 存在,二者间的转化主要受氧化-还原电位控制。氧化条件下, $As(III)$ 氧化为 $As(V)$,后者被吸附到粘粒矿物、铁锰氧化物及其水化氧化物和土壤有机质上,并且还可以和铁矿以砷酸铁的形式共沉淀。而淹水还原条件下,铁、锰等氧化物/氢氧化物结合的砷因铁、锰还原而释放,砷化合物的溶解度增加, $As(V)$ 逐步还原为 $As(III)$ ^[33],同时,水稻通过水通道和细胞膜直接渗透主动吸收 $As(III)$ ^[34]。淹水条件下稻米总砷可达富氧条件下的10~15倍,籽粒无机砷是富氧条件下的2.6~2.9倍^[35]。干湿交替条件下种植出的水稻稻米砷含量较持续淹水条件下的低^[36]。

针对农田镉、砷污染,应视具体情况采取不同的水分管理。同时,还要综合考虑不同生育时期作物镉、砷吸收与水分的相关关系,如水分管理对稻米镉含量的影响大小顺序为开花期>抽穗期>分蘖期>乳熟期,灌浆期是糙米吸收砷的关键时期^[37]。如果农田涉及镉、砷复合污染,需结合作物品种、土壤性质等其他因素,谨慎权衡水分管理措施。

2.3 土壤钝化调控抑制作物镉、砷吸收

土壤钝化调控是实现镉、砷污染农田安全种植的重要途径之一。钝化材料分为无机、有机及无机-有机复合材料,主要通过调节土壤理化性状,以及与重金属发生沉淀、吸附、络合、氧化-还原等反应,降低镉、砷生物有效性。土壤钝化调控成本低、见效快、对土壤破坏小,适合于我国大面积轻中度镉、砷污染情况。

对镉和砷,钝化剂有一定的针对性和选择性。铁基氧化物,包括 Fe_2O_3 、 Fe_3O_4 及其水化物,表面含有丰富的羟基位点-OH,能以专性和非专性吸附的方式与砷酸根、亚砷酸根离子结合形成内表面和外表面螯合物,对砷具有较高的吸附容量^[38]。某些微量元素钝化效果较好,硒^[39-40]、硅^[41-42]可显著降低作物对镉、砷吸收。秸秆、生物炭等有机钝化材料通过含有的羧基、羟

基、巯基等活性官能团与重金属发生络合、螯合作用,还可通过增加CEC、稳定土壤结构间接固定重金属。蚕沙生物炭可使弱酸可提取态和可还原态镉含量分别降低42.07%和35.19%,可氧化态和残渣态镉含量分别增加292.59%和339.29%^[43]。施加腐植酸对碱性土壤中砷向较稳定形态转化有显著的促进作用^[44]。值得注意的是,有机肥矿化分解后易与重金属形成有利于植物吸收的小分子有机结合态^[45]。通过表面修饰得到的无机-有机复合材料具有较大的应用价值,例如通过枝接巯基、氨基等官能团到无机氧化物基体上,可提高镉、砷的负载量及吸附选择性^[46]。

2.4 叶面调理阻控作物镉、砷吸收

叶面喷施调理剂可阻控作物吸收重金属。喷施锌可降低番茄^[47]、水稻^[48]镉吸收。喷施硅能促进镉、砷在细胞壁沉积,抑制作物镉、砷吸收和向地上部迁移^[49-50]。喷施硫酸亚铁、柠檬酸铁和EDTA二钠亚铁可降低菜心镉吸收,其机理在于植物对镉的吸收与转运与铁的吸收转运系统紧密相关,细胞质膜的铁转运蛋白在镉的吸收过程中起着重要作用^[51]。硫酸亚铁、氯化锰、氯化铜、硼酸和硼砂处理都能有效地抑制镉从秸秆向籽粒转移^[52]。徐向华等^[53]研究发现,喷施硒硅复合溶胶可有效缓解水稻砷毒害、显著抑制稻米砷积累。李慧敏等^[54]研究表明,叶面喷施不同浓度的铈、硅溶胶及不同掺杂比的铈硅复合溶胶,生菜的地上部鲜重升高了9%~58.8%,而砷含量降低了23%~48%。叶面调理是一种方便、可行、能有效阻控镉、砷吸收的方法,其机理一是利用元素间的拮抗作用来抑制植物对重金属的吸收,二是调节作物生理功能、提高抗氧化酶活性。

2.5 镉、砷低吸收作物品种选择与替代种植

作物对镉、砷吸收存在显著的种间、种内差异。蔬菜吸收镉按科属可分为低镉积累(豆科)、中镉积累(禾本科、百合科、葫芦科和伞形科)和高镉积累(藜科、十字花科、茄科、菊科)三类^[55]。刘维涛等^[56]研究发现15种大白菜对镉的吸收、转运差异显著。蒋彬和张慧萍^[57]研究了239份水稻品种稻米镉、砷含量,发现镉含量在 $0.01\sim1.98\text{ mg}\cdot\text{kg}^{-1}$ 之间,砷含量在 $0.08\sim49.14\text{ }\mu\text{g}\cdot\text{kg}^{-1}$ 之间,品种间差异极为显著。Mei等^[58]、谈宇荣等^[59]也发现不同稻作品种对砷的耐性和吸收具有显著差异。其他多种作物,如小麦^[60]、大豆^[61]、菜心^[62]等,对镉的吸收都存在显著的种间差异。作物低积累重金属虽存在基因型与环境的交互作用,但亦有主要受遗传因素控制的低积累表型品种^[63-64]。对于中轻度污染农

田,可通过选育抗性强、镉、砷低积累作物品种实现污染农田安全种植。对于重度污染土壤,可改变食用农产品用途(如稻米用于酿酒),或改种非食用农产品或花卉苗木,通过种植结构调整实现污染农田安全利用。

2.6 秸秆移除削减农田镉、砷

含镉、砷的作物秸秆移除可逐渐减少农田土壤重金属总量。水稻、小麦、玉米三大作物的谷草比分别约为1.0、1.0和1.2^[65],依据我国粮食平均产量^[66],平均亩产秸秆量分别达到460、360、470 kg。以水稻为例,参考唐非等^[67]提出的糙米与茎叶镉含量线性关系,若糙米镉含量按照国家标准(GB 2762—2012)0.2 mg·kg⁻¹计,一年种植早晚两季,秸秆移除每年每667 m²能带走镉量为688 mg,相当于带走4.3 μg·kg⁻¹土(0~20 cm耕作层),加上稻谷至少带走1.15 μg·kg⁻¹土,理想状态下镉超标农田(0.3 mg·kg⁻¹)连续种植55 a可实现耕作层镉的清除。当然实际与理想相差较远,但秸秆移除对削减农田镉、砷的贡献是毋庸置疑的。可筛选种植秸秆高富集、而籽粒低积累的作物品种,利用边生产边修复的方法。也可优化种植模式,如南方水稻—油菜典型轮作模式,水稻、油菜秸秆均可高富集镉,通过秸秆移除,在保障农田安全生产基础上,逐步降低土壤镉含量。

3 镉、砷污染农田安全种植的几点思考

3.1 建立基于耕地—农产品污染等级的安全种植技术体系

我国土壤环境质量标准与安全利用等主要考虑土壤污染程度,但实际上,不同农作物对镉、砷等重金属的敏感性与吸收特征差异迥异,农田土壤污染分类还应充分考虑农作物类别。镉、砷污染农田安全利用,归根结底是通过调控土壤、作物来实现。受污染耕地安全利用,应遵循农业生产规律,同步关注土壤与作物,结合食品污染物限量,构建耕地—农产品污染等级方案,在此基础上,建立基于耕地—农产品污染等级的安全种植技术体系。

湖南省于2014年启动的重金属污染耕地修复及农作物种植结构调整试点工作是个较好的尝试,修复耕地分为三类:达标生产区(稻米镉含量在0.2~0.4 mg·kg⁻¹)、管控生产区(稻米镉<0.4 mg·kg⁻¹且土壤镉≤1.0 mg·kg⁻¹)、替代种植区(稻米镉>0.4 mg·kg⁻¹且土壤镉>1.0 mg·kg⁻¹)。各省市或地区土壤类型与性质、农作物类型有其地域差异性,可建立地方性的耕

地—农产品污染等级方案,然后本着技术节约、成本节约原则,采取适宜的安全种植(集成)技术。

3.2 集成农艺措施与VIRL安全种植技术模式

大田作物在整个生育期,由于外界环境因素复杂,单独的品种选择、水肥管理、土壤调控或叶面调理等措施,难以确保农产品达标,集成农艺措施对于实现作物安全种植可能更有保障。湖南省针对镉污染,创建了“VIP+n”降镉技术模式,即“低镉品种(Variety)+合理灌溉(Irrigation)+调节酸度(pH)”。“n”指使用土壤钝化剂、叶面/根际阻控剂及其复合配方等。该技术模式降镉效果显著^[68],已成为湖南省重点推广模式。但对砷污染农田不适合。原因在于土壤砷的生物有效性随土壤pH值升高而升高,与镉几乎完全相反,对于砷及砷镉复合污染农田,调节农田土壤酸度基本没必要。

根据镉、砷的土壤环境化学行为差异,笔者在此提出一种新的普适性集成农艺安全种植模式:VIRL技术模式,V代表作物品种(Variety)选择,包括低吸收品种筛选及替代作物种植;I代表农业投入品(Input)控制和灌溉(Irrigation)调控,镉和砷采取相反的水分管理;R主要代表根区(Root zone)调控,即土肥调控与钝化修复,包括酸度调节,同时还代表秸秆移除(Removal of straw);L代表叶面(Leaf blade)调控,主要喷施降镉、降砷的相关元素肥料或其他物质。该模式将源头控制(农业投入品)、过程阻控(作物本身镉、砷吸收特性,影响作物地下部与地上部镉、砷吸收的各个环节)、末端治理(秸秆移除修复)高度统一起来,然后根据耕地—农产品污染等级,采取或紧或松的关键(联合)技术调控,实现农田的安全种植。VIRL英文意为金属箍,可将此模式形象为紧箍咒技术模式,该模式亦适用于其他大部分重金属污染及复合重金属污染情况。

3.3 镉、砷复合污染同步防控问题与展望

农田镉、砷复合污染普遍存在,由于二者的生物有效性受土壤酸碱度和氧化—还原状况的影响几乎完全相反,实际防控效果往往顾此失彼。其复合污染防控,一是要加强共性防控关键技术研发,包括同步钝化土壤镉砷材料的研制、同步阻控作物镉砷吸收叶面调理剂研发、低吸收镉砷作物品种筛选等。二是要根据实际情况,辨别主次矛盾,采取针对性的防控措施。如稻田、菜地、麦田等不同种植体系,要综合权衡土壤水分状况的影响、作物对镉砷吸收差异的影响等,从上述VIRL安全种植技术模式中选取有效的技术措施。

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