综 述 Reviews

水稻砷的吸收机理及阻控对策

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摘要: 水稻积累砷的能力较其他农作物强, 稻米是我国人群从食品中摄入无机砷的主要来源, 降低稻米砷含量对增进农产品质量安全有重要意义。本文阐述了稻田砷的生物地球化学转化特征及水稻对不同形态砷的吸收、运输与储存机理, 提出阻控稻米砷积累的对策, 并讨论了需要进一步研究的问题。

关键词: 砷; 水稻; 吸收; 运输; 阻控

Mechanisms of Arsenic Uptake by Rice and Mitigation Strategies

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Abstract: Rice has a greater ability to accumulate arsenic in the grain than other cereal crops. Consumption of rice constitutes a major dietary source of inorganic arsenic for the population in China. Decreasing arsenic accumulation in rice is of great importance to food safety. Here, the biogeochemical transformations of arsenic in the paddy environment and the mechanisms of arsenic uptake, transport and storage in rice are reviewed. Strategies to mitigate excessive arsenic accumulation in rice are discussed. Knowledge gaps are also identified.

Key words: arsenic; rice; uptake; transport; mitigation

无机砷是致癌物质, 人体无机砷的摄入主要来自饮用水和食物。稻米是食物中无机砷的最重要来源, 大约占我国人群无机砷平均摄入量的60% (Li等2011)。近年来, 稻田砷生物地球化学循环、水稻砷的吸收与运输机制、稻米砷对人体的健康风险等问题引起国内外学者的高度重视(Zhu等2008; Zhao等2010b; Gilbert-Diamond等2011; Meharg和Zhao 2012; Banerjee等2013)。本文围绕以上几方面内容加以阐述, 并提出阻控水稻砷积累的措施。

1 稻田砷的生物地球化学循环特征

稻田的季节性淹水与排水, 驱动了土壤中一系列的氧化还原反应, 对砷的循环及其生物有效性产生了深刻的影响。随着稻田土壤的淹水, 土壤中微生物的活动导致氧气、硝酸盐等电子受体的耗竭, 紧接着便是锰、铁氧化物及五价砷[As(V)]的还原(Borch等2010)。铁氧化物是土壤固相中吸附As(V)的主要物质, 它们的还原与溶解导致吸附的砷进入土壤溶液(Takahashi等2004; Xu等2008; Stroud等2011; Yamaguchi等2011)。此外, As(V)还原为三价砷[As(III)]后, 被土壤固相吸附的强度降低, 也导致更多的砷从固相解吸进入土壤溶液(Takahashi等2004; Yamaguchi等2011)。土壤中的还原反应往往伴随着质子的消耗(pH上升), 这个过程也促进砷[尤其是As(III)]的解吸(Yamaguchi等2011)。好氧条件下土壤溶液砷[主要是As(V)]浓度一般不超过1 $\mu mol \cdot L^{-1}$ (Zhao等2010b), 而在淹水条件下, 有些砷污染水稻土的土壤溶液砷[主要是As(III)]浓度可高达80 $\mu mol \cdot L^{-1}$ (Stroud等2011)。因此, 稻田淹水导致土壤砷的溶解度和生物有效性大幅度增加(Takahashi等2004; Xu等2008; Li等2009b; Stroud等2011), 这是水稻与其他旱作作物相比积累较多砷的一个重要原因, 将水稻旱作或进行干湿交替可以大幅度降低稻米砷的含量(Xu等2008; Li等2009b; Norton等2012b)。

稻田土壤淹水所产生的还原性条件还促进了

砷的甲基化。砷的甲基化由土壤微生物介导, 由砷甲基转移酶所催化, 其编码的基因(*arsM*)已经在多个微生物中被克隆并验证了功能(Qin等2006, 2009; Yin等2011)。土壤中哪些微生物参与了砷甲基化目前还不清楚。已知一些厌氧的硫还原菌和甲烷产生菌含有*arsM*基因(Lomax等2012; Jia等2013a; Zhao等2013a), 处于淹水还原条件下的水稻土可能有利于厌氧的砷甲基化菌生长及活性, 从而促进砷的甲基化。种植于旱作条件下的水稻籽粒甲基砷含量极低, 而淹水条件下的水稻籽粒甲基砷含量大幅度增加(Xu等2008; Li等2009b)。向土壤施加有机质也会促进砷的甲基化、砷的挥发和水稻对甲基砷的积累(Mestrot等2009, 2011; Huang等2012; Jia等2013b)。不同地方生产的稻米砷形态有明显差异, 亚洲稻米往往以无机砷为主(约80%), 产自美国南部的稻米二甲基砷(DMA)可占一半以上, 欧洲稻米介于二者之间, 这些地域性差异可能与土壤微生物区系有关(Zhao等2013b)。

水稻根际的特异性对砷循环有着重要影响。为了适应淹水还原条件, 水稻根系通过其通气组织向根际释放氧气, 导致亚铁氧化并在根表形成以水铁矿为主要成分的红棕色铁膜(Liu等2006; Frommer等2011)。铁膜对砷[尤其是As(V)]有很强的吸附能力, 因此, 水稻根表铁膜往往富集较高浓度的As(V) (Liu等2006; Seyfferth等2010; Frommer等2011)。铁膜对水稻砷吸收及向地上部运输的影响较为复杂, 短期试验中, 铁膜降低了水稻根系对As(V)的吸收, 但增加了对As(III)的吸收(Chen等2005)。有些研究表明铁膜形成可以降低水稻地上部砷的积累(Deng等2010; Lee等2013), 另一些研究则显示铁膜对As(III)在水稻地上部积累有促进作用(Liu等2005)。不同水稻品种铁膜形成能力与地上部或籽粒砷的积累往往没有显著相关(Liu等2006; Lee等2013)。铁膜的复杂效应可以从以下几方面加以解释, 一方面, 铁膜的形成促进根表砷的富集; 另一方面, 铁膜又起到阻碍根系吸收砷[尤其是As(V)]的屏障作用; 此外, 新生根及根尖一般没有铁膜覆盖(Seyfferth等2010), 而这些又是养分和污染物吸收的主要部位。铁膜形成的总量不一定反映根表铁膜的覆盖率, 而后者可能与铁膜的屏障效应关系更为密切。有研究表明, 不同水稻品种根系的泌氧能力与水稻籽粒和秸秆砷含量有显著的负相关(Mei等2009), 这可能与根表铁膜形成有关(Mei等2012), 但也可能与根际As(III)氧化能力关系更为密切, 因为As(III)氧化为As(V)后更容易被铁膜吸附。

2 水稻吸收砷的机理

淹水条件下的水稻土壤溶液中砷的形态以As(III)为主, 通常占70%~90%, 其余的部分为As(V)和少量的甲基砷[单甲基砷(monomethylarsonic acid, MMA)和二甲基砷(dimethylarsinic acid, DMA)] (Khan等2010; Stroud等2011; Zhao等2013a)。由于不同形态砷的化学性质不同, 植物根系对它们的吸收机理也不同。

亚砷酸(H_3AsO_3)有较高的解离常数(pK_a=9.2), 因此, 在土壤及植物细胞内通常的pH条件下(pH<7.5), As(III)主要以非解离的中性分子存在。近年来的研究表明, 水稻根系主要通过两种不同类型的细胞质膜转运体将As(III)吸收进入根系并向木质部装载(Ma等2008)。第一种类型是NIP水通道蛋白, 负责将As(III)吸收进入细胞中, 水稻根系中OsNIP2;1 (即Lsi1)的表达量很高, 主要表达在外皮层和内皮层细胞膜的向外一侧, 是吸收As(III)的主要途径; 第二种类型是Lsi2, 它是一种介导底物外溢的膜转运体, 表达量也很高, 主要表达于外皮层和内皮层细胞膜向内的一侧, 负责将细胞内的As(III)朝中柱方向的质外体溢出(Ma等2008)。这两类转运蛋白的主要功能是吸收运输硅(Si) (Ma等2006, 2007), 由于亚砷酸(H_3AsO_3)的物理化学性质与硅酸(H_4SiO_4)较为相似, 因此可以通过Lsi1和Lsi2非专性地吸收进入水稻根系。与Lsi1相比, Lsi2对砷在水稻地上部累积的作用更大(Ma等2008), 说明砷向木质部的输送是控制地上部砷积累的关键步骤。水稻是硅的超积累植物, 其含量大大超过其他矿质元素, 硅对水稻的抗逆能力起到重要的作用, 因此水稻吸收硅的能力很强, 吸收As(III)的能力也很强。水稻之所以积累较多砷, 一方面是稻田的还原条件导致As(III)活化, 另一方面是水稻根系拥有旺盛的Si/As(III)吸收途径(Zhao等2010b)。水稻吸收硅和As(III)能力强的另一个重要原因在于Lsi1和Lsi2的极性分布有利于这些底物向中柱的运输(Ma等2006, 2007), 大麦和玉米中

与水稻同源的Lsi2也具有转运Si的功能, 但它们在大麦和玉米根系内皮层细胞膜上的分布没有极性(Mitani等2009), 这一特征可能解释了在同样条件下大麦向木质部装载及向地上部运输As(III)的能力显著低于水稻(Su等2010)。

除OsNIP2;1之外, NIP水通道蛋白的其他成员对As(III)也具有不同程度的透性(Bienert等2008; Ma等2008; Kamiya等2009; Zhao等2009), 而对硅酸的透性仅局限于少数几个成员。通过定向突变改变NIP蛋白结构中影响底物选择性的过滤器氨基酸残基, 对硅酸透性的影响也大于对As(III)透性的影响(Mitani-Ueno等2011)。这些结果表明NIP通道蛋白对As(III)的选择性较低。硅积累能力低的植物, 可以通过对硅酸无透性的NIP通道蛋白(如拟南芥的AtNIP1;1)吸收As(III) (Kamiya等2009)。

与As(III)不同, As(V)的化学性质与磷酸盐相似, 因此As(V)主要通过磷酸盐吸收途径进入植物根系细胞(Zhao等2009)。在水培试验中, 水稻Os-PHF1 (phosphate transporter traffic facilitator 1)和OsPT1突变体吸收磷和As(V)的能力大幅度降低, 而过量表达磷酸盐转运体OsPT8或OsPT1则显著提高水稻对磷和As(V)的吸收(Wu等2011; Kamiya等2013), 这些结果充分说明了As(V)与磷酸盐共享吸收途径。As(V)对磷酸盐吸收途径具有反馈调控作用, As(V)胁迫抑制了缺磷对*OsPT2*、*OsPT4*和*OsPT8*等基因表达的诱导(Kamiya等2013), 从而减少对As(V)的吸收。有证据表明, As(V)不但迅速抑制拟南芥磷酸盐转运体*AtPHT1;1*的表达, 而且使AtPHT1;1蛋白从质膜上下载并通过内吞途径进入液泡, 这个过程与WRKY6转录因子的参与有关(Castrillo等2013)。水稻是否存在类似拟南芥的负调控机制目前尚不清楚。转录组学研究表明, As(V)或As(III)胁迫对水稻很多基因表达产生正的或负的调控(Norton等2008; Yu等2012)。虽然As(V)与磷酸盐共享吸收途径, 但是在淹水栽培条件下, 由于As(V)不是砷的主要形态, 或者由于As(V)容易被根表铁膜吸附, 磷酸盐吸收途径对水稻砷的积累贡献不大(Wu等2011)。

As(V)和磷酸盐的一个重要差别在于前者很容易被还原, 而后者则很难被还原。即使在供应As(V)的条件下, 多数植物体内砷以As(III)的价态

为主(Zhao等2009), 说明植物具有较高的As(V)还原能力。以前认为植物中催化As(V)还原的主要酶是ACR2 (Dhankher等2006), 但是拟南芥ACR2突变体As(V)的还原能力并没有下降(Liu等2012), 由此推测植物体中可能存在多种As(V)还原酶。水稻含有2个*ACR2*基因序列, 在大肠杆菌或酵母异源表达时具有还原As(V)的能力(Duan等2007), 但在水稻体内的功能尚不清楚。As(V)在水稻或其他植物根系中还原后, 所形成的As(III)很容易被排放到介质中(Xu等2007; Liu等2010; Zhao等2010a), 外溢的As(III)可占吸收的As(V) 60%~80%, 如果没有As(III)的外溢, 植物在吸收As(V)之后的砷积累量将大幅度增加。As(III)外溢可能通过具有双向透性的NIP水通道蛋白(Zhao等2010a), 还可能有其他未知膜转运体参与。将酵母的As(III)外溢转运体ACR3在水稻中过表达, 可以促进As(III)外溢并减少水稻对砷的积累(Duan等2012)。

除了无机砷外, 水稻籽粒还含有一定量的有机砷, 可占总砷含量的10%~90% (Zhao等2013b), 其主要形态是DMA, 有些样品还含有少量MMA和四甲基砷。以前认为, 植物本身具有将无机砷甲基化的功能(Nissen和Benson 1982), 最近的研究结果表明, 植物中的甲基砷来自于土壤或生长介质中的微生物, 植物本身很可能不具有将砷甲基化的能力(Jia等2012; Lomax等2012)。水稻对甲基砷的吸收速率低于无机砷(Abedin等2002), 这可能与甲基化降低了底物的亲水性有关。MMA和DMA具有较低的pK_a (分别为4.2和6.1), 因此在土壤溶液中呈解离和不解离的形态, 不解离的MMA和DMA可以通过水稻根系的Lsi1 (OsNIP2;1)通道蛋白进入细胞中, *lsi1*突变体吸收MMA和DMA的能力与野生型相比分别下降了80%和50% (Li等2009a), 而硅酸/As(III)的外溢转运体Lsi2则不能运输甲基砷。MMA和DMA解离的比例随介质pH升高而增加, 而水稻对二者的吸收则随着pH升高而下降, 表明不解离的MMA和DMA是水稻吸收的主要形态(Li等2009a)。

3 水稻砷的储存与长距离运输

As(III)与巯基的亲和性强, As(III)与蛋白质的巯基结合可影响酶的蛋白构型及活性, 影响一系列的代谢过程。As(III)可与1~3个巯基结合, 结合

强度随着巯基的数目增加而增加, 因此, As(III)特别容易与含有2~3个相邻巯基的蛋白质或多肽结合。体外实验表明, 当多肽的两个半胱氨酸巯基相邻距离少于14个氨基酸残基(CX$_{0~14}$C)时, 与As(III)结合能力较强(Kitchin和Wallace 2006)。根据拟南芥基因组预测的35 386个蛋白质中, 有23 578个蛋白具有间隔0~14氨基酸残基的双巯基, 其中11 559个蛋白可以与As(III)形成三巯基结合(Finnegan和Chen 2012)。质体丙酮酸脱氢酶复合体中的硫辛酰胺脱氢酶含有相邻的二巯基, 是拟南芥植物受As(III)毒害的一个重要靶标(Chen等2010)。

植物解毒As(III)的主要机理是合成富含巯基的植物螯合素(phytochelatins, PCs), 络合As(III), 并进一步将As(III)-PC络合物运输进入液泡中加以储存。植物体内存在多种As(III)-PC或As(III)-PC/GSH络合物(Raab等2005; Liu等2010; Zhang等2012)。与PCs的络合及在液泡中储存不但对解毒As(III)起重要作用(Ha等1999; Liu等2010), 而且降低了As(III)在植物体内的移动性(Liu等2010; Duan等2011)。采用同步辐射X-射线荧光光谱和纳米二次离子质谱技术研究表明, As与S (硫)大量富集于水稻根系中柱鞘、内皮层、茎节及叶鞘的韧皮部陪伴细胞的液泡中, 二者有极为密切的相关性(Moore等2011, 2014), 这也暗示水稻中砷的主要储存形态是As(III)-PC或As(III)-PC/GSH络合物。已知ABCC1/2是拟南芥液泡膜上运输PCs或As(III)-PC的转运体(Song等2010), 类似功能的水稻转运体还未见报导。

砷可以通过木质部和韧皮部进行长距离运输, 非超积累植物体内无机砷的移动性总体较低(Zhao等2009)。与其他非超积累植物相比, 水稻是木质部As(III)移动性较强的植物(Zhao等2009; Su等2010)。即便如此, 在短期(2~4 d)试验中水稻根系吸收的^{73}As标记As(III)仅有10%运输到地上部, 其中仅3.3% (即根系总吸收量的0.33%)运输到穗子, 将As(III)供应给水稻旗叶, 2 d内叶片吸收的标记As有2%~3%运输到穗子(Zhao等2012)。无机砷由根系向地上部运输的途径是木质部, 而向水稻籽粒运输的主要途径则是韧皮部(Carey等2010; Zhao等2012)。水稻茎节中富含多种维管束组织, 对养分及污染元素在叶片和穗之间的分配起重要作

用。节比茎、叶含有更高浓度的砷, 其中韧皮部陪伴细胞液泡是砷富集的主要场所(Moore等2014), 这可能起到防止砷向韧皮部筛管装载的作用。

与无机砷相比, 甲基砷(尤其是DMA)在木质部和韧皮部的移动性要高得多(Carey等2010, 2011; Ye等2010)。在水培试验中, 水稻根系供应DMA的籽粒与茎叶As浓度比例是供应无机砷的100倍以上(Lomax等2012)。DMA在植物体内的高移动性可能与其不能为PCs络合继而不能在液泡中储存有关, 这也解释了为什么DMA倾向于在水稻籽粒中富集。此外, DMA与无机砷在水稻籽粒中的分布也有所不同, 无机砷主要富集于籽粒表皮的维管束迹(ovular vascular trace), 而DMA更容易进入胚乳中(Carey等2010; Zheng等2013)。如果稻米砷以无机形态为主, 糙米加工为精米可以显著降低砷的浓度, 但米糠则含有较高浓度的无机砷(Sun等2008)。关于不同形态砷在韧皮部装载与卸载机理目前仍不清楚。

4 阻控稻米砷累积的对策

稻田水分管理是阻控水稻砷吸收的有效措施。旱作、干湿交替或垄沟栽培方式均可降低水稻土中砷的活化, 从而减少水稻砷吸收和在籽粒中的积累(Xu等2008; Li等2009b; Zhao等2010b; Norton等2012b), 但是会增加重金属镉的吸收(Arao等2009; Meharg和Zhao 2012; Hu等2013), 因此不宜在镉污染的稻田采用。

硅是水稻的重要养分。由于As(III)主要通过硅的吸收途径进入水稻, 硅酸可以竞争性地抑制As(III)的吸收(Ma等2008), 此外, 水稻在高硅条件下$Lsi1$和$Lsi2$表达下调, 也会导致As(III)吸收减少。不同水稻土中硅的有效性与水稻砷的积累呈显著的负相关(Bogdan和Schenk 2008; Khan等2010)。在温室盆栽试验中, 施用硅肥可显著降低水稻砷的吸收及籽粒中无机砷的浓度(Li等2009b), 但是会增加DMA的浓度, 这是因为硅可以减少DMA被土壤固相吸附或增进DMA解吸, 从而提高其对水稻的有效性(Liu等2014)。与无机砷相比, 五价的DMA对动物和人体的毒性较小, 但是如果五价的DMA被还原为三价的DMA, 则毒性大幅度增强(Styblo等2000; Zhao等2013b)。

不同水稻品种稻米砷含量差异较大, Norton等

(2012b)比较了300多个品种在不同环境条件下籽粒砷浓度的差异, 发现变幅为3.5~35倍。虽然基因型与环境的交互作用较为明显, 但是仍然可以选出一些在不同环境条件下具有稳定的低积累表型的品种(Norton等2012b), 指明了通过品种筛选和培育低砷品种的可能性。关于水稻籽粒砷积累的遗传基础仍然不甚清楚, 已有一些研究报导了控制籽粒砷含量的QTLs及上位互作效应(Zhang等2008, 2014; Norton等2010, 2014), 但是这些QTLs往往因不同试验条件或不同遗传群体而异, 此外, 抽穗期长短对籽粒砷含量也可能有间接影响(Norton等2012a)。

国内外对采用砷超积累植物修复砷污染土壤已进行了大量研究。在温室盆栽条件下, 种植蜈蚣草(*Pteris vittata*)可以显著降低土壤砷的有效性并降低水稻籽粒砷(尤其是DMA)的含量(Ye等2011)。这种植物修复方法在大田条件下的效果如何, 尚需进一步研究。

5 展望

近年来关于稻田砷的生物地球化学循环及水稻吸收砷的机理研究取得了很大进展, 但是仍有许多问题有待进一步研究。例如, 稻田土壤中介导砷氧化、还原、甲基化的主要微生物群落及关键功能基因, 影响水稻根际砷生物有效性的关键因子, 水稻As(V)还原及As(III)外溢的基因, 液泡储存砷的机理, 砷在韧皮部装载及向籽粒运输的机理, 水稻品种间砷积累自然变异的遗传基础及分子育种技术等。今后的研究应加强应用遗传和分子生物学手段, 应用离子组学方法(Salt等2008), 结合现代分析化学及亚细胞砷形态定位技术(Zhao等2014), 揭示不同形态砷的吸收、运输机理及调控网络, 为有效阻抗稻米砷的积累提供理论依据和技术途径。

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