

· 综述 ·

砷耦合还原的微生物协同机制及其环境效应

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毛腾, 陈国梁, 屈志慧. 砷耦合还原的微生物协同机制及其环境效应[J]. 生物工程学报, 2024, 40(12): 4480-4492.

MAO Teng, CHEN Guoliang, QU Zhihui. Microorganism-mediated arsenic reduction and its environmental effects[J]. Chinese Journal of Biotechnology, 2024, 40(12): 4480-4492.

摘要: 砷(arsenic, As)是一种常见的有毒污染元素, 微生物介导的砷形态转变是砷生物地球化学循环的重要组成部分。在砷的各类微生物代谢过程中, 砷的耦合还原对环境影响较大, 也是容易被忽视的过程。本文主要从砷的生物地球化学循环出发, 介绍了甲烷氧化、厌氧铵氧化、铁(Fe)-硫(S)氧化与砷耦合还原的微生物协同机制, 有机质、pH 值以及氧化还原电位是影响砷耦合还原的主要因素。砷经耦合还原后, 毒性和迁移性大大增加, 可能会增加砷污染的风险。因此, 进一步明确碳(C)、氮(N)、Fe、S 等这些元素在砷耦合过程中的影响以及挖掘出更多的微生物耦合还原过程, 在防治砷污染方面具有重要意义。

关键词: 砷; 生物地球化学循环; 耦合还原; 微生物

Microorganism-mediated arsenic reduction and its environmental effects

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Abstract: Arsenic (As) is a common toxic pollution element. The microorganism-mediated

资助项目: 湖南省自然科学基金(2023JJ30230); 湖南省教育厅优秀青年基金(21B0451); 湖南省教学研究与改革项目(HNJG-2022-0174); 大学生创新创业训练计划(S2024105340120)

This work was supported by the Natural Science Foundation of Hunan Province (2023JJ30230), the Outstanding Youth Fund of Hunan Provincial Education Department (21B0451), the Teaching Research and Reform Project of Hunan Province (HNJG-2022-0174), and the National College Students' Innovation and Entrepreneurship Training Program (S2024105340120).

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Received: 2024-07-01; Accepted: 2024-09-06; Published online: 2024-09-06

transformation of arsenic forms is an important part in the biogeochemical cycle of As. In the various microbial metabolic processes involving As, the coupling reduction of As has a great impact on the environment and is a process that is easily overlooked. From the biogeochemical cycle of As, this review introduces the microorganism-mediated methane oxidation, anaerobic ammonium oxidation, and iron (Fe)-sulfur (S) oxidation coupled with As reduction. Organic matter, pH, and redox potential are the main factors affecting the coupling reduction. After the coupling reduction, the toxicity and migration of As are greatly enhanced, which may increase the risk of As pollution. Therefore, it is of great significance to clarify the influences of carbon, nitrogen, Fe, S and other elements on the coupling process and explore more microbial processes coupled with As reduction for the prevention and control of As pollution.

Keywords: arsenic; biogeochemical cycle; coupling reduction; microorganism

砷(arsenic, As)是一种有毒元素,常伴生于各种黑色或有色金属如煤、铁、金、铜、铅、锌、锡等矿产资源中,并随着这些矿产资源的开发和利用,逐渐释放至地表环境^[1-2]。目前在全球范围内,包括来自印度、巴基斯坦、孟加拉国、美国以及中国等国家的数百万人受到砷污染的影响^[3]。由于受污染土壤和地表水中过高的砷含量,砷污染在许多国家和地区引起了广泛关注^[4]。

在各种无机砷化合物中,As(V)毒性相对较小,通常以稳定的矿物形式存在,然而亚砷酸盐 As(III)毒性大且具有较强的流动性,往往更容易进入生物体内^[5]。与其他重金属不同,砷甲基化产物中,三价有机砷化合物的毒性甚至要高于三价无机砷,五价有机砷则相反,即毒性大小为三甲基胂(trimethyl-arsine, TMA)^{III} > 单甲基胂(monomethyl-arsine, MMA)^{III} > 二甲基胂(dimethyl-arsine, DMA)^{III} > As(III) > As(V) > MMA^V ≈ DMA^V > 三甲基氧化胂(trimethyl arsenic oxide, TMA₂O)。微生物甲基化挥发的最终产物 TMA₂O 以及在海洋中发现的砷甜菜碱和砷胆碱等有机形式的砷毒性远低于无机砷^[6]。

微生物的种类繁多,在自然界中承担着重要的生态功能^[7],在砷的生物地球化学循环过程中微生物也发挥着重要作用,如戴尔福特菌

(*Delftia* sp. BAs29)^[8]、赖氨酸芽孢杆菌(*Lysinibacillus* sp.)和沙福芽孢杆菌(*Bacillus safensis*)^[9];罗氏砷杆菌(*Arsenicibacter rosenii* SM-1)^[10]和硫酸盐还原菌(*Desulfuromonas*)^[11-12];不动杆菌(*Acinetobacter gandensis*)和代尔夫特食酸菌(*Delftiatsuruhatensis*)^[13];脂环酸芽孢杆菌(*Alicyclobacillus mali* FL18)^[14]和短波单胞菌(*Brevundimonas aurantiaca* PFAB1)^[15]等微生物可以分别通过对砷的氧化还原、甲基化、巯基化等作用降低砷的生物毒性^[16]。最近的一些研究表明,微生物介导的砷耦合还原对周边环境有着较大的影响^[15-16]。本文主要从砷的生物地球化学循环出发,详细介绍了砷在土壤及地下水中耦合还原微生物的协同机制,并探讨了微生物砷耦合还原对环境的影响,以期对砷污染的防治提供支持。

1 砷的生物地球化学循环

砷的生物地球化学循环是一种复杂的现象(图1)。土壤及水体中的无机砷可以通过微生物的氧化还原及甲基化过程转化为有机砷并挥发到大气中,从而将砷以气态形式释放并迁移,挥发性含砷化合物在大气中被氧化,然后随雨水或大气干沉降进入土壤或水中,最终完成砷在土壤、水体和大气中的循环^[17]。

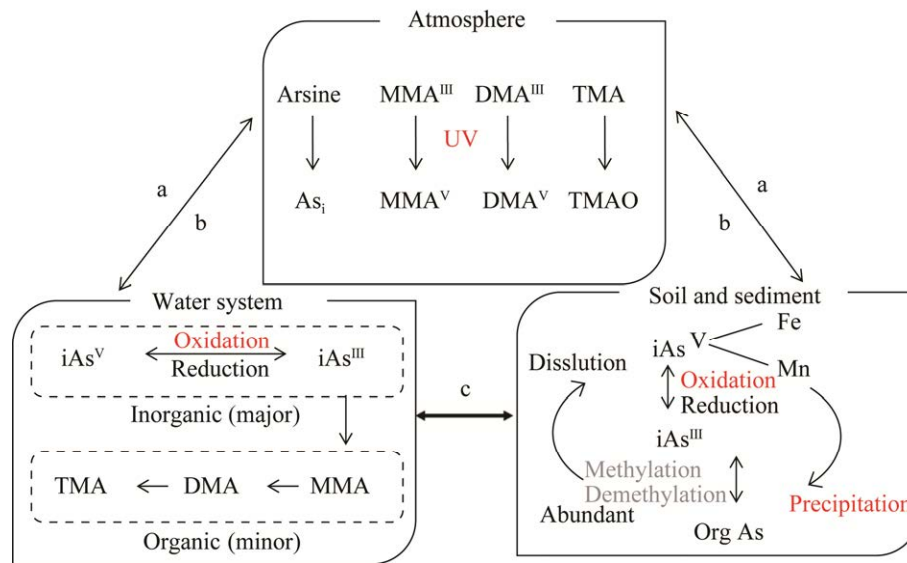


图1 砷的生物地球化学循环^[17] a: 微生物砷甲基化及挥发; b: 大气沉降; c: 表面吸附、溶解-沉淀、氧化-还原、有机螯合、微生物作用等

Figure 1 Arsenic biogeochemical cycles^[17]. a: Microbial ss methylation and volatilization; b: Atmospheric subsidence; c: Surface adsorption, solution-precipitation, oxidation-reduction, organic chelation, Microbial action, etc.

微生物直接或间接的砷代谢活动是砷地球化学行为的主要驱动力。微生物对砷的转化(砷的生物地球化学过程)包括氧化还原、甲基化和去甲基化、有机螯合、表面吸附和解离以及离子共沉淀^[18]。其中,砷还原、有机砷的去甲基化和吸附砷的解离形成剧毒的As(III),导致砷的迁移率和毒性增加,而砷氧化、甲基化、有机螯合和共沉淀产生的挥发性甲基砷(例如DMAs和TMAs)、有机砷和硫化砷毒性较小,可有效减少砷的生物毒性^[17]。

微生物不同代谢过程的主要功能基因如表1所示。

2 砷耦合还原微生物协同机制

砷的化学形态在很大程度上决定了砷的迁移和毒性^[4]。砷的耦合还原在自然界中广泛存在,是由多种微生物共同作用,不仅限于砷还

原菌,如甲烷氧化耦合砷还原^[20-21]、地下水中As-C-N-S微生物耦合代谢过程中砷还原^[20-21]、土壤中As-Fe-S微生物的氧化还原过程中砷的还原释放等^[22]。砷经耦合还原后,由As(V)结合态转变成了更易迁移、更易溶解也更具毒性的As(III),极大地促进了砷的释放,从而增加砷污染环境的风险。

表1 微生物不同代谢过程的主要功能基因^[19]

Table 1 Main functional genes of different microbial metabolic processes^[19]

Metabolic process	Major functional gene
Arsenic reduction	<i>arrA, arrB, arrC, arrD, arsD, ACR2</i>
Arsenic oxidation	<i>aioA, aioB, arxA, arsC</i>
Organoarsenic oxidation	<i>arsH, arsV</i>
Methylation and demethylation	<i>arsM, ArsI</i>
Migration and transport of arsenic	<i>Acr, arsB, arsA, arsP, arsW, arsK</i>

2.1 甲烷氧化耦合砷还原

在过去的 30 年中,全球大气甲烷平均含量的增加引起了科学界的极大关注^[23]。微生物厌氧甲烷氧化(anaerobic oxidation of methane, AOM)在甲烷调节中发挥重要作用,有助于减少海洋和淡水生态系统中甲烷的释放^[24]。最初的研究发现 AOM 与海洋生态系统中的硫酸盐还原耦合,其中厌氧甲烷氧化古细菌(anaerobic methane oxidation archaea, ANME)是主要的功能微生物^[25]。随后,AOM 与硝酸盐/亚硝酸盐的还原耦合过程也得到了广泛研究^[26-27]。近年来,有研究证明一些重金属也可以作为电子受体与 AOM 耦合而被还原,如 Fe(III)、Mn(IV)、Cr(VI)、Se(VI)、V(V)、Sb(V)等^[28-30]。

AOM 耦合砷还原于 2020 年在湿地土壤中首次被报道,Shi 等^[20]将 7 个不同地区砷酸盐污染的湿地土壤作为研究对象,并使用同位素标记的甲烷进行实验,发现 AOM 和砷酸盐还原耦合释放的砷占土壤砷释放总量的 26%–49%,其中砷以溶解性高和毒性大的亚砷酸盐形式存在。研究人员利用定量 PCR 技术和宏基因组学分析,定位了甲烷氧化和砷还原的活性基因,揭示了参与耦合反应的功能微生物,并重构了甲烷厌氧氧化耦合砷还原的生物学代谢通路^[20],结果表明甲烷氧化古菌首先通过逆向产甲烷途径活化甲烷并获得电子,随后电子被传递至细胞周质中的砷还原酶或者共生的砷还原菌中,进一步实现了砷还原(图 2)。

此外,研究还发现一类好氧产甲烷菌可能耦合非产甲烷菌微生物还原砷酸盐,但在这个过程中需要氧化甲烷的产物(甲醇或甲酸盐)来作为以上这两种微生物群体的电子载体^[31]。根据热力学方程(1)–(7)^[31]可知,当 1 mol 甲烷氧化时,好氧甲烷氧化耦合砷酸盐可以比 AOM 耦合砷酸盐还原释放更多的能量。

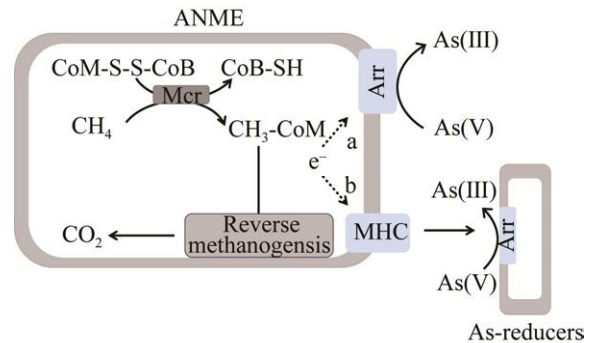
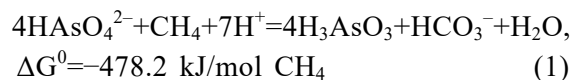


图 2 厌氧甲烷氧化耦合砷酸盐还原微生物机制^[20]

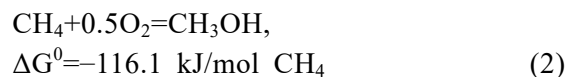
a: 厌氧甲烷氧化古菌独立进行氧化还原耦合过程; b: 厌氧甲烷氧化古菌通过逆向产甲烷途径产生电子, 然后通过多血红细胞色素转移至砷酸盐还原微生物中完成耦合过程. Mcr: 甲基辅酶; MHC: 多血红素细胞色素; Arr: 呼吸砷酸盐还原酶; ANME: 厌氧甲烷氧化古细菌.

Figure 2 Microbial mechanism of anaerobic methane oxidation coupled with arsenate reduction^[20]. a: Anaerobic methane oxidizing archaea independently carry out the REDOX coupling process; b: The anaerobic methane-oxidizing archaea produce electrons through the reverse methanogenic pathway, which may then be transferred to arsenate reducing microorganisms through polyhaemoglobin cytochrome to complete the coupling process. Mcr: methyl-coenzyme M reductase; MHC: Multi-haem cytochrome; Arr: Respiratory arsenate reductase.

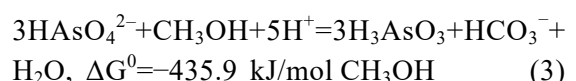
AOM 与砷酸盐还原耦合反应:



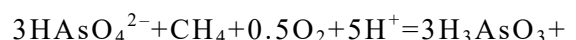
甲烷氧化制甲醇:

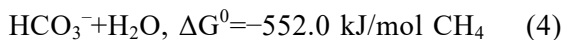


甲醇基砷酸盐还原:

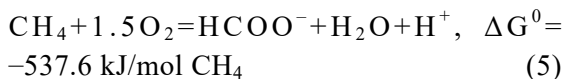


甲醇连接的整体反应:

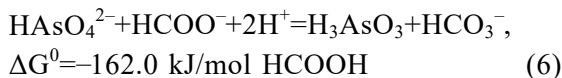




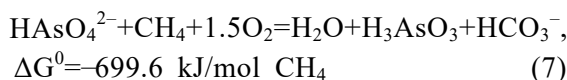
甲烷氧化制甲酸盐:



甲酸盐基砷酸盐还原:



甲酸盐连接的整体反应:



Shi 等^[32]对实验室培养物和田间土壤样品

进行了微观培养,发现了在甲烷、氧气和砷酸盐共存的情况下,好氧甲烷氧化(aerobic methane oxidation, aeMO)与砷酸盐还原耦合的微生物协同途径;研究表明,环境中砷酸盐还原对甲烷氧化的依赖性极强,该过程中的主要功能微生物是分属于变形菌门(Proteobacteria)和疣菌门(Verrucomicrobia)的需氧产甲烷菌,同时也证明了甲酸盐是还原砷酸盐的种间电子载体。该过程由需氧甲烷氧化菌和伯克霍尔德氏菌的协同作用完成(图3)。与之前的AOM耦合砷酸盐还原不同,这个过程需要微量的氧气来活化甲烷,氧是一种比砷酸盐更有利的热力学受体^[33],因此,在缺氧环境中,甲烷氧化消耗大量氧气后,共存的砷酸盐可以更有效地被还原。同时,该研究^[33]也表明了,在缺氧的情况下,AOM耦合效应强于aeMO,而在氧气存在的情况下则相反。在这两个耦合过程中,甲烷最终被氧化为CO₂的同时也为砷酸盐还原提供了电子载体(甲酸盐),而还原产物As(III)具有更大的毒性和生物利用度,会对生态系统的健康构成严重威胁。

2.2 微生物 As-N-S-Fe 耦合代谢过程中砷还原

砷的生物地球化学循环与N、S、Fe等其他元素循环密切相关,由于功能性微生物群落

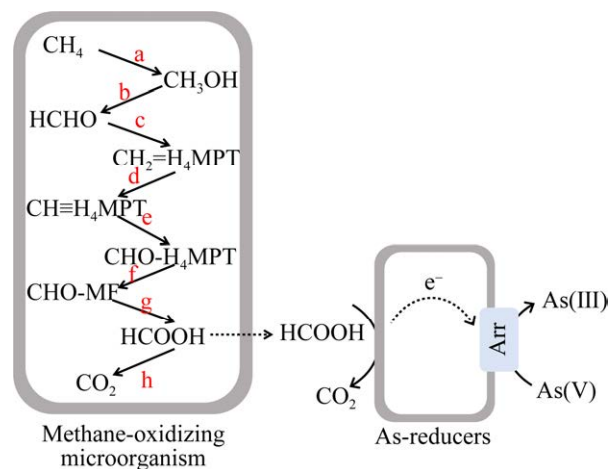
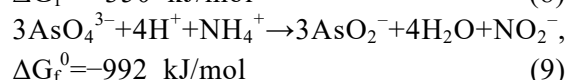
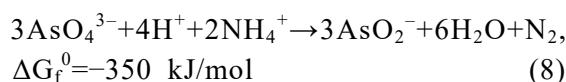
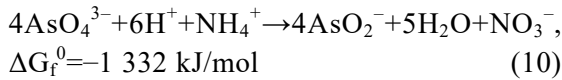


图3 有氧甲烷氧化耦合砷酸盐还原微生物机制^[32]
a: 甲烷单加氧酶; b: 甲醇脱氢酶; c: 甲醛活化酶; d: 亚甲基脱氢酶; e: 甲烯基水解酶; f/g: 甲酰转移酶; h: 甲酸脱氢酶

Figure 3 Mechanism of microbial reduction by aerobic methane oxidation coupled with arsenate^[32].
a: Methane monooxygenase; b: Methanol dehydrogenase; c: Formaldehyde activating enzyme; d: Methylene dehydrogenase; e: Methenyl hydrolase; f/g: Formyltransferase/hydrolase complex; h: NAD-dependent formate dehydrogenase.

之间的内在相互作用,因此在这些元素的生物地球化学循环过程中,微生物种群之间产生了复杂的耦合效应^[34]。例如,微生物Fe和As的还原可以使用有机物、S以及甲烷作为电子供体^[20]。地下水中微生物介导的砷生物地球化学过程对砷的形态、毒性、迁移性和环境行为影响很大。由于大量氮肥的使用,土壤和地下水中N的微生物代谢极为活跃^[35]。同时,在缺氧环境中也有利于微生物对As的还原。因此在砷污染的稻田土壤中可能存在厌氧铵氧化与砷还原的耦合过程。根据热力学方程(8)–(10)^[36]可知,厌氧铵氧化与砷酸盐耦合还原是可行的。





该过程由铵氧化微生物提供电子载体, 砷酸盐作为电子受体被还原。在土壤及地下水复杂的环境中, 可作为微生物铵氧化过程电子受体的还有亚硝酸盐和 Fe(III) 等^[37]。通过排除残余电子受体对铵氧化的影响, 有研究人员利用 ¹⁵N 进行土壤实验研究, 根据 ¹⁵N 标记的 N₂ 含量来确定电子受体的还原, 结果发现 As(V) 的加入显著提高了 ¹⁵N 标记的 N₂ 含量, 此外, As(V) 还原产生的 As(III) 浓度与加入 As(V) 含量呈显著正相关^[36]。由于缺乏对该过程主要功能微生物代谢能力的了解, 其中的微生物机制尚不明确。

铁(氢)氧化物是沉积环境中的常见矿物, 它们通常是砷、锑、镉和钒等有毒重金属元素的主要载体, 在地下水环境的生物地球化学过程中发挥着重要作用^[38-41]。然而, 它们结构的不稳定性使其容易受到生物或非生物过程的影响, 导致矿物溶解、有毒重金属元素的释放和区域范围内的地下水质量下降^[42]。值得注意的是, 在缺氧条件下, 微生物可以使用 As(V)、Fe(III)、SO₄²⁻ 作为电子受体氧化有机物, 产生 As(III)、Fe(II) 和 S²⁻^[22]。溶解后生成的 Fe(II) 可与硫化物形成 FeS 矿物, 或与 Fe(III) 矿物表面结合形成绿锈、磁铁矿等 Fe(II)-Fe(III) 矿物。次生矿物吸附性质的变化将影响砷在固相和水相之间的分布^[43]。当大量的 As(V) 吸附在铁矿物上时, 由于矿物形态的变化, As(V) 会经历解吸-再吸附过程, 一部分最终会迁移到水相^[44]。相反, 当含有大量 As(III) 的铁矿物发生硫化反应时, 会形成流动性更强的硫代砷酸盐, 从而增加地下水中砷的积累。硫代砷酸盐的形成不仅促进了砷向水相的迁移, 而且还阻碍了次生矿物的形成, 导致可用于砷吸附的载体减少^[45]。因此, 微生物在铁硫矿物的溶解和重组过程中,

都直接或间接地参与了砷的还原, 存在着显著的耦合氧化还原效应, 这也可能影响土壤环境质量和农田生态风险, 其中主要的微生物和非微生物的相互转化过程如图 4 所示。

2.3 微生物耦合砷还原的影响因素

微生物是促进砷的氧化还原、溶解释放以及迁移转化的推动者, 也是砷的生物地球化学循环的主要驱动力。因此, 所有影响功能微生物

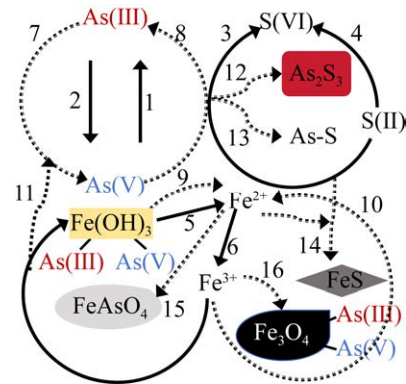


图 4 微生物介导的 As-Fe-S 的相互转化^[46] 1: 微生物 As(V) 还原; 2: 微生物 As(III) 氧化; 3: 微生物硫化物氧化; 4: 微生物硫化物还原; 5: 微生物 Fe(III) 还原; 6: 微生物 Fe(II) 氧化; 7: 非生物 As(III) 氧化; 8: 硫化物诱导 As(V) 还原; 9: 硫化物诱导 Fe(III) 还原; 10: Fe³⁺ 诱导的硫化物氧化; 11: Fe³⁺ 诱导的 As(III) 氧化; 12: 砷化砷沉淀; 13: 硫代砷水溶液的形成; 14: 硫化铁沉淀; 15: 砷酸亚铁沉淀; 16: 次生 Fe(II) 矿物的形成

Figure 4 Microbe-mediated As-Fe-S interconversion^[46]. 1: Microbial As(V) reduction; 2: Microbial As(III) oxidation; 3: Microbial sulfide oxidation; 4: Microbial sulfide reduction; 5: Microbial Fe(III) reduction; 6: Microbial Fe(II) oxidation; 7: Abiotic As(III) oxidation; 8: As(V) reduction induced by sulfide; 9: Fe(III) reduction induced by sulfide; 10: Fe³⁺ induced sulfide oxidation; 11: Fe³⁺ induced As(III) oxidation; 12: Arsenic sulfide precipitation; 13: Formation of thioarsenic aqueous solution; 14: Iron sulfide precipitation; 15: Ferrous arsenate precipitation; 16: Formation of secondary Fe(II) minerals.

物活性以及基底有效性的环境因素均会直接影响砷还原的效率。

可溶性有机质是土壤有机质中最活跃的化学物质,包括低分子量游离氨基酸、碳水化合物、有机酸和大分子量的酶、多糖、酚和腐殖质等。一方面,有机质可以利用表面官能团(COOH、OH和苯酚)与砷竞争矿物表面的吸附点位;另一方面,有机质可以与砷形成络合物从而增加砷的迁移转化^[47]。Chen等^[48]的研究发现,在重金属污染的土壤中加入生物炭可有效改变土壤的pH值、有机质和氮含量,从而调节微生物活动,促使还原态重金属含量增加。生物炭不仅可为微生物提供充足的营养物质和有利的生存空间以提高其活性,一些具有氧化还原活性官能团和石墨化结构的生物炭还可以充当“电池”和“导体”,有效促进电子转移,从而提高微生物修复效率^[49]。Cheng等^[50]通过生物炭和重金属固定化细菌(液化沙雷氏菌, *Serratia liquefaciens* CL-1)的结合,降低了有效性重金属含量,增加了土壤pH值、有机质含量和抗性基因丰度,从而减少了小麦籽粒对重金属的吸收。因此,生物炭作为一种低成本、多官能团有机质,在土壤重金属修复过程中可能会在一定程度上促进砷的耦合还原。

Yang等^[51]在稻田根际土壤中分别加入醋酸、草酸和柠檬酸,探究了砷转化迁移的微生物效应,结果表明,在有机质氧化与异化还原耦合之后,As(V)可以直接或间接被还原。有机质的加入,促进了土壤固相中砷的释放,但也显著富集了含有As(III)甲基化功能基因(*arsM*)的微生物。

pH值作为重要的环境因子,对微生物生长活性、群落结构、砷形态转化有显著影响^[5]。土壤中不同pH下的砷形态如表2所示。研究发现,酸性环境中的几种嗜酸细菌、古细菌以及嗜中性Fe(III)和硫酸盐还原细菌在pH中性和弱碱性环境中可将Fe(III)矿物的还原溶解,形成Fe/S次级产物,释放砷并将其还原为As(III)^[53]。Zhou等^[54]研究了在不同pH条件下由矿山酸性废水中富集培养的微生物所介导的Fe/S氧化偶联砷形态转化,结果表明,pH变化显著影响了微生物对矿物质的吸附和微生物群落结构的演变,从而进一步影响了矿物生物溶解和Fe/S氧化过程砷的还原释放。此外,Jiang等^[55]在研究中发现,地下水中常见的硫酸盐还原菌代谢过程中产生的小分子有机酸、硫化氢和二氧化碳,降低了周围环境的pH值,从而促进了碳酸盐结合态中砷的溶解释放。

表2 土壤中不同pH下砷形态^[52]

Table 2 Arsenic speciation in the soils with different pH^[52]

Valence state of arsenic	Form of arsenic	pH
As(III)	H ₃ AsO ₃	At pH 0–9, the most dominant form (53%–100%)
	H ₂ AsO ₃ ⁻ /HAsO ₃ ²⁻	
As(V)	H ₃ AsO ₄	pH 1–3
	H ₂ AsO ₄ ⁻	pH 3–6
	HAsO ₄ ²⁻	pH 7–11
	AsO ₄ ³⁻	pH 12–14
As(V)	H ₂ AsO ₄ ⁻	pH 4–9
	HAsO ₄ ²⁻	
As(V)	H ₂ AsO ₄ ⁻ (96%)	pH 3–4
	HAsO ₄ ²⁻ (73%)	pH 6–7

土壤氧化还原电位会显著影响砷的形态, 从而影响其溶解度、迁移率和生物利用度。如地下水位的季节性变化会改变土壤中的氧化还原条件, 从而影响其耦合还原过程^[56]。由于亚砷酸盐和砷酸盐的溶解度和迁移率不同, 其受氧化还原条件的影响很明显。一般来说, 砷在土壤中的溶解度随着氧化还原电位(Eh 值)的降低而增加。As(V)在氧化环境下占主导地位, 但在缺氧条件下(还原环境), 相对不溶的砷酸盐 As(V)被还原为更易溶解的亚砷酸盐 As(III)^[57]。因此, 缺氧条件更有利于砷的耦合还原, 例如目前已发现的厌氧甲烷氧化^[20]、铵氧化耦合砷还原过程^[36]。表 3 展示了土壤不同氧化还原条件下的 As 形态的变化。

3 微生物耦合还原对环境的影响

砷在环境中的毒性、迁移性和归宿很大程度上取决于其化学形态, 砷经耦合还原后, 由 As(V)结合态转变成了更易迁移、更易溶解也更具毒性的 As(III), 极大促进了砷的释放。As(III)由于其较少被吸附所以具有较大的迁移性, 并且 As(III)的毒性远大于 As(V)的毒性, 约为其 60 倍^[18]。因此, As(III)更容易进入生物链循环而产生危害, 从而增加砷污染环境的风险^[58]。研究发现, 我国高砷地下水形成主要原因是由于沉积物层原生微生物对有机物的降解, 导致 Fe、Mn 氧化物的溶解, 在碱性环境下砷的耦合还原, 促使砷在地下水中不断迁移和富集^[59]。Xu 等^[60]的研究发现, 在砷污染的稻田土壤淹水环境中, 微生物异化铁还原和砷酸盐的还原导

致孔隙水中的 As(III)浓度大幅增加, 而硫酸盐的添加刺激了微生物对硫酸盐的还原, 环境中高浓度的 Fe^{2+} 和 S^{2-} 与 As(III)形成的次生矿物可有效降低孔隙水中的砷含量。同时, 砷污染的生物修复作为一种低成本、环保和可持续的策略, 目前已得到广泛关注^[4,61-63]。Chen 等^[64]的研究发现, 硫可以通过促进巯基化合物、植物螯合素等的合成, 通过与 As(III)络合来增加对植物对砷的富集, 然而微生物砷耦合还原后易与硫生成不溶性的硫化物, 可能会减少植物对硫的吸收。许多植物对 As(V)的耐受性比 As(III)更强, 且对土壤砷吸收主要以 As(V)形式存在^[65-66], 因此, 砷经耦合还原后可能阻碍植物对砷的吸附。然而, 微生物主要以 As(III)作为底物进行甲基化, 砷耦合还原过程似乎更有利于微生物的修复。

砷的耦合还原对环境中的甲烷、N 等循环也有着重要影响。甲烷作为一种温室气体, 其全球变暖潜能值是二氧化碳的 25 倍^[67]。据报道, 厌氧氧化消耗了陆地生态系统中大约 30%的甲烷, 在一定程度上减少了温室气体的排放^[67]。稻田土壤氮肥的使用, 刺激了微生物的厌氧铵氧化, 缺氧条件对微生物砷还原更有利, 此外, 考虑到铵的消耗, 再加上其与砷还原的耦合效应^[36], 对稻田土壤中 N 循环及氮肥的有效利用产生了重要影响。同时, 地下水中铵、砷和溶解铁共存是含水层系统中的普遍现象, 它们具有很强的氧化还原耦合效应, 从而影响了氮循环和地下水中砷、铁的迁移转化^[68]。因此, 厌氧铵氧化与砷耦合还原对提高氮肥效率以及防治氮损失和砷污染具有重要的意义。

表 3 土壤中不同氧化还原电位下砷形态的形成^[52]

Table 3 Arsenic speciation in the soils with different redox potential^[52]

Redox condition	-200-0 mV	0-100 mV	100-200 mV
Arsenic speciation	As(V) is reduced to As(III)	Partial dissolution of As(V)	As(V) predominates and is co-precipitated with iron and manganese oxides

4 总结与展望

砷的耦合还原与砷的生物地球化学循环过程密切相关, 微生物介导的砷转化过程是由不同环境下生物体内的一系列酶催化的, 并且这些酶与环境中 N、Fe、S 等其他元素的生物地球化学循环耦合。此外, 环境中有机质含量、pH 以及氧化还原电位是微生物砷耦合还原的主要影响因素。

目前, 砷污染修复不断由物理化学手段向生物修复方向发展, 在微生物对砷的各种直接或间接的代谢过程中, 砷耦合还原对环境的影响较大, 是一个不可忽视的过程。一方面, 砷耦合还原增加了环境砷污染的迁移和转化; 另一方面, 砷耦合还原为砷甲基化过程提供了更多的反应底物, 对生态健康以及作物安全产生了重大的影响。因此, 进一步研究砷耦合还原与微生物砷甲基化挥发过程的结合, 可以为砷污染的治理提供新的视角。砷耦合还原过程涉及了多种微生物, 而目前不同微生物的种间电子传递方式尚不明晰, 重金属驱动的甲烷氧化过程中的电子转移途径比依赖单一途径更为复杂。因此, 未来还可以结合分子生物信息工具挖掘出更多的微生物耦合还原过程, 包括电子传递方式、关键功能酶等以及影响因子, 揭示砷污染的内在机制, 为砷的生物修复提供进一步的支持。

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