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Aluminium Phytotoxicity and Plant Acclimation to Acidic Soils

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ABSTRACT

Aluminium toxicity is an important factor inhibiting plant productivity in acidic soils. Thus, in the present review, a short focus is drawn to the Al risk assessment. In fact, this review aimed to provide sufficient background informations about techniques used to assess the potentially toxic aluminium species in environmental samples and knowledge about the mechanisms of aluminium toxicity and resistance in plants. In order to give a solution for the alleviation of the aluminium phytotoxicity in acidic soils, a special emphasis is paid to mechanisms of exclusion of aluminium from sensitive root tips and internal mechanisms of tolerance of high aluminium tissue levels. The most recently transgenic approaches are considered and combined with the physiological and biochemical approaches towards improving aluminium stress adaptation.

Key words: Aluminium, acidic soils, plant acdimation, phytotoxicity

INTRODUCTION

Aluminium (Al) is the most abundant metal and the third most common element in the earth's crust. Al toxicity is the primary factor limiting crop productivity in acidic soils, which comprise 40% of the world's arable land (Foy *et al*., 1990). Thus, it is an important factor limiting food production in many developing countries. As soil becomes more acidic, phytotoxic forms of Al are released into soil to high levels that affect root system structure, whole plant growth and seed yield. Previous works demonstrated that the root apex is the primary site of Al-induced root growth inhibition. In fact, Al can interact with a number of extracellular and intracellular substances like interaction within the root cell walls, disruption of plasma membrane and plasma membrane transport system, interaction with apoplastic and/or symplastic constituents (Horst *et al*., 2010). An important response to stress by aerobic cells is the production of Reactive Oxygen Species (ROS) (Giannakoula *et al*., 2010). Metals including Al are known to induce lipid peroxidation and oxidative damages in various plant systems and act as catalysts in ROS production (Giannakoula *et al*., 2008). These ROS produced in the cell are detoxified by both non enzymatic and enzymatic antioxidant system. These ROS, if not detoxified, can cause serious damage to proteins, lipids and nucleic acids (Achary *et al*., 2008; Zhang *et al*., 2010).

Crop productionn acid soils can be sustained by the application of lime (which is often not economic or practical because of its slow movement of lime especially in the deeper layers of subsoils (Foy *et al*., 1990) or by the application of gypsum (R'bia and Smiti, 2010). Furthermore, the production of cultivars with improved tolerance to acid soil stress is a solution to address this problem. In recent years, extensive researches have been focused on this subject, including

evaluation of germplasm for Al tolerance and the physiological, biochemical and molecular responses of plants to Al toxicity (Sasaki *et al*., 2004; Sledge *et al*., 2005; Narasimhamoorthy *et al*., 2007; Chandran *et al*., 2008a).

FORMS AND AVAILABILITY OF ALUMINUM IN THE SOIL

Al is the most abundant metal of the Earth's crust, constituting approximately 7% of its mass. The soluble forms of Al in the acid soils have various sources.

Aluminum exists in the soil in various mineral forms. It can be included in the hydroxides (gibbsite), the aluminosilicates (feldespaths, kaolinite, imogolite), the sulfates (jurbanite) and the phosphates (variscite) (Exley, 2003). The dissolution of Al starting from these various forms is controlled by several factors, whose principal ones are the pH, the ionic force and nature of the soil solution ions (Ritchie, 1995). The release of the ion Al^{3+} from the hydroxides or kaolinite is optimal at low pH (less than 3.5). Under these conditions, all the Al sites are occupied by protons H^+ (Ahn *et al*., 2001). The structure of the soil also influences the dissolution of Al. Indeed, the aggregation of the argillaceous particles prevents the H^+ protons from reaching their adsorption sites which decreases the rate of Al release (Furrer *et al*., 1991).

The major part of the soil solution $A1^{3+}$ ion comes from exchangeable Al which is related to specific surfaces of the soil by electrostatic forces (Pineros *et al*., 2002). Generally, the exchanges of Al^{3+} are external in the case of kaolinite and internal in the case of illite or smectite. Between the layers of silicated minerals, Al is present in the form of hydrolized polymers. It is then non-exchangeable but can react to the pH changes (Ritchie, 1995).

The availability of Al^{3+} in the soil solution is function not only of mineral dissolution or the exchanges with inorganic surfaces (Exley, 2003), but also of the soil-content in organic substances (Zhang *et al*., 2010). The reactions of Al with the organic substances in the soil were studied by several authors (Stevenson and Vance, 1989; Huang *et al*., 1995; Ritchie, 1995). These studies showed that Al can react with soluble or insoluble organic substances. The active fraction of the organic compounds, with high molecular weight (>1000), is represented by the humic substances whose insoluble form accounts for 25 to 67% of the totality of the soil organic matter (Stevenson and Vance, 1989). This form which adsorbs specifically Al contains carboxyl groups (ionizing in pH acids) which represents the total Cation Exchange Capacity (CEC) of the organic matter (Zhang *et al*., 2010). It also presents hydroxyls phenolic group which dissociate with basic pH (Ritchie, 1995). In addition, Tipping and Woof (1990) showed that the release of Al starting from the insoluble humic substances is slower in the presence of high calcium concentrations. The soluble form of the organic matter includes the humic acids, the low-weight fulvic acids and organic molecules (with low molecular weight) such as the citrate (Ritchie, 1995). These compounds can form complexes with Al and, thus, play the role of detoxificating.

The binding of Al to the organic matter of the soil depends on several factors: Constants of intrinsic connection to the carboxyl groups, the number of adsorption-sites, interactions between the sites, pH, the ionic force and the competition of other cations (Tipping and Woof, 1990). According to Noble *et al*. (1988), the chemistry of Al in solution is in close relationship with the pH. In solution, the monomeric species $A1^{3+}$ prevails under the acid conditions, while with higher pH, monomeric species $Al(OH)^{2+}$ and $A1(OH)_2^+$ are the major forms. With pH close to the neutrality, gibbsite, which represents a solid phase, is formed. The $Al(OH)_4$ form dominates under the basic conditions (Delhaize and Ryan, 1995). At the plant level, the toxicity of Al relates to only some of its soluble forms, whereas others have only low or no toxicity (Fageria *et al*., 1988). Thus, the

organic Al (Al-Citrate, Al-Fulvate...), the inorganic (Al-Sulfate.) and the polymeric forms are little or not toxic (Noble *et al.*, 1988). The forms of Al, which are generally considered as the most toxic are the inorganic monomers such as Al^{3+} and hydroxides (Alva *et al.*, 1986; Blamey *et al.*, 1990). However, the relative toxicity of the various monomeric inorganic Al forms is difficult to establish (Fageria *et al.*, 1988). Some authors consider that the Al^{3+} form is the most toxic. This result is established in the case of wheat (*Triticum aestivum*) and probably for the other monocotyledons (Rincon and Gonzales, 1992; Sasaki *et al.*, 2002). For some dicotyledons species, the hydroxide forms are recognized as the most toxic (Kinraide, 1991). According to Blamey *et al.* (1990), the forms Al^{3+} and $Al(OH)_2^+$, are rather responsible to the inhibition of the root growth of *Soya*. The pH as well as the presence of calcium or other cations may influence the expression of toxicity (Kinraide, 1991).

UPTAKE OF ALUMINUM BY THE PLANT

Kinetic studies carried out on the excised roots of several plant such as: *Brassica oleraceae, Lactuca glossed*, *Pennisetum clandestinium* and *Triticum aestivum* (Zhang and Taylor, 1991), showed that the Al uptake is biphasic: a linear initial phase that saturates quickly followed by a slower and almost linear phase. The uptake during the first phase represents the accumulation of Al in the apoplast, this Al is exchangeable because it can be easily desorbed by a citrate solution (Zhang and Taylor, 1991). The Al of the linear phase represents the portion that accumulated in the cytoplasm (Pettersson and Strid, 1989) or related to the apoplast and, thus, dependent on the metabolism (Zhang and Taylor, 1991; Giannakoula *et al.*, 2008).

ACCUMULATION AND DISTRIBUTION OF ALUMINUM INSIDE THE PLANT

The high accumulation of Al takes place on a level of the root apex (tip, meristem and elongation zone) which constitutes the most damaged zone root (Delhaize and Ryan, 1995; Silva *et al.*, 2010). According to Rincon and Gonzales (1992) and Silva *et al.* (2010), the root apex of the sensitive wheat cultivar *(Triticum aestivum)* accumulates eight times more Al than the tolerant cultivar. For *Zea mays,* aluminum is localized in the apoplastic spaces of the cells of the root epidermis (Rasmussen, 1968). The presence of impermeable bands of Caspary on a level of the maize root exodermis, represents a physical barrier which limits the entry of Al in the apoplast of the cortical cells (Vazquez *et al.*, 1999). After a long-period exposure, Al is localized on a level of external cortical cells (Wagatsuma *et al.*, 1987). Matsumoto (2000) distinguished 3 types of accumulating Al plants: (1) species, which accumulate Al in roots and leaves. The leaf Al concentration exceeds 1000 ppm in 12 pteridophytes from Venezuela (Olivares *et al.*, 2009). The tea plant (*Nicotina rustica*) is undoubtedly the most accumulating species whose leaves contain more than 20.000 ppm of Al, particularly, on the thick epidermis cells (Matsumoto, 2000; Zhang *et al.*, 2010). For species which accumulate Al in the leaves, it is possible that soluble complexes participate in the transport of the metal from roots to leaves and in the vacuole they represent the final stock form (Olivares *et al.*, 2009). (2) tolerant species which accumulate aluminum on their roots without being able to transport it to leaves part such as *Medicago sativa*. (3) species which exclude metal, such as wheat and barley (Foy *et al.*, 1990).

Al, a polyvalent cation under the acid conditions, is fixed on the negative charges of the free space of Donnan. These negative charges are essentially those of the pectic residues (Rengel *et al.*, 1995). The external root membrane represents a tank for the Al accumulation (Taylor, 1991). It accumulates about 70 to 90% of the total root Al (Giannakoula *et al.*, 2008). Al is binded to the free

carboxyl groups of the polygalacturonic acids. The presence of a high local Al concentration and/or of a raised pH on the root apoplast lead to the polymerization of Al (Vazquez *et al*., 1999).

The hydrophobic nature of double-layered lipidic of the membrane prevents the entry of ionic A1 in the cytoplasm. However, small quantities can cross the membrane, probably by endocytose of neutral complexes, proteins binded to the membrane, or through lesions created by the stress (Delhaize and Ryan, 1995; Giannakoula *et al*., 2008). In the symplast of the root apex, more than the half of a total Al of the roots was detected (Matsumoto, 2000). The symplastic majority of Al is located in the cytosol (48-64%), the rest is distributed between the nucleus (21-40%) and the mitochondria (10-16%) (Aniol, 1984). In the cytosol, Al is especially complexed by substances with high molecular weight such as proteins (Aniol, 1984) or with phosphatic compounds (Ward *et al*., 2010). An intracellular pH between 6.5-7.5 and the abundance of potential ligands involve a strong reduction in the cytoplastic concentration of Al^{3+}. This is explained by the strong affinity of Al for many important molecules involved in the metabolism (Haug *et al*., 1994). Al can either inhibit the vital function of the ligand on which it is binded (enzymes, calmoduline, tubuline, ATP, GTP and DNA) (Achary *et al*., 2008) or affect the other metabolic processes by the formation of this complex (Delhaize and Ryan, 1995).

MORPHOLOGICAL, PHYSIOLOGICAL, METABOLIC AND MOLECULAR ASPECTS OF ALUMINUM PHYTOTOXICITY

The Al, solubilized in the acid grounds, inhibit the growth of the plants, particularly that of roots (Sasaki *et al*., 1996). This inhibition is the most known of the symptoms of toxicity by Al (Delhaize and Ryan, 1995). Even micromolar concentrations of Al can affect the growth of roots at the first hours of exposure (Delhaize and Ryan, 1995). In the presence of toxic Al concentrations, the roots are severely damaged, with formation of nodules in the terminal zone (Rasmussen, 1968). Al effects are not restricted to roots, but also extended to aerial organs. In fact, leaves develop a red colour indicating a phosphorus deficiency (Rasmussen, 1968). Al also inhibits the development of the root-hairs (El-Saht, 2001). The apical zone of the root, strongly damaged, becomes thick, short and brownish (Foy *et al*., 1990). Previous works demonstrated that the exposure to Al of this zone only (from 2 to 3 mm) is enough to start the inhibition of the root growth (Ryan *et al*., 1995). When Al is selectively applied to the elongation zone or to the totality of the root except the apex (apical meristem), the growth is not affected (Ryan *et al*., 1995). Moreover, Vazquez *et al*. (1999) described fast changes in the ultrastructure of the root cap cells as response to Al. Ryan *et al*. (1995) showed that the root cap does not have a crucial role in the mechanism of toxicity by suggesting that the root apical meristems is the primary site of toxicity. On the other hand, it has been suggested that Al could act indirectly via signals which make intervene the root cap and the root growth hormones (Matsumoto, 2000).

According to several studies, the inhibition of the root growth is associated to a reduction in the mitotic activity of the meristematic zones (Matsumoto, 1991). The accumulation of Al in the cell nucleus was observed in several plant species (Liu and Jiang, 1992). Matsumoto (1991) suggested that the formation of a DNA-Al complex would be responsible to the inhibition of the cellular division. Indeed, this author showed that for onion (*Allium cepa*), a reduction of the number of metaphases in the root tip cells. Whereas, Achary *et al*. (2008) provided evidence that Al induced oxidative stress leading to DNA damage in root cells of *Allium cepa*.

Some authors attributed the harmful effect of Al on the growth to an inhibition of the cellular elongation rather than to that of the cellular division (Rengel *et al*., 1995). More recently, Sasaki *et al*. (1996) demonstrated that, in two sensitive and tolerant wheat cultivars, the inhibition

of the root elongation is correlated to a lignification of the elongation zone. The cortical cells in this root portion are remarkably hypertrophied following the increase in their diameter. This hypertrophy was described by other authors and would be due to a change of cell-growth mode (Nichol *et al*., 1993). The thickening apical extremity of the root cap is initially due to an increase in the size of the cortical cells (Matsumoto, 2000). In addition, a stimulation of the root growth in the presence of low Al concentrations was described in acid conditions (Foy *et al*., 1990). This can be explained by an alleviating of the toxicity of the H^+ ions by Al (Kinraide, 1991). The beneficial effects of Al can be also ascribed to a larger solubilization of iron which increase its capacity to inhibit the growth of the harmful microorganisms living in partnership with the roots (Rufyikiri *et al*., 2000) or to a phosphate ion inactivation. Indeed, it was shown that the phosphate reduce the growth of some plant species (Ward *et al*., 2010). On the other side, Al tolerance could be benefic for the survival of microorganisms in Chilean volcanic soils which are characterized by low pH and high concentrations of Al in the soil solution (Jorquera *et al*., 2010). Indeed, their study showed that the loss of genes encoding for Al tolerance (The occurrence of Al-tolerance plasmids was investigated in the rhizosphere) may affect competitiveness particularly in the rhizosphere where competition is strong. Thus, the rhizosphere of pasture and crop plant growing in Chilean volcanic soil harbors genetic mobile elements which could play a role in the adaptation of bacterial populations to environmental stressors, such as Al-toxicity.

Al toxicity can cause a deficiency of some other mineral nutrients, more particularly Ca, Mg, K or P (Foy *et al*., 1990; Tan *et al*., 1993; Ward *et al*., 2010). This toxicity is often expressed as being a Ca deficiency (Foy *et al*., 1990; Sasaki *et al*., 2002). The interaction of Al with the ways of ionic transport is considered as one of the mechanisms of toxicity (Kochian, 1995; Taylor, 1991). Furthermore, the breaking of calcium homeostasis, which occurred at early stage of Al toxicity, causes stimulation of gene expression. Thus, in wheat, TaMDR1 (Triticum aestivum MDR) a gene encoding multidrug resistance (MDR) is induced by aluminium and inhibitors of calcium flux (Sasaki *et al*., 2002).

Several authors showed that, in the presence of Al, the uptake of certain divalent cations is reduced, particularly Ca and Mg and that their accumulation in the roots is reduced (Jan, 1991; Keltjens, 1995; Rengel *et al*., 1995; Olivares *et al*., 2009). Kinetic studies revealed the existence of a competition in the uptake of these cations with Al (Rengel *et al*., 1995). The presence of high Mg or Ca concentrations in the nutrient solution seems to decrease the toxic effects of Al (Keltjens, 1995; Olivares *et al*., 2009). The amelioration of the growth observed in the presence of these cations, is explained by an alleviation of the inhibited uptake of these elements (R'bia and Smiti, 2010). For the dicotyledons, Ca is more effective in the reduction of the toxic effects of Al than Mg, while the opposite is observed for the monocotyledons (Keltjens, 1995).

Al blocks the channels of Ca^{2+} in the plasma membrane of root apical meristems (Rengel *et al*., 1995). This effect is measurable in the minutes or even the seconds which follow the treatment (Huang *et al*., 1995). This can lead to a decrease of the Ca uptake causing its deficiency in the cytoplasm and a consequent disturbance of the cellular homeostasis (Rengel *et al*., 1995). The structure as well as the function of cells is consequently affected. Moreover, the inhibition of the Ca uptake involves a limitation of its transport to the leaves, this in order to maintain a normal Ca concentration in root cells (Huang *et al*., 1995).

Al inhibits the Mg uptake for many plant species (Tan *et al*., 1993). In this context, Keltjens (1995) reported that the increase in Al and H^+ concentrations cause a decrease in the uptake of Mg in wheat. The presence of these cations with high concentrations decreases the binding of Mg to the sites of exchange of nutrients. This results in a decrease in its uptake.

Some authors observed an increase in the K^+ concentration in the plants treated by Al (Giannakoula *et al.*, 2008; Silva *et al.*, 2010), whereas others noted the opposite (Olivares *et al.*, 2009; R'bia and Smiti, 2010). In addition, Al inhibits the K^+ channel in the plasma membrane. This effect was observed in *Zea mays* (Olivetti and Etherton, 1991) and in pea (Matsumoto, 1991). The coexistence in culture medium of a high concentration of Ca and Al can partially alleviate the inhibiting effect of this metal (R'bia and Smiti, 2010).

Al inhibits the uptake of phosphate and its accumulation in leaves (Fageria *et al.*, 1988). According to these authors, Al binds to the sites of adsorption on cell wall- root tip. The amorphous forms of Al hydroxides precipitate phosphate in solution. For this reason, phosphorus deficiency is one of the principal factors which limit the vegetable production in the presence of Al (Ward *et al.*, 2010). Al and phosphate are co-localised on the wall of the external cortical cells of the treated roots (Ownby, 1993; Vazquez *et al.*, 1999).

Many studies showed a decrease of the nitrate uptake (Keltjens, 1995; Durieux *et al.*, 1993; Lazof *et al.*, 1994). On the other hand, Nichol *et al.* (1993) showed a stimulation in the NO_3^- uptake which is associated to an increase or a small change in the nitrate reductase activity (Keltjens, 1995).

Ridolfi and Garrec (2000) showed that an excess of Al and a deficiency in Ca and Mg generate an alteration of the stomatal functionning and the net carbon assimilation of beech leaves. In fact, under the action of Al, the photosynthetic activity is partly reduced because of the stomatal closing (Moustakas *et al.*, 1996; Zhang and Liu, 2005). Al induces an alteration of the membrane permeability which affects the carbon metabolism and the stomatal regulation (Moustakas *et al.*, 1996). Aluminium influence the photosynthetic performance in Al-sensitive and Al-tolerant maize inbred lines. In fact, the Photosystem 2 activity and the Chlorophyll content were most severely affected in Al-sensitive maize line (Mihailovic *et al.*, 2008).

Al-Inhibits the H^+- ATPase activity by permanently altering the plasma membrane surface potentials in squash roots (Ahn *et al.*, 2001). Furthermore, Al can affect the activities of various enzymes of the intermediary metabolism, particularly those which are involved in the phosphorylation of sugars and/or the deposit of polysaccharides in the cell wall (Foy *et al.*, 1990). The effect of Al on the metabolism of the root apical meristems was examined in two cereals which differ by their tolerance to Al, the wheat (sensitive) and rye (tolerant). For the sensitive cultivar, the activities of, glucose 6-phosphate dehydrogenase (G_6PDH) and the 6-phosphogluconate dehydrogenase (6-PGDH) decrease in the presence of Al. These changes in the enzyme activities are accompanied by a reduction in the concentration of glucose 6-phosphate (G_6P) (approximately 90%) in wheat. This reduction is the result of a decrease in the root glucose concentration and in the hexokinase activity, which is responsible for its phosphorylation (Slaski, 1994). Al can also disturb the activities of many other enzymes. In fact, Copeland and De Lima (1992) showed that Al decreases the ADH activity in wheat roots. Sucrose synthase and lactate dehydrogenase activities also increase, but not to a greater extent. The increase in the ADH activity indicates a deviation of the carbohydrate metabolism from oxidation to fermentation, as shown for many plant species subjected to a hypoxia (Horchani *et al.*, 2010) or low temperatures (Christie *et al.*, 1991). The reaction catalyzed by the ADH provides the reducing power (NADH) allowing the glycolysis under anaerobic conditions. These biochemical changes can result from a reduction of the cellular permeability to O_2 and/or from a deterioration of the mitochondria functions (Slaski, 1994).

RESPONSES TO THE STRESS BY ALUMINIUM: MECHANISMS OF TOLERANCE

Some studies suggested that the plants which maintain a pH relatively high in the nutrient solution are tolerant to Al, whereas the plants which showed a faster acidification of the culture medium are sensitive (Taylor, 1991). Moreover, Blamey *et al.* (1990) showed that a variation of pH from 4.5 to 4.6, in the nutrient solution leads to a reduction of 26% in the Al concentration. Therefore, these pH changes induced by *Triticutn aestivum* could be a mechanism of tolerance to this metal. However, in 1990, Blamey et *al.* (1990) showed that for two varieties of *Lotus,* different by their tolerance to Al, the pH of the nutrient solution did not change. The plants which maintain a pH relatively high, in the root apoplast or in the rhizosphere, can generate a pH barrier in the soil-root interface which can reduce the solubility and limit the Al entry in the symplast (Blamey *et al.*, 1990; Wenzl *et al.*, 2001).

The tolerance to Al can be expressed by a preferential accumulation of this metal in the cell wall, from which results a reduction of transport to the symplast. Indeed. the root apoplast represents a privileged site for the accumulation of Al (Taylor, 1991). This metal can be extracted by a citric acid solution (Zhang and Taylor, 1991) and represents, probably, Al in the free space of the wall or Al fixed to the cation exchange sites of the apoplast (Horst *et al.*, 2010).

In addition to the root apoplast, the plasma membrane can play the role of a barrier which limits the Al entry (Taylor, 1991; Ahn *et al.*, 2001). The presence of a metabolic inhibitor, the DNP, reduced the effectiveness of this barrier. This effect is observed in some plant species which show an increase in the Al uptake when they are exposed to metabolic inhibitors (Wagatsuma *et al.*, 1987). Thus, the exclusion of Al is an active process in which the membrane plays a crucial role (Taylor, 1991; Zhang and Taylor, 1991; Ahn *et al.*, 2001).

The phosphate, released actively from the roots, forms an insoluble complex with Al. The precipitation of Al in the form of hydroxides, in the membrane surface, could restrict its transport in root (Vazquez *et al.,* 1999). Ward *et al.* (2010) showed that an active efflux of phosphate is important to determinate the tolerance to Al.

The Al efflux can constitute a possible mechanism of tolerance (Zhang and Taylor, 1991). Indeed, the working of a pump, excluding Al, maintains a low concentration of this metal in the cytoplasm (Taylor, 1991; Matsumoto, 2000). The efflux of Al which is carried out against an electrochemical gradient must be coupled to the hydrolysis of ATP or another energy source (Taylor, 1991). In the presence of DNP, there is inhibition of this pump and thus the stimulation of the Al uptake (Zhang and Taylor, 1991). But, the effect of the DNP can result in an inhibition of the exudation of ligands and/or phosphate which binded Al in the rhizosphere (Taylor, 1991). Therefore, the efflux of Al could not be distinguished from the mechanism of exudation.

Internal mechanisms can take place if those which limit the entry of Al in the symplast are ineffective or not achieved (Taylor, 1991). Because of the high affinity of Al for several compounds such as the inorganic phosphate, nucleotides, the ARN, the DNA..., the low Al concentrations in the cytoplasm are very toxic (Haug *et al.*, 1994; Taylor, 1991). For maize plant, in response to Al treatment, proline (Pro) concentration increased three-fold in roots of tolerant plants, while a slight increase was observed in roots of sensitive-line plants. A substantial carbon surplus (two-fold increase) was observed in roots of the Al-tolerant maize line. Carbohydrate concentration remained almost unchanged in roots of Al-sensitive line plants. Al treatment triggered the enhancement of lipid peroxidation in the sensitive line, while no change was observed in lipid peroxidation level (the production of malonaldialdehyde (MDA) remains constant) in the tolerant maize line (Giannakoula *et al.*, 2010). These data provide further support to the hypothesis that a mechanism

exists that excludes Al exclusion mechanism from the roots of the tolerant maize line, as well as an internal mechanism of tolerance that minimizes accumulation of lipid peroxides through a higher Pro and carbohydrate content related to osmoregulation and membrane stabilization (Giannakoula *et al.*, 2008).

Although the compartmentation in the vacuole was considered as a possible mechanism of tolerance for other metals, there is no evidence that such a mechanism plays a role in the case of Al (Taylor, 1991). For *Zea mays*, Vazquez *et al. (*1999) demonstrated that the vacuolar concentrations of soluble inorganic phosphates decrease in the presence of Al. This result can reflect the formation in the vacuole, of insoluble Al-phosphate compounds. However, these authors observed also a reduction in the concentration of total phosphate as response to Al. This led to suppose that stress by Al reduces the acquisition of phosphate and consequently its deficiency (Ward *et al.*, 2010).

Some metals, in particular Cd, Zn, Cu and Pb induce the synthesis of low- molecular-weight protein, the phytochelatins, which can have a role in the mechanisms of tolerance to metals. In *Triticum aestivum,* in response to a thermal shock, newly synthesized proteins are able to confer a protection against the Al stress (Pettersson and Strid, 1989). These authors suggested that the tolerance induced by a thermal shock could be the result of a high production of phytochelatins. This result is confirmed by Christie *et al.* (1991), which observe at *Zea mays, an* increase in the rate of the glutathion which is a precursor of the phytochelatins. Al tolerance in maize is also correlated with increased level of proline (Giannakoula *et al.*, 2008).

The synthesis of enzymes, which function normally in the presence of Al in the cytosol, constitutes a possible mechanism of tolerance (Taylor, 1991). By studying the mechanism of inhibition of the Magnesium transport by Rengel *et al.* (1995) showed that the transport system of Mg in the tolerant cultivar of *Lolium multiflorum* has a larger affinity for Mg than in the sensitive one. Taylor (1991) reported that in the cytosol, Al binds to enzymes leading to an inhibition of their activities. In *Secale cereal, Triticum aestivum, Hordeum vulgare and Avena sativa,* the degree of tolerance is correlated to the activity of the NAD kinase. The maintenance of a normal activity of this enzyme represents a potential mechanism of tolerance (Slaski, 1994). The response of the antioxidant enzymes, superoxide dismutase (SOD) and peroxidase (POD), to Al stress was studied, in roots of two inbred maize lines (*Zea mays* L.). Giannakoula *et al.* (2010) showed that increased activities of the SOD and POD were found in Al-treated roots of the tolerant maize line, in which the level of membrane lipid peroxidation remained almost unchanged. These results suggest that Al toxicity may be mediated by oxidative stress and that the better protection of the Al tolerant maize roots against Al-induced oxidative damage results, at least partially, from the increased activity of their antioxidative system (Giannakoula *et al.,* 2010).

The exudation of chelate ligands, in the rhizosphere, can protect the plants from the toxic effects of Al. Indeed, these ligands are able to form stable complexes, with this metal, reducing then its activity (Taylor, 1991). The organic acids exudation by roots could be an efficient mechanism for the Al exclusion (Jones and Kochian, 1982). In fact, the organic acids are involved in many chemical reactions in the soil. Among these chemical reactions, the detoxification of metals and the increase in the solubility of some nutritive elements (Kochian, 1995). The reactions of detoxification are a complexation reactions which occured by the carboxyl groups in the soil solution (Jones *et al.*, 1996). In this last, the malate can make, for the plant, more available microelements such as Fe, Mn and Zn (Jones *et al.*, 1996). In the same way, the citrate stimulates the release of Fe starting from the solid phase Fe $(OH)_S$ (Gerke, 1992; Jones and Kochian, 1982). By chelating Al, the organic

acids reduce its toxicity (Delhaize and Ryan, 1995; Pellet *et al*., 1995). Indeed, at certain species of plants such as *Agrostis stolonifera, Medicago sativa, Oryza sativa* and *Trifolium subterraneum,* it was shown that the Al-EDTA complex is less toxic than free Al (Ma *et al*., 2001). In plant tea (*Camellia sinensis*), Morita *et al*. (2008) showed that the Al-oxalate complex is less toxic than the inorganic form of Al. The addition of citrate or succinate, in the nutrient solution, restores the growth of *Triticum aestivum* in the presence of Al (Ownby, 1993).

The malate exists in the cytosol in the form of a divalent anion. Its transport outside the cell must be compensated either by an equal efflux of cations or by an equal uptake of anions in order to maintain the electroneutrality of the cytosol (Delhaize and Ryan, 1995).

In wheat, the tolerance for Al is correlated to a malate efflux starting from root tips (Delhaize and Ryan, 1995). The wheat cultivars (sensitive and tolerant), show differences in the malate efflux (Basu *et al*., 1994) which could be a general mechanism of tolerance in wheat (Ryan *et al*., 1995). This role is showed by the fact that the malate efflux is specifically stimulated by Al and that the addition of the malate, in the nutrient solution, protects the sensitive cultivar against Al toxicity (Delhaize and Ryan, 1995).

The released malate can either be binded to the anion exchange sites of the soil solid phase, or remain free in solution or can be degraded by the micro-organisms of soil (Jones *et al*., 1996). It is able to form complexes with Al of the soil solution. Jones *et al*. (1996) showed that the complexation of Al by the malate in the soil solution occurs at the expense of the other cations (Fe, Mn, Cu, Zn, Ca, Mg). This results show that the A1-malate$_2$ complex present the greater stability. In the soil solution, the malate can reduce the activity of $A1^{3+}$ ions by chelation. It follows a local increase in the pH and so a reduction of the $A1^{3+}$ activity by pH effects (Delhaize and Ryan, 1995). The mucilage secreted by the root cap can contain concentration of malate, sufficient for protect the root apex from the inhibiting effect of Al (Henderson and Ownby, 1991).

The malate efflux, from the cytosol toward the external solution, is against the electrochemical gradient and involves channels on a level of the plasma membrane (Delhaize and Ryan, 1995). In the Al mechanism of action on the opening of the channel permeable to the malate, exist 3 possible ways by which Al stimulates the opening of the channel: (1) Al interacts directly with the protein channel and causes a change of its conformation and so an increase in its permeability; (2) Al interacts with a specific receptor of the membrane or directly with this last and via second messengers in the cytoplasm; (3) Al enters the cytoplasm and deteriorates the activity of the channel, either directly by binding to him or indirectly through transduction signals. Basu *et al*. (1994) showed that the malate efflux at the tolerant plants is accompanied by *de novo* synthesis of malate. On the other hand, Ryan *et al*. (1995) showed that the activities of the phosphoenol pyruvate carboxylase (PEPC) and the malate dehydrogenase, two important enzymes in the malate synthesis pathway, are not different at the sensitive and tolerant cultivars. These tolerant cultivars have the same capacity to synthesize the malate on a level of their root tips. The tolerant cultivar is then more efficient to transport the malate out of its tip (Delhaize and Ryan, 1995). These informations are confirmed by Ward *et al*. (2010), which showed that the phosphorous status can influence the response to Al^{3+} by inducing a greater utilisation of PEPC-derived organic acids for Al^{3+} detoxification. Furthermore, Sasaki *et al*. (2004) showed that the enhanced Al tolerance exhibited by some cultivars of wheat is associated with the Al-dependent efflux of malate from root tips. Malate forms a stable complex with Al that is harmless to plants and, therefore, this efflux of malate forms the basis of an hypothesis to explain Al tolerance in wheat. These authors reported that ALMT1 (aluminum-activated malate transporter), that co-segregates with Al tolerance in F2

and F3 populations derived from crosses between near-isogenic wheat lines that differ in Al tolerance. The ALMT1 gene encodes a membrane protein, in *Medicago truncatula*, which is constitutively expressed in the root apices of the Al-tolerant line at greater levels than in the near-isogenic of Al-sensitive line (Chandran *et al.,* 2008b). Heterologous expression of ALMT1 in Xenopus oocytes, rice and cultured tobacco cells conferred an Al-activated malate efflux. Additionally, ALMT1 increased the tolerance of tobacco cells to Al treatment. These findings demonstrate that ALMT1 encodes an Al-activated malate transporter that is capable of conferring Al tolerance to plant cells (Sasaki *et al.*, 2004; Chandran *et al.,* 2008a). This transgenic approach was also used by Sledge *et al.* (2005) and Narasimhamoorthy *et al.* (2007) to valorize the *Medicago truncatula* germplasm as a potential source of Al stress resistance. In fact, *Medicago truncatula* Gaertn., a close relative of alfalfa (*M. sativa* L.), is negatively affected by Al toxicity. The objective of these studies was to assess the variation for Al tolerance among *M. truncatula* accessions, with the long-term goal of identifying Al tolerance genes to be used for alfalfa improvement. Barley (Hordeum vulgare) is considered to be most sensitive to Al toxicity among cereal species. Al tolerance in barley has been assessed by several methods, such as nutrient solution culture, soil bioassay and field screening. Genetic and molecular mapping research has shown that Al tolerance in barley is controlled by a single locus which is located on chromosome 4H. Molecular markers linked with Al tolerance loci have been identified and validated in a range of diverse populations (Wang *et al.*, 2006). Transgenic barley (*Hordeum vulgare L.*) expressing the wheat aluminium resistance gene (TaALMT1) shows enhanced phosphorus nutrition and grain production when grown on an acid soil (Delhaize *et al.*, 2009).

Several plant species such as bean and maize exude citrate instead of malate (Pineros *et al.*, 2002). The tolerant cultivar of bean (*Phaseolus vulgaris*) exudes approximately ten times more citric acid than the sensitive cultivar in response to Al (Miyasaka *et al.*, 1991). In the same way, at maize, the exudation of citric acid is more important at the tolerant cultivar (Pellet *et al.*, 1995). The detoxification of Al by the citric acid involves the formation of a very stable complex. The other organic acids, such as succinate or malate appear less efficient than the citric acid (Ownby, 1993). Released in the soil solution, the citrate is able to be fixed to Al of the soil solid phase (Jones and Kochian, 1982; Pineros *et al.*, 2002) estimated at 10 - 20% the citrate complexed with Al in the soil solution and the remainder is complexed with other divalent cations such as Ca, Fe and Mg. When it is selected in absence of insoluble phosphate, it exudes more of citrate and becomes consequently more sensitive to Al than the wild-type (Koyama *et al.*, 1990). These results show that the exudation of citrate by the tolerant line is induced by a phosphate deficiency and not by a direct toxicity of Al. The tolerant line is able to use insoluble phosphate by releasing the citrate. This one forms a stable complex with Al. Thus, the inorganic phosphate is released (Koyama *et al.*, 1990).

The phytotoxicity of Al could be limited by the formation of stable complexes with the organic acids in the cytosol. In general, the Al stress decrease the root and foliar concentrations in organic acids. This reduction is more important at the sensitive cultivars (Foy *et al.*, 1990). The tolerant cultivars are able to preserve normal concentrations of organic acids through an immobilization, a compartmentation, a detoxification or by a mechanism which limits the entry of Al in the cytosol (Foy *et al.*, 1990). On the other hand, at the sensitive cultivars, the inhibition of the key enzymes in the biosynthesis pathway or the degradation of the organic acids leads to an accumulation of the substrates and a reduction of the reaction products (Taylor, 1991). Thus, at *Triticum aestivum,* the presence of Al induces an increase of the cis-aconitic acid concentration on the leaves and reduces the fumaric acid (Foy *et al.*, 1990). The differential tolerance with Al at the maize cultivars is not

correlated to the root and foliar concentrations changes in organic acids (Foy *et al*., 1990). The formation of Al complexes with the organic acids in the cytosol is not probable, considering the low solubility of the ion $A1^{3+}$ ($6H_2O$) by the presence of Al (OH) $_3$, with pH close to the neutrality of the cytoplasm. Other oxygen donor ligands can have an important role in the detoxification of Al in the cytosol (Taylor, 1991). Ma *et al*. (2000) shows that in triticale, a hybrid between wheat and rye, aluminum tolerance genes on the short arm of chromosome 3R are linked to organic acid release. In fact, the action of the genes for Al tolerance on the short arm of triticale chromosome 3R is highly specific to Al. The marked lag phase in the inhibition of root elongation and the release of organic acids (malate and citrate) implies that the expression of genes on the short arm of triticale chromosome 3R is induced by Al and that these genes are necessary for the release of organic acids.

CONCLUSION

Our review shed light on comprehensively understanding how plants detoxify aluminum to survive in an acidic environment and shows that investigations into Al phytotoxicity and detoxification mechanisms are extremely complex. In fact, the severe problem of Al phytotoxicity is a challenge for plant molecular biology and a target for cooperation between plant and soil scientists. Thus, for resolving this problem from the practical point of view, the plant mechanisms leading to a decrease of $A1^{3}$+ activity at the membrane level has been studied under growth conditions which really reflect the ionic environment of the rhizosphere soil under field conditions. Therefore, further researches, reproduced in solution culture studies, several soil factors that have been shown to have a significant influence on the response of plants to Al-toxicity. These soil factors which can influence Al-tolerance responses in plants, are taken into account in the nutrient solution in the last studies, are soil compactation, mycorrhizal infection and soil organic matter.

Important progress and further investigations, made in the last decade at the molecular level, have clarified that differences in Al-tolerance between genotypes are due to differences in both plasma membrane composition and metabolic pathways leading to enhanced capacity for Al chelation. Therefore, this review shows that it is crucial to identify and select plants able to withstand increased environmental cues as natural selective pressures. Some genes, involved in both internal and external detoxification of Al at different cellular levels, were identified and transferred from one germplasm to another. This transgenic approach is very useful and should be coupled with the acidic soils amendments and with the others approaches of detoxification either by microorganisms or by chelation processes.

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