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Review

Mechanisms of organic acids and boron induced tolerance of aluminum toxicity: A review

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ABSTRACT

Aluminum is a major limiting abiotic factor for plant growth and productivity on acidic soils. The primary disorder of aluminum toxicity is the rapid cessation of root elongation. The root apex is the most sensitive part of this organ. Although significant literature evidence and hypothesis exist on aluminum toxicity, the explicit mechanism through which aluminum ceases root growth is still indefinable. The mechanisms of tolerance in plants have been the focus of intense research. Some plant species growing on acidic soils have developed tolerance mechanisms to overcome and mitigate aluminum toxicity, either by avoiding entry of Al^{3+} into roots (exclusion mechanism) or by being able to counterbalance toxic Al^{3+} engrossed by the root system (internal tolerance mechanism). Genes belonging to ALMT (Aluminum-activated malate transporter) and MATE (Multidrug and toxin compounds extrusion) have been identified that are involved in the aluminum-activated secretion of organic acids from roots. However, different plant species show different gene expression pattern. On the other hand, boron (B) (indispensable micronutrient) is a promising nutrient in the tolerance to aluminum toxicity. It not only hinders the adsorption of aluminum to the cell wall but also improves plant growth. This review mainly explains the critical roles of organic acid and B-induced tolerance to aluminum by summarizing the mechanisms of ALMT, MATE, internal detoxification, molecular traits and genetic engineering of crops.

1. Introduction

Acid soils comprise up to 40% of the world's potentially arable lands. Aluminum is the third most abundant element after oxygen and silicon (Von Uexküll and Mutert, 1995). In Australia, ~50 Mh, approximately half of the agriculture soils are acidic (Ryan, 2018) and red soils in China cover an area of 102 Mh (accounting for over 20% of the country's total land area) and are mainly distributed in the tropical and subtropical regions of China (He et al., 2004). Aluminum is usually present as oxides and aluminosilicates that are non-toxic to plants. However, as soil pH drops down ($pH \leq 5$), it transforms to toxic Al^{3+} which can be easily taken up by plants and can interfere with normal plant growth mechanisms (Kochian, 1995; Ryan et al., 2001). In acidic soils, aluminum toxicity is a major limiting factor for crop development and productivity due to loss of basic cations (Ca^{2+}, Mg^{2+} and K^{+}) and increased concentration of soluble Al^{3+} and limited availability of indispensable nutrients (especially phosphorus, molybdenum and magnesium). The loss of these cations creates a charge imbalance, which is then compensated by the discharge of proton. Inhibition of root elongation is the major symptom of aluminum toxicity (Ma and Furukawa, 2003), which becomes apparent within a short period and even a small concentration of aluminum may induce root growth inhibition (Kochian, 1995). The roots are the most sensitive part of the plant (Eticha et al., 2005) and more recently, the transition zone or distal elongation zone of the root has been regarded as the most sensitive to aluminum (Li et al., 2016). Generally, root elongation is characterized by cell division and cell elongation, nevertheless, interruption of cell elongation is considered a major cause of inhibition of root growth. Aluminum toxicity also reduces the uptake of water, nutrients and interferes with cellular activities in sensitive species (Ma and Furukawa, 2003; Kochian et al., 2005). Acid soils also disturb the existence and persistence of soil rhizobia, affecting the efficacy of nodulation and N-fixation in legume species (Graham and Vance, 2003).

Apoplastic binding of aluminum is considered as the most critical and predominate mechanism in the expression and resistance to aluminum toxicity (Eticha et al., 2005; Yang et al., 2011a). Al^{3+} is trivalent cation and is strongly attracted by negatively charged ions present on the cell wall (Horst et al., 2010). Aluminum may interrupt the cell wall properties, interfere with the transport of molecules across the membrane, disrupt the plasma membrane and impair many

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intercellular processes that are essential for proper functioning of cell processes (Kochian, 1995). The pectin matrix of the cell wall, carboxylic groups, cellulose, and hemicellulose possess a great affinity for aluminum ions and binding of Al^{3+} to these compounds results in the alteration of cell wall composition, structure, and architecture of cell wall components (Yang et al., 2011a). However, the exact mechanism of inhibition of root elongation by aluminum toxicity is still not clear (Tandzi et al., 2018). Moreover, molecular mechanisms underlying aluminum toxicity are not well known because of aluminum interference with multiple sites in the symplast and apoplast (Matsumoto, 2000; Kochian et al., 2015; Bojórquez-Quintal et al., 2017; Singh et al., 2017).

The mechanisms of tolerance in plants have been the attention of intense research. In this review, we discussed different aluminum tolerance mechanisms and summarized the aluminum-induced secretion of organic acids in different plants. We also highlighted the role of micronutrient boron in aluminum tolerance in plants. Mechanisms of protection of roots may include, (1) exclusion mechanism through root exudation and chelating ligands, (2) internal detoxification and/or compartmentalization into the vacuole, (3) less binding of aluminum to the cell walls (see the section of boron-induced tolerance of aluminum).

2. Strategies of aluminum tolerance in plants

2.1. Exclusion mechanism of aluminum tolerance

Some plant species growing on acidic soils have developed tolerance mechanisms to overcome and resist aluminum toxicity (Ma et al., 2001; Barbierbrygoo et al., 2011; Kochian et al., 2015). These mechanisms of aluminum tolerance in plants make them stronger to grow under harsh conditions of phytotoxicity by detoxifying aluminum (Ma and Furukawa, 2003; Kochian et al., 2005), either by the exclusion of aluminum from root tips or intrinsic detoxification of aluminum ions that were already absorbed by plant roots (Sade et al., 2016). In plants, aluminum tolerance is achieved by mechanisms involving organic acids (OA) (Klug and Horst, 2010; Ryan, 2018). A number of aluminum tolerant plants have been identified that are able to secrete organic acids from roots (Ryan et al., 1995; Yang et al., 2013; Chang et al., 2016) which prevent direct contact of aluminum with the sensitive tissues within the cell or on the root apex. The organic acids form a stable complex with aluminum ions (Ma et al., 2001; Sharma et al., 2016). Most of the plants that are in the categories of aluminum excluders also need the shielding of root tips from toxic aluminum ions present in the immediate surface of roots. The exclusion of phytotoxic aluminum from roots and homeostasis of essential nutrient are prerequisite mechanisms of tolerance to aluminum (Kichigina et al., 2017). It is quite impossible for plants to detoxify all aluminum present in the soil, therefore, plants only neutralize a part of Al^{3+} which surrounds root apex. Thus, the first response of plant is the detoxification of toxic aluminum surrounding root apex which has the potential to enter into root cells. This could be a primary target of organic acids (Delhaize et al., 1993a). Several plant species also detoxify metals other than aluminum like Fe, Zn, Cd, and Ni (Chen et al., 2017). The increase of rhizosphere pH has been reported to be a mechanism of aluminum resistance, as it can reduce the solubility of Al^{3+} and ultimately aluminum toxicity (Yang et al., 2011a).

Although many organic acids are secreted from roots, however, some of them are effective in tolerance to aluminum. The effective organic acids typically include citrate, malate, oxalate, and acetate (Ma et al., 1998; Ma and Hiradate, 2000; Matsumoto, 2000), and are considered excellent chelating agents involved in the adaption of plants to toxic environmental conditions including aluminum stress (Igamberdiev and Eprintsev, 2016). The exudation of organic acid is carried out by plant roots in response to high concentration of aluminum ions (Yang et al., 2008). There are considerable reports that show the priority of secretion of organic acids in response to aluminum (Delhaize et al., 1993b). In some cases, the citrate might be more dominant than malate and oxalate. However, all these organic acids function in the neutralization of toxic aluminum (Sasaki et al., 2004; Furukawa et al., 2007). It can be assumed that organic acids shield the root apex by forming defensive scabbard (Klug and Horst, 2010).

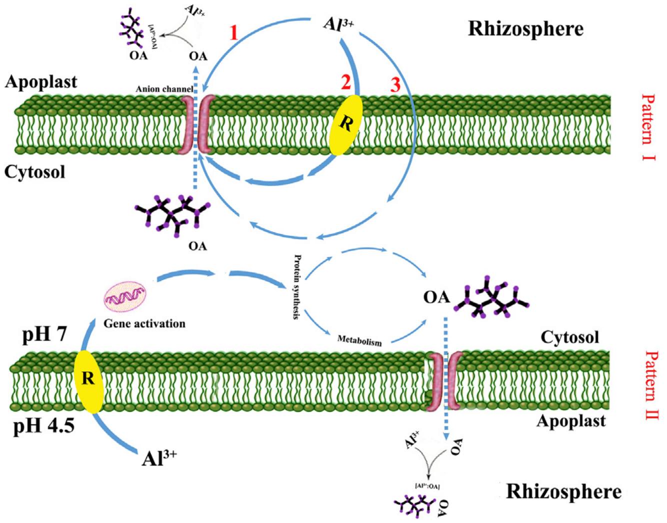

Fig. 1. Models for the aluminum (Al)-stimulated secretion of organic acid anions (OA) from plant roots. For Pattern I-type responses, Al activates an anion channel on the plasma membrane that is permeable to organic acid anions. This stimulation could occur in one of three ways: (1) Al^{3+} interacts directly with the channel protein to trigger its opening; (2) Al^{3+} interacts with a specific receptor (R) on the membrane surface or with the membrane itself to initiate a secondary-messenger cascade that then activates the channel; or (3) Al^{3+} enters the cytoplasm and activates the channel directly, or indirectly via secondary messengers. The Al-activated efflux from maize probably occurs by mechanism 1; the mechanism activating malate efflux from wheat is not known. In the Pattern II response, Al interacts with the cell, perhaps via a receptor protein (R) on the plasma membrane, to activate the transcription of genes that encode proteins involved with the metabolism of organic acids or their transport across the plasma membrane. Organic acid anions form a stable complex with Al, thereby detoxifying Al^{3+} in the rhizosphere. Experiments have identified some of the components shown in the model for Pattern I whereas the components depicted for Pattern II are entirely speculative.

Organic acid secretions from roots are usually categorized into two patterns based on their time of exudation upon the exposure of aluminum; Pattern-I (P-I) and Pattern-II (P-II) (Fig. 1) (Ma et al., 2001; Ma, 2005). In pattern-I, there is no apparent delay between the aluminum exposure and release of organic acids, usually occurs within 15–30 min (Ma and Hiradate, 2000) while pattern-II involves the exudation of organic acids in a delay process generally after a few hours (4–10 and sometimes more than 48 h) of Al^{3+} exposure (Li et al., 2000). For example, in *Urochloa decumbens*, secretion of the organic acid is achieved after a lag phase of 72–96 h (Arroyave et al., 2017). Pattern-I indicates the preexisting mechanism of release of organic acids, only it needs Al^{3+} to activate transporters and does not require stimulation of novel proteins (Ryan et al., 2001). On the other hand, pattern-II requires activation of novel proteins and genes that are involved in the organic acid metabolism or in the transport of organic acids anions (Ma et al., 2001).

The secretion and transport of organic acids need a medium and are mostly carried out by anion channels and transporters situated on the plasma membrane. Studies using the patch clamp technique (measures the transport activity directly) have confirmed that aluminum-activated exudations of organic acids are mediated by anion transporters or anion channels (Pineros and Kochian, 2001; Pineros et al., 2002), and inhibition of these transporters affect the secretions of organic acids (Zheng et al., 1998). Increasing evidence exhibits that the influence of this anion channel depends on the species of organic acids (OA)