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REVIEW

Microbiology of inorganic arsenic: From metabolism to bioremediation

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Arsenic (As) contamination of drinking water and soils poses a threat to a large number of people worldwide, especially in Southeast Asia. The predominant forms of As in soils and aquifers are inorganic arsenate [As(V)] and arsenite [As(III)], with the latter being more mobile and toxic. Thus, redox transformations of As are of great importance to predict its fate in the environment, as well as to achieve remediation of As-contaminated water and soils. Although As has been recognized as a toxic element, a wide variety of microorganisms, mainly bacteria, can use it as an electron donor for autotrophic growth or as an electron acceptor for anaerobic respiration. In addition, As detoxification systems in which As is oxidized to the less toxic form or reduced for subsequent excretion are distributed widely in microorganisms. This review describes current development of physiology, biochemistry, and genomics of arsenic-transforming bacteria. Potential application of such bacteria to removal of As from soils and water is also highlighted.
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[**Key words:** Arsenate reduction; Arsenite oxidation; Arsenic contamination; Biogeochemical cycle of arsenic; Bioremediation]

Although arsenic (As) is commonly known as a toxin, it is ubiquitous in the environment (1); however, its abundance in the earth's crust is low (0.0001%) and its background concentrations in soils are generally less than 15 mg kg^{-1} (2,3). Nevertheless, local concentrations can vary depending on parent materials and geological history of the region. For example, Himalayan-derived sediment is the source of groundwater As contamination in large areas of south and southeast Asia (4). In Bangladesh and West Bengal, India, approximately 60–100 million people rely on drinking water that contains As in excess of the World Health Organization standard (5). Direct consumption of rice irrigated with As-contaminated water is another significant route of human exposure (6). Accordingly, health problems associated with exposure to As are a worldwide concern. Although As has both toxic and therapeutic properties, chronic exposure to As has caused a wide variety of adverse health effects including dermatological conditions and skin and internal cancers (7). In addition, recent studies have indicated that gestational As exposure is associated with increased cancer incidence in adulthood (8).

Anthropogenic discharges such as air emissions, soil amendments, mining operations, and wood preservation have also resulted in elevated As levels (9). Indeed, As has become a prevalent soil contaminant throughout the world (9,10). Accumulated As in contaminated soils has the potential to leach into ground and surface water, and direct exposure from ingestion, inhalation, and dermal routes can impact animal and human health. In Japan, the Soil Contamination Countermeasures Law was enacted in 2003 to address issues caused by harmful substances, including As.

Although As can exist in four oxidation states (V, III, 0, −III) with a variety of inorganic and organic forms, inorganic arsenate [As(V)] and arsenite [As(III)] predominate in aquatic and soil environments (11–13). As(V) is present as negatively charged oxyanions ($H_2AsO_4^-/HAsO_4^{2-}$) at moderate pH. These oxyanions are strongly adsorbed to the surface of common soil minerals such as Fe and Al (hydr)oxides. As(III) primarily exists as uncharged $H_3AsO_3^0$ with a pKa of 9.2, and is therefore less adsorptive and more mobile than As(V) in most environments (12). In aerobic environments, As(V) is found to be the predominant species and immobilized in solid phase. In contrast, As(III) is more prevalent in anoxic environments, which leads to mobilization into the aqueous phase (14).

Microorganisms can mediate redox transformations of As via As(V) reduction and As(III) oxidation (2). To date, a wide variety of As(V)-reducing and As(III)-oxidizing prokaryotes have been isolated from various As-contaminated environments (2,15), and a recent study suggested that they are also distributed in the natural environment containing background levels of As (16,17). Because both As(V) reduction and As(III) oxidation directly affect the mobility and bioavailability of As, microbial activities play a key role in biogeochemical As cycling. Such microbial processes have the potential to promote As removal from contaminated soils/waters when used as intended. This article outlines the latest physiology and phylogeny for microbial metabolism of inorganic As and highlights their advances as bioremediation techniques.

AS(III) OXIDATION

Aerobic As(III) oxidizers The bacterial oxidation of As(III) was first reported in 1918, although the finding went largely unnoticed until 1949, when Turner isolated 15 strains of heterotrophic As(III)-oxidizing bacteria (18–20). Currently, physiologically

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diverse As(III) oxidizers are found in various groups of *Bacteria* and *Archaea* and include both heterotrophic As(III) oxidizers (HAOs) and chemolithoautotrophic As(III) oxidizers (CAOs) (2,21,22). Heterotrophic As(III) oxidation is generally considered a detoxification mechanism that converts As(III) into less toxic As(V), although it may be used as a supplemental energy source (23). In contrast, CAOs use As(III) as an electron donor during fixation of CO_2 coupled with reduction of oxygen (24). Anaerobic CAOs have also recently been isolated (see below). In addition, some researchers have reported curious facultative anaerobic HAOs capable of either aerobic As(III) oxidation or anaerobic As(V) reduction (25,26). In recent studies, As(III) oxidizers were isolated from As-rich environments (27,28), as well as metal-contaminated soil containing low levels of As and uncontaminated garden soil (29,30).

Arsenite oxidase, which was first isolated in 1992 (31), has been identified in both CAOs and HAOs (24,32). In both cases, the enzyme contains two subunits, a large subunit containing a molybdopterin center and a [3Fe–4S] cluster and a small subunit containing a Rieske [2Fe–2S] cluster (33,34). Although homologous genes encoding these two subunits were formerly assigned different names (*aoxB-aoxA*/*aroA-aroB*/*asoA-asoB*), nomenclature for genes involved in prokaryotic aerobic As(III) oxidation was recently unified and the name *aio* was newly assigned; therefore, the large and small subunit are denoted *aioA* and *aioB*, respectively (35). AioA is similar to the molybdenum-containing subunits in the DSMO reductase family and distantly related to the catalytic subunit of respiratory As(V) reductase (ArrA) (2,21,22).

Homologs of genes encoding AioA are found in phylogenetically diverse strains including members of α-, β-, γ-*Proteobacteria*, *Bacteroidetes*, *Actinobacteria*, *Firmicutes*, *Aquificae*, *Deinococcus-Thermus*, *Chlorobi*, *Chloroflexi*, *Nitrospira*, and *Crenarchaeota* (Fig. 1). These genes are found clustered in several groups in the AioA-based tree, with strains in the phyla including thermophiles basically forming distinct phylogenetic branches from mesophiles. The major mesophile branches are divided into two groups, group I, which is mainly composed of α-*Proteobacteria*, and group II, which is primarily composed of β- and γ-*Proteobacteria*. This pattern suggests that these groups probably originated from respective proteobacterial divisions. However, there are considerable inconsistencies between the AioA-based phylogeny and 16S rRNA-based classification, suggesting that horizontal gene transfer plays a role in the propagation of *aio* genes in prokaryotes (36). In some cases, two identical copies of the *aioA* gene have been found in same strain. For example, the DGGE profile of *Thiomonas arsenivorans* DSM 16361 showed two bands corresponding to two distinct *aioA*-related sequences (37), whereas two copies of *aioA* in *Ancylobacter* sp. OL1 were clustered more closely (38).

aioA-like genes have been amplified from a variety of As-rich environments including mine, arsenical pesticide- or smelter-impacted sites, and geothermal sites (36,37,39–43). Additionally, Engel et al. (44) recently detected *Chloroflexi* and *Proteobacteria*-related *aioA* sequences from the same microbial mat collected at a geyser. Taken together, these investigations suggest that the diversity of *aioA* genes in prokaryotes is wider than previously suspected. Moreover, *aioA*-like genes have been obtained from soil or sediments containing background levels of As (16,45), indicating that diverse aerobic As(III) oxidizers reside in the environment, regardless of As contamination.

Anaerobic As(III) oxidizers In 2002, Oremland et al. (46) isolated an anaerobic As(III)-oxidizing bacterium, strain MLHE-1, from anoxic bottom water of Mono Lake, CA, USA, which is an alkaline soda lake known for its high concentration of As(V) (200 μM). Strain MLHE-1, later proposed as *Alkalilimnicola ehrlichii* sp. nov. (47), is a chemolithoautotrophic bacterium that can couple As(III) oxidation to nitrate reduction under anaerobic conditions. A purple sulfur bacterium, *Ectothiorhodospira* sp. PHS-1, was also isolated from red-pigmented biofilms in Mono Lake (48). This strain can use As(III) as the electron donor for anoxygenic photosynthesis and produces As(V) anaerobically under light conditions. Interestingly, both of these bacteria appear to lack *aioA* genes and instead possess genes that are much more closely related to *arrA* (49,50) (Fig. 2). This gene, designated *arxA*, is required for chemoautotrophic growth on As(III) and nitrate by strain MLHE-1. In addition, *arxA* is strongly induced by As(III) in strain PHS-1. Thus, it is possible that ArxA is a novel type of As(III) oxidase that forms a distinct phylogenetic clade within the dimethyl sulfoxide (DMSO) reductase family. *arxA*-like genes have recently been found in a nearly complete genome sequence of uncultured bacterium within the candidate division OP1 (51) and in a reconstructed complete genome of the dominant organism (RBG-1) in deep sediment of the Colorado River, CO, USA (52). As(III)-oxidizing denitrifying chemoautotrophs (strains DAO-1 and DAO-10 within the classes β- and α-*Proteobacteria*, respectively) have been isolated from As-contaminated soils, but it is still unclear which genes are required for As(III) oxidation (53).

AS(V) REDUCTION

A wide variety of bacteria known as As(V)-resistant microbes (ARMs) can reduce As(V) via detoxification systems (15,54). As(V) usually enters bacterial cells through phosphate transporters (Pit or Pst). Once inside, As(V) is reduced to As(III) by a cytoplasmic As(V) reductase (ArsC) with the aid of glutathione or ferredoxin as the reducing power. As(III) is finally excreted out of the cells via a membrane efflux pump, ArsB or Acr3 (55). In some cases, an ATPase ArsA is bound to ArsB to facilitate As(III) efflux, conferring an advantage to organisms exposed to high levels of As. As(III), which enters bacterial cells through aquaglyceroporin, may also be extruded by the same system.

In addition to the detoxifying As(V) reduction, certain bacteria can reduce As(V) as the terminal electron acceptor for anaerobic respiration. Such bacteria are defined as dissimilatory As(V)-reducing prokaryotes (DARPs). These bacteria are phylogenetically diverse, including members of *Firmicutes*, γ-, δ-, and ε-*Proteobacteria* (Fig. 2) (15). The respiratory As(V) reductase (ARR) consists of a larger catalytic subunit ArrA and a smaller subunit ArrB (56). ArrA is a member of the DMSO reductase family containing a molybdenum center and a [4Fe–4S] cluster, while ArrB contains three to four [4Fe–4S] clusters. ARR of *Alkaliphilus oremlandii* and *Shewanella* sp. ANA-3, which are both As(V)-respiring bacteria, was recently found to be biochemically reversible (57), showing both As(III) oxidation and As(V) reduction activities upon *in vitro* gel assay. Richey et al. (57) suggested that the physiological role of ARR depends on the electron potentials of the molybdenum center and [Fe–S] clusters, additional subunits, or constitution of the electron transfer chain.

As sorption onto metal oxide minerals, especially on iron (hydr) oxides, is an important process controlling the dissolved concentration of As in various environments. As(V) is strongly associated with iron and aluminum (hydr)oxides, whereas As(III) is more mobile than As(V) (58). Thus, reductive dissolution of As-bearing iron (hydr)oxides by dissimilatory iron-reducing bacteria can cause As release (59,60). In addition, direct reduction of As(V) adsorbed onto soil minerals by DARPs may be another important mechanism of As mobilization (61,62). ARMs are generally not considered to be involved in As release because ArsC, the cytoplasmic As(V) reductase, is not able to directly reduce As(V) adsorbed onto soil minerals (63). Therefore, ARR is believed to be responsible for As(V) reduction in solid phase, although how periplasmic ARR transfers

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