

## **Al<sup>3+</sup> - Ca<sup>2+</sup> INTERACTION IN PLANTS GROWING IN ACID SOILS: AL-PHYTOTOXICITY RESPONSE TO CALCAREOUS AMENDMENTS**

**C. Meriño-Gergichevich<sup>1</sup>, M. Alberdi<sup>2</sup>, A.G. Ivanov<sup>3</sup> and M. Reyes-Díaz<sup>2\*</sup>.**

<sup>1</sup>Programa de Doctorado en Ciencias de Recursos Naturales, Universidad de La Frontera, Temuco, Chile. <sup>2</sup>Center of Plant- Soil Interaction and Natural Resources Biotechnology, Scientific and Technological Bioresource Nucleus (BIOREN), Universidad de La Frontera, Casilla 54-D, Temuco, Chile. <sup>3</sup>Department of Biology and the Biotron, University of Western Ontario, London, Ontario, N6A 5B7 Canada. \*Corresponding author: [reyesm@ufro.cl](mailto:reyesm@ufro.cl)

### **ABSTRACT**

High aluminum (Al) concentrations as Al<sup>3+</sup> represent an important growth and yield limiting factor for crops in acid soils (pH ≤ 5.5). The most recognized effect of Al-toxicity in plants is observed in roots. However, damages in the upper parts (including stem, leaves and fruits) may also be present. In addition, Al-toxicity triggers an increase in reactive oxygen species (ROS), causing oxidative stress that can damage the roots and chloroplasts, decreasing normal functioning of photosynthetic parameters. Al-toxicity may also increase or inhibit antioxidant activities, which are responsible to scavenge ROS. As result of the negative effects of toxic Al, root metabolic processes, such as water and nutrient absorption, are disturbed with a concomitant decrease in calcium (Ca) uptake. Ca plays a fundamental role in the amelioration of pH and Al-toxicity through Al-Ca interactions improving physiological and biochemical processes in plants. Ca is a useful amendment for correcting these negative effects on crops growing in acid soils. This is an agronomic practice with alternatives, such as limestone or gypsum. There is little information about the interaction between amendments and Al-toxicity in physiological and biochemical processes in crops. Thus, the main objective of this review is to understand the interactions between Al<sup>3+</sup> and Ca amendments and their effects on the physiology and biochemical responses in crops growing in acid soils.

**Keywords:** Acid soils, aluminum, amendments, calcium, gypsum.

### **INTRODUCTION**

Andisols are acid soils developed from volcanic materials (Nanzyo *et al.*, 1993; Iamarino and Terribile, 2008). These soils comprise an acidity ranging from 4.5 to 5.5 (Samac and Tesfaye, 2003), a high organic matter (OM) content (Mora *et al.*, 2002; Takasu *et al.*, 2006a), low phosphorus (P) availability (Mora *et al.*,

2007) as well as low Ca, magnesium (Mg) and molybdenum (Mo) contents (Kleber and Jahn, 2007) and high levels of extractable Al and manganese (Mn) (Toma and Saigusa, 1997).

At pH ≤ 5.5, Al-toxicity is the main stress factor for plants (Poschenrieder *et al.*, 2008; Ryan and Delhaize, 2010),

which limits crop production (Jones and Kochian, 1997; Mora *et al.*, 1999). Acidic conditions enhance the presence of trivalent cation ( $Al^{3+}$ ) (Lidon and Barreiro, 2002; Kochian *et al.*, 2005), which is the most toxic of all Al species available to plants (Delhaize and Ryan, 1995; Hoshino *et al.*, 2000). Al-toxicity results in alterations of the physiological and biochemical processes of plants and consequently their productivity (Kumar Roy *et al.*, 1988; Mora *et al.*, 2006). The decrease in root growth is one of the initial and most evident symptoms of Al-toxicity at micromolar ( $\mu M$ ) concentrations in plants (Rengel and Zhang, 2003), inducing reduced capacity for water and nutrient uptake. Upper organs may be also affected by Al phytotoxicity (Reich *et al.*, 1994; Peixoto *et al.*, 2002). At the cellular level, toxic Al triggers an overproduction of oxygen reactive species (ROS) in cells (Blokina *et al.*, 2003; Ma, 2005), which alters the functionality of the biomembranes favoring oxidative damage in plants (Boscolo *et al.*, 2003; Guo *et al.*, 2006). The scavenging of ROS in plants can be regulated by enzymatic and non-enzymatic antioxidant systems (Shao *et al.*, 2008).

To overcome the limitations of Al phytotoxicity, Ca amendments are an agronomic practice commonly used to reduce acidity and Al-toxicity in acid soils (Toma and Saigusa 1997; Mora *et al.* 2002). Ca application to different crops is carried out by different economically viable options, such as lime and gypsum or phosphogypsum (PG) (Campbell *et al.*, 2006; Takahashi *et al.*, 2006a,b). They are often applied to soils to restore Ca and Mg availability for plants and adjust soil acidity (Carvalho and van Raij, 1997). There are many studies reporting the beneficial Ca effects in ameliorating Al-toxicity in different crops growing in acid soils (Illera *et al.*, 2004; Mora *et al.*,

2002) which resulted in an production increase of important commercial crops as soybean (*Glycine max*) (Caires *et al.*, 2006; Bachiaga *et al.*, 2007), wheat (*Triticum aestivum*) (Caires *et al.*, 2002), coffee (*Coffea arabica*) (Hue, 2005), tomato (*Lycopersicon esculentum*) (Tuna *et al.*, 2007) and others.

Although the effects of different Ca amendments on the physical and chemical properties of acid soils are well documented, limited information is available about the effectiveness of calcareous amendments on plant physiological and biochemical processes such as water and nutrient uptake, photosynthesis and antioxidant systems. Therefore, the aim of this review is to summarize the effects of Al-toxicity in plants, the interactions between toxic Al and different Ca amendments and their effects on the physiological and biochemical responses in cultivated plants growing in acid soils.

## GENERAL CHARACTERISTICS OF ANDISOLS

### Andisols and their properties

Andisols are typical soils developed from volcanic materials (Takahashi *et al.*, 2007), covering from 110 to 124 million hectares around the world (Sparks, 2004). It has been established that Andisol distribution is not restricted to volcanic areas and/or volcanic parent material (Iamarino and Terribile, 2008). These soils generally possess excellent physical properties such as low bulk density ( $<0.90 \text{ Mg m}^{-3}$ ), high permeability and high water-holding capacity (Takahashi *et al.*, 2007; Iamarino and Terribile, 2008). These soils are unique in terms of their aggregate structure, with well-defined and stable intra- and inter-aggregate spaces. Therefore, they commonly have a

relatively large specific surface area. Chemically, Andisols are characterized by high phosphate sorption capacity, acidity, Al and Mn toxicity (mainly non-allophanic Andisols), and are rich in cations such as silicon (Si), Al, iron (Fe), Ca, Mg, potassium (K) and sodium (Na) (Nanzyo *et al.*, 1993; Kameyama and Miyamoto, 2008).

#### **Aluminum forms in acid soils**

According to Kochian (1995), Al is the third most abundant element in the earth's crust, comprising about 7% of the total mass of the earth (Delhaize and Ryan, 1995; Zhang *et al.*, 2007). Lidon and Barreiro (2002) reported that rocks contain from 0.45 to 10% Al. Yakimova *et al.* (2007) considered that Al is one of the most abundant toxic elements with the ability to contaminate soil, water and trophic chains. Nonetheless, the specific biological functions of Al for animals and plants are unknown, and so it is not regarded as an essential nutrient (Poschenrieder *et al.*, 2008). Fortunately, in terms of agronomic activity, most Al is bound to insoluble forms such as aluminosilicates and/or precipitated as Al hydroxide sulfate (Takahashi *et al.*, 2006a,b). Al is solubilized from silicates and oxides (not toxic forms) to Al<sup>3+</sup>, which is phytotoxic only under conditions of low pH (Delhaize and Ryan, 1995; Wang *et al.*, 2006).

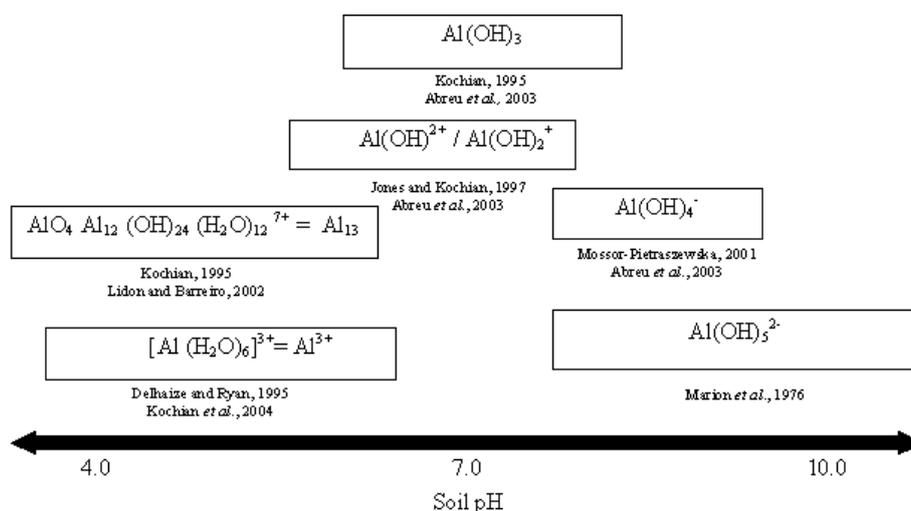
Numerous studies have reported that there are various Al forms in soils in monomer, polymer or solid phase, and that their concentration depends on the degree and duration of hydrolysis of the Al compounds (Delhaize and Ryan, 1995) (Figure 1). Rout *et al.* (2001) found a significant correlation between low pH and high concentrations of phytotoxic Al species, which is related to the reduction of exchangeable bases in the soil solution

(Mora *et al.*, 2006). Soil acidification is associated with inappropriate agricultural practices (Rengel, 1996), heavy winter precipitation that causes the loss of bases (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) due to leaching (Mora *et al.*, 2006), use of ammoniacal fertilizer (urea) and nutrient uptake by plants (Mora *et al.*, 2006). Hede *et al.* (2001) reported that the mineralization of OM may also contribute to Al-toxicity, resulting in a hydrogen ions (H<sup>+</sup>) release to soil environment reducing its pH, which determine an increase of Al<sup>3+</sup> release.

#### **Detrimental effects of aluminum on plants**

In the case of acid soils such as Andisols, a major stressful condition for plants and hence a constraint on agricultural production is Al-toxicity (Ma *et al.*, 2002; Langer *et al.*, 2009; Ryan and Delhaize, 2010), which occurs in approximately 40% of the planet's arable soils (Mossor-Pietraszewska, 2001).

Concentration dependence of Al-toxicity has been studied in various crops. Although Al concentrations in the nutrient solutions are within the micromolar range (25-1,600  $\mu$ M), they are sufficient to induce morphological and physiological damage in some crops, and even more significant changes in seedlings (Rengel, 1996). Many plants have no more than 0.2 mg Al g<sup>-1</sup> dry weight (DW) in their leaves, because the translocation of Al to the upper parts of the plant is very slow. However, plants such, as tea (*Camellia sinensis*), may contain up to 30 mg Al g<sup>-1</sup> DW in adult leaves (Mossor-Pietraszewska, 2001; Han *et al.*, 2007). Consequently, the tea plant is one of the 400 species classified as an accumulator of toxic metals in its tissues. Among others, rye (*Secale cereale*), cranberries (*Vaccinium spp.*) and some members of



**Figure 1.** Monomeric and polymeric forms of Al and pH of soil according to various authors. When pH is lower than 5.5 soluble forms available for plants are predominant.  $Al^{3+}$  and  $[AlO_4 Al_{12} (OH)_{24} (H_2O)_{12}]^{7+}$  ( $Al_{13}$ ), Al species are the most toxic to plants.

the *Proteaceae* family have also been described as effective accumulators of toxic metals (Bakker *et al.*, 2000).

There are several studies demonstrating that metabolic and morphological damages exerted by toxic Al species in plants and animals are often expressed by a dramatic decrease in productivity (Hoshino *et al.*, 2000). For example, Wang *et al.* (2006) reported that there was more than USD 600 million in estimated Al-toxicity-related losses in the agricultural sector in Australia in the first years of the 21<sup>st</sup> century (with a large area of acid soils with a high content of toxic Al). Mora *et al.* (2006) measured the effect of  $Al^{3+}$  on forage production and animal metabolism and reported that high concentrations of  $Al^{3+}$  correlates with a poor quality of pastures and higher risk of agricultural losses, including weight gain in livestock. In an earlier study, Chaney (1989) argued that 1,000 mg Al  $kg^{-1}$  should be the maximum level in the animal diet, although no report is given

regarding time units. Many studies considered that Al-toxicity is an important stress factor for plants (Ma 2005; Poschenrieder *et al.*, 2008), limiting plant growth, development and the subsequent performance of commercial crops (Rout *et al.*, 2001; Wang *et al.*, 2006) in various parts of the world with acidified soils (Rengel, 1996). It has been reported that Al inhibits the absorption of nutrients, especially Ca, Mg, Fe and Mo and less available P (Poschenrieder *et al.*, 2008) as well as promotes Mn and  $H^+$  toxicity (Wang *et al.*, 2006). Rout *et al.* (2001) mentioned that Al-induced effects in leaves resemble P deficiencies. Some other studies also demonstrated that Al excess induced similar if not identical effects to those observed under Ca and Fe deficiencies in rice (*Oryza sativa* L.), sorghum (*Sorghum bicolor*) and wheat.

The first and most recognized effect of Al-toxicity in plants is the inhibition of the division and elongation of meristematic cells and thereby the

reduction in root growth (Panda *et al.* 2003; Mora *et al.*, 2006). Under Al-toxicity, roots become thinner and darker in color resulting in lower efficiency for water and nutrient absorption; this effect is more pronounced in seedlings than in adult plants (Foy *et al.*, 1978). Other effects include a decrease in cell respiration; a major interference with the enzymes involved in biosynthesis of cell wall polysaccharides which results in elevated rigidity of the cell wall (Wang *et al.*, 2006).

In species susceptible to Al presence, symptoms of root damage have been linked to Al binding with carboxylic groups of pectins (Lidon and Barreiro, 2002), interruption in the synthesis of cellulose and/or accumulation of calose as well as mitosis inhibition in radical apices (Delhaize and Ryan, 1995) through blockage in DNA synthesis (Lidon and Barreiro, 2002). It has been reported that Al can induce programmed cell death in barley (*Hordeum vulgare*) roots after 8 hours of exposure to Al treatment (0.1-50 mM) due to the presence of ROS (Pan *et al.* 2001).

Despite the numerous reports on various effects of Al-toxicity in roots, and the fact that Al inhibits photosynthesis in many species (Lidon and Barreiro, 2002), there is a lack of detailed information about its effects on the structural integrity and functional performance of the photosynthetic apparatus (Poschenrieder *et al.*, 2008).

## **CALCIUM AND ALUMINUM IN PLANTS AND THEIR INTERACTIONS**

### **General role of calcium in plants**

Ca plays a key role as an essential nutrient in plants (White and Broadley, 2003). It is related to its role as a regulator of growth and development (Hepler, 2005) and is

indispensable in a number of metabolic functions/pathways (Plieth, 2005). As a divalent cation, Ca<sup>2+</sup> plays a structural role in cell walls and cell membranes. It also participates in root and stem elongation (White and Brodley, 2003). Ryan *et al.* (1997) indicated that a high quantity of this mineral is present in the apoplast, where it maintains cell and tissue viability. Its fundamental role in the structure and rigidity of the cell wall has been recognized and studied since the nineteenth century (Silva *et al.*, 2005; Shukry *et al.*, 2007). Ca forms ionic and covalent bonds with carboxylates of pectins in the polysaccharide matrix of the cell wall, which is relevant for growth and texture of plants, fruits and mature vegetables (Poovaiah *et al.*, 1988; Gilroy *et al.*, 1993). Hepler (2005) discussed about antagonistic interaction between Ca<sup>2+</sup> and indol acetic acid (IAA), where this acid is a chelator of Ca and Mg, thus allowing cell division and cell elongation. However, many report providing clear evidence that the inhibition of cell elongation by Ca does not prevent to IAA from stimulating cell wall synthesis.

At cell membrane level, Ca<sup>2+</sup> interacts with phospholipids, stabilizing the lipid bilayer and the structural integrity of membranes, thus controlling membrane permeability through interactions between phospholipids and membrane protein (Poovaiah *et al.*, 1988; Hepler, 2005). On the other hand, Ca<sup>2+</sup> plays a major role in extra- and intracellular signaling (Yocum, 2008). It regulates enzymatic activity (Cheng *et al.*, 2002), as well as homeostasis in both the chloroplast and mitochondria-activating ATP kinases and produces electrochemical potential (Ryan *et al.*, 1997). Ca is also involved as a second messenger in various signal transduction pathways in eukaryotic cells (Sanders *et al.*, 2002; Silva *et al.*, 2005), and is modulated at intracellular level in response to many signals such as

hormones, light, mechanical disruption, abiotic and biotic stress (Cheng *et al.*, 2002; Sanders *et al.*, 2002).  $\text{Ca}^{2+}$  is also involved in the photosynthetic process as an essential activator of the Mn redox chemistry that culminates in the release of  $\text{O}_2$  from photosystem II (PSII) in water photolysis (Hommann, 2002; Yocum, 2008), a process that could be inhibited when substituted by other cations such as  $\text{K}^+$ , rubidium ( $\text{Rb}^+$ ) and cesium ( $\text{Cs}^+$ ) (Ono *et al.* 2001). These results can be used to evaluate the role of Al in the photosynthetic apparatus. However, in an earlier study, Ca role in photosynthesis was evaluated by inducing Ca deficiency in sugar beet (*Beta vulgaris*) plants (Terry and Huston 1975). The authors reported that Ca deficiency had no effect on leaf carbon dioxide ( $\text{CO}_2$ ) uptake, photoreduction of ferricyanide or ATP formation via cyclic and non-cyclic electron transport in chloroplast and concluded that the  $\text{Ca}^{2+}$  requirement for efficient functioning of photosynthesis is very minimal. According to Hommann (2002) and Yocum (2008), PSII contains a set of intrinsic proteins such as (PsbA, B, C, D, E, and F) that can be restored by  $\text{Ca}^{2+}$  action.

#### **Physiological interactions of Ca-Al in plants**

It is accepted that the first plant responses to  $\text{Al}^{3+}$  damage appear in roots, resulting in a decrease in nutrient uptake (Wang *et al.*, 2006). Although Al-effects on roots have been intensively studied, the Al effects on leaf structure and functions of the photosynthetic machinery are poorly understood. In this way, some reports indicated that Al-induced leaf necrosis (Kumar Roy *et al.*, 1988; Zhang *et al.*, 2007), leaf yellowing (Foy, 1984), stunted leaf growth (Wang *et al.*, 2006) and late leaf maturity (Rout *et al.*, 2001) are effects of Al-toxicity. These changes were

accompanied by a reduction in chlorophyll content (Wang *et al.*, 2006) and photosynthesis rate (Reich *et al.*, 1994) and abnormal chloroplast structure (Akaya and Takenaka, 2001; Peixoto *et al.*, 2002). High Al/Ca ratios resulted in a reduced photosynthetic capacity and increased respiration in Scots pine (*Pinus sylvestris*) (Reich *et al.*, 1994). In relation to photosynthetic efficiency (PE) of a unicellular green alga *Euglena gracilis* (strain Z, Department of Plant Physiology, University of Lund, Sweden), this process was reduced after short-term exposure (1h) to 15.0 mg Al ( $\text{AlCl}_3$ )  $\text{L}^{-1}$ , although in long-term (7 days) experiments, PE was partially recovered (Danilov and Ekelund 2002). Moreover, Al-toxicity also affected the transpiration rate by reducing stomatal aperture (Kumar Roy *et al.*, 1988; Wang *et al.*, 2006). Reyes-Díaz *et al.* (2009) reported that photochemical and non-photochemical parameters, such as maximum quantum yield of PSII (Fv/Fm), effective quantum yield of PSII ( $\Phi\text{PSII}$ ), electron transport rate (ETR), and non-photochemical quenching (NPQ), respectively, differentially decreased in three cultivars of highbush blueberry (*Vaccinium corymbosum*) growing in hydroponic solution, due to short-term Al treatments (100 $\mu\text{M}$   $\text{AlCl}_3$ ).

The Ca-Al relation is strongly associated with growth and development in a wide variety of plants (Schaberg *et al.*, 2006). This interaction has been related to the toxicity that Al exerts on plants, which is principally mediated by  $\text{Ca}^{2+}$  deficiency. By contrast, its addition alleviates the toxic effects caused by  $\text{Al}^{3+}$  (Rout *et al.*, 2001; Rengel and Zhang, 2003). These interactions are the factors that must affect uptake and Ca translocation in plants growing in acid soils ( $\text{pH} \leq 5.5$ ) (Mossor-Pietraszewska, 2001). It has also been shown that Al excess competes or inhibits Ca and/or Mg

absorption capacity, which affects normal plant development (Watanabe and Osaki, 2002; Silva *et al.*, 2005). Thus, Al<sup>3+</sup> is a powerful inhibitor of Ca<sup>2+</sup> uptake in roots. According to Delhaize and Ryan (1995) and Kochian (1995), three mechanisms are proposed to explain Al-Ca interactions, as follows:

***Inhibition of Ca<sup>2+</sup> transport via symplasm by Al<sup>3+</sup>***

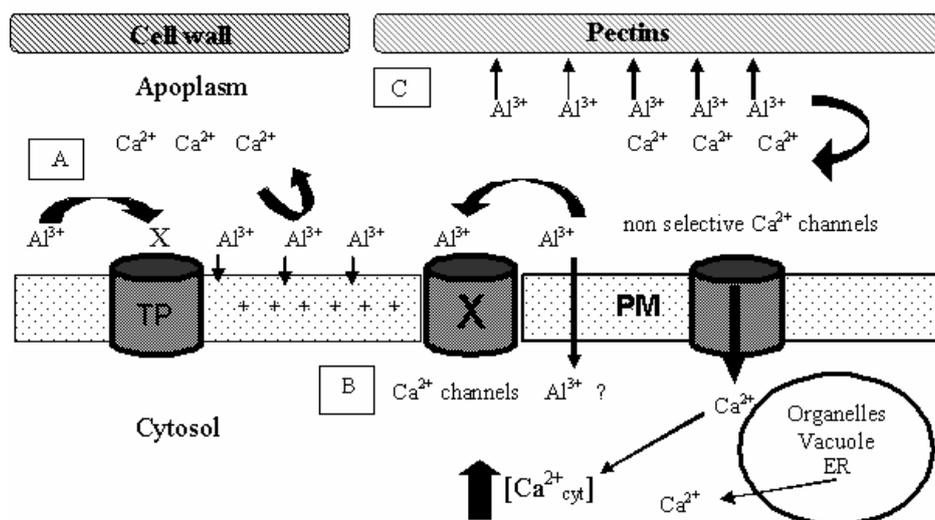
The surface charge of plasma membranes as well as the transmembrane potential can be modulated by Ca<sup>2+</sup> channel activity by affecting ion transport and other processes (Rengel and Zhang, 2003). Al<sup>3+</sup> is known to affect cell membrane structure and permeability by blocking the Ca<sup>2+</sup> channels (Ryan and Kochian, 1993; Plieth, 2005). Al<sup>3+</sup> may inhibit the influx of divalent cations as Ca<sup>2+</sup> into cells more than monovalent cations, but it stimulates the anion cell influxes. Binding of Al<sup>3+</sup> to cell membrane phospholipids and transport proteins, reduces the net negative membrane surface charge, permitting the movement of anions and restricting that of cations (Huang *et al.*, 1992) (Figure 2A). Thus, the alleviation of Al<sup>3+</sup> toxicity through Ca<sup>2+</sup> addition causes a reduction in the negative potential of the plasma membrane, leading to a drop in the electrostatic attraction of the toxic Al<sup>3+</sup> cation (Kinraide, 1998). Therefore, it is proposed that high external Ca<sup>2+</sup> decreases the Al<sup>3+</sup> amount entering the cytoplasm in root cells (Babourina *et al.*, 2005). Rengel (1992a) studied the mechanism of Al inhibition of net <sup>45</sup>Ca<sup>2+</sup> uptake by *Amaranthus tricolor* and concluded that Al ions affect net <sup>45</sup>Ca<sup>2+</sup> uptake by acting as a Ca<sup>2+</sup>-channel blocker (i.e. by binding to the verapamil-specific channel-receptor site) as well as by interfering with the action of the GTP proteins involved in the

regulation of transmembrane Ca<sup>2+</sup> fluxes. However, they found no effects of Al on the plasma membrane Ca<sup>2+</sup>-ATPase. Rengel (1992b) suggested that Al may disturb the symplasmic Ca<sup>2+</sup> homeostasis by altering the Ca<sup>2+</sup> flux pattern across the plasma membrane. The disturbance of transmembrane Ca<sup>2+</sup> fluxes may prevent an increase in cytosolic Ca<sup>2+</sup>. Huang *et al.* (1992) evaluated also the Ca<sup>2+</sup> transport mechanism in two wheat cultivars with contrasting tolerance to Al<sup>3+</sup> at pH 4.5. In the sensitive cultivar, Al<sup>3+</sup> induced an inhibition of Ca<sup>2+</sup> uptake, indicating that Al effects did not involve Al-Ca interactions in the cell wall. This suggested that Al inhibits Ca<sup>2+</sup> influx across the root cell membrane, through blockage of Ca<sup>2+</sup> channels (Figure 2A). Lindberg and Strid (1997) found that in two wheat Al-sensitive cultivars, subjected to a concentration of 50 mM of Al (as AlCl<sub>3</sub>), different effects on the transmembrane electrical potential (hyperpolarizations and depolarizations) of root cells when Al was added and after the plants were removed from the Al treatment. Besides rapid changes in cytosolic pH, K<sup>+</sup> and Ca<sup>2+</sup>-free concentrations were evidenced.

***Disruption of Ca<sup>2+</sup> homeostasis in cytoplasm by Al<sup>3+</sup>***

Cytosolic Ca<sup>2+</sup> concentration in plant cells is approximately 100-200 nM, and is typical for all eukaryotes (Lecourieux, *et al.*, 2006), while in apoplastic fluid and some cellular organelles Ca<sup>2+</sup> concentration is 104 to 105 times more (Hepler, 2005).

Ca intake to cells through permeable ion channels in the plasma membrane (White and Broadley, 2003) is gated by voltage changes, stretch and ligands such as IP<sub>3</sub>, cADP-R, glutamate, G proteins, among others (Rengel and Zhang, 2003).



**Figure 2.** Three mechanisms of Ca-Al interactions at cellular level. (A) Inhibition of Ca<sup>2+</sup> transport via symplasm by Al<sup>3+</sup>, (B) Disruption of Ca<sup>2+</sup> homeostasis in cytoplasm by Al<sup>3+</sup> and (C) Ca<sup>2+</sup> displacement by Al<sup>3+</sup> from apoplasm. (ER) Endoplasmatic reticulum, (PM) plasma membrane, (TP) transport protein.

The cytosolic Ca<sup>2+</sup> plays an important role as a regulator of cell expansion and division (Jones *et al.*, 1998) and it is known that its changes under controlled homeostasis permit cell viability (Bush, 1995). At very low external pH, the related control mechanisms cannot avoid a decrease in cytosolic pH; then the plant activates responses as an increase in Ca<sup>2+</sup> free concentrations (Plieth, 2005). Under acid conditions, exposure to Al<sup>3+</sup> generates a disturbance of pH homeostasis and cytoplasmic Ca<sup>2+</sup> (Ma *et al.*, 2002), which affects metabolic processes, such as cell division and elongation (Zhang and Rengel, 1999) (Figure 2B). Ma *et al.* (2002) correlated the increases of cytoplasmic Ca<sup>2+</sup> in rye root tip cells under two Al concentrations (50 and 100 mM AlCl<sub>3</sub>) with a slight increase in Ca<sup>2+</sup> at 50mM and 100 mM it produced a higher increase of cytoplasmic Ca<sup>2+</sup> (46%). The last value triggered an inhibition of root growth after two hours of Al exposure. These disruptions are

generally believed to be a primary trigger of Al-toxicity (Ma *et al.*, 2002). Other authors have indicated that this homeostasis disruption leads to an inhibition of Ca<sup>2+</sup>-dependent signal transduction, affecting cell division and cell elongation (Rengel, 1992a; Kochian, 1995; Jones *et al.*, 1998).

#### *Ca<sup>2+</sup> displacement by Al<sup>3+</sup> from apoplasm*

The importance of Ca in the cell wall is due to its role in the interaction of Ca<sup>2+</sup>-pectate as a regulator of growth and antagonism with IAA (Hepler, 2005). Cell wall components and intercellular spaces are a critical site in the apoplast, as this is the first contact site of the roots with potentially toxic Al species in a soil solution (Ryan *et al.*, 1997; Rengel and Zhang, 2003). In plants growing in acid soils, Al<sup>3+</sup> reacts with these cell wall components in roots (Rengel, 1996), particularly with Ca-pectate (Blamey *et*

*al.*, 1997), where Al<sup>3+</sup> binds to carboxyl groups (Poschenrieder *et al.*, 2008). Ma *et al.* (2007) mentioned that almost 85-99% of total Al corresponds to apoplastic content, and Ca<sup>2+</sup> is displaced from negative binding sites by Al<sup>3+</sup> in the apoplasm (Kinraide, 1998), because Al<sup>3+</sup> binds more strongly than Ca<sup>2+</sup> to pectin, a major constituent of cell walls (Rengel and Zhang, 2003) (Figure 2C).

### **Biochemical Ca-Al interaction in plants**

Under normal conditions, the physiological processes in higher plants produce relatively small amounts of ROS through the successive reduction of O<sub>2</sub> to H<sub>2</sub>O (Scandalios, 2002; Khan *et al.*, 2007). The term ROS includes free radicals as superoxide anion (\*O<sub>2</sub><sup>-</sup>) and hydroxyl (\*OH), and molecules such as H<sub>2</sub>O<sub>2</sub>, singlet oxygen (<sup>1</sup>O<sub>2</sub>) and ozone (O<sub>3</sub>) (Guo *et al.*, 2004; Khan *et al.*, 2007), which are a constant threat produced by photosynthetic organisms (Mittler *et al.*, 2004; Kochian *et al.*, 2005). The main sources of ROS in plants are organelles with a highly oxidizing metabolic activity or with an intense rate of electron flow such as chloroplasts, mitochondria and peroxisomes (Yamamoto *et al.*, 2002; Mittler *et al.*, 2004).

Various biotic or abiotic environmental stresses induce an increase in the ROS production (Foyer and Noctor, 2005) in plants, which can cause oxidative damage in different biomolecules such as lipids, proteins and nucleic acids (Guo *et al.*, 2004; 2006). Heavy metals are an important factor in the increased ROS production and oxidative stress in plants (Tamás *et al.*, 2005). The higher Al<sup>3+</sup> toxicity in acid soils, such as Andisols (Ma, 2005), triggers enhanced ROS production in plant cells accompanied by a strong correlation with oxidative stress in plants (Ma *et al.*, 2007). Although Al itself is not

a transition metal and can not catalyze redox reactions, it probably has a pro-oxidant function through \*O<sub>2</sub><sup>-</sup> formation (Yamamoto *et al.*, 2003; Tamás *et al.*, 2005). Thus, prolonged exposure to Al may be accompanied by enhanced peroxidation of phospholipids, membrane proteins and oxidative damage in all plant systems leading to cell death (Pan *et al.*, 2001; Panda *et al.*, 2003).

The oxidative damage triggered by Al<sup>3+</sup> can also induce ion loss, protein hydrolysis and even DNA strand breakage (Guo *et al.* 2006). Meriga *et al.* (2004) reported that the primary target of an Al-induced increase in ROS is plasma membranes, causing increased peroxidation of phospholipids and protein (Šimonovičová *et al.*, 2004). This trivalent ion can induce death in root tip cells in Al-sensitive maize cultivars by increasing the amount of ROS and protein oxidation (Boscolo *et al.*, 2003). In addition, Yamamoto *et al.* (2002) suggested that Al affects mitochondrial activity, thereby inhibiting cell growth.

A number of studies have reported that in parallel to increased ROS levels, Al stress also induces an increase in the antioxidant activity to reverse the deteriorating effects of these toxic species and increase the tolerance of plants to Al stress (Guo *et al.*, 2006; Khan *et al.*, 2007). For example, an enhancement of antioxidant activities was reported in roots of intact plants and cultured cells of *C. sinensis* subjected to Al treatments (Ghanati *et al.* 2005). Similarly, the antioxidant activities in root cells were stimulated in barley plants subjected to pH 4.0 and 100 μM Al (AlCl<sub>3</sub>) (Guo *et al.*, 2004). Okamoto *et al.* (2001) also reported that tolerance of photosynthetic organisms is mainly related to defense systems rather than prevention of oxidative damage. ROS scavenging and elimination in plants is regulated by non-enzymatic and enzymatic antioxidant

systems, which are highly compartmentalized (Shao *et al.*, 2008). The enzymatic antioxidant set includes enzymes such as superoxide dismutase (SOD), catalase (CAT), ascorbate peroxidase (APX) and glutathione reductase (GR), among others (Ma *et al.*, 2007). Various molecular compounds have also been reported to play effective (non-enzymatic) antioxidant functions: ascorbate and glutathione in hydrophilic conditions (Shao *et al.*, 2008),  $\alpha$ -tocopherol (Foyer and Noctor, 2005), vitamins C and E (Huang *et al.*, 2005),  $\beta$ -carotene (Stahl and Sies, 2003), (poly)phenols (Prior *et al.*, 2005) salicylic acids (SA) and flavonoids (Mittler *et al.*, 2004) including compounds such as flavones, isoflavones, flavonones, anthocyanins and catechins (Prior *et al.*, 2005).

$\text{Ca}^{2+}$  may also be involved in plant tolerance to different stresses by regulating antioxidant metabolism (Jiang and Huang, 2001).  $\text{Ca}^{2+}$  and  $\text{Ca}^{2+}$ -binding proteins such as calmodulin are involved in signaling events associated with ROS sensing through the activation of G proteins and the activation of phospholipids signaling, which results in the accumulation of phosphatidic acid (Foyer and Noctor, 2005). The localization of ROS signals in specific cell sites may be similar to that of  $\text{Ca}^{2+}$  signals in response to many stimuli (Mittler *et al.*, 2004). A cross-talk between  $\text{Ca}^{2+}$  and ROS originating from cell membrane-bound-NADPH oxidase is also involved in abscisic acid ABA-dependent signal transduction, inducing an effective antioxidant defense and enhancement of antioxidant enzyme as SOD, CAT, APX and GR activities (Jiang and Huang, 2001).

As mentioned above, the amelioration of Al-toxicity has been related to the use of cations such as Ca and Mg (Guo *et al.*, 2004), but the information related to Al-

Ca interaction and their effect on antioxidant activity in plants is scarce. In this context, Guo *et al.* (2006) found that Ca has a stimulating effect and increases the antioxidant enzymatic activity of SOD, POD and CAT in barley exposed to Al (100  $\mu\text{M}$ ). Furthermore, short-term Al-toxicity at high Al concentration (5mM) was mitigated by Ca and Mg by stimulating antioxidant enzyme activities in Japanese cedar needles (*Cryptomeria japonica*) (Takami *et al.* 2005). It is suggested that Ca/Al ratio also correlates with a SOD and CAT activity increase either with short-term or long-term treatment. Indeed, the application of lime (Calcitic) and P enhanced the antioxidant enzymes (POD and APX), improving the nutrition, thus, increasing the dry matter and yield of white clover growing in Andisols (Mora *et al.*, 2008). External Ca addition to two grass species, tall fescue (*Festuca arundinacea*) and Kentucky bluegrass (*Poa pratensis*), growing in nutrient solution increased also the activity of CAT, APX and GR, reduced lipid peroxidation and raised the relative water content (RWC) and chlorophyll (Chl) content (Jiang and Huang, 2001). Additionally, external  $\text{Ca}^{2+}$  treatment ( $\text{CaCl}_2$ ) allowed maize seedlings to keep relatively higher activities of antioxidant enzymes SOD, CAT and APX and lower levels of lipid peroxidation compared with  $\text{Ca}^{2+}$ -deficient treatments (Gong *et al.*, 1997). In contrast, Ogawa *et al.* (2000) demonstrated that although the active oxygen scavenging enzymes SOD and CAT were stimulated in hooky cypress (*Chamaecyparis obtusa*) treated with 5 mM Al ( $\text{AlCl}_3$ ), whereas Ca addition suppressed the antioxidant enzymes.

#### **Alleviation of Al-toxicity by $\text{Ca}^{2+}$**

There are many reports about the beneficial Ca effects on the amelioration

of Al-toxicity in different crops growing in acid soils (Mora *et al.*, 1999; Mora *et al.*, 2002). Akaya and Takenaka (2001) reported that Al-toxicity effects on the photosynthesis of *Quercus glauca* could be ameliorated by basic cations, especially Ca<sup>2+</sup> and Mg<sup>2+</sup>. Other studies have shown that soil pH increases after the application of Ca amendments due to the displacement of Al<sup>3+</sup> and H<sup>+</sup> by Ca<sup>2+</sup> from the exchange sites into the solution (Alva and Sumner, 1988; Mora *et al.* 1999).

It has also been recognized that the Ca/Al molar ratio (Ritchey and Snuffer, 2002) is a good indicator of Al stress in nutrient solutions (Akaya and Takenaka, 2001; Ritchey and Snuffer, 2002) and may be used to predict acidity effect on plant growth and development. Indeed, it has been demonstrated that there is a 50% risk of a negative effect on tree growth when the Ca/Al ratio in soil solution is below 1.0 (Takami *et al.* 2005). Furthermore, this indicator may not be quite useful for Andisols due to their high OM content, which could be complex Al ions (Takahashi *et al.*, 2006b). It has been shown that Ca has a beneficial effect on root hair growth and elongation in soybean plants affected by Al<sup>3+</sup> toxicity (Sanzonowicz *et al.*, 1998).

In addition, Ca nutrients play an important role in fruit growth and quality in different crops, such as melons (Takasu *et al.*, 2006a), blueberries (Blatt and Mc Rae, 1997) and crop yields of wheat (Caires *et al.*, 2002), red clover (Zheljazkov *et al.*, 2006), brussels sprouts (Carter and Cutcliffe, 1990) and ryegrass (Mora *et al.*, 1999, 2002). Moreover, a higher concentration of Al in the soil solution resulted in a reduction in foliar concentrations of Ca, Mg, Mn and Zn, decreased net photosynthesis and respiration processes, and reduced weight and length of shoots in red spruce (*Picea rubens*) (Schaberg *et al.*, 2000). Watanabe

and Osaki (2002) have also reported a negative relationship between the accumulation of Al in leaves and other essential minerals. Kinraide (1998) reported that the short-term ability of Ca to alleviate Al<sup>3+</sup> toxicity utilizes three mechanisms: 1) Displacement of Al<sup>3+</sup> by electrostatic effects on the cell surface, most probably by blocking plasma membrane channels to the toxic cation (Kinraide, 1998); 2) Restoration of Ca<sup>2+</sup> on cell membrane surface with Ca addition, when Al has reduced surface negativity (Kinraide *et al.*, 2004); 3) Interactions between Ca<sup>2+</sup> and Al<sup>3+</sup> (Silva *et al.*, 2005). Kinraide (1998) highlighted that in order to inhibit Al<sup>3+</sup> (1  $\mu\text{mol L}^{-1}$ ) effect a Ca<sup>2+</sup> concentration approaching 1  $\text{mmol L}^{-1}$  is necessary.

#### **Use of Ca as amendments in acid soils**

Many studies report the beneficial Ca effects in different crops growing in acid soils (Mora *et al.*, 2002). Currently, Ca application is carried out through different practical alternatives (Campbell *et al.*, 2006; Takasu *et al.*, 2006a,b) including: common liming oxides (CaO), hydroxides [Ca(OH)<sub>2</sub>], silicates of Ca or Ca-Mg, carbonates as calcites (CaCO<sub>3</sub>) and dolomites [CaMg(CO<sub>3</sub>)<sub>2</sub>], and sulfate salts (Tisdale *et al.*, 1985) as mined gypsum and gypsum by-product such as PG, titanogypsum or red gypsum (Garrido *et al.*, 2003; Illera *et al.*, 2004).

Liming is a very common practice in approximately 22 countries that are benefitting substantially from well established liming practices (Scott *et al.*, 2000) for restoring available Ca for plants (Mora *et al.*, 1999; 2002), correcting acidic soils (Scott *et al.*, 2000), alleviating Al and Mn toxicity (Illera *et al.*, 2004) and avoiding metal leaching as cadmium (Cd), copper (Cu) and lead (Pb) in polluted soils (Campbell *et al.*, 2006).

In general, the responses of cultivated

plants to Ca application are positively correlated with an increase in both top and roots DW, crop yield and improvement in quality in different crops such as soybean (Caires *et al.*, 2006; Bachiega *et al.*, 2007), blueberries (Blatt and Mc Rae, 1997), wheat (Caires *et al.*, 2002), coffee (Hue, 2005) and tomato (Tuna *et al.*, 2007). However, its use strongly depends on crop types, placement, deep requirement, soil texture and OM soil content, as well as pH, time and/or frequency of liming and the nature and cost of the amendment material (Schuman *et al.*, 1994; Takasu *et al.*, 2006a).

### **CALCAREOUS AMENDMENT TYPES**

#### **Lime (calcite and dolomite)**

The major limestones are CaCO<sub>3</sub> and [Ca Mg (CO<sub>3</sub>)<sub>2</sub>] (von Willert and Stehouwer, 2003). The addition of CaCO<sub>3</sub> is associated with various reaction steps with H<sub>2</sub>O soil: forming Ca<sup>2+</sup> that later can be up taken by roots or lost by water drainage (Tisdale *et al.*, 1985) and HCO<sub>3</sub><sup>-</sup> that increases soil pH (Scott *et al.*, 2000). The major direct benefits of limestone application are the pH increase in soils, particularly those having levels below 5.0-5.5 (Mora *et al.*, 2006) and a decrease of toxic concentrations of Al and Mn (Hue, 2005; Caires *et al.*, 2006). The indirect benefits of limestone application to acid soils are more effective cationic exchange capacity (CEC) (de Castro *et al.*, 1999), additional supply of Ca<sup>2+</sup> as well as Mg<sup>2+</sup>, if dolomitic limestones are used (Pavan *et al.*, 1984), and enhanced P availability by inactivation of Fe and Al (Tisdale *et al.*, 1985). Indeed, a reduction of P adsorption and increased productivity in two Chilean Andisols treated with calcitic and dolomitic limes have been reported (Mora *et al.* 1999). Other indirect

benefits are improved micronutrient availability with adequate range of liming (Tisdale *et al.*, 1985) and amelioration of the nitrification and nitrogen (N) fixation (Campillo *et al.*, 2005). Deep incorporation of lime increases also roots development, resulting in an increased crop production (Sumner *et al.* 1986; Carvalho and van Raij 1997).

In addition to the lime effects on soils discussed above, there are well documented beneficial effects of lime use on different crops growing in acid soils. Hue (2005) reported that lime amendments were positively correlated with a good growth of coffee plants. Mora *et al.* (2002) found that lime increased the growth and reduced the weed presence in perennial pastures of ryegrass (*Lolium perenne*) and white clover (*Trifolium repens*) growing in Andisols. Redente and Richards (1997) used lime plus NPK fertilizer. These applications increased shoot and root biomass of wheatgrass (*Agropyron spicatum*) plants growing in smelter soils. This amendment reduced the trace element availability for plants and their concentrations in shoot biomass. In this context, Garland and Wilkins (1981) found that barley roots subjected to Pb toxicity increased their biomass and length when Ca concentration was increased from 12 to 72 mM. Recently, Han *et al.* (2007) showed a significant reduction (20-50%) in Pb concentrations in roots and stems in tea plants growing in acid soils after the second year of lime application. However, in watermelon (*Citrullus lanatus*), Locascio and Hochmuth (2002) showed that it is not necessary for soils low in toxic elements such as Mn and Al, additional Ca from lime [0 to 4.5 ton per hectare (t ha<sup>-1</sup>)], since only a 10% increase was found in the first growing season and no effect was found in the second growing season. On the other hand, application of 4 t ha<sup>-1</sup> of dolomite in a European forest of *Picea*

*abies* increased the development of fresh fine roots and decreased the degraded lignin (Rosenberg *et al.*, 2003). Similar results were found earlier by Bakker *et al.* (1999a) in a forest of sessile oak (*Quercus petraea*) limed with  $CaCO_3$ . Lime application significantly reduced the incidence of fungus *Pythium coloratum* infection in carrot (*Daucus carota*) (El-Tarabily *et al.*, 1997).

### Phosphogypsum

PG is a primary by-product of phosphoric acid in the fertilizer industry (Kumar, 2002). The chemical composition of PG varies depending on the phosphate rock used as a source in the production process (Korcak, 1988). It contains mainly Ca (total concentration of 116,800 mg kg<sup>-1</sup> and exchangeable concentration of 45,430 mg kg<sup>-1</sup>) and  $SO_4^{2-}$  (total concentration 83,200 mg kg<sup>-1</sup>) as well as small amounts of other elements such as P, Si and fluoride (F) (Campbell *et al.*, 2006). PG has been suggested as a possible mechanism for toxic Al alleviation by complexation with F in the pH range of 4.1-5.3 (Alva and Sumner, 1988).

PG contains also trace amounts of barium (Ba), chromium (Cr), Cu, nickel (Ni), zinc (Zn) and some radionuclides not hazardous for handling (Garrido *et al.*, 2003). PG byproducts are available in different regions of the world (Carvalho and van Raij, 1997). Its annual production is estimated to be 5 million t in India (Kumar, 2002), 27.2 million t in the United States (Florida) (Korcak, 1988) and nearly 2.4 million t in Brazil (Carvalho and van Raij, 1997). The recommended amounts of PG for use in agriculture vary from 500 to 1000 kg ha<sup>-1</sup> (Mays and Mortvedt, 1986).

PG has been used as an alternative for Ca and  $SO_4^{2-}$  addition for correcting both surface and deep acidity and Al-toxicity in acid soils such as Andisols, Oxisols and

Ultisols (Toma and Saigusa, 1997; Garrido *et al.*, 2003) (Table 1). It is used alone or in combination with other synthetic organic polymers for preventing runoffs and erosion in agricultural soils exposed to heavy rainstorms (Tang *et al.*, 2006). Alva and Sumner (1990) found that PG (2 t ha<sup>-1</sup>) increased Ca content in plant tissues and growth of both alfalfa tops and roots (*Medicago sativa* cv. Hunter River) and soybean cv. Lee crops. These changes were attributed to amelioration of subsoil acidity (60 to 80 cm), ligand exchange among  $SO_4^{2-}$  and OH<sup>-</sup>, and a decrease in exchangeable Al. In a subterranean clover pasture growing under acidic soil conditions, PG mixed with  $CaCO_3$  and gypsum at a rate 2,500 kg ha<sup>-1</sup> reduced  $Al^{3+}$  concentration in solution and on exchange sites at 0-5 cm, but no significant changes were observed deeper in the soil (Smith *et al.*, 1994). A similar experiment with a raised pH in wheat var. Jabato growing under greenhouse conditions was performed by Peregrina-Alonso *et al.* (2006). Pavan *et al.* (1984) showed effects of PG amendment to a depth of 60 cm, obtaining increased root density and decreased Al in apple trees (*Malus domestica*) growing in Brazilian Oxisols. The improvement of Ca, Mg and  $SO_4^{2-}$  uptake by plants and pH correction together with a decreased Al level in acid soil in Thailand were performed on sugar corn crops by Dam-ampai *et al.* (2007), who obtained an enhanced DW. In wheat, Mariscal-Sancho *et al.* (2009) studied the effects of PG (1.4 to 84.2 t ha<sup>-1</sup>) on biomass production and composition. They found an increase in biomass F, Al and Si at lower of PG rates (0 - 16.8 t ha<sup>-1</sup>), but not at higher rates (67.3 t ha<sup>-1</sup>). However, the highest PG rates increased plant Al and F contents, with the last reaching toxic levels for the consumer. Similarly, in a soil pot culture with canola, provided with 0.30, 0.75, and 1.50 g kg<sup>-1</sup> PG over 33 days, shoot and

root growth increased with a maximum increase of root fresh weight (FW) at dose 0.30 g kg<sup>-1</sup>. This growth is correlated with an improvement in Ca uptake (Takasu *et al.*, 2006b). Saigusa and Toma (1997) explained that Ca applied as PG had an average movement of 55% in subsoil related to 5% of lime in non-allophanic Andisols.

Literature report negative toxic PG effects on soils and plant production. Mays and Mortvedt (1986) applied 0, 22, and 112 t ha<sup>-1</sup> in soils sown with corn (*Zea mays*), wheat, and soybean, to know the effects on crop growth and uptake of Cd and radium (Ra) when added PG. It was demonstrated that, corn production decreased at a high PG rate (112 t ha<sup>-1</sup>), but wheat and soybeans were not affected. Nutrient elements and Cd and Ra contained in grains and soils were not affected by PG application. These experiments revealed that PG origin has an influence on PG radioactive composition. Papastefanou *et al.* (2006) experimented with PG amendments in soils and detected an increase in such radionuclides as radium-226 (<sup>226</sup>Ra) (derived from a uranium series), from 50 to 479 Becquerel (Bq) kg<sup>-1</sup> in the evaluated rice plants, and recommended previous PG checking for agricultural purposes. According to the U.S Environmental Protection Agency, controlled PG use is permitted if <sup>226</sup>Ra levels are ≤10 pCi g<sup>-1</sup> (Korcak, 1988). In another research, Al-Oudat *et al.* (1998) obtained lower levels of radionuclides (1.1 Bq kg<sup>-1</sup> DW) in *Trifolium pilulare* and barley var. Arabi Abyad in both the vegetative parts and grains of barley, in addition to increased plant height, shoot number and DW in both crops (40 to 60% in barley). An interesting response by the photosynthetic apparatus was found by Krutilina *et al.* (2000) when barley and corn seedlings were amended with PG (10

t ha<sup>-1</sup>). Negative effects on the photoactivity of chloroplasts (21.00 and 14.25, respectively) were found even lower than the control. These effects may be explained by an imbalance of Ca/Mg or Ca/Fe relations in plants that inhibit photosynthetic activity despite an increase of chlorophyll (Chl) a, b and Chl a+b content in both species compared with a non-amended control.

### Gypsum

Calcium sulfate (CaSO<sub>4</sub> x H<sub>2</sub>O also CaSO<sub>4</sub> x 2H<sub>2</sub>O calcium sulfate dihydrate and plaster of Paris, CaSO<sub>4</sub> 1/2H<sub>2</sub>O calcium sulfate hemihydrate) (Mandal and Mandal, 2002), more commonly known as gypsum, occurs geologically as an evaporate mineral associated with sedimentary deposits (Korcak, 1988). Currently, gypsum application may be an interesting option as an amendment in soils under acidic conditions because its most important property (from an agricultural point of view) is its water solubility (2.5 g L<sup>-1</sup> in water), which is higher than calcite lime (0.5 g L<sup>-1</sup> in water) (Korcak, 1988). It represents also an important source of Ca<sup>2+</sup> and sulfur (S) (Bolan *et al.*, 1993) for plant nutrition and, according to some authors, it can improve mineral content in vegetal tissues, such as N, P, K, Ca, Mn, S and Zn (Caires *et al.*, 2006; Tuna *et al.*, 2007).

Gypsum use benefits the chemical properties of soils. It increases subsoil Ca (Caires *et al.*, 2006), decreases subsoil acidity (Toma *et al.*, 1999) and reduces exchangeable Al (Ritchey and Snuffer, 2002; Hue, 2005). With respect to physical properties, the benefits of gypsum include increased infiltration (Sahin *et al.*, 2003; Chen *et al.*, 2009), increased soil aggregation (Chen *et al.*, 2009), decreased Na adsorption (Gambaudo, 2004), improved or increased

**Table 1.** Effects of PG dose applications on different plant crops in acid soils.

Doses (t ha <sup>-1</sup> )	Species	Effects	Authors
2.0	Alfalfa Soybean	Top and root growth Increasing Ca content in plant tissues	Alva and Sumner, 1990
2.5	Subterranean clover	Decreasing exchangeable Al Reduced Al <sup>3+</sup> concentration in solution and at exchange sites (0-5 cm)	Smith <i>et al.</i> , 1994
2.0	Apple tree	Increased root density and decreased Al <sup>3+</sup> (60 cm depth)	Pavan <i>et al.</i> , 1984
0.5	Sugar corn	Improvement of Ca, Mg and SO <sub>4</sub> <sup>2+</sup> uptake by plants Decreasing of Al level	Dam-ampai <i>et al.</i> , 2007
10.0	Barley Corn	Negative effects on photoactivity of chloroplast Increased chorophyll a, b and a+b content	Krutilina <i>et al.</i> , 2000
4.0	Melon	Increased dry matter weights Top and root growth	Takasu <i>et al.</i> , 2006a

root development (Takahashi *et al.*, 2006a) and decreased soil compactation (Gambaudo, 2004). Other benefits are an increase in the hydraulic conductivity of soil after consecutive gypsum applications (Sahin *et al.*, 2003), and a reduction in metal toxicities has also been documented (Campbell *et al.*, 2006).

An important gypsum characteristic is the reduction of toxic Al and the increase in the Ca status in subsoil (Toma *et al.*, 2005) (Table 2), without or only slightly altering pH conditions (Takahashi *et al.*, 2006a). If the pH ranges from 4.5 to 8.4, the addition of gypsum will have no effect on the soil pH (Franzen *et al.*, 2006). It has been reported that the reduction of Al<sup>3+</sup> exchangeable by gypsum precipitation of Al-hydroxy-sulfate minerals or aluminum sulfate (AlSO<sub>4</sub><sup>+</sup>) formation is considerably less toxic for plants (Saigusa and Toma, 1997; Garrido *et al.*, 2003). For Alva *et al.* (1991) the role of SO<sub>4</sub> in the reduction of Al-toxicity is very important in subsoil, where Al

complexes organic ligands. According to Shamshuddin *et al.* (1991), Al complexing organic ligands after gypsum application in acid soils in Malaysia resulted in an increase in AlSO<sub>4</sub><sup>+</sup> activity and a decrease in Al<sup>3+</sup> activity, which correlated with increased corn yields. Mora *et al.* (1999) reported that gypsum application to ryegrass growing in an Andisol rich in OM resulted in a considerable yield increase and a 50% reduction in Al concentration with no significant changes to pH. This characteristic is very important, for example in crops such as blueberry (*Vaccinium spp.*), which must be developed in acid conditions (pH 4.0-5.2), but that are sensitive to Al-toxicity (Lyrene and Muñoz, 1997). A similar situation occurs with another *Ericaceae* like rhododendron (*Rhododendron spp.*) growing in pH soil ranging from 3.8-6.0, depending on the species (Giel and Bojarczuk, 2002). In these cases, gypsum is a good alternative for amending,

because the CaCO<sub>3</sub> excess in the soils has a negative effect on their performance. According to Takahashi *et al.* (2006a) in Andisols the Al release by gypsum will depend of OM content, being more effective in soil with a lower humic substance content, also Toma *et al.* (2005) showed that gypsum application in a non-allophanic Andisol was more effective on a soil horizon with lower humus content. Brady *et al.* (1993) studied the effects of three monomeric Al species, Al<sup>3+</sup>, Al(OH)<sub>2</sub><sup>+</sup> and Al(OH)<sub>2</sub><sup>2+</sup>, and their influence on root growth in soybean amended with calcium sulfate (500-2000 mM). The negative effects of these species on root development were inhibited at gypsum concentration of 500mM. The effects of gypsum application on different crops in alleviating Al-toxicity has been well

studied in soil and its horizon as well as at different pH, depths and OM contents (Favaretto *et al.*, 2006), but these effects are relatively less studied in respect to plant physiology responses. In this context, gypsum amendment in nutrient solution (Ca 0, 25, 75 or 225 mM) with Al (200 mM) increased the mean mineral content in leaves in special cations, such as Ca and Zn (mg kg<sup>-1</sup>), reduced Al in leaf tissue and increased the respiration rates (Schaberg *et al.*, 2000). According to Caires *et al.* (2006), the surface gypsum application resulted in an improved root growth of soybean and elevated nutrients and water uptake together with an improvement in S, P and K content in grains. Bakker (1999b) also concluded that gypsum increased the fine root biomass and length of oak growing in acid soils, even four to five years after

**Table 2.** Effects of gypsum doses application on different plant crops in acid soils.

Doses (t ha <sup>-1</sup> )	Crop Species	Effects	Authors
2.0	Ryegrass	Yield increase and 50% reduction of Al concentration	Mora <i>et al.</i> ,1999
0.5- 4.3	Brussels sprout	Raised Ca and S tissue level, marketable yields. Increasing B, Mn, Fe, and Zn in the leaf tissue	Carter and Cutcliffe, 1990
4.0	Lowbush blueberry	Increased foliar content of N, P, K, S, Mn, and Ca; length of stem, live buds, and quantity of blossoms	Sanderson and Eaton, 2004
4.0	Lowbush blueberry	Raised N, K, Ca, Mn and S and significantly reduced Mg and Fe	Sanderson, 2004
2.5	Highbush blueberry	Increase in root and leaf Ca content	Korcak, 1992

application. In brussels sprouts grown in a low-calcium soil, gypsum application (0.5- 4.3 t ha<sup>-1</sup>) raised tissue Ca levels and marketable yields significantly as well as increasing leaf S, boron (B), Mn, Fe, Ca and Zn content (Carter and Cutcliffe, 1990). Applying gypsum (4 t ha<sup>-1</sup>) with NPK fertilizer (300 kg ha<sup>-1</sup>) on lowbush blueberry (*Vaccinium angustifolium*) growing in acid soil increased foliar content of N, P, K, S, Mn and Ca, in addition to increasing the stem length, live buds and the blossom quantity (Sanderson and Eaton, 2004). In 2004, Sanderson evaluated the responses in lowbush blueberry to gypsum (4 t ha<sup>-1</sup>) under field assays. This surface amendment elevated N, K, Ca, Mn and S and significantly reduced Mg and Fe in comparison with the control. Korcak (1992) reported on the increase in root and leaf Ca content in highbush blueberry (*V. corymbosum*), which did not affect soil pH significantly. However, Hanson and Berkheimer (2004) declared that gypsum only increased Ca levels in soils in highbush blueberry, but that these levels were not affected in the leaves and fruits.

Little is known about the effects of gypsum on biochemical responses in plants affected by the presence of Al-toxicity (Boscolo *et al.*, 2003; Šimonovičová *et al.*, 2004). There is only information about Ca-Al interactions on biochemical responses (see above). This calls for further research in order to examine such phenomena. However, Guo *et al.* (2006) demonstrated that Ca (0.5, 1.0 and 3.0 mM) addition in barley seedlings growing in nutrient solution reduced Al-toxicity efficiently, which is reflected in an increase in root growth, a decrease in Al concentration and malondyaldehyde (MDA) content, and increased SOD, POD, and CAT activities compared with Al-only treatment (100mM) (Guo *et al.*, 2006). Finally,

calcium sulfate is also important because it can reduce the uptake of toxic levels of soil pollutants, such as high selenium (Se) (Mathews and Joost, 1989; Arthur *et al.*, 1993).

#### **Comparative effectiveness of calcareous amendments**

Soil pH could affect soil microbial activity and populations, soil chemical reactions and nutrient availability (Mullen *et al.* 2007). The progressive acidification of soils by different natural and anthropological factors has negative effects and growers must apply various amendments to sustain their crop production (Wang *et al.*, 2006). In acid soils like Andisols, the amendments depend on conditions like agronomic management, OM content and fertility levels, local climatic conditions and crop type (Tisdale *et al.*, 1985). There are a number of studies evaluating the qualities of different amendments in different crops and reporting on the advantages and disadvantages of these treatments.

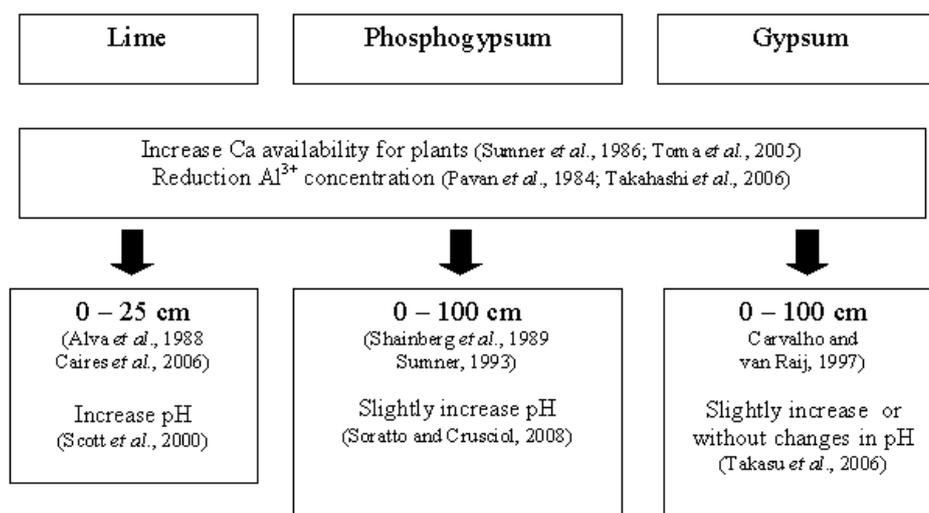
#### **Surface applications and subsoil effects**

Liming is a practice largely used to neutralize the acidity of the surface soil layers, but does not seem to be effective in acidity amelioration at a subsoil level (Carvalho and van Raig, 1997). However, the deep lime incorporation requires the implementation of specific equipment and results in higher costs, which makes it unfeasible for use by small farm (Carvalho and van Raig, 1997). Alternatively, the surface application of gypsum or PG allowing leaching into subsoils has resulted in higher water and nutrient uptake by plant roots (Alva *et al.*, 1988; Sumner, 1993). These effects are attributed to an increase in Ca content and a reduction in Al-toxicity at deeper soil layers (Toma *et al.*, 2005). In addition,

both gypsum and PG are the most mobile sources of Ca than CaCO<sub>3</sub> (von Willert and Stehouwer, 2003). In this context, the experiments reported by Sumner *et al.* (1986) demonstrated that deep lime incorporation into the soil (100 cm) and surface gypsum application increased root development in alfalfa growing in acid soils.

Lime applications also resulted in a complete Al<sup>3+</sup> precipitation, increased soluble Ca levels and a 50% increase in yields. Surface application of gypsum resulted in a progressive reduction in soluble Al and increase in soluble Ca, creating a similar but lesser effect than liming and also resulted in 25% yield increases. Pavan *et al.* (1984) reported that gypsum was more effective in lowering Al concentration within the 100 cm depth profile, while lime effects were observed only in the upper 20 cm. Caires *et al.* (2006) showed that gypsum ameliorate subsoil pH and Al-toxicity, increasing Ca and S level in wheat

leaves. A comparative evaluation of lime, gypsum and PG demonstrated that lime treatment (CaCO<sub>3</sub>, 2500 kg ha<sup>-1</sup>) increased exchangeable Ca and decreased exchangeable Al in the 0-5 cm soil layer, but no significant changes were observed below 5 cm, which suggested limited lime leaching. By contrast, gypsum and PG reduced these values to a 25 cm depth profile (Smith *et al.* 1994). Mc Cray *et al.* (2007) incorporated dolomite limestone (4.03 t ha<sup>-1</sup>) and PG (10 t ha<sup>-1</sup>) into the surface soil layer (15 cm). It was shown that PG moved downward much more rapidly than lime, increasing soil solution Ca ion activity to a depth of 80 cm within 5 months of application. Yield responses to PG were attributed to increased root growth below 20 cm, resulting from the increased Ca ion activity over a three-year period. CaCO<sub>3</sub> addition in two horizons (A and B) of non-allophanic Andisol in Japan reduced Al amounts complexed organically, as well as exchangeable Al, after 30 days of application (Takahashi *et*



**Figure 3.** Comparative effectiveness related to amendments at different soil layers.

*al.* 2006b). Gypsum ( $4.3 \text{ g kg}^{-1}$  and  $8.6 \text{ g kg}^{-1}$ ) has also improved the root growth of burdock (*Arctium lappa* cv. Kantan) on horizon B of the Andisol (Takahashi *et al.* 2006a) (Figure 3).

The amendment plays a role in root disease responses to manageable soil chemical factors, such as pH or Ca saturation. Allmaras *et al.* (1987) evaluated lime and gypsum treatment on a wheat-peas culture rotation and measured the propagated density of *Fusarium solani* ssp. *pisi* in the 0 to 15 cm soil layer. They found a decrease in the density of propagation (37%) of this fungus species by effect of lime, meanwhile between 15 to 45 cm of depth soil gypsum reduced its propagation density in 22%, therefore concluded that Ca can improve the resistance of the membrane in pea-root to attack by *Fusarium* pathogens, or allowing greater microbial antagonism.

#### **Effects on pH and mineral content**

Gypsum treatment does not affect soil pH as much as limestone (Figure 3), but results in increased Ca, S and Mn contents and decreased P and Mg levels (Ritchey *et al.*, 1995). On the other hand, limestone impact on soils is carried out by increasing pH (Scott *et al.*, 2000). Ritchey and Snuffer (2002) concluded that gypsum reduced both Mg in soil solution and orchard grass leaves (*Dactylis glomerata* L.) and tall fescue (*Festuca arundinacea* Schreb), but lime (dolomitic limestone) raised magnesium range in leaves.  $CaCO_3$  Application raised pH from 5.7 to 6.0 in the Andisol and increased foliar and root Ca content in coffee plants (Hue, 2005). By contrast, gypsum did not increase pH, but raised Ca content in leaves (Hue, 2005). Hanson and Berkheimer (2004) added Lime ( $1,100 \text{ kg ha}^{-1}$ ) in field assays for five seasons, and the soil pH values increased from 4.2 (1996) to 5.0 (2001),

whereas gypsum ( $550 \text{ kg ha}^{-1}$ ) amendment had a slighter effect and increased pH from 4.2 to 4.6 in the same period of time, while leaf Ca contents did not change significantly.

#### **CONCLUSIONS AND PERSPECTIVES**

The first symptoms of  $Al^{3+}$  damage in plant roots growing in acid soils have been well established; however, the effect on the upper parts such as stems, leaves and/or fruits remain a matter of controversy, despite the negative effects of  $Al^{3+}$  on photosynthesis, photochemical parameters and cellular respiration have been well established. Al presence in plant tissues has been correlated to decreased leaf nutrient content, especially  $Ca^{2+}$  and  $Mg^{2+}$ , and damage to the chloroplast and mitochondrial membranes.  $Al^{3+}$ -induced damage and toxicity are also related to  $Ca^{2+}$  interactions at apoplast and symplast levels and the regulation of cytosolic  $Ca^{2+}$  homeostasis. Both cations compete for the active sites of membrane structures to form ligands. This interaction is not fully understood, since each cation inhibits the other cation depending on the state of the membrane. The few reports regarding the interaction between  $Ca^{2+}$  and  $Al^{3+}$  have demonstrated that  $Ca^{2+}$  decreases the enzymatic antioxidant activity of SOD, CAT and POD, concomitant with a decrease in the toxic  $Al^{3+}$  levels. Nevertheless, other authors suggest that the antioxidant ability could be favored by the interaction between  $Ca^{2+}$  and  $Al^{3+}$ . The knowledge of the non-enzymatic antioxidant defense against Al stress is less recognized than the enzymatic one. Further studies are needed to better understand the mechanisms involved in the Ca-Al interactions that affect such physiological and biochemical processes

as photosynthesis, respiration, antioxidant activities, signal transduction and cellular homeostasis in plants growing in acid soils like Andisols.

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