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水稻对砷吸收的机理及控制砷吸收的农艺途径研究进展

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摘要： 全世界约一半人口以大米为主食，亚洲人口主食对水稻的依赖程度甚至超过 90%。当前全球各地均存在不同程度的砷(As)污染，水稻容易在籽粒中积累砷，从而使砷通过食物链进入人体，威胁人体健康。水稻中砷含量水平为几个到几百个 ng/g 不等，砷从土壤进入水稻的过程涉及复杂的物理化学过程和形态转化，最终主要以砷酸、亚砷酸及砷的巯基、甲基配位等形态储存于大米中。田间水管理、施肥以及添加土壤改良剂等方法都可以控制稻田农田生态系统中水稻对砷的吸收，但是每种技术都有其优势和局限性。水稻农田生态系统中砷生物地球化学及水稻对砷的吸收和代谢等诸多因素都影响着水稻及谷粒中砷的浓度。综合考虑农艺活动对土壤中 pH、氧化还原条件、有机质结构和共存元素等因素的影响，考虑不同的地域特征和经济因素，是在生产实践中实现控制水稻对砷吸收的关键。综合运用多种农艺方法进行水稻耕作是未来控制水稻吸收砷的重要途径；新型农艺方法在控制水稻吸收砷过程中的应用，气候变化对大米吸收砷的影响，以及非破坏原位与活体分析技术在砷形态分析中的应用，是未来在全球尺度上更科学有效地控制大米中的砷含量、降低人体砷暴露风险的关键，也是未来的重点发展方向和艰巨挑战。

关键词： 水稻；砷；铁膜；灌溉；水管理；施肥；土壤改良剂；健康地质

要点：

(1) 水稻吸收砷的过程会受到土壤 pH、氧化还原条件、有机质和共存元素等关键因素的影响。
(2) 综合运用田间水管理、施肥和土壤改良剂是经济、有效地控制水稻吸收砷的重要途径。
(3) 气候变化可能会在全球尺度上增加水稻中砷的含量水平。
(4) 拓展砷的形态分析技术是未来开展砷在环境中迁移转化和毒性研究的关键。

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砷(As)是自然环境中普遍存在的一种变价元素，是一种无阈值类致癌物质，可导致人体皮肤癌等多类癌症，并可能诱发心血管和神经系统疾病[1-2]。砷在环境中无处不在，自然界中砷主要来自地壳，砷通常以无机化合物的形态(主要为毒砂)赋存于岩石中，平均浓度 <10mg/kg[3]。随着岩石的风化，砷的无机含氧阴离子(如亚砷酸根和砷酸根)进入环境中，在环境中具有较强的地质背景特征。由于地理环境因素致使居民长期摄入过量砷，从而导致地方性砷中毒事件在世界各地均有报道，成为最突出的健康地质问题之一。矿山开采、肥料、农药和电池工业等人为活动，也会带来砷在环境水体和土壤中的污染和扩散，并通过用水和食物链等途径进入人体，威胁人类健康[4-6]。

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水稻(*Oryza sativa* L.)是一类多熟农作物,大米是世界上消费最多的主食之一[7],它提供了人类所需70%的能量和50%的蛋白质[8]。预计到2050年,大米产量需要增长60% ~70%才可以满足届时亚洲人口增长对主食的需求[9]。砷在大米中的含量普遍高于玉米等多种作物,大米中砷含量水平为几个到几百个ng/g不等。在一些特殊的砷污染地区,大米中的砷含量可高达700ng/g[10]。已有研究证实大米和大米制品是导致全球范围内人口摄入过量砷的重要途径之一[11],而南亚和东南亚人群风险最高[12]。在欧洲和美国人群饮食结构中来自大米的砷摄入量仅次于海产品,位居第二[13]。已有研究发现食用含有砷的大米,会显著增加人类尤其是婴幼儿的癌症风险[14]。因此,如何在增加大米产量的同时,控制大米中的砷含量成为保障未来食品安全和控制健康风险的重要问题之一。

控制大米中砷浓度、减少人体砷摄入的方法有多种。最普遍、最直接的方法自然是降低水稻种植土壤中的砷含量[15];其次,也可以通过改进大米烹饪方式[16]等途径来减少砷的人体摄入;而更为经济有效的方法,则是通过水稻灌溉、施肥等农艺活动减少水稻对砷的吸收,降低大米中砷含量,这也是当前国际上农业科学、环境科学和食品安全等领域的前沿热点问题。不同的农艺活动在控制水稻吸收砷的过程中会受到复杂的环境因素作用,且存在不同程度的局限性,探索特定条件下合理的农艺活动以控制水稻对砷的吸收显得尤为关键。

本文探讨了砷在大米中的赋存水平、形态特征及砷的形态分析方法,讨论了水稻对砷的根部吸收和向上转运机理及影响水稻吸收砷的环境因素,并在此基础上比较和评述了目前具有较好应用前景的控制水稻中砷含量的农艺学方法。本研究认为,综合运用多种农艺方法进行水稻耕作,是未来控制水稻对砷吸收的重要途径;新型农艺方法在控制水稻吸收砷过程中的应用,气候变化对大米中砷食品安全问题带来的深刻影响,以及砷形态非破坏原位与活体分析技术研究,是未来在全球尺度上更科学有效地控制大米中的砷含量、降低人体健康风险的关键,也是我们面临的艰巨挑战和未来重点发展方向。

1 水稻中的砷形态及其健康风险

水稻可以吸收土壤中不同形态的砷,并在吸收和输送砷的过程中发生砷的形态转化。认识水稻中砷的浓度水平和形态特征,建立不同形态砷的分析方法,对于控制水稻中砷的含量、降低人体健康风险具有重要意义。

1.1 水稻中砷的主要形态及含量特征

自然界中砷的形态复杂多变。目前,在环境和生物样品中已发现了近一百种不同的砷形态[17]。在生物样品中,最常见的砷形态主要包括亚砷酸盐[As(Ⅲ)]、砷酸盐[As(Ⅴ)]、一甲基砷酸[MMA(Ⅴ)]、一甲基亚砷酸[MMA(Ⅲ)]、二甲基砷酸[DMA(Ⅴ)]、二甲基亚砷酸[DMA(Ⅲ)]、砷胆碱(AsB)、四甲基砷(Tetra)[18]。砷形态受砷的原子结构特征和配位原子特性影响,当参与生物代谢过程时,每个砷原子可与C(甲基)、O和(或)S(硫醇)等元素(基团)共享3个或5个电子。砷的形态也与其所处的生物环境相关,在不同条件下还会发生形态转化。

大米中存在As(Ⅲ)、As(Ⅴ)、DMA(Ⅴ)、MMA(Ⅴ)和AsB等几种典型的砷形态[19-20]。一项对巴西大米中砷的研究发现了5种砷形态,其含量范围为8~88ng/g,是总砷浓度的3.6% ~39%[21]。此外,有研究比较了印度、日本和泰国大米中砷的形态,发现大多数大米样品中含有砷(25.81 ~312.44 ng/g),其中包括3.54 ~25.81ng/g的AsB、9.62 ~194.93ng/g的As(Ⅲ)、17.63 ~78.33ng/g的As(Ⅴ)、9.47 ~73.22ng/g的MMA(Ⅴ)以及13.43 ~101.15 ng/g的DMA(Ⅴ)[22]。除了这5种砷形态,也有报道揭示了大米中含有四甲基砷(Tetra)等其他砷形态,约占大米中总砷浓度的5.8%[23]。此外,水稻也可以通过甲基化降低无机砷的毒性[24-25]。

1.2 砷的毒性特征及大米砷摄入特征

砷的毒性与其化学形态密切相关。通常来说,As(Ⅲ)毒性高于As(Ⅴ),无机砷毒性高于有机砷,这是由于无机砷更容易与细胞中的含巯基酶结合,影响细胞的代谢和生理功能。砷的毒性通常随其甲基化程度升高而降低[26],这也表明甲基化代谢产物(如MMA和DMA)可能是生物的解毒产物。一些有机砷,如DMA(Ⅴ)和MMA(Ⅴ),可诱发氧化性组织损伤或直接干扰细胞分裂过程,具有致癌性[27]。

通过食用大米及其加工食品,人体可以摄入不同水平和不同形态的砷。世界卫生组织对大米中无机砷的含量限制值为0.2mg/kg,然而,由于每个地区地质背景和人群饮食结构存在差异,故而不同人群通过食用本地大米带来的砷暴露风险也不同。研究发现巴西几个不同地区人群从本地大米中摄入的无机砷可达到每日人体临界耐受摄入量的10%[21]。人体中

砷的形态与大米中的砷形态有关。研究发现人体的尿液和血液中的 AsB 和大米中 AsB 浓度呈正相关[22]。因此，随着每个地区大米中砷的含量、形态、毒性以及人群饮食结构的差异而产生的健康风险问题已成为不可忽视的食品安全和健康地质问题之一，对大米中的砷标准制定和砷的健康风险评价需要综合考虑不同地区以及大米中砷的形态差异。

1.3　砷形态的典型分析方法

化学破坏分析和原位形态分析是两类重要的砷形态分析方法，在环境和生物样品的砷形态分析中有广泛应用，两类方法各具优势，也都存在一定的局限性。

化学破坏分析法的主要原理是将样品中的砷化学提取到溶液中并通过联用技术进行定性和定量检测，如气相色谱 - 原子吸收光谱、气相色谱 - 原子荧光光谱、气相色谱 - 微波诱导等离子体发射光谱、气相色谱 - 电感耦合等离子体质谱、高效液相色谱 - 电感耦合等离子体质谱，其优点在于可以对 ng 级别的砷形态进行精确的定量分析，是比较主流和成熟的砷形态分析技术。但化学破坏分析法存在以下几个局限性：首先，化学提取会带来砷的形态转化，导致分析失误。例如，DMMTA 的毒性与无机砷相当，而普通的酸提取会将 DMMTA 转化为DMA(Ⅴ)[28]。如果提取介质的 $\mathrm{pH} > 7.2$ 时，As(Ⅲ)可能会被氧化为 As(Ⅴ)[29]。有研究表明 2% 的酸提取浓度可以有效降低大米中的砷形态转化[30]。从植物中提取砷形态时，一些砷的络合形态可能会发生改变，例如 PC - As(Ⅲ)复合物可能游离成植物螯合素(PC)和游离As(Ⅲ)[29]。其次，色谱技术对于某些砷形态的分离能力有限，从而导致将多种砷形态错误地记入同一种砷形态的定量数据中。如采用阴离子交换色谱进行砷形态分离时，Tetra 和 As(Ⅲ)会共洗脱，造成两种形态被错误地定性和定量分析[23]。

与化学破坏分析法相比，原位形态分析技术如 X 射线吸收光谱(X - ray absorption spectroscopy，XAS)技术可以在不化学破坏样品的情况下获得砷与周围原子的配位特征以及样品中砷的形态及其质量分数[31]。近年来 XAS 技术在地质、环境和生物样品中 As 的原位形态定性和定量分析中有广泛应用，例如已有研究应用 XAS 技术分析了超富集蕨类植物中 As 的形态，并揭示了 As(Ⅲ)在蕨类植物体内可以转化为 As 的巯基结合态[32]。XAS 技术也存在一些挑战，如样品中砷含量较低时，难获得高信噪比的 XAS 谱图，含量较低的砷形态可能在线性拟合中误差较大，某些不同形态的砷可能具有十分接近的 XAS 特征谱图，也会给定性分析带来一定的挑战。

水稻中砷的吸收和代谢，以及砷的毒性都与砷的形态密切相关，因此水稻中砷的形态分析技术对研究水稻吸收砷及砷的人体健康风险具有重要意义。由于大米中的砷浓度通常 <300ng/g，而部分形态的砷浓度只有几个 ng/kg，这为大米中砷的形态分析带来一定的挑战。

2　水稻对砷的吸收和输送机理

水稻对砷存在特殊的吸收、输送和解毒机制，了解砷从土壤进入水稻根系、向上输送并进入籽粒中的途径，是控制水稻对砷的吸收、减少大米中砷含量的重要前提。

2.1　铁膜在水稻吸收砷过程中的作用

根是水稻吸收砷的主要部位，为适应厌氧环境，水稻非常容易在根表形成一层金属氧化膜[33]，主要为赤铁矿(α - FeO)、磁赤铁矿(γ - FeO)、针铁矿(α - FeOOH)、纤铁矿(γ - FeOOH)和无定形氢氧化铁等[34]，称为铁膜或铁斑块。铁膜本身的形成受到复杂因素的影响，铁膜的形成对砷进入水稻起着决定作用。

首先，铁膜的形成能力与根系泌氧水平及根际氧化还原条件有关。根际铁氧化过程受到根系泌氧水平的影响[35-36]，而高根系泌氧基因型的水稻可诱导更多的铁膜[37-38]。由于不同的生长时期水稻根系的泌氧水平不同，根系铁膜含量也存在差异。例如根系泌氧从分蘖期到抽穗期迅速增加，但在灌浆期显著减少，导致成熟期铁膜显著减少[39]。也有研究发现铁膜的形成与硫代硫酸盐歧化反应生成的硫化物还原有关[40]。当土壤由淹水环境转为干燥环境时，土壤基质从还原性条件转变为好氧性条件[41]，可溶性二价铁被氧化成不溶性三价铁氧化物，减少了可溶性铁离子对根际的供应，抑制了铁膜的形成[41-42]。

其次，铁膜在水稻吸收砷的过程中可以对土壤中的砷起到吸附、屏蔽或缓冲作用。铁膜对很多金属和类金属都具有很好的吸附能力。多项研究发现铁膜中 Cd、As、Sb、Hg、Se、Pb 等与 Fe 浓度呈显著正相关[43-46]。铁膜对砷的吸附作用主要机理是，铁膜中的铁氧化物/氢氧化物与砷有很强的亲和力，它在砷进入根系之前将砷吸附，从而减少根系吸收。水培条件下，水稻根系铁膜的形成可以显著降低水稻对砷的吸收[47-48]。水稻根表铁膜可以吸附约 73% ~90% 的砷，是水稻植株吸收和转运砷的屏障[49-51]。然而，

也有研究发现,虽然随着根表铁膜数量的增加,根际砷浓度也随之增加,而水稻中的砷浓度并没有增加,说明铁膜是砷进入水稻体内的缓冲带[45]。铁膜对不同形态砷的吸附能力存在差异。与As(Ⅲ)相比,氧化物对As(Ⅴ)有较高的亲和力,在缺氧土壤条件下,As(Ⅴ)与Fe(Ⅲ)、Fe(Ⅱ)离子的快速共沉淀有利于As的固定,防止其还原为As(Ⅲ),因此As(Ⅴ)在土壤溶液中的生物利用度较低[52]。研究表明As(Ⅲ)是淹水条件下土壤中主要的砷形态,但铁膜吸附的As(Ⅴ)约占总砷的78%[53-54],表明铁膜可以更有效吸附As(Ⅴ)。

2.2 砷在水稻中的吸收转运、向上输送和进入谷粒的特征及影响因素

在水稻根系中,砷主要通过共用Si、P等重要营养元素的转运体进入根中,不同形态的砷具有不同的转运体。As(Ⅴ)作为磷酸盐类似物通过OsPT8等PO_4^{3-}转运体被吸收。而As(Ⅲ)可以通过$Si(OH)_4$转运体,如水蛋白通道OsNIP2;1(Lsi1),被水稻吸收[55]。部分甲基砷,如DMA(Ⅴ)和MMA(Ⅴ),也可以被$Si(OH)_4$转运蛋白吸收[56]。水稻根部对甲基砷的吸收能力低于对无机砷的吸收能力[19]。

不同形态的砷的向上输送通道和输送速度存在差异。砷在水稻中的向上输送也是通过共用转运蛋白发生,水稻中Lsi1和Lsi2两种Si转运蛋白都可以介导硅酸从根细胞通过质外体沿中柱向芽的输送,也因此可以向上输送As(Ⅲ)[57-58]。有研究发现与巯基结合的还原形态砷在植物中通过液泡膜和囊泡向上运输[59-60]。有机砷在植物体内的向上输送效率高于无机砷[61]。

砷进入水稻谷粒的过程会受到水稻中砷的形态、水稻中其他元素含量、水稻的生长时期以及土壤中砷的含量影响。首先,不同形态的砷在谷粒中的输送和装载效率存在差异。韧皮部是As(Ⅲ)向籽粒运输的主要组织,在韧皮部和木质部,有机砷比As(Ⅲ)的流动性强得多。韧皮部也会拦截砷进入籽粒,有研究发现韧皮部节点拦截了90%的砷[62]。其次,植物体中的营养元素也会影响砷向籽粒的转移,例如茎中氮浓度升高时,砷从茎到籽粒中的转运系数降低[63-64]。同时,在水稻不同的生长发育阶段,谷粒中砷的装载途径也不同。有研究发现水稻开花前吸收的砷主要通过韧皮部由茎叶组织运输到达籽粒,而开花后吸收的砷主要通过木质部运输到达水稻籽粒[65]。此外,水稻籽粒中的砷浓度也与土壤中砷的浓度有关。在土壤砷含量较低时,谷粒中砷含量随着土壤中砷浓度增加而增加,在土壤砷浓度较高时趋于稳定[66-67],这是由于砷浓度的增加使水稻某些代谢活动受到干扰,从而阻碍了砷向籽粒的装载[66]。

3 土壤中影响水稻吸收砷的因素

水稻从土壤中吸收砷的能力主要与土壤中砷的浓度、形态和生物有效性有关,受到pH、氧化还原特征、土壤有机质结构、共存元素以及水稻品种等因素的影响[68-71]。

3.1 土壤pH和氧化还原条件对土壤环境中砷的形态和可迁移性的影响

土壤pH和氧化还原条件在不同的地域存在很大差异,它们可以决定土壤中砷的主要形态,从而决定着土壤中砷的生物有效性和可迁移性。

首先,土壤pH和氧化还原条件都会影响土壤中砷的主要形态,从而影响水稻对砷的吸收。在氧化条件下,砷酸(H_3AsO_4)是$pH<2$时的优势形态,$H_2AsO_4^-$和$HAsO_4^{2-}$是pH在2~11范围内的优势形态。在还原条件下,亚砷酸(H_3AsO_3)是优势形态,在较低的pH水平下转化为$H_2AsO_3^-$,在较高的pH水平下($pH>12$)转化为$HAsO_3^{2-}$[72-73]。因此,不同地区的水稻田pH和氧化还原条件直接决定了砷在进入水稻根系之前的主要形态特征。

pH会影响砷在土壤中的吸附和释放。通常,土壤酸化时,铁和铝氧化合物的溶解会促进砷的释放和迁移[74-75],从而促进水稻对砷的吸收。然而,也有研究发现高pH会促进水稻对砷的吸收。例如在pH 6.5~8.5时,土壤pH与水稻籽粒总砷浓度呈正相关[76]。这是因为高pH值会引起负表面电荷,从而促进As(Ⅲ)和As(Ⅴ)在土壤溶液中的解吸。同时,在pH值相对较高时,土壤黏土含量较低,也会促进砷的释放[77]。pH对不同形态的砷在固液中的分配也存在差异。流动相的pH值不仅影响着流动相缓冲盐的组分构成,也影响着不同形态砷化合物的离子形式,在液相分离过程中起着至关重要的作用[78]。例如,与As(Ⅴ)相比,As(Ⅲ)更容易从土壤固相释放到土壤溶液中,在低pH条件下,两者溶解度有很大差异[70]。与As(Ⅲ)相比,As(Ⅴ)在土壤-溶液体系中的分配更容易受到pH的影响[79]。

土壤氧化还原条件也会影响砷的吸附和释放。还原条件下水稻根际的砷溶解度更高,导致水稻中含有更高浓度的砷[80-81]。在Eh值降低时,土壤中的Fe在铁还原菌的联合作用下发生还原溶解[82],

吸附在铁氧化物上的砷被解吸并释放到根际溶液中[83]。

3.2　土壤有机质对砷的吸附和释放的影响

土壤中的有机质分子大小、结构、官能团特征和溶解性存在很大差异,不同的有机质对水稻吸收砷的过程有不同的影响。天然有机物的存在主要通过竞争有效的吸附位点、形成络合物、改变位点表面的氧化还原化学性质和砷形态来控制砷的吸附和释放[84]。

首先,土壤有机质可以通过从氧化物表面抢夺砷的吸附点位,从而导致砷在土壤溶液中的释放。金属氧化物与土壤有机质具有很强的亲和力,可与—COOH、苯酚/邻苯二酚的—OH 官能团发生配体交换反应,与砷竞争吸收位点[85-87],造成砷的解吸和释放。例如,腐植质在赤铁矿和针铁矿上与砷存在共同的吸附点位,从而导致砷从赤铁矿和针铁矿表面解吸下来。腐植质还可以通过非生物氧化还原促进砷从土壤中释放[88-89]。

其次,有机质对砷具有很高的亲和力,可以形成有机质-砷的络合物[90-92]。例如,可溶性腐植质可以直接与 As(Ⅴ)[93-94]或 As(Ⅲ)络合[95]。另外,一些有机质具有发达的孔结构,可以通过物理吸附促进砷扩散到孔中[96]。例如,生物炭含有可通过表面络合控制砷吸附的氧化官能团(即醇、酚和羧基)[97-100]。已有研究发现腐植质、铁和 As(Ⅲ)或 As(Ⅴ)的三元络合物形成的桥接作用是控制砷络合形态的主要机制[101-103]。土壤中的 pH-Eh 可以通过与腐植质相关的 FeOOH 或 MnOOH 的还原性溶解将砷释放[104]。

有机质对砷的络合可能会增加,也可能会降低砷的生物可利用性。例如,溶解性有机质在土壤中具有很好的迁移能力,它将原本被吸附的砷抢夺下来后,促进了砷的可移动性。但是溶解性有机质与砷络合所形成的不溶性复合物也会降低土壤溶液中砷的生物可利用性[105]。

3.3　土壤环境中的共存元素对水稻吸收砷的影响

水稻的生长和代谢需要多种元素参与,如磷、硅、硫、铁和锰等,这些共存元素可以和砷发生竞争或协同吸收作用,对水稻吸收砷的影响也是不可忽视的。

首先,由于水稻中不同形态的砷有不同的吸收通道,与砷共用通道的物质都可能与砷的吸收形成竞争关系。由于 As(Ⅲ)和 As(Ⅴ)会分别与 $Si(OH)_4$ 和 PO_4^{3-} 共用相同的吸收通道,Si 和 P 与砷存在竞争吸收关系[106-107]。同时,还有一些可以共用 Si 和 P 吸收通道的元素如硒[Se(Ⅳ)][108-109],也与砷存在竞争吸收关系。研究也证实培养液中添加 Se(Ⅳ)能显著降低砷在水稻幼芽中的积累[110]。

其次,在水稻生长过程中,很多氧化还原过程与一些特殊的元素或物质相关,它们通常与砷的形态转化密切相关,且受到的影响因素也较为复杂。如硫的生物地球化学过程在水稻生长环境中的氧化还原条件的周期性变化中有主导作用,水稻生长季节长期淹水导致土壤缺氧,可以加剧硫代硫酸盐歧化反应,改变砷的形态。Mn 和 Fe 在水稻土壤中也可以参与氧化还原反应。砷污染稻田土壤中的锰氧化物可能通过 FeOOH 的还原溶解而阻碍高迁移率 As(Ⅲ)的释放[111-112]。在水稻根部形成的锰斑块可能会更容易促进水稻根际中的 As(Ⅲ)氧化[113]。

另外,有些元素对砷在水稻中的解毒能力有重要作用。如硫在某些砷解毒的蛋白质表达过程中有重要作用,可以介导木质部的 As(Ⅲ)外排[28]。硫还可以促进水稻根中植物螯合素(PC)和谷胱甘肽(GSH)的形成[114],与砷络合并进行液泡隔离[115]。水稻中 NO 的抗氧化能力可以抑制活性氧,保护细胞免受非生物胁迫[116]。外源供应的 NO 对水稻砷诱导的毒性有显著的抗性,并且对砷诱导的氧化应激有改善作用[117]。

此外,一些其他的共存毒性元素可能会干扰到植物的生长和代谢,从而抑制水稻对砷的吸收。例如有研究发现汞(Hg^{2+})对 As(Ⅲ)和 As(Ⅴ)的吸收均有抑制作用,但是这种抑制作用可能是 Hg 对植物带来的应激反应导致的,而非 Hg^{2+} 与 As(Ⅲ)和 As(Ⅴ)对水通道蛋白的竞争作用导致[118]。

4　控制水稻对土壤中砷吸收的途径与农艺方法

水稻的耕种离不开田间水管理、施肥和添加土壤改良剂等农艺活动,它们是维持水稻生长、保证大米产量的必要环节,合理的农艺方法可以在一定程度上控制水稻对砷的吸收。

4.1　田间水管理对水稻吸收砷的控制

合理的灌溉和田间水管理可以将稻田土壤溶液中的总砷含量控制在较低水平。常规水稻耕作会经历淹水(还原)和非淹水(氧化)条件,淹水条件下水稻对砷的吸收量比非淹水条件下高 10~15 倍[81]。间歇性灌溉和有氧水管理都可以在满足水稻对水的生长需求的条件下,尽量保持土壤中的好氧环境,从

而减少大米中砷的积累[119-120]。这是因为这两种水管理方式可以改变水稻土壤-水系统的理化性质。在连续的淹水环境下，土壤中As(Ⅴ)转化为As(Ⅲ)[121-122]，根际中无机砷的微生物甲基化可能会提高稻田土壤溶液中甲基砷的含量，并在大米中积累[123]。在间歇灌溉和有氧水管理条件下，水稻土壤溶液中As(Ⅴ)/As(Ⅲ)比率较高[124]，籽粒中甲基化砷含量的比例趋于下降，水稻籽粒中的无机砷含量远低于持续淹水下水稻籽粒中的无机砷含量[125]。可见，与持续灌溉相比，在间歇性灌溉和有氧水管理条件下，水稻谷粒总砷中，无机砷和甲基化砷形态的浓度都得到了很好的控制[126]。

此外，田间水管理时也需要充分考虑降雨的影响。有报道显示持续的降雨可以导致土壤中51~250mg/m^{2}的砷被释放[127]。而在旱季灌溉耕作后，降水会使得水稻表层土壤的砷含量降低。因此，需要进一步研究自然降雨对稻田环境中砷动力学的影响。

间歇性灌溉和有氧水管理虽然可以降低水稻中的砷，但也存在一定的局限性。它的耗水量是淹水耕作的三分之一[126]，降低了农业耗水，但同时却减少了大约25%的水稻产量[126-128]。这是因为在这种田间水管理方式下，相对干燥的土壤环境限制了根系生长，降低了水稻的吸水率[129]。从人体健康角度来看，这种田间耕作方式是有益的，但是从经济角度，这种作业方式会降低当地居民的经济收入。

因此，如何科学有效地在不同的降水条件下，通过水管理方式实现降低粮食减产损失—节水—降低砷暴露风险的最佳平衡，将是未来水稻田间水管理的重要方向。

4.2 施肥对水稻吸收砷的控制

4.2.1 施用磷肥

由于As(Ⅴ)和PO_4^{3-}共用相同的吸收通道，在砷污染的稻田中施用磷酸盐可以控制水稻植物中As(Ⅴ)的吸收，PO_4^{3-}的施用量和土壤性质都会影响磷肥对控制水稻吸收As(Ⅴ)的效率。在田间管理时，可以用水稻根际环境中较高的PO_4^{3-}/As(Ⅴ)比来衡量水稻对As(Ⅴ)的吸收能力，比值越高，水稻中的As(Ⅴ)吸收能力越低。但有研究显示，在砷污染(9~102mg/kg)的稻田中施用PO_4^{3-}肥料并没有成功地抑制水稻植物中砷的吸收和积累[130]。还有研究发现，添加PO_4^{3-}甚至会增加水稻植株和谷粒中的总砷浓度。PO_4^{3-}的添加将水稻铁膜中的总砷吸附比从70%降低到10%，水稻根和芽中总砷的比例反而增加了20%~60%[131]。主要原因是PO_4^{3-}和As(Ⅴ)在土壤基质和根部铁膜上存在竞争性吸附，磷酸盐的过多添加可能会增加土壤溶液中As(Ⅴ)的浓度，反而不利于降低水稻对砷的吸收。因此，因地制宜地衡量砷污染情况和PO_4^{3-}最佳添加量，才可以达到降低稻米中砷的目的。

通过施加磷肥降低水稻中砷的方法也存在其局限性。如磷肥市场价格不低，其在一些欠发达地区广泛应用于水稻田中的可行性不高[132-133]。同时，由于很多磷肥(三重超级磷酸盐、磷酸一铵、磷酸二铵和磷酸岩石)中普遍含有砷和镉等元素，长期添加这样的磷酸盐磷肥反而会增加水稻田中砷和镉的输入[134-135]。此外，磷肥非常容易地因地表径流和垂直浸出而流失，会加剧河流、湖泊和水库中的富营养化。

4.2.2 施用硅肥

由于As(Ⅲ)与$Si(OH)_4$占用相同的吸收通道，施用硅肥可减少水稻对As(Ⅲ)的吸收。根际中Si/As(Ⅲ)含量比值的增加是降低水稻植物吸收As(Ⅲ)的关键因素。有研究发现，随着砷污染水稻土中Si添加量逐渐增加，水稻组织中的As(Ⅲ)/总砷比值显著降低[136-137]。

硅的添加对控制水稻吸收As(Ⅲ)的效率受到多种因素影响。首先，硅施用量会影响水稻对砷的吸收效果，有研究添加了0.375g/kg硅肥但是并没有降低水稻中砷的积累[138]。这是由于土壤颗粒中$Si(OH)_4$和As(Ⅲ)之间的竞争吸附，硅的施用会提高稻田土壤溶液中的As(Ⅲ)水平，从而增加水稻对As(Ⅲ)的吸收。其次，不同的硅种类也对控制水稻吸收砷有不同的作用。有研究发现不同硅酸盐矿物(硅藻土和SiO_2凝胶)对水稻谷粒中砷的积累有不同的影响[139]。SiO_2凝胶的添加显著降低了稻米中的总砷含量，而硅藻土的施用并未降低稻米中的总砷含量[139]。因此，优化稻田中硅的施用类型和比例含量对于降低水稻中的砷吸收是非常重要的。

施用硅肥来控制水稻吸收砷也存在一定的局限性，如成本较高等，从而限制了这种方法的适用性。有研究发现，由于水稻每年吸收的硅为270 kg/ha[140]，水稻植株本身就是一种较好的硅肥原料，将水稻的秸秆、稻壳等堆肥后还田，随着硅的缓慢释放而达到减少水稻中砷的吸收可能是另一种经济有效的控制水稻砷吸收的方法[141]。

4.2.3 施用硫肥

施用硫肥可以控制水稻中的砷吸收。有报道显示施用硫肥显著降低了水稻叶片中砷的积累[142]。

相似的研究结果在小麦[143]、大麦[144]和茄属植物[145]中都有报道。

通过添加硫降低水稻吸收砷的机制与磷肥和硅肥不同，它主要参与了水稻吸收砷的氧化还原过程和解毒过程。首先，硫的添加可通过改变根际的矿物结构来减轻水稻砷的积累。在淹水条件下，土壤－水系统中的SO_4^{2-}还原为S^{2-}[122]，稻田土壤溶液中的As(Ⅲ)可以与S^{2-}反应并沉淀为As_2S_3[146]，从而降低了As(Ⅲ)的生物可利用性。其次，硫的添加可以改变水稻对砷的代谢。有研究者发现添加硫(5.0mmol/L)可以降低Lsi2的转录水平，介导木质部的As(Ⅲ)外排[28]。硫还可以促进水稻根中植物螯合素(PC)和谷胱甘肽(GSH)的形成[147]，这些硫醇对As(Ⅲ)具有很高的亲和力，As(Ⅲ)－硫醇复合物可以通过水稻根部的C型ATP转运蛋白(OsABCC1)转运进行液泡隔离[115]。存在于韧皮部液泡膜中的OsABCC1还介导了As(Ⅲ)－硫醇复合物的转运，以促进其液泡隔离[148]。

在实践中硫肥的添加对控制水稻吸收砷的效果受到水稻品种等多种因素的作用。尽管许多研究表明，水稻籽粒中砷含量较低的水稻品种其根部的PC含量均显著较高，但近期有研究发现了相反的结果，某些水稻品种中高浓度PC并不一定会降低水稻籽粒中总砷的含量[149]。有研究发现在硫施用量下降的情况下，某些水稻籽粒中的砷积累量也会降低。而一些特殊的水稻品种(如IR64)即使不添加硫，其谷粒中的砷也比较低[150]。

施用硫肥的局限性在于它可能会加剧稻田中硫代砷酸盐的形成[151]。在还原条件下通过从As(Ⅲ)中交换OH^-/SH^-配体和硫的氧化会形成硫代砷酸盐[152－153]。一氧化二硫砷酸盐具有与As(Ⅴ)相似的毒性，其生成的酸碱度范围可以跨越pH 2.5～8.0[154－155]。与As(Ⅲ)和As(Ⅴ)不同的是，硫代砷酸盐与Fe(Ⅲ)的氢氧化物(FeOOH)的络合能力较小，因此更容易被水稻吸收[156]。S^{2-}/As(Ⅲ)比和S(0)/As(Ⅲ)比、pH值以及微生物的可用性等不同因素都会影响硫代砷酸盐的形成[152－154]。因此，在使用硫添加调控水稻吸收砷时，考虑硫代砷酸盐化学行为和毒性至关重要。

4.3　添加土壤改良剂

添加土壤改良剂可以改变土壤理化性质和土壤结构，如添加铁、锰和生物炭等添加剂，可以改变砷在土壤和根系中的吸附能力从而控制水稻对砷的吸收，在未来的在田间管理中具有较好的应用前景。

4.3.1　添加铁

外部添加铁(例如氧化铁、含铁工业副产品和混合铁源)可提高水稻土壤对砷的吸附能力，从而降低水稻中砷的积累。通过向土壤中添加铁而降低水稻对砷的吸收主要是应用了土壤中铁氧化物对砷的吸附能力。

首先，铁的改良剂可以直接影响稻田环境中铁的含量。当将Fe(0)和Fe(Ⅱ)化合物施用于稻田土壤时会被氧化，形成结晶度较差的铁氧化物[157]。在FeOOH的配位结构中，OH_2和OH取代砷离子形成单齿、双齿或双核桥连络合物[158－159]，促进砷吸附在FeOOH上。其次，铁的添加可以使得水稻根部形成Fe(Ⅲ)膜，从而吸附更多的As(Ⅴ)和As(Ⅲ)[45]。但是，由于稻田环境中氧化还原化学的变化，砷吸附到Fe(Ⅲ)铁膜上的过程是可逆的。在淹水条件下，随着氧化还原电位降低，铁膜和稻田土壤中的FeOOH还原为Fe(Ⅱ)[122]，会使得FeOOH上吸附的砷以As(Ⅲ)的形式释放到土壤溶液中。

施用铁添加剂时，需要考虑施用量的问题。铁源的比表面积和铁源的溶解度等吸附特性需要在施用到稻田土壤中之前进行评估，因为这些特性极大地决定了砷的吸附能力[160]。较高的铁施用量会使得水稻根部铁膜过厚，从而阻碍根部的养分吸收和氧气扩散[161]。

添加铁源还需要考虑土壤有机质、土壤理化性质及水稻的生长阶段等问题。例如，天然有机物可以被吸附到FeOOH上，从而减少了As(Ⅲ)和As(Ⅴ)吸附到FeOOH上[162]。同样，PO_4^{3-}与FeOOH具有很强的亲和力，也会抑制As(Ⅴ)吸附到FeOOH上[163]。铁改良剂对水稻谷粒中砷积累的影响还与植物的生长阶段有关。例如在谷粒成熟阶段，铁的添加显着降低了砷在水稻植株中的积累[164]。因此，随着水稻耕种地区的土壤理化性质的差异和植物生长阶段的不同，通过添加铁来控制水稻对砷的吸收其效果也会有偏差。

添加含铁改良剂在经济上有一定优势，但也需要考虑其局限性。比如，铁源添加也可能会引入其他污染物。同时，铁添加会导致土壤酸化，并对土壤理化性质及土壤中其他元素的吸附平衡产生进一步扰动。

4.3.2　添加锰

添加锰的主要作用是在根部形成锰斑块，从而吸附砷来控制水稻对砷的吸收。锰氧化物通常以细

颗粒或结核的形式存在于土壤中。有研究发现，在被砷污染的水稻土中，以1200mg锰/kg土的比率施用合成的锰氧化物（主要为菱锰矿），可使稻草和谷物中的总砷浓度降低30%～40%[165]。补充氧化锰会减缓稻田中Eh的降低[111]。

添加锰也有一定的局限性。已有研究表明锰氧化物由于其较低的零点电荷点pH（pH_{zpc}＝1.8～4.5）而不能将砷吸附在水稻土中[166]。在水稻成熟阶段，锰氧化物不再对砷起吸附作用[165]。此外，外源锰添加也可能带来新的污染，例如带来饮用水中的锰污染（锰含量400mg/L），从而增加人类健康的风险。过量的氧化锰在稻田土壤溶液中的溶解也会在水稻植株中引起生物毒性。

4.3.3 添加生物炭

生物炭是在低水平的有氧环境下热分解有机生物质（热解）产生的。通过添加生物炭可以控制水稻对砷的吸收，此方法具有很好的环境和经济效益[167-168]。生物炭的原料类型、热解温度、速率和时间都会决定它的理化性质［如pH、孔体积、孔径、官能团、pH_{zpc}、阳离子交换容量（CEC）等］和营养成分[169-170]。在污染的土壤中添加生物炭可以观察到金属迁移率和生物利用度的显著降低[171-172]。生物炭会增加土壤溶液中溶解的有机碳浓度，因此，As－DOC复合物的形成也会将砷吸附在稻田土壤中[96]。更重要的是，生物炭中通常含有磷和硅等与砷存在竞争吸收的元素。向土壤中施用5%和10%（质量比）的污水污泥生物炭，其PO_4^{3-}含量增加了3.5～4.9倍[96]，因此导致水稻籽粒中总砷吸收的减少。掺入富含Si的稻壳生物炭（1%）可使谷物中的无机砷降低30%[141]。此外，某些生物炭还可以减少水稻中无机砷和甲基砷的形态[96]，这可能是生物炭添加促进了可挥发砷的形成。

添加生物炭有时并不能降低水稻对砷的吸收，这与诸多复杂因素有关。有报道显示，某些生物炭也会导致砷在水稻谷粒和植株中的增加[173-174]。生物炭有较高的表面积和孔结构，会影响微生物的活动，为微生物的生长提供稳定的栖息地。例如生物炭的应用导致还原Fe（Ⅲ）细菌的含量增加。与稻草施用相比，与Fe（Ⅲ）还原密切相关的梭状芽胞杆菌、脱硫杆菌等的相对丰度增加[173]。生物炭中高浓度的盐含量导致土壤溶液中的电导率增加，并促进还原Fe（Ⅲ）的细菌与Fe（Ⅲ）矿物之间的电子转移[175]，使得残留在FeOOH中的As（Ⅴ）可以As（Ⅲ）的形式释放到土壤溶液中。此外，生物炭会改变水稻土壤中的理化性质，增加砷的释放。例如，生物炭的施用会增加土壤pH，导致可溶性矿物质溶解[174]，造成砷的释放。

生物炭的表面修饰对控制水稻吸收砷非常重要。铁和锰已经成功用于生物炭的表面修饰[176-177]。用零价纳米铁对生物炭进行改性会增加改性生物炭的表面积，从而显著增加生物炭中的反应位点[176]。因此，生物炭和铁或/和锰的复合材料可以减少水稻组织中砷的积累[174-178]。深入研究水稻土壤－水系统中砷形态与原始/改性生物炭之间相互作用以及最佳生物炭施用量，是未来通过施用生物炭减少水稻砷吸收的关键。

综上，表1总结了目前控制水稻吸收砷的主要农艺学方法、机理以及局限性。每种农艺学方法都具有控制水稻中砷含量的应用价值和潜力，但是也都同时存在局限性，因此，在实际使用时需要综合考虑各项因素，因地制宜，以达到最好的控制效果。

表1 降低水稻对土壤中砷吸收的主要农艺学方法及其主要机理和局限性

Table 1 Main agronomic methods for reducing the absorption of arsenic in soil by rice and its main mechanism and limitations

主要农艺学方法	主要机理	局限性
间接性灌溉/有氧水管理	防止As（Ⅴ）还原为As（Ⅲ），通过减少甲基化降低水稻对砷的吸收	水稻减产
施用磷肥	与As（Ⅴ）竞争吸收通道	成本高；带来新的砷和镉的输入；造成水体富营养化
施用硅肥	与As（Ⅲ）竞争吸收通道	成本高，需要控制施用比例和肥料类型
施用硫肥	参与砷的氧化还原，降低砷的有效性	产生硫代砷酸盐等二次污染物质；需考虑水稻品种
添加土壤改良剂（铁、锰、生物炭）	改变根系－土壤－添加剂之间对砷的吸附能力	改良剂中存在的重金属元素可能会对土壤造成新的污染；土壤酸化

5 结语和展望

鉴于全球尺度范围内人们对水稻的依赖程度以及水稻中砷吸收问题的普遍特征，开展水稻对砷的吸收机理及其影响因素的研究，探索实用有效的方法降低大米中的砷吸收，从全球尺度评估未来水稻对砷的吸收趋势、控制方法和水稻中砷的含量和形

态特征带来的人类健康风险，在未来环境科学、农业科学和食品安全等研究领域将继续占据重要的地位。

首先，物理化学方法及田间水管理等方法都可以控制稻田农业生态系统中砷进入水稻的含量，但是每种技术都有其优势和局限性。水稻农业生态系统中砷生物地球化学及水稻对砷的吸收和代谢等诸多因素都影响着水稻及谷粒中砷的浓度。综合考虑农艺活动对土壤中 pH、氧化还原条件、有机质结构和共存元素等因素的影响，考虑不同的地理因素、土壤特性、经济因素，是在生产实践中真正实现控制水稻对砷吸收的关键。在方法推广前，综合进行短期和长期的田间实验验证是必不可少的前提。

第二，除了田间水管理、施肥以及添加土壤改良剂等常见的农艺方法，还有一些其他方法也可以降低水稻大米中砷的含量。例如，在水稻田中同时耕种一些砷的超富集植物（如蜈蚣草）、藻类植物或植入一些新型的细菌改变土壤的氧化还原环境；此外，筛选并推广某些已有的对砷吸收能力较低的水稻品种，或者改良水稻品种的基因类型，使其降低对砷的吸收，也是当前的研究热点。

第三，温度升高会增强植物蒸腾作用和土壤中酶的活性，促进微量元素从有机物中释放出来，从而更容易被植物吸收[179]。面对全球气候变化等全球环境因素变化问题，评估粮食作物中砷的食品安全问题，尤其是水稻中砷的吸收问题具有很强的现实意义。

第四，东南亚等全球大米重要产地地质背景中砷的普遍释放作用极大地增加了水稻对砷的吸收，从而增加了人群砷暴露带来的健康风险，不同地区环境因素差异会导致大米中砷的含量、形态、毒性存在差异，并随着人群饮食结构的差异引发复杂的健康地质问题。因此，开展地质环境中砷释放带来的水稻砷的食品安全和健康问题也将是未来重要的研究方向。

最后，目前砷形态分析技术能定性和定量的砷种类还非常有限，这也限制了未来降低植物和人体对砷的吸收及加强食品安全领域的发展。今后主流的砷形态分析技术中需要进一步考虑如何改进前处理技术，减少砷在化学前处理过程中的形态转化，同时提升 LC－ICP－MS 技术分析过程中色谱的分离能力，实现通过 XAS 技术更科学地解谱和拟合，提高原位形态定性和定量分析的准确性，提升对 ng/g 甚至更低级别砷形态的定性和定量分析技术水平。

6　参考文献

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A Review of Research Progress on the Absorption Mechanism of Arsenic and Agronomic Pathways to Control Arsenic Absorption

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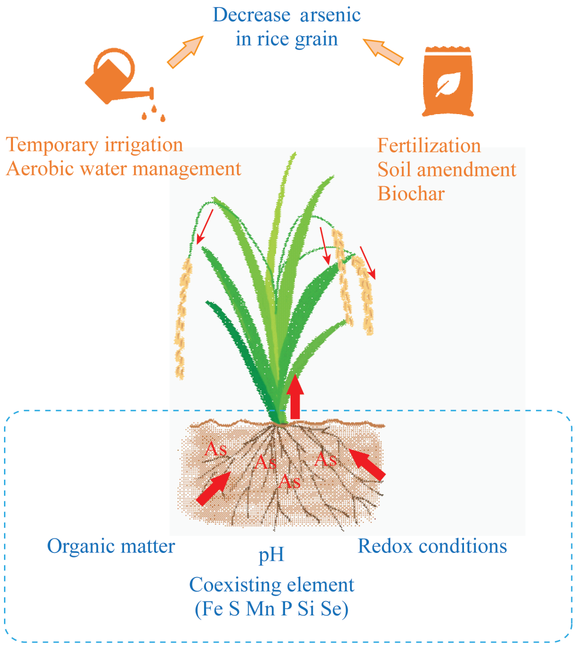
HIGHLIGHTS

(1) Soil pH, redox conditions, organic matter and coexisting elements are the key factors affecting As absorption by rice.

(2) The comprehensive use of field water management, fertilization and soil amendments is an important way to control the absorption of As in rice.

(3) Climate change may increase the level of As in rice on a global scale.

(4) Expanding the As speciation analysis is the key to carrying out research on the transport, transformation and toxicity of As in the environment in the future.


Decrease arsenic
in rice grain
Temporary irrigation
Aerobic water management
Fertilization
Soil amendment
Biochar
As
As
As
As
Organic matter
pH
Redox conditions
Coexisting element
(Fe S Mn P Si Se)

ABSTRACT

BACKGROUND: Rice is the staple food of about half of the world's population, and the dependence of Asian staple food on rice exceeds 90%. There are varying degrees of arsenic (As) pollution all over the world. As can accumulate in rice and enter the human body, causing health problems.

OBJECTIVES: To reveal the mechanism of As absorption in rice.

METHODS: The content and species characteristics of As absorbed by rice and the species analysis techniques were reviewed. The mechanisms of As absorption, tolerance and detoxification by rice were summarized.

RESULTS: The content of As in rice ranged from a few to several hundred ng/g. The process of As entering the rice from the soil involved complex physical and chemical changes and species transformation. Arsenic mainly existed in the form of arsenate, arsenite, thiol and methyl coordination in rice. Field water management, fertilization and soil amendments controlled the absorption of As in rice. Each technique had their advantages and disadvantages. Soil pH, redox conditions, organic matter and coexisting elements were the key factors affecting As absorption by rice. Agronomic methods can control the absorption of As by rice. Many factors such as arsenic biogeochemistry and the absorption and metabolism of arsenic in rice agroecosystems affect the concentration of arsenic in rice and grain. Comprehensive consideration of the effects of agronomic activities on soil pH, redox conditions, organic matter structure and coexisting elements, and different geographic factors such as soil characteristics and economic factors were the keys to realize the control of arsenic absorption by rice in production practice.

CONCLUSIONS: Comprehensive use of multiple agronomic methods for rice farming is an important way to control the absorption of arsenic in rice in the future. Application of new agronomic methods in the control of arsenic absorption by rice, the impact of climate change on arsenic absorption by rice, and application of non-destructive *in situ* and *in vivo* analysis techniques for As speciation analysis, are keys for more scientifically and effectively controlling the arsenic content in rice and reducing the risk of human As exposure on the global scale in the future. These are also the key development directions and challenges in the future.

KEY WORDS: rice; arsenic; iron plaque; aerobic irrigation; water management; fertilization; soil amendment; healthy geology