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Review

The central role of hydrogen sulfide in plant responses to toxic metal stress

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ABSTRACT

With the increase of industrial wastes, sewage irrigation, chemical fertilizers and pesticides, metal contamination is increasingly serious. How to reduce the environmental risk has become a compelling problem in cultivated land. As a gaseous signal molecule, hydrogen sulfide (H_2S) is involved in multiple plant responses to toxic metal stress. Metal stress rapidly triggers endogenous H_2S production and exogenous H_2S alleviates metal toxicity in plants. To elucidate the role of H_2S in metal tolerance, the physiological and molecular mechanisms of H_2S in alleviating metal toxicity is necessary to be reviewed. Here, the latest progress on endogenous H_2S metabolism and the role of H_2S in plant responses to toxic metal stress were summarized and discussed. The mechanisms of exogenous H_2S in alleviating metal toxicity is proposed.

1. Introduction

With soil pollution becoming of a serious issue, the effects of metal stress on plant growth have attracted wide attention. The main toxicants that produce metal stress in plants come from mining, exhaust emissions, sewage irrigation, and use of metal products. Due to anthropogenic activities, the content of metals in the environment is beyond the normal range, resulting in the deterioration of environmental quality and ecosystem health. Widely concerned metals include copper (Cu), zinc (Zn), cadmium (Cd), aluminum (Al), arsenic (As), chromium (Cr), and lead (Pb). Excess exposure to metals inhibit seed germination and seedling growth, damage the antioxidant enzymes and membrane system, induce chromosome aberration, and lead to plant death. In addition, metal ions also seriously interfere with plant metabolism by inducing secondary stress such as nutrient imbalance, a large number of free radicals, and oxidative stress. The characteristics of metal stress are accumulation toxicity and root damage. Owing to the diversity of metals, the effects of metal stress are associated with plant species, injured tissue, metal types, and duration of treatment. Soil characteristics (pH, clay, organic matter, and redox potential) control the solubility, mobility, and bioavailability of metals. The toxicity of metal contaminants to plants brings environmental risks (Hooda, 2010). How to reduce the environmental risk has become a compelling problem in cultivated lands. However, plants alleviate the damage of metal stress by the corresponding mechanisms in the course of long-term evolution. Metal tolerance mechanisms include the restriction of metal absorption and transport on the roots, vacuolar compartmentation, the chelation with metallothioneins (MTs), phytochelatins (PCs) or organic acids, and the repair of damaged proteins by heat shock proteins. The improvement of plant metal tolerance by transgenic technology and bioremediation technology open up new way to repair metal pollution.

Similar to nitric oxide (NO) and carbon monoxide (CO), hydrogen sulfide (H_2S) is considered as the third gaseous signal molecule, which exists in bacteria, invertebrates, vertebrates, plants, and mammals (Wang, 2012). The emission of H_2S was originally detected from cucumber, squash, pumpkin, cantaloupe, corn, soybean, and cotton with the help of sulfur-specific flame photometric detector (Wilson et al., 1978). Hydrogen sulfide not only plays an important roles in plant growth and development, but also influences plant responses to environmental stress (Jin and Pei, 2015). H_2S inhibits the absorption and transport of metals, reduces the accumulation of metals in plants, and improves the stress tolerance of plants to metal stress. Although the reducing capacity of H_2S is lower than that of glutathione (GSH) and cysteine (Kabil and Banerjee, 2010), H_2S as a reductive substance, can directly scavenge reactive oxygen species (ROS), such as superoxide (Mitsuhashi et al., 2006), peroxynitrite and hypochlorite (Whiteman et al., 2004), and hydrogen peroxide (H_2O_2) (Geng et al., 2004). Similarly, there is the connection between H_2S and the mechanisms of ROS with production of H_2S in plants. To elucidate the role of H_2S in metal tolerance, the physiological and molecular mechanisms of H_2S in alleviating metal toxicity is necessary to be reviewed. In this review, the latest progress on endogenous H_2S metabolism and the role of H_2S in plant responses to toxic metal stress were summarized and discussed. The mechanisms of exogenous H_2S in alleviating metal toxicity is proposed. This will provide novel strategies for the genetic improvement of plant tolerance to metal stress.

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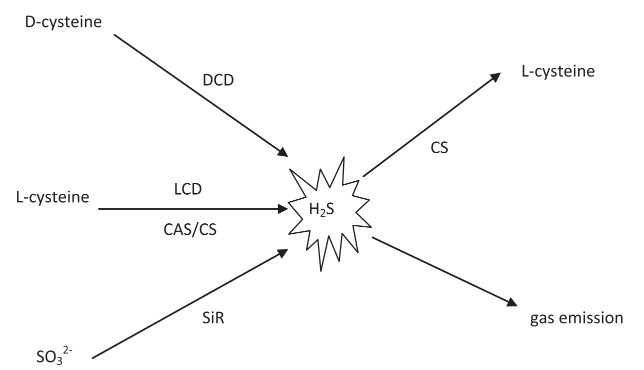

Fig. 1. H_2S metabolism in plants. CAS, cyanoalanine synthase; CS, cysteine synthase; DCD, D-cysteine desulfhydrase; LCD, L-cysteine desulfhydrase; SiR, sulfite reductase.

2. Endogenous H_2S metabolism in plants

Endogenous H_2S metabolism includes synthesis and decomposition of H_2S in plants (Fig. 1). The H_2S synthesis is composed of L-cysteine desulfhydrase (LCD), D-cysteine desulfhydrase (DCD), sulfite reductase (SiR), cyanoalanine synthase (CAS), and cysteine synthase (CS) pathway (Rausch and Wachter, 2005). LCD degrades L-cysteine to produce H_2S, ammonia (NH_3), and pyruvate, which exists in the cytoplasm, nucleus, and mitochondrion of plant cells. D-cysteine, as the substrate, is degraded by DCD to generate H_2S in mitochondrion. The sulfite ion is reduced by SiR to produce H_2S with an electron donor ferredoxin (Fed) in chloroplast. In cytoplasm and mitochondrion of plant cells, CAS can convert cyanide and L-cysteine into cyanuric acid and H_2S. Known as O-acetylserine (thiol) lyase (OAS-TL), CS catalyzes O-acetylserine (OAS) and H_2S to form cysteine in the cytoplasm, chloroplast, and mitochondrion. This reversible reaction can produce H_2S. Under the action of CS, excessive H_2S further is reduced to cysteine or protein/polypeptide containing cysteine except gas emission. The cysteine-degrading and H_2S-releasing enzymes have been characterized in higher plants (Papenbrock et al., 2007). Dependent on the balance between the generation and removal of endogenous H_2S, H_2S homeostasis is crucial importance for the adaptation of plants to metal stress.

Researchers suggest that metal stress rapidly triggers endogenous H_2S production (Table 1). The increase of endogenous H_2S content is associated with the enhancement of metal tolerance in plants. Cd^{2+} induced endogenous H_2S synthesis in *Medicago sativa* (Cui et al., 2014). 10 mM Cr^{6+} treatments for 24 h caused H_2S emission by 166.7% in *Setaria italica* through the up-regulation of *LCD*, *DCD*, and *DES1* expression (Fang et al., 2014a). The increase of H_2S content was dependent on NO in bermudagrass response to Cd stress (Shi et al., 2014). During the process of *Arabidopsis* response to Cd stress, abscisic acid (ABA)-related transcription factor WRKY regulated the transcript of *LCD* and *DES* to produce H_2S (Liu et al., 2015a). 0.5 mM Cd stress induced H_2S by 20% in rice seedlings (Mostofa et al., 2015). Salicylic acid (SA) enhanced the activity of LCD to activate H_2S production in the regulation of Cd tolerance in *Arabidopsis* (Qiao et al., 2016). In roots of *Brassica rapa* L. ssp. *pekinensis*, H_2S content was increased by 52.6% under 20 mM Cd treatment for 24 h (Zhang et al., 2015). The changes of endogenous H_2S content in plants under metal stress are related to the species, genotypes, and tissues of plants, different metals, metal concentrations, and the duration of treatment. That is, whether H_2S exerts toxic or protective effect is dependent on the concentration and location of H_2S in plants.

3. Exogenous H_2S alleviates metal toxicity in plants

Other authors have reported that exogenous H_2S can induce stress tolerance to toxic metals, such as Al, As, Cd, Cr, Cu, Pb, and Zn, thus alleviating metal toxicity in plants (Table 2). Hydrogen sulfide protects plants against the negative effects of toxic metals, which is related to the way and concentration of H_2S supply. Aluminum toxicity is one of the major limiting factors for crop productivity in acidic soil (Kochian et al., 2004). The pre-incubation of H_2S donor NaHS in wheat seeds alleviates Al-induced stress by increasing antioxidant capacity (Zhang et al., 2010a). The reduction of Al uptake and the elevation of ATPase and photosynthetic performance contribute to the alleviating role of H_2S on Al toxicity in barley seedlings (Dawood et al., 2012). H_2S-ameliorated Al toxicity in barley seedlings is related to the activation of antioxidant enzymes, the increase of citrate secretion, and the enhancement of plasma membrane H^+-ATPase (Chen et al., 2013). Exogenous H_2S alleviates Al toxicity in *Brassica napus* by improving photosynthetic parameters, nutrient concentration, and ultrastructural changes (Ali et al., 2015).

Arsenic and its compounds are common environmental pollutants, which are detrimental to plant growth and human health. Through up-regulation of the AsA-GSH cycle, H_2S alleviate toxic effects of As in pea seedlings. Furthermore, NO might be involved in the reduction of As accumulation (Singh et al., 2015). Besides, H_2S also has an alleviating effect against Cd toxicity in plants. NaHS as a donor of H_2S, alleviated Cd toxicity in alfalfa seedlings and NO was involved in this process (Li et al., 2012). Through the up-regulation of antioxidant enzymes and the activation of tonoplast Cd^{2+}/H^+ antiporters, H_2S alleviated Cd toxicity in *Populus euphratica* cells (Sun et al., 2013). Exogenous H_2S improved plant growth, enhanced photosynthetic parameters, regulated elements uptake, enhanced antioxidant activities, and alleviated ultrastructural changes in *Brassica napus* under the condition of high Cd stress (Ali et al., 2014a).

Exogenous H_2S improved Cd tolerance in bermudagrass by modulating ROS and osmolytes with NO together (Shi et al., 2014). By governing reduced (homo) glutathione and ROS homeostasis, LCD/DCD-mediated H_2S enhanced Cd tolerance in alfalfa seedlings (Cui et al., 2014). H_2S protected rice against Cd stress by reducing oxidative stress and maintaining mineral homeostasis (Mostofa et al., 2015). As a downstream signal, H_2S was involved in SA-induced Cd tolerance in *Arabidopsis* (Qiao et al., 2016). By up-regulating the activities of antioxidant enzyme, H_2S alleviated Cd-induced cell death in roots of *Brassica rapa* L. ssp. *pekinensis* (Zhang et al., 2015).

Calcium-dependent protein kinases (CDPKs) enhanced Cd tolerance in *Arabidopsis* via H_2S-mediated decrease in oxidized glutathione (GSSH) content (Qiao et al., 2016). By enhancing the activities of

Table 1
Reports on the effects of metals on H_2S content in plants.

Plant species	Tissue	Metals	Concentration and duration of treatment	H_2S content	References
Medicago sativa	Root	Cd^{2+}	200 μM/12 h	increase	Cui et al. (2014)
Sataria italica	Leaf	Cr^{6+}	10 mM/24 h	increase	Fang et al. (2014a)
Cynodon dactylon	Leaf	Cd^{2+}	750 μM/6 days	increase	Shi et al. (2014)
Arabidopsis	Leaf	Cd^{2+}	50 μM/2 days	increase	Liu et al. (2015a)
Oryza sativa	Leaf	Cd^{2+}	500 μM/3 days	increase	Mostofa et al. (2015)
Arabidopsis	Root	Cd^{2+}	100 μM/72 h	increase	Qiao et al. (2015)
Brassica rapa	Root	Cd^{2+}	5 mM/48 h	increase	Zhang et al. (2015)