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Effects of microbial processes on the fate of arsenic in paddy soil

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Arsenic (As) is a metalloid toxic to organisms including humans. Arsenic in rice represents a significant exposure pathway for the general population, particularly for those subsisting on rice. Arsenic transformation, namely reduction, oxidation and methylation, in soil-rice systems has fundamental impacts on its mobility and toxicity. In addition to soil chemical properties (pH, Eh, metallic oxides, organic matter), microorganisms play critical roles in As transformation and mobility in paddy soil, such as through ArsM (As(III) S-adenosylmethyltransferase) and interactions with iron oxides or organic matters. Arsenic species in paddy soil directly influence As speciation in rice grain because the methylated As species in rice are mainly derived from microbial methylation in paddy soil. This paper aims to provide an overview on the status of the knowledge and gaps on the chemical aspects of As transformation in soil-rice system in conjunction with microbial ecology and functional genes. In addition, potential pathways (manipulation of microorganisms in paddy soil and genetic engineering) to decrease total As and/or inorganic As in rice grain are proposed.

arsenic, microorganisms, transformation, soil, rice

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Inorganic arsenic is classified as a well-known non-threshold carcinogen [1]. The toxicity of arsenic (As) to humans has been well documented and reviewed [2,3]. Numerous studies have reported that the increase in soil As concentration can cause an enhancement of As accumulation in rice grain and in turn threaten human health through food chain [4–8]. Rice consumption contributes a large proportion of inorganic As via dietary intake for those who rely on rice as the staple food [9–11]. The consumption of rice can contribute up to 60% of inorganic As ingestion through diet in China [11]. In addition, many people in the United States are also exposed to potentially harmful levels of As through rice consumption [12].

The mobility and toxicity of As in soil environment depend largely on its chemical species. In addition to abiotic factors (pH, Eh of soils, adsorption of metallic oxides and organic matter (OM), etc.), it has been suggested that microorganisms play a major role in modulating As speciation (reduction, oxidation and methylation) and its mobility [13,14]. The rates and directions of As biotransformation in soil-plant systems largely depend on the microbial communities, both functional diversity and the expression of functional genes under various environmental conditions. By using molecular tools, it is now possible to unravel the microbial processes in the soil that governs the fate and toxicity of As.

Understanding the speciation and bioavailability of As in contaminated soils affected by microorganisms is also necessary for reducing total As and/or inorganic As in rice grains. Herein, we review the microbial effects on the fate of As in paddy soil-rice systems in conjunction with soil chemical properties, discuss further research needs and propose some potential mitigation strategies of As accumulation in rice grains through manipulating microbial activities and/or communities.

1 Arsenic species in paddy soil

Arsenic exists primarily as inorganic arsenate (As(V)) and arsenite (As(III)) in paddy soil [15]. Organic As such as

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monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine (TMA) which may have been derived from microbial and algal biomethylation could also be present in paddy soils as a minor component [14,16].

The behavior and fate of As in soil environment depend largely on its speciation, different As species vary greatly in their toxicity to organisms. Inorganic As species As(V) and As(III) are generally considered to be more toxic than organic species for many organisms [4]. Arsenite is more mobile and toxic than As(V) [17] because it is neutral under normal environmental conditions and therefore poor adsorption on soil particles [18]. Trimethylarsine (TMA) is volatilizable and thought to be nontoxic [19,20].

2 Abiotic factors influencing the speciation and mobility of arsenic

The proportion of As(III) and As(V) in soils depends mostly on soil chemical conditions including the redox potential (Eh) and pH. Arsenic, with As(V) being the stable form in well-aerated soils shows a low solubility [21], because As(V) is strongly adsorbed on most mineral constituents such as iron or aluminum (hydr)oxides and aluminosilicates [22] (Figure 1). Under reducing conditions (paddy soil), oxygen is depleted since oxygen diffusion in water is four orders of magnitude lower than those in air [23–25]. Arsenate is reduced to As(III) readily, becoming the dominant form [26–28], and As becomes more mobile in soil solution due to the increased concentration of As(III). Ferric (hydr)oxide undergoes reductive dissolution under anaerobic conditions, this process also causes As release from soils or iron oxide minerals [29,30]. Redox reactions in soils are mainly controlled by microbial activities [31]. Microbial reduction processes in the soil is accompanied by changes in the pH: A pH increase in acid soils due to consumption of protons and a pH decrease in alkaline soils due to increasing pressure of CO_2 (P_{CO_2}) can be observed after flooding [32]. Yu and Patrick [33] suggested that redox changes from 59 to 177 mV are accompanied by pH changes of 1 unit depending on soil properties. In addition, a rise in soil pH generally causes a release of anions such as As(V) from their adsorption sites. As pH increases, the number of positively charged sites on minerals decreases, which lowers the sorption capacity of negatively charged oxy-anions of As [34,35].

The mobility of As in soils depends largely on the retention and release along the surfaces of iron, manganese, and aluminum oxides or hydroxides [22,36,37]. Iron oxide is believed to be the dominant factor controlling the bioavailability and mobility of As in the soil [38]. In paddy soil under flooding conditions, ferric iron is reduced to ferrous iron, and As sequestrated on iron oxide is then released to soil pore water [29,30]. This is in fact one of the key reasons why rice often contains much higher As than upland crops [7]. In addition, re-crystallization of ferrous iron to more stable phases could trap As again [39,40] (Figure 1).

Organic matter (OM) additions can mobilize As in soils. The release of As was observed in soils after the application of organic matter [41,42]. Many functional groups such as COOH, phenol, catechol and OH on OM surface result in a

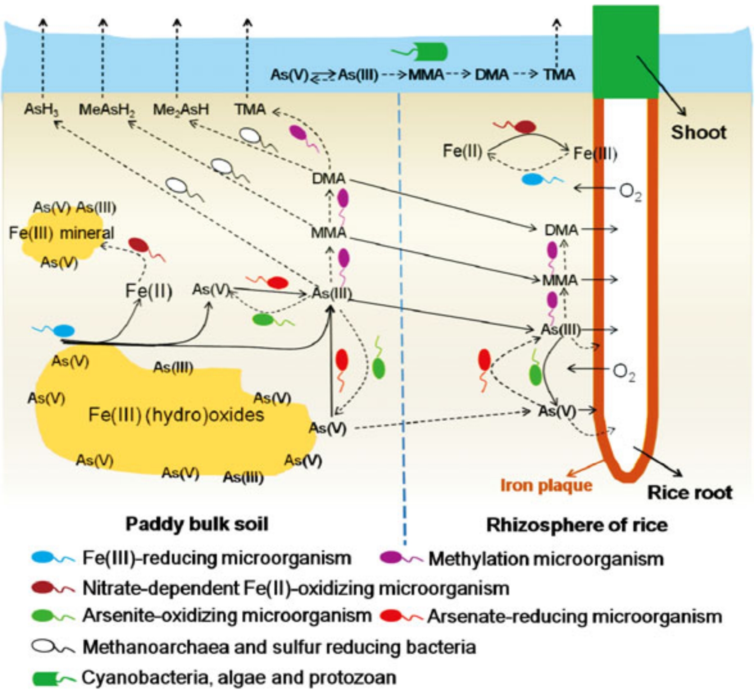

Figure 1 Arsenic mobilization and transformation drove by microorganisms in flooded paddy soil. Arrows with solid and broken lines indicate dominant and minor processes, respectively.

strong affinity of OM with metal oxides, thus OM can compete with As for adsorption sites of metal oxides [43]. It was reported that dissolved organic carbon (DOC) played a dominant role in As solid-solution phase partitioning in paddy soil [44].

Phosphorus (P) and silicon (Si) can also influence the mobility of As in soils and the uptake by rice. It has been reviewed that the presence of phosphate adversely affects As(V) immobilization in soils [26]. Phosphate is an analog to As(V) and is the major species of P present in soils [45]. Phosphorus applications caused a desorption of As retained in soil particles [46,47]. In addition to P, Si competes with As(III) for binding sites on iron oxide surfaces in soils to influence As solubility in pore water [48,49]. Furthermore, because As(III) is taken up by rice roots mainly through the Si uptake pathway, the increase in Si concentration in soil solution can significantly reduce As accumulation in rice straw, husk and grain and even decrease the percentage of inorganic As in rice grain [50,51]. The fact that the dominant species taken up by rice roots in paddy soils is As(III) leads to a considerable effect of silicon in soil solution on As uptake.

3 Arsenic speciation and mobility modulated by microorganisms in paddy soil

3.1 Arsenic speciation modulated by micro-organisms

The transformations of As species in soils including oxidation, reduction, methylation and volatilization, are commonly driven by microorganisms [52–54], and these transformations were summarized in Figure 1. Most living organisms have developed As resistance mechanisms or even make use of As for their ordinary physiology although As is very toxic [55]. Microbial oxidation of As(III) is believed to be a detoxification mechanism of microorganisms because As(V) is less toxic than As(III) [55,57]. On the other hand, As(III) can also be as an electron donor in the process of bacterial metabolism. Similar to As(III) oxidation, As(V) reduction includes two pathways. One is the dissimilatory reduction where As(V) is the terminal acceptor of electrons in bacterial anaerobic respiration. The other is the detoxification mechanism of microorganisms including As(V) reduction and As(III) efflux out from cells [55]. A recent report suggested that the constant and high (more than 80%) As(III) proportion of total As in solution phase of paddy soil was attributed to microbial activity [30].

In addition to oxidation and reduction, methylated As can be formed by various aerobic and anaerobic microorganisms [56]. Arsenic methylation occurring in the soil greatly affects the toxicity and fate of As in paddy soils (Figure 1). Widespread ArsM homologues in prokaryotic and eukaryotic microorganisms can catalyze this process, and many methylated intermediates and trimethylarsine as the end are produced in this process [53,57–59]. It has been reported that bacteria, anaerobic archaea and halophiles in soils or sludges can methylate As [60–63]. Arsenic biomethylation has been observed in numerous cyanobacteria and algae as well [14,57]. Furthermore, methylcobalamin-dependent nonenzymatic methylation of As has been reported for numerous anaerobic prokaryotes [64]. In particular, autotrophic sulfate-reducing bacteria as well as methanoarchaea, which are abundant in paddy fields [65,66], were suggested to be responsible for this process [63]. Methylated species of As(III) and volatile arsenicals were detected when the cyanobacteria were treated with As(III) or As(V) [57]. Microorganisms play a crucial role in the biogeochemical cycle of As especially for cyanobacteria which are ubiquitous in aquatic environments, including paddy soil, wetland and ocean [67]. *Tetrahymena pyriformis*, a protozoan living in fresh water, and possibly in paddy soils as well, could also methylate and even volatilize As [58,68]. All these organisms are ubiquitous in the freshwater systems like paddy soil. Arsenic methylation is proposed to play an important role in As cycling among terrestrial, aquatic and atmospheric environments [69,70].

3.2 Interactions of microorganisms with organic matters

The application of OM (as exogenous nutrition) stimulates the growth of various indigenous microorganisms, including As methylaters which facilitate As methylation and volatilization from soil, and the “volatilization ability” varied between the types of organic matters [13,20]. As mentioned above, the addition of organic matters will enhance the mobilization of As thus increasing its bioavailability for methylaters, and favoring methylation processes. In addition, OM amendment changes the physicochemical properties (such as pH, Eh) of paddy soils, which can also affect communities and activities of microorganisms, further influence As methylation and subsequent volatilization [13]. It was reported that pH changes can influence the microbial process to affect As methylation or volatilization: a decrease in soil pH enhanced microbial-mediated As volatilization [71]. On the other hand, dissolved organic matter (DOM) also works as a labile substrate for iron reducing bacteria and as an electron shuttle to enhance microbial iron reduction resulting in the release of As adsorbed on iron oxides [72,73].

3.3 Interactions of microorganisms with iron oxides

(1) In bulk soil. Microbial activities and diversities play critical roles in As mobilization through influencing iron oxidation and reduction [29] (Figure 1). Paddy soils have a unique characteristic of periodical alternations between anoxic and oxic conditions, providing ferric iron-reducing bacteria with abundant electron acceptors and decomposition of organic matter for growth [74]. So it can be assumed that dissimilatory iron-reducing bacteria are abundant in paddy soils. Dissimilatory iron-reducing consortia in As-

contaminated paddy soils are phylogenetically diverse [75]. Decreasing activities or abundance of iron-reducing bacteria may cause less ferrous iron and more ferric oxides existing in soils and thus immobilization of As.

In addition, nitrate-dependent ferrous iron oxidizing microorganisms which can oxidize ferrous iron under flooding conditions were also found in paddy soils [76]. Nitrate-dependent ferrous oxidation may lead to more As co-precipitation with, or adsorption to ferric minerals in the soil to reduce As bioavailability and thus uptake by rice plants [77] (Figure 1). This is an essential pathway to manipulate As in soil-rice systems through regulating anaerobic iron oxidizing bacteria. However, it is still at the beginning in capitalizing this option, as little is known about the microbial community responsible for iron oxidation and also its diversity and population dynamics in relation to environmental conditions.

(2) In rhizosphere soil. Different from the bulk soil, wetland plant such as rice release oxygen and oxidants from the root into the rhizosphere, ferrous iron is then oxidized to ferric iron and deposits on root surface forming iron plaque [78]. Iron plaque is an important biogeochemical component in soil-rice systems affecting the uptake of As by rice plant [79,80] (Figure 1). Because it has a high capacity to sequestrate As due to high specific surface area of iron (oxyhydr)oxides and co-precipitation of As with ferric iron [81]. Synchrotron-based analysis of root iron plaque revealed that As in iron plaque was sequestered mainly with amorphous and crystalline iron (oxyhydr)oxides, and that As(V) was the predominant species [81]. The amount of iron plaque is significantly affected by the aerenchyma tissue and radial oxygen loss (ROL) by root [82]. It was indicated that iron plaque increased and As concentration in rice grains decreased significantly with increasing ROL [82,83]. Developed aerenchyma tissue in root could significantly restrain As in root and then reduce As accumulation in rice shoot [83]. It has also been shown that iron plaque on rice root has higher affinity to As(V) than to As(III), and iron plaque may even enhance As(III) uptake by rice [84,79]. Overall, iron plaque may act as a 'buffer' for As(V) in the rhizosphere.

Arsenate has much higher affinity for iron oxide as compared to As(III), therefore As(V) is much less mobile than As(III) in the soil, implying that the oxidation of As(III) is likely to reduce As uptake by rice [79,81]. As mentioned above, dominant As on iron plaque is As(V), indicating the occurrence of As(III) oxidation in the rhizosphere, but the microbial-mediated As(III) oxidation in soil is largely unknown. Bacterial As(III) oxidase genes are phylogenetically diverse and ecologically widespread [85]. Microbial oxidation of As(III) to As(V) occur under both aerobic and anaerobic soil conditions, which significantly enhance the immobilization of As in the soils, due to the fact that As(V) can more easily co-precipitate with ferric iron or be adsorbed by ferrihydrite [86]. In the rhizosphere soil, it remains unclear whether the activity of As(III) oxidizing bacteria (expression of *aroA*-like gene [85]) is elevated by the root exudates or the oxygen released from the rice roots to result in more As(V) binding on iron minerals in soil and iron plaque on rice roots, thus to reduce the bioavailability of As to rice roots.

Moreover, abundant iron reducing bacteria also exist in rice rhizosphere, these reducing bacteria improved the reduction rates of ferric iron in the rhizosphere [87], and then accelerate the release of As retained in iron plaque to soil solution. Ferric reducing bacteria account for about 12% of total bacteria cells in the rhizosphere comparing with only <1% in the bulk soil [88].

Ferric iron reduction is a widespread trait of members of the archaea as well [89–91]. Slobodkin et al. [89] isolated thermophilic anaerobic archaea from petroleum reservoirs, which was capable of dissimilatory ferric iron reduction. Hori et al. [92] demonstrated the involvement of archaea in ferric iron reduction in rice paddy soil by ^{13}C-acetate probing. Abundance of archaea with ferric iron reduction was low and ferric iron reduction by archaea would not be an important process.

Arbuscular mycorrhizal fungi (AMF) can form symbiosis with rice roots [93], and can enhance As tolerance and decrease the ratio of grain/straw As concentration of rice plants [94]. Mycorrhizal inoculation could reduce the uptake of As(V), As(III) and MMA by rice plants. It was likely that mycorrhizal roots released some signaling molecules to down-regulate the expression of Si transporter Lsi1 (OsNIP2;1 aquaporin) or combine with Lsi1 as a substrate [95], but requires further investigations.

Oxidizing/reducing bacteria in rice rhizosphere and their interactions with iron plaque corporately influence As speciation and mobility and thus rice uptake. Symbiotic AMF also affects As uptake by rice. Manipulation of related microbial communities or activities is an optional pathway which influences As mobility in rice rhizosphere.

4 Dissolution of iron plaque and arsenic release

Once rice is harvested, rice root may be subjected to anaerobic decomposition, and As sequestrated by iron plaque maybe released and become As hot spot for the subsequent crops (rice or other crop plants). In addition, root turnover during the entire growth period of rice plant can be fast, and dead root can also be hot spot of As release. It is therefore very important for the dissolution of iron plaque to the release of As from iron plaque into soils. The dynamics of As mobilization after rice harvest has been evaluated recently by microcosm experiments and the results suggested that As sequestrated in the iron plaque can be quickly released into soil solution as a result of iron reductive dissolution under flooded conditions [96]. Iron plaque dissolution is the main cause of As release and bacterial activity play crucial roles in this process [29]. The quick and prominent increase in As concentration in soil solution after rice harvest may seasonally affect surface and groundwater systems, which will raise environmental risks, and thus warrant further investigation.

5 Benefits of microbial arsenic methylation and volatilization

It is clear now that methylated As species in rice plant (mostly in the grain) is originated from soil, where microorganisms are responsible for the production of methylated species [97,98]. DMA levels detected in the solution amended by MMA or As(III) with the growth of rice seedlings decreased dramatically after the addition of antibacterial agent chloramphenicol [97]. No methylated As could be detected in plants (rice, tomato and red clover) cultured in a sterile hydroponic solution fed with inorganic As [98]. Thus, higher plants appears to lack the capacity of methylating As(III). However, methylated As can be taken up by rice roots and has a high translocation efficiency to grains attributed to its poor -SH (sulfhydryl) coordination [99]. The translocation efficiency of DMA to the rice grain is over an order of magnitude greater than inorganic species in As-fed excised panicles. It is because that DMA is more mobile than As(III) in both the phloem and the xylem [100]. Organic As (DMA and MMA) was mainly distributed in reproductive tissues rather than vegetative tissues. Much higher translocation efficiency of DMA in rice plant was also found than that of inorganic As. There are different pathways on the unloading of inorganic As and DMA in rice grain [101]. Inorganic As species are primarily (90%) translocated via the phloem, whereas DMA is translocated via both phloem (55%) and xylem (45%). Leaf-fed As(III) was not translocated to the filling rice grain but sequestered into leaf cell vacuoles compared with the readily mobility of DMA and MMA [102].

The increase in As methylation and volatilization directly enhance the proportion of methyl As in soils or reduce total As amount of the soil respectively. The enhancement of methylated As percentage in paddy soils could subsequently increase the methyl As proportion in rice grain to minish the food toxicity to rice consumers. Thus, it is of practical significance to promote As methylation and/or volatilization through manipulating the activity of methylaters.

6 The manipulation of arsenic methylation and volatilization

It has been suggested that As biovolatilization from paddy soils contributes 0.9% to 2.6% of global As emissions. About 419–1252 t/year As are emitted into the atmosphere from paddy soils, which are 15- to 45-times higher than from sea spray (26.5 t/year), 3- to 10-times higher than from forest fires (125 t/year), even up to 240 mg ha^{-1} year^{-1} arsines were released from paddy soils with only 11.3 mg/kg As [20,103,104].

Because OM addition can significantly increase As methylation and volatilization from the paddy soil through changing abundances or activities of the bacteria capable of oxidization, reduction, and methylation of As [13]. It is a potential way that increasing organic As (decreasing inorganic As) in rice grain through increasing methylated As or As volatilization in paddy soil. The organic matter from various sources exhibited large difference in inducing As volatilization and the mechanisms require further investigation.

Although higher plant is believed to be unable to methylate As by itself and no gene encoding ArsM has as yet been identified in the genome of any higher plants, genes capable of As methylation widely exist in many microorganisms [14]. Recently, Meng et al. [105] expressed an *arsM* gene from the soil bacterium *Rhodopseudomonas palustris* in Japonica rice and then monomethylarsenate (MAs(V)) and dimethylarsenate (DMAs(V)) were detected successfully in the roots and shoots of the transgenic rice, and the transgenic rice could give off 10-fold greater volatile arsenicals than the wild type. It will be possible for engineering plants genetically to volatilize As or transform more inorganic As to less toxic methyl As in rice grain.

Genetic engineering is a potential strategy for both phytoremediation (phytovolatilization) and reduction of As in rice grain. To maximize As volatilization or As removal from soil or minimize As accumulation in rice grain, more genes involved in As metabolism (reduction, methylation, efflux, etc.) need to be further identified and manipulated. Zhu and Rosen [106] have proposed substantial pathways for genetic engineering that can be manipulated for phytoremediation.

7 Perspectives and conclusions

It is now clear that As transformation is largely driven by microorganisms in soils in addition to chemical properties of the soil, the rate and direction of As transformation depend on the abundance and structures of microbial communities and the expression of functional genes (responsible for reduction or oxidation of arsenic, iron and nitrogen, and also arsenic methylation). Despite the recent advances, it is still early to link the microbial community to actual biogeochemical processes in soil-rice systems, and further information on novel functional genes, and their expression pattern is needed before we can build up predictive models to forecast the fate and health risks of As in this system. In this regard, functional metagenomics tools will play a role.

Although higher plants can reduce As(V) to As(III), as far as we know they cannot methylate As(III), therefore microorganisms in paddy soil, particularly in the rhizosphere, play a critical role in As transformation. Some functional genes can be used to characterize the relationship between environmental conditions, microbial community and As fate. Soil amendments with organic matters can modulate As transformation, which is mediated by soil microorganisms. The functional genes related to As methylation could also be expressed in higher plants (such as rice) and volatilize As through plants. Genetic engineering may offer the possibility of reducing the accumulation of As in rice grain. Nonetheless, our knowledge on the related functional genes is very limited, and requires further studies, particularly using functional metagenomics tools.

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