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ARSENIC IN PLANTS: UPTAKE AND METABOLISM MECHANISM

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Review Article

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ABSTRACT

The two inorganic forms of arsenic, arsenate (As^{V}) and arsenite (As^{III}), easily enter through root cells but with distinct mechanism. Inside the cell, As^{V} readily converted to As^{III}. As^{V} have analogy with inorganic phosphate (iP) therefore, replaces iP from different reactions thereby disturbing the cellular metabolism; while being dithiol reactive compound As^{III} binds and inactivates the enzymes having dithiol cofactors or closely present cysteine residues. Arsenic induces overproduction of reactive oxygen species (ROS) which interferes with the amino acid and protein metabolism, carbon metabolism, and nitrogen and sulphur assimilation pathways.

Keywords: Arsenate (As^{V}); arsenite (As^{III}); inorganic phosphate; metabolism

INTRODUCTION

Arsenic (As) is 20th most occurring element in the earth crust anda well-known toxin which arguably has influenced human history more than any other toxic compound (Singh *et al*., 2015). Presently, millions of people are suffering from As poisoning due to intake of As-contaminated groundwater especially in South and Southeast Asian countries (Nordstrom, 2002). Arsenic in soil mainly comes from arsenical mining, insecticides, wood preservatives, herbicides and irrigation with As-contaminated groundwaters. Excessive As uptake by crop plants is leading to food safety problems. From the recent findings by Zhu *et al*. (2008) it was clear that rice (*Oryza sativa*) efficiently uptake As from paddy field, translocate its high concentration to grains, which is causing health risk to people consuming large quantities of rice in their diet. Therefore, to develop mitigation strategies to encounters the problems of food chain contamination by As, it is necessary to know that how plants uptake and metabolite As, from the soil. Interestingly, the role of ferns as As-hyperaccumulators has attracted attention (Ma *et al*., 2008), so future studies are focusing to understand the mechanism behind this unusual process along with assessment of phytoremediation potential of different As hyperaccumulators. Therefore in this review, we will focus on the As speciation, uptake, toxicity, tolerance and hyperaccumulator mechanism of the plants and highlight the knowledge gaps that require further research.

Arsenic uptake, translocation and metabolism inplants

While studying the effect of As on plant cellular metabolism, it becomes mandatory to reflect the As species in soils, their entrance medium/path in plant cell, inter conversion of one species to another, and their translocation to different parts of the plants. During As translocation from root to shoot, some plant species respond only to high level of As, while other will respond only to low level of particular As species. The hyperaccumulator plants amazingly accumulate high

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concentration of As in their aerial tissues/parts compared to that of roots; while non-accumulators retainsmost of the As in roots, and much lower concentrations of As in aerial parts/shoot. Undoubtedly, the knowledge of different plant parts in response to different As species, will help in designing the strategies to develop plants which will be highly suitable to deal with the As load of the environment.

Arsenic uptake and transport in plants

Arsenic exists as inorganic and organic species, arsenate (As^{V}) and arsenite (As^{III}) are the two dominating inorganic forms in aerobic (soil) and anaerobic (water; flooded paddy fields) environment. The concentration of organic species of As^{V} (monomethylarsonic acid (MMA^{V}), dimethylarsinic acid (DMA^{V}) and trimethylarsine oxide ($TMAO^{V}$) is very low in soil; where methylated species are dominating in anaerobic soils than aerobic soils (Abedin *et al*., 2002). As^{V} show analogy with inorganic phosphate (iP) therefore easily transported through iP transporter (PHT) proteins across the plasma membrane (Wu *et al*., 2011), and As^{V} also competes with iP for its uptake through same transport channels in plants. Under iP deprivation condition, As^{V} donot allow iP to enter into plant by increasing iP deprivation signals; while excessive iP outcompetes As^{V} by protecting plants from toxicity (Tu and Ma, 2003). Within plant cell, As^{V} easily can move from one organelles to other by crossing the internal membranes through iP transporters. As^{V} can be found in the xylem, having most likely been loaded into the xylem vessels by PHT proteins (Wu *et al*., 2011). As^{V} also found in the xylem vessels loaded by PHT proteins (Wu *et al*., 2011). Although, roots of the As non-hyper-accumulator plants have the ability to strongly retain As like in *Arabidopsis* only 3% of total As uptake by roots was translocated to shoot (Quaghebeur and Rengel, 2003).

The As^{III} enters through nodulin 26-like intrinsic proteins (NIPs; Ma *et al*., 2008), which belongs to aquaporin family. The silicon transporter (OsNIP2;1/OsLsi1) have been found associated with AsIII uptake protein in rice roots; while As^{III} efflux from rice root cells to the xylem is via OsLsi2 silicon transporter (Ma *et al*., 2008). In yeast, As^{III} uptake majorly occurs through hexose permeases; although plant proteins show strong homology with hexose permeases of yeast; however As^{III} entry through these proteins in plants still not known. In *Pteris vittata* (an As hyperaccumulating fern), As^{III} is not arrested in root instead rapidly transported to fronds via xylem (Su *et al*., 2008), where it is sequestered in vacuoles to extremely high levels. Arsenic is non-essential, toxic metalloid, through its entrance to roots it inhibits root extension and proliferation and upon translocation to shoots, it severely obstruct growth and development of plants by arresting biomass accumulation, negotiating plant reproductive capacity by hampering fertility, yield and fruit production (Garg and Singla, 2011).

Arsenic metabolism in plants

After As^{V} supplementation to plants, it was noticed that more than 90% As found in the root and shoots was in the form of As^{III} (Dhankher *et al*., 2002; Xu *et al*., 2007), which suggests that AsV is rapidly reduced to As^{III}, thereby indicating the first As detoxification pathway adopted by plants (Pickering *et al*., 2000). As^{V} reduction in to As^{III} could be both non-enzymatically and enzymatically. In the non-enzymatic pathway, two molecules of GSH reduces As^{V} to As^{III}, by forming a GSH dimer (disulphide bond formation between GSH-GSH), which rapidly recycled into two molecule of GSH by glutathione reductase (GR; Foyer and Noctor, 2011). While arsenate reductase (ACR), an enzyme isolated from yeast and bacteria directly reduces As^{V} to As^{III} (Mukhopadhyay *et al*., 2000).

Arsenic toxicity in plants

The earlier studies clearly suggests that phytotoxicity of As depends on As species and As uptake by different plants have been ordered as As^{III}> As^{V}> MMA^{V}> DMA^{V} while its tranlocation order from root to shoot is DMA^{V}>MMA^{V}>As^{V} ≥As^{III}; however, no one is constantly toxic.The order reveals that DMAV with lowest uptake have highest phytotoxicity (Raab *et al*., 2007), which is 18 times more toxic than As^{III} in animals. Due to similarities with iP, As^{V} replaces iP from the various biochemical reactions (As^{V} sensitive reactions) viz. cellular metabolism (glycolysis and oxidative phosphorylation) and biosynthesis (phospholipid metabolism), information storage and retrieval (DNA and RNA metabolism), and cellular

signalling (protein phosphorylation/ dephosphorylation) (Gresser, 1981). The leading iP-needed reaction is the phosphorylation of ADP to ATP by the F1Fo-type ATP synthases complex present in inner mitochondrial membrane and thylakoid membrane of plastids; where mitochondrial enzyme uses As^{V} instead iP and produces ADP-As^{V} and uncouples both the reactionsby blocking ATP production (Gresser, 1981). Similar to ATP synthase reaction, the GAPDH enzyme of glycolysis replaces iP by As^{V} with similar kinetics to that of iP-dependent reaction. The phosphorolysis of different nucleosides is catalysed by purine nucleoside phosphorylase (PNP) by producing free nucleotide base and ribose-1-phosphate, where replacement of iP with As^{V} produces ribose-1-As^{V}, the reaction called arsenolysis with similar KM value to that of iP-dependent reaction (Park and Agrawal, 1972).

In contrary to this, As^{III} is highly reactivetoward thiol groups, which can bind up to three sulfhydryl groups and makes As^{III} as cross-linking agent like GSH. It could also bind with the single molecule of poly-thiol compound like phytochelatins (PC; Cys-rich GSH polymerization product). The stability of AsIII complexes increases with the increasing number of formed bonds, thus greater stability of As^{III}-trithiol complexes suggesting the fact that As^{III} favourably binds zinc-finger proteins containing three or more Cys residues (Zhou *et al*., 2011). As^{III} binding to dithiols will be greater when sulfhydryl groups are in close proximity to one another (CX0–14C) but the ideal spacing for trithiols is not known. As^{III} is an inhibitor of several enzymes like at about 115µM As^{III}, half maximal inhibition of pyruvatede hydrogenase was found while MMA^{III} is a more powerful inhibitor of GR and thioredoxin reductase (Lin *et al*., 1999) like enzymes and at very low concentration it displace Zn^{2+} from a zinc-finger protein of DNA repair and gene expression. As^{III} either taken up by roots directly or formed due to reduction of As^{V}, combines with sulfhydryl rich protective molecules viz. GSH and PC (Pickering *et al*., 2000; Liu *et al*., 2010). As^{III} favorably by binding with polythiols forms As^{III}-PC3 complexes over PC2 or oxidized GSH complexes (Raab *et al*., 2005), which then transported to vacuoles for dumping thereby restricting its transport to aerial parts of plant. Therefore, As toxicity in plants depends on how efficiently As^{III} is deactivated by thiol compounds and dumping into vacuoles; however in *P. vittata*, little As^{III} binds to PC in roots, instead it is transported to fronds through xylem and sequestered as free As^{III} in vacuoles (Pickering *et al*., 2006).

As^{V} and As^{III} exposure in plants induced overproduction of ROS like superoxide radical ($O_2^{\bullet -}$), hydrogen peroxide (H_2O_2) and hydroxyl radical (OH), which damage amino acids, nucleic acids, proteins, purine nucleotides and cause lipid peroxidation of membranes (Mallick *et al*., 2011) thereby disturbing the redox status of the cell. Although pants have evolved defence strategies to encounter ROS toxicity like superoxide dismutase (SOD) converts highly toxic $O_2^{\bullet -}$ into less active but longer lasting H_2O_2, which either directly or indirectly can be neutralized by catalase. Besides catalase, there are two component systems in plants to regulate H_2O_2 level in cells. The first one comprises a group of non-enzymatic antioxidants such as anthocyanin, ascorbate (AsA), GSH, NPTs, PC, and carotenoids (Song *et al*., 2010). The second one is made up of monodehydroascorbate reductase (MDHAR), dehydroascorbate reductase (DHAR), and GR. Together, these enzymes efficiently recycle AsA and GSH to allow further cycles of H_2O_2 reduction (AsA-GSH cycle), which requires reducing powerin the form of NAD(P)H (Foyer *et al*., 2011), thus AsA-GSH cycle play an important role in maintaining ROS balance in plants.

Concluding remarks

Excellent work have been done till date on As metabolism in plants starting from its uptake, analogy with iP, transportation, sequestration, binding with sulfhydryl group, detoxification, oxidative injuries and antioxidant defence system to encounter As toxicity. However, some loopholes in understanding the mechanism like accumulation of large quantity of As by As-hyperaccumulators without any injury/ poisoning, raises the question that how the As-hyperaccumulators cells are skilled of keeping As^{III} away from vital metabolic targets during sequestration and translocation process? Or Which part of plants are most susceptible to As toxicity and why? Why low concentrations of As stimulates growth? The answer of all these questions will provide great insights into the mode of action of As in plants in near future.

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