三种含钙物质对土壤砷植物有效性的影响

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摘要：综述含钙物质(生石灰(CaO)、熟石灰($Ca(OH)_2$)及石灰石($CaCO_3$))对土壤理化性质(pH 值、有机质成分及其含量)、土壤微生物群落结构和 As 赋存形态及生物有效性的影响与机制,及其对植物 As 吸收积累和 As 耐性的影响与机制.综述内容可为准确理解含钙物质影响土壤 As 的生物有效性和植物对 As 吸收积累的过程机制,进而合理选择含钙物质调控土壤理化性质降低土壤 As 生物有效性及其生态环境风险提供理论依据和技术参考,对保障土壤种植安全和作物食品安全具有一定现实意义.

关键词：钙；砷；生物有效性；吸收；积累；种植安全；食品安全

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Effects of three calcium substances on plant bioavailability of arsenic in soil. MA Sheng, YANG Xiao-li, LIU Chao-zhu, XU Qi-jing, LIU Xue* (Institute of Ecology and Environment/Institute of Environment Remediation and Health, Southwest Forestry University, Kunming 650224, China). *China Environmental Science*, 2022,42(12)：5785~5795

Abstract：This paper reviewed effects of calcareous materials (mainly including CaO, $Ca(OH)_2$ and $CaCO_3$, and others) on soil physicochemical properties (pH, composition and content of soil organic matter), microbial community, and As bioavailability, including impacts on As tolerance in plants, uptake and accumulation of As by plants. The review can provide theoretical and technical references for accurately understanding mechanisms under effects of calcareous materials on As bioavailability in soils and uptake and accumulation of As by plants, and then contribute to rationally select calcareous materials to improve soil physicochemical properties and reduce As bioavailability and its environmental risks in soils. It has certain practical significances for ensuring planting safety and food safety in agricultural field.

Key words：calcium；arsenic；bioavailability；uptake；accumulation；planting safety；food safety

砷(As)在土壤广泛分布,主要是无机砷(As_i)形式,如砷黄铁矿(FeAsS)、雄黄矿(As_4S_4)、雌黄矿(As_2S_3)等[1-3].因具有高毒性和“三致”效应[4-5],As 及其化合物被列为优先控制有害物质[6-8].2014 年《全国土壤污染状况调查公报》显示[9],我国土壤 As 点位超标率达 2.7%.As 为锡(Sn)、铅(Pb)、锌(Zn)等矿产资源伴生元素[2].我国西南地区砷矿产资源分布集中,矿山采冶区周边土壤 As 污染问题突出.研究表明,云南个旧、广西大厂锡矿周边农田土壤 As 含量分别达 132mg/kg 和 109mg/kg,是农用地土壤污染风险筛选值(20mg/kg)的 6.6 倍和 5.5 倍[10-11].此外,贵州、湖南锑矿和广西铅锌矿周边农田土壤 As 含量分别为 44.3mg/kg、15.0~363mg/kg 和 109mg/kg,分别为贵州土壤风险筛选值(30mg/kg)、湖南土壤 As 地质背景值(14mg/kg)和广西土壤 As 地质背景值(22mg/kg)的 1.47 倍、1.1~26 倍和 5 倍.重要的是,土壤 As 可被作物吸收,会引发人体健康风险.文献报道,As 含量 66.4mg/kg 土壤生长的空心菜叶 As 含量达 0.73~91.1mg/kg[12],是食品污染物限值(0.5mg/kg, GB 2762-2017)的 1.46~182 倍.此外,As 含量 78.9mg/kg 土壤生长的小麦籽粒 As 含量达 0.19mg/kg,对成人和儿童有致癌风险(致癌风险值 $>1\times10^{-4}$)[13].研究发现,我国部分区域土壤种植的蔬菜有 As 污染风险[14-16].综上,土壤 As 污染可引起食品安全风险和人体健康风险,需要通过研究土壤环境因子对 As 生物有效性的影响,降低或阻控农作物(尤其谷物和蔬菜)对 As 的吸收和积累.

钙(Ca)是土壤常见矿质元素,亦是植物必需大量元素.在植物体内,Ca 在维持细胞形态、调节离子平衡和渗透压等方面具有重要作用[17].此外,Ca^{2+}作为细胞的第二信使,参与其对环境信号转导[18].碳酸盐是土壤钙的主要来源,经风化和溶解后以 Ca^{2+}形式进入土壤,进而被土壤颗粒吸附[19].此外,由于具有来源广泛、价格低廉和施用简便等特点,石灰类等含

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钙物质常被用于酸性土壤改良和土壤重金属污染修复.土壤中 Ca 通常可分为水溶态、吸附交换态、有机态、矿物态 4 种赋存形态[20],其中,水溶态和吸附交换态钙是可被植物有效利用的形态,有机物态钙在矿化分解后转化为植物可吸收利用的有效态钙,矿物态钙难以被植物利用[21].含钙物质通过调控土壤理化性质(pH 值、有机质成分和含量)、微生物群落结构等影响土壤 As 赋存形态和生物有效性,进而影响植物对 As 吸收积累.

我国已探明砷矿的储量达 397 万 t,主要分布在西南地区[2].该区域的 As 背景值高(27.8mg/kg)且广泛分布石灰性土壤,其中碳酸钙($CaCO_3$)含量为 3.91~92.7g/kg[22].由于西南地区的包括 As 在内的有色金属矿开采冶炼活动频繁,周边土壤中 As 含量高达 44.3mg/kg[23].此外,在农业生产中,污水灌溉以及使用含 As 农药和化肥(如磷肥)也会导致土壤 As 含量升高.生石灰(CaO)、熟石灰($Ca(OH)_2$)及石灰石($CaCO_3$)等含钙物质因其钝化作用常被用于 As 污染土壤修复[24-25].然而,亦有研究发现,含钙物质($Ca(OH)_2$、CaO_2 等)可提高土壤 pH 值,促进 As 的解吸和置换,从而提高 As 的活动性和生物有效性,表明含钙物质对 As 的钝化和活化作用共存.因此,有必要理解含钙物质对土壤中 As 生物有效性的影响与过程作用机制,及其对植物 As 吸收积累的影响.由此,本文综述了含钙物质对土壤理化性质的影响,重点阐述含钙物质和土壤理化性质对土壤 As 赋存形态和生物有效性的影响,进而对植物 As 吸收积累的影响,以及 Ca^{2+} 对提高植物 As 耐受性的作用.

1 含钙物质对土壤理化和生物化学性质的影响

土壤中 As 价态和赋存形态影响其活动性、生物有效性和生物毒性效应.含钙物质影响土壤理化性质(pH 值、有机质含量和有机质组分等)、土壤微生物,进而影响土壤中 As 价态和赋存形态.

1.1 提高土壤 pH 值

土壤酸化是目前农业生产中面临的严重问题,导致农作物发育不良、降低营养元素(磷(P)、硼(B)、钼(Mo)等)有效性、土壤微生物失衡以及土壤板结等问题.此外,土壤 pH 值降低使重金属活性增强,导致土壤中活性态铁(Fe)、铝(Al)、锰(Mn)积累,对植物产生毒性效应.除酸沉降等自然因素外,长期施用氮肥是导致土壤酸化的主要人为因素[26-27].添加外源含钙物质可增加土壤中 Ca^{2+} 含量,通过离子交换减少土壤胶体吸附态 Al^{3+},同时中和土壤溶液中 H^+,提高土壤 pH 值,缓解土壤酸化[28].例如,Beckie 等[29]在酸性土壤施加 4.5~6.7t/hm^2.$Ca(OH)_2$ 使土壤 pH 值提高 0.5~1.1.Frank 等[30]和钟倩云等[31]研究发现,施用 $CaCO_3$ 使土壤 pH 值分别提高 1.0~1.6 和 0.48.因此,含钙物质对提高土壤 pH 值具有一定作用,对类金属阴离子(AsO_4^{3-}、AsO_3^{3-}等)具有潜在活化作用.

1.2 影响土壤有机质含量和成分

有机质是土壤重要组分,影响土壤养分含量和土壤结构、带电性和吸附性等.施加少量(5~20g/kg) $CaCO_3$ 时,Ca^{2+} 易与有机质结合,在其表面形成钙质层,阻碍有机质与土壤微生物接触,降低有机质的矿化分解;而施加大量 $CaCO_3$ (30~100g/kg)则提高土壤微生物活性,促进有机质矿化分解.例如,李瑞东等[32]对贵州黄壤研究发现,添加 30g/kg $CaCO_3$ 使有机质矿化速率降低 42.5%.类似地,黄媛等[33]研究发现,5~20g/kg $CaCO_3$ 使红壤有机质矿化速率降低.李忠等[34]研究发现,40~120g/kg $CaCO_3$ 使土壤有机质分解速率提高 4%~6%.黄媛等[33]研究发现,50g/kg $CaCO_3$ 对石灰土和红壤有机碳矿化速率贡献率分别达 6.01%~9.64%和 24.2%~34.1%.含钙物质不仅影响土壤有机质矿化分解速率及含量,亦影响有机质的成分分布.例如,胡乐宁等[35]研究发现,在喀斯特地区土壤中,由于 Ca^{2+} 易与胡敏酸和富里酸结合形成难溶性物质,总 Ca 及各形态 Ca 含量与腐殖酸含量呈正相关性.陈家瑞等[36]亦发现,喀斯特地区石灰性土壤中 Ca 含量与土壤总有机碳、胡敏酸、胡敏素含量成正相关.因此,含钙物质可通过影响有机质矿化分解速率进而影响土壤有机质含量,通过与不同成分的反应影响有机质的成分分布.有机质富含大量带电基团,能与含 As 离子(AsO_4^{3-}、AsO_3^{3-}等)发生吸附或解吸附反应,从而影响土壤中 As 赋存形态和生物有效性[37].

1.3 影响土壤微生物群落结构和数量

微生物活性是重要的土壤生物化学性质,也是反映土壤质量的重要指标[38].含钙物质通过影响土壤 pH 值和提高土壤 Ca^{2+} 含量直接或间接影响土壤微生物活性,然而其影响效应因土壤类型不同而异,相对而言对酸性土壤的影响更加显著.例如,外源添

加 1.2g/kg 过氧化钙(CaO_2)可使水稻土壤 pH 值升高 0.32,使可培养细菌、真菌和放线菌数量分别提高 114%、33.6%和 44.7%,其原因是过氧化钙不仅提高土壤 pH 值和氧化还原电位,亦可提高土壤温度,促进土壤碳氮等营养元素释放,从而提高土壤微生物活性[39].添加 2250kg/ha 生石灰(CaO)使酸性土壤(pH=5.4)微生物群落的 Shannon 和 Simpson 指数分别提高 5%和 5.58 倍,微生物的碳利用能力提高 1 倍,其原因与土壤 pH 值、有机质以及氮磷钾可利用性的改善有关[40].Li 等[41]对酸性黑土研究发现,0.04%~0.48% $CaCO_3$ 主要通过提高土壤 pH 值和氮磷有效性影响土壤微生物物种丰度和群落结构,比如使土壤微生物活性提高 42%,细菌数量由 2.74×10^{11} 增至 5.39×10^{11},而真菌数量由 1.96×10^{9} 降至 1.24×10^{9},并改变细菌群落结构(降低 *Firmicutes*、*Patescibacteria*、*Armatimonadetes* 和 *WS2* 相对丰度,增加 *Gemmatimonadetes* 和 *Rokubacteria* 相对丰度)和真菌群落结构(增加 *Basidiomycota*、*Glomeromycota* 和 *Chytridiomycota* 相对丰度),并利用冗余分析发现土壤 pH 值是主要影响因素($CaCO_3$ 使土壤 pH 值由 5.10 升至 7.49).Sangsub 等[42]对温带松树林土壤(pH=4.2~4.9)研究发现,石灰石($CaCO_3$)通过影响土壤 pH 值(升高 2.37)直接影响土壤细菌和真菌群落结构:细菌 OUT、Chao1、Shannon 指数分别提高 233、324 和 0.46,真菌 OUT 提高 13;石灰石($CaCO_3$)使细菌 *Firmicutes* 种群数量减少,*Bacteroidetes* 种群数量增加,同时交换性铝含量降低,进而降低其对微生物的毒性.Shangguan 等[43]对磷脂脂肪酸(PLFAs)分析发现,7.5t/hm^2 $Ca(OH)_2$ 使酸性土壤(pH=4.7~5.6)的 PLFAs 含量由 93.4mmol/g 降至 58.5mmol/g,说明土壤微生物丰度明显降低;而在中性或碱性土壤(pH=6.5~7.5)中则情况相反,这与不同 pH 值条件下土壤微生物群落结构的差异性有关.因此,含钙物质主要通过提高土壤 pH 值和增加 Ca^{2+}含量影响土壤微生物群落结构和数量,酸性土壤响应大于中性或碱性土壤,同时土壤类型、矿物质类型及其含量、土地利用方式及污染程度等也是重要影响因素.值得注意的是,土壤微生物能与土壤中 As 发生氧化、还原和甲基化反应,影响 As 的形态转化和活动性,进而影响植物对 As 的吸收和积累[44–45].

2　含钙物质对土壤砷生物有效性的影响

相较于总量,重金属的生物有效性可更直接地反映其活动性、生物有效性及生物毒性[46].土壤中 As 的生物有效性与其赋存形态和价态密切相关[47].含钙物质通过影响土壤 Ca^{2+}、pH 值、有机质及微生物作用(氧化、还原、甲基化以及与铁(Fe)或硫(S)循环耦合等[44–45])直接或间接影响土壤中 As 的活动性和生物有效性.

2.1　Ca^{2+}的影响

表 1　含钙物质对土壤砷生物有效性的影响

Table 1　Effects of calcareous materials on As bioavailability in soils

作用	土壤	土壤砷 (mg/kg)	钙种类	土壤砷生物有效性	参考文献
钝化	水稻土	25	2000kg/ha $CaCO_3$	有效态 As 含量减少 40%~50%, pH 值升高 0.3	[54]
		54	0.09% (*W*/*W*) CaO	有效态 As 含量降低 7.52%,pH 值升高 0.3	[55]
	石灰土	80	2g/kg(*W*/*W*) $CaCO_3$	水溶态 As 含量降低 17.2%,钝化率 9.78%	[50]
	场地土	278	16.9mmol/L Ca^{2+}	与 3.38mmol/L 无机磷配合施用,土壤 As 钝化率~100%	[53]
	耕地土	85	0.22g/kg (*W*/*W*) $CaCO_3$	有效态 As 含量 1200μg/L 降低至 1000μg/L	[56]
		26	0.4% (*W*/*W*) $Ca(OH)_2$	有效态 As 含量 18.1μg/kg 降低至 12.8μg/kg	[51]
活化	矿区土	48~3421	3~25.6g/kg (*W*/*W*) (60% $CaCO_3$+40% $Ca(OH)_2$)	有效态 As 含量增加 28%,pH 值升高 2	[57]
		875	100mmol/kg CaO_2	有效态 As 含量 137mg/kg 升至 158mg/kg	[58]
无影响	底泥土	3	0.25~8g/kg (*W*/*W*) $CaCO_3$	有效态 As 含量无明显变化	[59]
	粉砂土	65	4% (*W*/*W*)白云石	有效态 As 含量所占比例基本不变	[60]

Ca^{2+}可与无机砷(As_i)形成砷酸钙沉淀,或被土壤碳酸盐矿物吸附[48],从而降低 As 的活动性和生物有效性[49](表 1).例如,田间 As 污染模拟试验发现,施加 2g/kg $CaCO_3$ 使土壤中水溶态 As 含量降低 17.2mg/kg[50];0.4% (*W*/*W*) $Ca(OH)_2$ 使土壤有效态 As(0.5mol/L, $NaHCO_3$ 浸提态)含量下降 29.4%[51];毒

性特性溶出法(TCLP)研究表明,5%~20% (*W*/*W*) $Ca(OH)_2$ 使土壤有效态 As 含量由 10.3mg/L 降至 0.495mg/L[52].此外,Neupane 等[53]结合水相地球化学模型和 X 射线衍射技术(XRD)研究发现,在 278mg/kg As 土壤中,当 16.9mmol/L Ca^{2+} 与 3.38mmol/L 无机磷(P_i)共存时,As 可与钙磷化合物($Ca-P_i$)形成共沉淀使土壤 As 钝化率达~100%.

2.2 土壤 pH 值的影响

土壤中 $CaCO_3$ 等含钙物质含量强烈影响土壤 pH 值,外源添加石灰类含钙物质能有效中和土壤 H^+,进而提高土壤 pH 值.pH 值是影响土壤 As 生物有效性的重要因素[57].土壤 pH 值与土壤 As 赋存形态变化、土壤胶体对 As 吸附-解吸附过程以及溶解-沉淀过程密切相关.在酸性环境(pH=4~6.5)利于土壤中 Fe、Al 及 Mn 等氧化物对 As 吸附,而碱性环境(pH=7.0~8.5)有利于 As 解吸附和释放.土壤 pH 值升高引起土壤溶液 As 含量增加的原因包括:(1)土壤所带负电荷量增加,导致土壤对 As 的吸附量减少;(2)当 OH^- 含量增加时,土壤胶体吸附的 As_i 被置换,使土壤溶液中 As 含量增加;(3)当 pH 值>8 时,促进土壤物质分散或溶解,导致 As 解吸量增加[61].例如,Brian 等[62]研究发现,OH^- 有利于土壤中被铁氧化物所吸附的 As(V)解吸.陈静等[63]对红壤研究发现,pH 值影响 As 吸附-解吸附过程,土壤对 As 的吸附量随 pH 值升高而降低:当 pH 值由 4.0 提高到 9.0 时,As 吸附量由 2750μg/g 降至 2500μg/g;而 As 解吸量随 pH 值升高而升高:当 pH 值由 4.0 提高到 8.0 时,As 解吸量由 1850μg/g 增至 2300μg/g.通常,酸性环境利于 As 吸附,碱性环境利于 As 解吸附.此外,外源添加 25.6g/kg $CaCO_3$ 使土壤 pH 值由 5.0 升至 8.0,使土壤可溶性 As 含量提高 10~400 倍,主要受 pH 值依赖性的吸附-解吸附过程调控,非溶解-沉淀过程调控[58].

2.3 土壤有机质含量和成分的影响

含钙物质不仅影响土壤有机质矿化分解速率及含量,亦影响有机质的成分分布.有机质是土壤重要组分,其含量与土壤营养状况直接相关.有机质通过影响土壤颗粒对 As 的吸附-解吸附过程,耦合铁氧化物还原过程,促进铁氧化物所吸附的 As 释放,以及改变土壤中 As 的化学形态,来影响土壤中 As 的活动性和生物有效性.有氧环境中,负电性有机质促进土壤 As 释放,增加其环境迁移能力.例如,Syu 等[64]研究发现,土壤溶液中 As 含量与溶解性有机碳(DOC)呈正相关性(R^2=0.79),DOC 与 As 竞争吸附位点导致 As 解吸,同时形成 As-DOC 复合物,使土壤溶液中 As 浓度进一步升高.类似地,50g/kg dw 天然有机质(牛粪、污泥和森林凋落物)使土壤溶液 As 含量增加 1.5~3 倍[65];15%有机质使土壤可溶性 As 含量增加 62g/kg[66];因腐殖酸在铁氧化物表面具有更强的吸附竞争力,腐殖酸对土壤 As 活化率高达 53.3%[67].Ko 等[37]研究发现,100mg/L 胡敏酸能将 As(III)氧化为 As(V),使其含量占总 As 的 20%.综上,有机质促进 As 从土壤固相解吸释放进入土壤溶液的主要机制包括吸附竞争、形成水性复合物和 As 氧化还原形态变化[68].在缺氧环境中(例如淹水农田、湿地等),有机质的巯基(–SH)会与 As 结合,降低 As 的生物有效性.例如,Verbeeck 等[69]研究发现,在淹水条件下,土壤有机质(SOM)作为电子供体,通过催化氧化还原或者作为竞争配体影响 As 的活动性和生物有效性.Langner 等[70]研究发现,天然有机物通过 As(III) 和 –SH 共价螯合,降低其迁移率.此外,Williams 等[71]研究发现,SOM 具有双重性,一方面通过竞争吸附位点促进土壤中 As 解吸释放,另一方面通过吸附或络合溶液中 As 降低其生物有效性.因此,有机质对土壤中 As 生物有效性的影响机制复杂,相关机制有待进一步深入研究.

2.4 土壤微生物的影响

土壤中微生物种类和数量巨大,对土壤生态系统健康具有重要影响[72].由于数量巨大、比表面积大、电荷丰富以及繁殖快等特征,土壤微生物对 As 的生物地球化学行为产生影响,通过生物转化(氧化、还原、甲基化)及介导 Fe 或 S 循环来影响土壤中 As 的活动性和生物有效性[45,73-75].目前,土壤-水稻系统中土壤微生物对 As 形态转化和生物有效性的研究成为研究热点之一,且重点研究如何通过调控功能微生物阻控植物对 As 的吸收积累.例如,Gustave 等[76]研究发现,降低土壤孔隙水溶解性有机物含量和 As 还原基因(*arsC*)丰度,稻米中 As 含量降低 67.9%.Xue 等[77]研究发现,*arsC* 基因和 *arsM* 基因丰度与土壤中总 As 和 As(III)浓度呈正相关性($P<0.05$),表明砷功能微生物能影响环境中 As 形态转化.微生物通过甲基化形成三甲基砷化物(TMAs)等是去除土壤中 As 的有效措施.例如,Di 等[78]认为,微生

物通过促进土壤中 As 甲基化并挥发,从而减少植物中 As 积累.此外,通过添加外源含硫物质(Na_2SO_4)调控硫还原菌(SRB)通过产生 H_2S 或耦合 Fe(III)还原菌(FeRB)降低土壤溶液中 As(III)浓度,从而降低土壤-水稻系统中 As 风险[79-81].Yamamura 等[82]研究发现,脱硫杆菌属(*Desulfitobacterium*)和脱硫孢菌属(*Desulfosporosinus*)通过还原溶解铁氧化物,使土壤溶解性 As 含量增加 0.8mmol/L.

3　含钙物质对植物砷吸收积累的影响

土壤中 Ca 含量约为 1.37%,含钙物质通过改变土壤 pH 值或形成难溶性的含 Ca 砷化物(Ca-As)影响 As 的生物有效性,进而对植物吸收积累 As 产生影响[83].在农业生产中,石灰类(CaO、$Ca(OH)_2$、$CaCO_3$ 等)含钙物质常被用作重金属钝化剂和土壤改良剂,以降低农作物对重金属的吸收积累[84-86].然而,含钙物质对土壤 As 生物有效性和植物 As 吸收积累影响的报道相对较少.前期研究表明,Ca^{2+}能够与 As_i 形成砷酸钙沉淀,降低土壤 As 的生物有效性,进而降低植物对 As 的吸收积累(表 2).例如,施用 20g/kg CaO_2 使土壤溶液中 As 含量降低 47.9%~70.6%,使糙米 As_i 含量降低 25%~45%[87];2.5g/kg CaO_2 使芹菜茎中 As 含量由 0.7mg/kg 降至 0.2mg/kg[88];1.52t/ha CaO_2 使萝卜(*Raphanus sativus* L.)、生菜(*Lactuca sativa*)和大白菜(*Brassica rapa*)茎叶中 As 含量分别降低 68%、68%~71%和 73%[89].此外,Zhai 等[90]在室内和大田试验发现,硫酸钙($CaSO_4$)和氧化铁(Fe_2O_3)复施使水稻谷粒 As 含量降低 46.8%.然而,亦有研究发现,尽管含钙物质能够降低土壤 As 的生物有效性,但对植物 As 吸收积累无显著影响.例如,水稻盆栽实验发现,$CaCO_3$ 虽使土壤交换态 As 含量降低 69%,但水稻各部位 As 含量未明显降低[31].产生不同结果的可能原因是:(1)土壤 As 生物有效性提取方法存在差异;(2)土壤 As 与 P 等营养元素的相互作用影响植物对 As 的吸收和积累;(3)不同植物对 As 的吸收和积累机制存在差异.

表 2　含钙物质对植物砷吸收积累的影响

Table 2　Effects of calcareous materials on As uptake and accumulation by plants

植物种类	基质	砷浓度	含钙物质及施加量	作用效果	文献
水稻(*Oryza sativa* L.)	水培	0.5~1mmol/L	10mmol/L $CaCl_2$	0.5 和 1mmol/L As(V)组,茎叶 As 含量分别减少 30%和 50%,根 As 含量分别减少 36%和 21%	[97]
	水稻土	16~8mg/kg	5~20g/kg CaO_2	糙米 As 含量降低 25%~45%	[87]
		14~36mg/kg	$CaCO_3$/$CaSO_4$	稻米 As 含量降低 16%~68%	[54]
		54mg/kg	0.09% (w/w) CaO	谷粒 As 含量降低 20%~30%	[55]
萝卜(*Raphanus sativus* L.) 生菜(*Lactuca sativa*) 大白菜(*Brassica rapa*) 雅顿生菜(*Lactuca sativa* L.)	耕地土	15mg/kg	0.38~1.52t/ha CaO_2	萝卜(*Raphanus sativus* L.)、生菜(*Lactuca sativa*)、大白菜(*Brassica rapa*)及雅顿生菜(*Lactuca sativa* L.)茎叶 As 含量分别降低 68%、71%、73%和 68%	[89]
芹菜(*Apium graveolens* L.)	水稻土	162mg/kg	2.5~5g/kg CaO_2	茎叶 As 含量由 0.7 降至 0.2mg/kg	[88]
豌豆(*Pisum sativum*)	水培	25~250μmol/L	1~10mmol/L $CaCl_2$	茎叶 As 含量降低 50%~88%	[98]
蚕豆(*Vicia faba* L.)		25~250μmol/L	1~10mmol/L $CaCl_2$	茎叶 As 含量降低 30%~50%,根 As 含量降低 13%~50%	[99]
玉米(*Zea mays* L.)	石灰土	80mg/kg	2g/kg $CaCO_3$	籽粒、根、茎、叶 As 含量分别降低 50%、13.9%、16.5%和 14.9%	[50]
金合欢(*Acacia ingramii*)	矿场土	1000mg/kg	750kg/ha $CaCO_3$	茎叶 As 含量由 50 增至 500mg/kg,As 转移系数为 0.02	[100]
蜈蚣草(*Pteris vittata*)	水培	10~50mg/L	2~4mmol/L $CaCl_2$	10 和 50mg/L As,分别使叶 As 含量由 350mg/kg 增至 500mg/kg dw 和由 1200mg/kg 降至 800mg/kg dw	[95]
		1mg/L	0.8mmol/L $CaCO_3$	叶片 As 含量增加 70%	[95]
	砂培	0.1~0.2mmol/L	2.5~5mmol/L $CaCl_2$	2.5mmol/L 和 5mmol/L Ca^{2+}处理相对 0.03mmol/L Ca^{2+}处理,叶片 As 含量分别降低 20.8%和 73.1%	[94]
	耕地土	85mg/kg	0.22g/kg $CaCO_3$	地上部 As 含量由 1000mg/kg 降至 200mg/kg	[56]

由于蜈蚣草(*Pteris vittata*)是世界上首次报道的 As 超富集植物,也是一种碱性钙质土指示植物[91-92],因此有必要对含钙物质对蜈蚣草 As 吸收积累的影响进行讨论.前期研究表明,Ca 明显促进蜈蚣草孢子萌发和羽叶生长[93].虽然蜈蚣草体内 Ca 与 As 存在交互作用,但相关机制尚不清楚.廖晓勇等[94]通过砂培实验发现,与 0.03mmol/L Ca^{2+}相比,2.5mmol/L 和 5mmol/L Ca^{2+}使蜈蚣草羽叶 As 含

量分别降低 20.8%和 73.1%.Fayiga 等[95]利用水培实验发现,10mg/L As 处理下,4mmol/L Ca^{2+}使蜈蚣草羽叶 As 含量由 350mg/kg 增至 500mg/kg,这可能与 Ca^{2+}对植物的营养作用有关;然而,50mg/L As 时,4mmol/L Ca^{2+}使蜈蚣草羽叶 As 含量由 1200mg/kg 降至 800mg/kg,可能由于在高饱和度溶液时,Ca^{2+}与 As 形成沉淀并沉积在植物根部,抑制根对 As 吸收积累.Fayiga 等[95]进一步研究发现,0.8mmol/L $CaCO_3$ 促进蜈蚣草生物量增加且羽叶 As 含量提高 70%.然而,土壤研究中类似结果较少,因土壤系统的复杂性,其过程和机制更为复杂.例如,Caille 等[96]研究发现,在自然污染土壤添加 4.6g/kg $CaCO_3$ 对蜈蚣草羽叶 As 含量无显著影响.目前,关于含钙物质对土壤 As 形态转化、生物有效性及其植物吸收积累影响的调控过程和机制仍不清楚,可通过加强土壤环境中不同含钙物质对不同植物 As 吸收积累影响差异性的研究,降低 As 污染土壤对作物食品安全和人体健康的风险.

4 含钙物质对植物砷胁迫的缓解作用

表 3 Ca^{2+}对植物砷胁迫的缓解作用

Table 3 Alleviation of Ca^{2+} on As stress in plants

植物种类	培养基质	砷浓度	含钙物质及施加量	缓解机制	参考文献
水稻(*Oryza sativa* L.)	水培	0.5~1mmol/L As(V)	10mmol/L $CaCl_2$	叶绿素 a 和叶绿素 b 含量分别降低 33%和 44%,诱导脯氨酸(Pro)含量增加 85%~177%,H_2O_2 含量增加 65%~89%,Ca^{2+}使其恢复;Ca^{2+}有助于脱氢抗坏血酸还原酶(DHAR)、谷胱甘肽还原酶(GR)、谷氧还蛋白(GRX)维持在正常范围内	[97]
蚕豆(*Vicia faba* L.)	水培	5μmol/L As(V)	30mmol/L $CaCl_2$	过氧化物含量由 14mmol/g/min 恢复至 8mmol/g/min,H_2O_2 含量由 35μmol/g 恢复至 25μmol/g,还原型烟酰胺腺嘌呤二核苷酸磷酸(NADPH)、葡萄糖氧化酶(GOx)和丙二醛(MDA)对 Ca^{2+}响应类似	[107]
	砂培	25~250μmol/L As(V)	1~10mmol/L $CaCl_2$	根 H_2O_2 含量增加 50%~79%,根丙二醛(MDA)含量增加 9%~473%,总叶绿素含量由 698μg/g 降至 298~499μg/g,Ca^{2+}使之恢复到正常	[99]
芥菜(*Brassica juncea* L.)	砂培	15~30mg/kg As(V)	250mg/kg $CaCl_2$	根 H_2O_2 和丙二醛(MDA)含量分别增加 36%~73%和 13%~29%,叶抗坏血酸(AsA)和谷胱甘肽(GSH)含量分别降低 14%~29%和 30%~49%,Ca^{2+}使上述指标基本恢复至正常水平; Ca^{2+}使根半胱氨酸(Cys)和植物螯合肽(PCs)含量处于正常水平	[106]
	水培	50μmol/L As(V)	12mmol/L $CaCl_2$	活性氧(ROS)含量增加,引起脂质过氧化,破坏细胞膜完整性,使总叶绿素含量和光合酶活性分别降低 10%~20%和 30%,Ca^{2+}增加总叶绿素含量,使光合酶活性基本恢复正常	[109]
		15~30mg/kg As(V)	250mg/kg $CaCl_2$	根 Mn、Cu、Mg 和 P 含量分别降低 11%、8%、6%和 39%,叶的分别降低 18%、11%、27%和 25%,Ca^{2+}有助于恢复体内矿质含量保持正常范围;叶绿素 a 和叶绿素 b 含量分别降低 7%~15%和 15%~24%,Ca^{2+}缓解其降低趋势;As 使 O_2^-、H_2O_2、MDA 含量分别增加 66%、36%和 12%,Ca^{2+}降低该类氧化应激标记物含量	[110]

Ca 对植物硼(B)[101]、氟(F)[102]、盐碱[103]、水分[104]及高温[105]等环境胁迫均具有明显的缓解作用.然而,关于 Ca 对植物 As 胁迫缓解作用的研究报道相对较少,且该方面研究大多涉及生理生化层面(氧化应激系统、光合作用及渗透胁迫等),相关分子机制研究较少(表 3).例如,0.5~1mmol/L As(V)使水稻幼苗(*Oryza sativa* L.)产生胁迫响应,叶片总叶绿素和抗坏血酸(AsA)含量分别降低 33%~44%和 33%~51%,脯氨酸(Pro)和谷胱甘肽(GSH)含量分别增加 85%~177%和 48%~82%,而添加 10mmol/L Ca^{2+}有助于上述指标恢复至正常水平[97].25~250μmol/L As(V)使豌豆(*Pisum sativum*)和蚕豆(*Vicia faba* L.)产生胁迫响应,使根和叶片积累过量过氧化氢(H_2O_2)和丙二醛(MDA),而添加 10mmol/L Ca^{2+}使豌豆根、叶 MDA 含量分别降低 60%和 30%~40%[98],使蚕豆幼苗叶片总叶绿素含量由 438 增至 1728μg/g,使 H_2O_2 和 MDA 含量降低 21%和 30%,表明 Ca^{2+}对豌豆和蚕豆的 As 胁迫具有明显的缓解作用.土培实验发现,250mg/kg Ca^{2+}可提高芸苔(*Brassica rapa*)幼苗抗氧化应激能力以缓解 As(V)毒性,使叶片 MDA 含量降低 30%,GSH 含量由 435nmol/g 升至 626nmol/g[106].Siddiqui 等[107]认为,Ca^{2+}对植物缓解 As 毒性的机制包括:(1)抑制根和叶细胞程序性死亡;(2)提高叶绿素、可溶性糖和 Pro 含量;(3)抑制 DNA 损伤和活性氧(ROS)产生;(4)提高抗坏血酸-谷胱甘肽途径相关蛋白表达量,包括抗坏血酸过氧化物酶(APX)、单

脱氢抗坏血酸还原酶(MDHAR)、脱氢抗坏血酸还原酶(DHAR)等.此外,关于植物体内 Ca 与 As 相互作用的分子机制有少量报道.例如,Li 等[108]对拟南芥(*Arabidopsis thaliana*)研究发现,Ca 依耐型蛋白(CPK31)通过降低水通道蛋白(NIP1;1)活性抑制植物对 As(III)吸收,进而提高植物对 As 耐性.目前,关于 Ca 对植物 As 胁迫缓解作用涉及的植物种类较少,且这方面研究大多关注生理生化层面(氧化应激系统、光合作用及渗透胁迫等),缺乏分子机制研究报道,可通过结合光谱学原位技术(激光扫描共聚焦显微镜(LSM 和同步辐射等)和分子生物学,从植物细胞壁、细胞膜和液泡等与 Ca^{2+}信号转导密切相关的细胞器系统性研究 Ca^{2+}对植物 As 吸收和积累的分子机制,有助于发现新的植物 As 转运通道和吸收转运的调控机制.

5　结论与展望

5.1　结论

5.1.1　施用石灰等含钙物质可改善土壤(尤其酸性土壤)理化性质,提高土壤 pH 值,改变土壤微生物群落结构.

5.1.2　含钙物质可通过形成砷酸钙沉淀钝化土壤中 As,降低其活动性和迁移性,但当土壤 pH 值增加到一定数值(pH>8.5)时可能会增土壤 As 环境风险.

5.1.3　一般而言,由于降低土壤 As 有效态含量,含钙物质能有效减少植物对土壤 As 吸收积累量,但也可提高土壤 As 生物有效性,这主要受土壤 pH 值和矿质含量(Fe、Al 和 Mn 氧化物或氢氧化物)等因素影响.

5.1.4　含钙物质通过降低 ROS 等活性物质含量,改善植物抗氧化能力和改善光合作用等途径提高植物对 As 耐受性.

5.2　展望

目前,关于含钙物质对土壤 As 迁移转化和植物 As 吸收积累的影响尚缺乏系统性深入研究,建议加强以下方面研究:

外源含钙物质影响土壤 As 生物有效性的环境因素复杂,一方面能形成钙砷沉淀降低其有效性,另一方面能通过提高土壤 pH 值促进土壤 As 释放,可利用 X 射线吸收精细结构(XAFS)和激光共聚焦扫描显微镜(CLSM)等原位表征技术,深入研究含钙物质对土壤 As 生物有效性调控的微观机制及其定量关系.

含钙物质显著影响土壤微生物丰度和群落结构,且土壤相关功能微生物群落与土壤As迁移转化密切相关,目前关于微生物生态学及基因水平的定性定量信息较少,可深入研究对含钙物质响应显著的微生物及其间接调控土壤 As 形态转化的分子机制.

对植物,Ca 不仅是重要营养元素,亦是重要信号分子,可以深入研究 Ca 影响植物 As 耐受性、吸收、转运和积累的过程与机制,并深入探讨植物体内 Ca 和 As 互作效应及其机制.这将有助于理解含钙物质对土壤 As 活动性和生物有效性的影响机制,对土壤 As 污染防控治理以及保障食品安全和人体健康具有重要现实意义.

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