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Arsenic Pollution in Agriculture: Its Uptake and Metabolism in Plant System

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Abstract

Arsenic is widely distributed in the soil, water, air and all living matters. Presently arsenic pollution through food-chain contamination is a major health concern worldwide. It poses menacing damage compared to arsenic pollution in drinking water. Arsenic may occur in both inorganic and organic forms. Arsenate can compete with phosphate within the plant cells disturbing the energy flow in the cell. Arsenite reacts with a number of enzymes and tissue proteins that can cause inhibition of cellular function and finally death. Arsenate is taken up by plants via phosphate uptake system, while arsenite is taken up through water channels or aquaporins in the roots. Arsenic is then transported from root to leaves through xylem. However, different forms of arsenic have different translocation efficiencies. Different crop plants have exhibited varying tendencies to accumulate arsenic in different plant parts in the following order, root > stem > leaf > economic produce. Plants can combat with arsenic accumulation either by formation of antioxidant enzyme system or by chelating the toxin with certain ligands (e.g. metallothioneins, phytochelatins) or by sequestering them in sub- or extra-cellular organelles and thus prevents the normal metabolic process from the interference of arsenic.

Keywords: Contamination; Phytochelatins; Sequestration; Stress; Toxicity

Abbreviations: WHO: World Health Organization; ROS: Reactive Oxygen Species; OH: Hydroxyl Radicals; Pht1: Phosphate Transporter 1; NIPs: Nodulin 26-like Intrinsic Proteins; MIPs: Major Intrinsic Proteins; MMA: Mono Methyl Arsenic Acid; DMA: DiMethyl Arsinic Acid; SH: Sulfhydryl; MTs: MetalloThioneins; PCs: Phyto Chelatins

Introduction

Arsenic, a metalloid, occurs naturally in the environment through various geological and anthropological activities [1] and poses a great environmental risk due to its widespread food-chain contamination and carcinogenic toxicity. Thousands of people of Bangladesh and India are now suffering from arsenicosis, and the World Health Organization (WHO) has described it as "the largest mass poisoning of a population in history". Arsenic contamination in groundwater and therefore the incidence of high concentrations of arsenic in drinking-water is a major public-health problem in many parts worldwide [2,3]. However, huge lifting of such contaminated groundwater for crop irrigation purposes has aggravated the problem to a vulnerable level leading to serious health hazards of more than 110 million people of South and Southeast [4]. It can be noted that only less than 10% of the total contaminated groundwater accounts for drinking purpose while major share (>90%) is used for crop-irrigational requirements and quantifying the influence of arsenic in soil–plant systems has received attention only recently [5]. The gradual build up of arsenic in the soil consequently is a continuous process [6]. These arsenic enriched soils are now being considered as major sources of contamination in the food chain and water supplies and of great concern to the entire ecosystem, arsenic being a potential carcinogen and mutagen as well [7]. Many rice soils have being supported by irrigation with highly-contaminated water for 10-20 years or more the arsenic build up is considered toxic for the crop now [8,9]. More than 1000 metric tons of arsenic is being added to soil every year in Bangladesh alone resulting in arsenic accumulation in soils and elevated uptake of arsenic by crops [10]. Food crops grown on arsenic contaminated soils are potentially important route of human exposure to arsenic, especially in populations with rice-based diets [11]. High accumulation of arsenic in rice plants threatens human health as almost 50% of the world population consumes rice as their staple food [12]. In this context, the knowledge of arsenic uptake by the plant roots and its metabolism within plant system would be very crucial.

Arsenic toxicity and plant response

The toxicity of arsenic compounds depends largely on its speciation means the oxidation state. The toxicity of arsenic compounds follows the order: arsine (-3) > organo-arsenic compounds > arsenites (+3) and oxides (+3) > arsenates (+5) > arsonium metals (+1) > native arsenic. Once being taken up by plants, arsenic may be toxic in a number of ways. Arsenic breaks the biochemical function of cells and severely impedes different plant metabolic processes viz. photosynthesis, transpiration, respiration and other physiological functions through reacting with proteins and enzymes, and ceases plant growth [13]. Arsenic exposure of plants causes considerable stress and leads to growth inhibition, physiological disorders and finally death [14]. Oxidative stress is one of the most common effects of arsenic accumulation in plants as it promotes overproduction of reactive oxygen species (ROS) including singlet oxygen ($^1O_2$), superoxide ($O^{2\cdot}$-),hydrogen peroxide (H_2O_2), and hydroxyl radicals (OH) [15]. Seed germination, biomass production and yields of a variety of crops are significantly reduced at elevated levels of arsenic [16]. Inhibitory affects of arsenic on seed germination have been reported in many crops such as rice [17], wheat [18] and vegetables [19]. Plants develop several others toxicity symptoms such as decrease in plant height [20], depressed tillering [21], reduction in root growth [22], decrease in shoot growth [23], reduction in photosynthesis rate [24], reduced number of filled grains/ panicle [25] and reduced crop productivity [26]. A specific form of arsenic toxicity in rice is straight head disease. It is a physiological disorder that causes panicle sterility and can visually be identified as empty panicles standing upright instead of bending downward at maturity.

Uptake of arsenic species into plant root

Arsenic can enter into the root symplast by crossing the plasma membrane of the root endodermal cells probably through the action of a membrane pump or it can enter the root apoplast through the space between the cells. Arsenic can be taken up by plants in both arsenite and arsenate forms through different mechanisms. Arsenate and phosphate share the same transport pathway in higher plants and it is via phosphate transporter [27]. The uptake mechanism involves co-transport of phosphate or arsenate and protons [27]. Phosphate transporter 1 (Pht1) family is involved in expression of over 100 phosphate transporters which are strongly expressed in roots [28]. Arsenite is the predominant form of arsenic in reducing environments and it is actively taken up by plants via nodulin 26-like intrinsic proteins (NIPs) which represent one of the four subfamilies of the plant major intrinsic proteins (MIPs), commonly called as aquaporins [29]. Organic arsenicals like monomethylarsenic acid (MMA) and dimethylarsinic acid (DMA) are usually minor arsenic species [30] and can be taken up by plants, but generally in less efficient manner than inorganic arsenate or arsenite [31, 22]. However, the uptake mechanism of MMA and DMA is still very unclear [32].

Transport to the leaves

After the entry into roots, a small fraction of arsenic is exported to the shoot via the xylem as oxy-anions (arsenate and arsenite). The flow of the xylem sap will transport to the leaves once the element is loaded into the xylem. It is then loaded into the cells of leaf from xylem again by crossing a membrane. Arsenite transport in rice roots shares the same efficient pathway as silicon and thus it is efficiently accumulated in rice [33]. Organic arsenic is more readily translocated within plant though its uptake is much lower as compared to inorganic arsenic [22]. However inorganic arsenic is readily translocated from root to shoot, and different crop plants exhibit different tendencies of accumulation and tolerance to arsenic. Some hyperaccumulator ferns likely Pteris vittata, Pteris cretica can efficiently translocate arsenic from root to frond and concentrate in that tissue suggesting the higher potentiality of ferns in phytoremediation [34].

Arsenic metabolism

The arsenic concentration tends to build up from the contaminated groundwater to the crop, via soil and contaminated irrigation water. The accumulation pattern follows the order of root > stem > leaf > economic produce for most of the crops examined which might be due to sluggish movement of arsenic that rendered it to be less mobile within plant body [35]. Following uptake by plant root, arsenic can be converted to a less toxic form through chemical conversion or by complexation at any point along the transport pathway. Arsenic is predominantly present in plant tissues as arsenite even if plants are exposed to arsenate and this probably occurs through the rapid reduction of arsenate to arsenite enzymatically by arsenate reductase and non-enzymatically by glutathione or ascorbic acid followed by formation of an arsenite-thiol complex. Thus arsenate does not have high enough cytoplasmic concentration to exert toxicity [36]. Consequent upon the reduction of arsenate to arsenite in plants, arsenic may further be biomethylated to MMA, DMA, tetramethylarsonium ions and trimethyl arsonium oxide leading to further oxidative stress [37]. Within plant system, arsenate can compete with phosphate due to their similarity in kind and arsenate replaces phosphate from ATP to form unstable ADP-As leading to the disruption of energy flow in cells [38]. However arsenite is also highly toxic to plants as it breaks enzymatic activity by reacting with sulfhydryl (-SH) group of enzymes and tissue proteins and finally leads to death [13]. Arsenic stimulates the formation of free radicals and reactive oxygen species (ROS) and it occurs probably through the conversion of arsenate to arsenite [39]. ROS can directly attack lipid layers of the plasmamembrane causing its peroxidation and consequently disintegration of bio-membranes. However ROS is readily scavenged by the antioxidant defence system of plants composed of non-enzymatic antioxidants (ascorbic acid, glutathione, phenolic compounds, alkaloids, non-protein amino acids, and α-tocopherols) and antioxidant enzymes (superoxide dismutase, catalase, ascorbate peroxidase, glutathione reductase,

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monodehydroascorbate reductase, dehydroascorbate reductase, glutathione peroxidase, and glutathione S-transferase) [40,41].

Moreover arsenic is most likely detoxified by complexation of arsenite to phytochelatins and then transported out of the cytoplasm into the vacuole [13]. Chelates are compounds that containing many ligand sites that attach to the metal and the tight binding power of the chelate then renders the metal non-toxic. Chelates like metallothioneins (MTs) and phytochelatins (PCs) facilitate metal transportation in organisms. While metallothioneins exist in many kinds of organisms, phytochelatins are only produced by certain species of plants, fungi, nematodes and all groups of algae including cyanobacteria. Phytochelatins, thiol (-SH) rich peptides (common structure [α-glu-cys]n gly are oligomers of glutathione and are synthesized from reduced glutathione (GSH) by the transpeptidation of γ-glutamyl-cystein dipeptides, through the action of the constitutive enzyme phytochelatin synthase. The arsenite-PC complexes are stable at acidic pH, but dissociate into phytochelatin and free arsenite, with the latter getting oxidized to arsenate above pH 7.5. The final step for the accumulation of most toxic heavy metals is the sequestration of it in extra- or sub-cellular compartments to prevent disruption of cellular processes. Sequestration usually occurs in the plant vacuole where the arsenite- PC complexes must be transported across the vacuolar membrane [32].

Conclusion

The entry of arsenic, through contaminated groundwater-soil-agricultural produce into the food-chain is being taken as a serious consideration in the recent times. It may occur in both inorganic and organic forms in the biosphere. Plants can accumulate both inorganic and organic forms of arsenic. Plants can take up arsenic from soil and subsequently translocate from roots to aerial parts with different pathways and rates. Arsenate is taken up via phosphate uptake systems while arsenite is entered into the plant through aquaporins. Arsenate and arsenite can exert toxicity by competing with phosphate in the energy metabolism and reacting with –SH groups of enzymes, respectively. Redox stress caused by the cellular reduction of arsenate to arsenite generates reactive oxygen species. Arsenicals have been shown to bind to a variety of cytosolic proteins and macromolecule constituents of tissues. Complexation of arsenite with certain ligands, like metallothioneins or phytochelatins and following by sequestration of them in sub- or extra-cellular organelles or formation of antioxidant enzyme systems are important detoxification mechanism in a wide range of plant species.

Future Studies

The regulation of arsenic speciation, an essential tool for characterization of arsenic in the soil-water-plant-human continuum, is poorly understood. Uptake mechanisms of organic arsenicals is still not clear, whether if their occurrence in plant biomass is well proven. Arsenic metabolism typically occurs through biomethylation of inorganic arsenicals to give MMA, DMA, tetramethylarsonium ions and trimethyl arsonium oxide which can further be metabolized to form arsenocholin, arsenobetaine and arseno-sugars. However, no evidence of such metabolism has been found in the plants, although these compounds have been measured in some terrestrial plants.

Certain microorganisms like yeast, bacteria can reduce arsenate to arsenite, and then exclude the arsenite from their cells through arsenite transporter. The studies on arsenic exclusion would be of worthy in terms of arsenic resistance of plants as well as of lower levels of this toxicant in the plant biomass. The investigation towards long-term risk analysis and possibility of reduction in crop yield from the continuous build-up of arsenic in the soil from contaminated groundwater would be valuable to understand and formulate future strategies for managing the risks posed by arsenic-contaminated soils to plants.

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