ALUMINIUM TOXICITY IN SOIL AND PLANTS

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Aluminium, an element with atomic number 13, is the most abundant metallic element and the third most abundant element (after oxygen and silicon) of all elements in earth crust. In soil, large quantities of Al are present in aluminosilicate minerals, and a very small portion appears in the soluble form, capable of influencing plant growth and development. Aluminium concentration in soil ranges from 1 to 30 percent (10000 to 300 000 mg Al kg^{-1}) (Lindsay, 1979). Aluminium (Al) is not considered as an essential nutrient for plants, but small concentrations can sometimes increase plant growth or bring other desirable effects. However, aluminium toxicity is a potential growth-limiting factor for plants grown in acid soils worldwide. Acid soils (with a pH of 5.5 or lower) are most prone to aluminium toxicity to limit agricultural production. The total Al concentration in the soil and the forms of Al species depend on the soil pH and the chemical environment of the soil solution (Kisnierinene and Lepeikaite, 2015). When pH drops below 5.5, aluminosilicate clays and aluminium hydroxide minerals begin to dissolve, releasing aluminium-hydroxy cations and $Al(H_2O)_6^{3+}$ (Al^{3+}), that then exchange with other cations. The toxic effect of different Al species on plant growth is in the order $Al_{13} > Al^{3+} > Al(OH)^{2+} > Al(OH)_2^{+} > Al(OH)_4^{-}$.

CHEMISTRY OF ALUMINIUM IN SOIL

Aluminium, in the earth's crust possesses approximately 8.1% of its content in weight, bound as oxides and complex aluminosilicates in minerals. In nature aluminium occurs with silicates, like mica and feldspar, as bauxite and cryolite (Na_3AlF_6) (Cotton et al., 1999). Soil pH determines the occurrence of Al either as precipitates or as conjugated organic and inorganic and molecular ions (Figure 1).

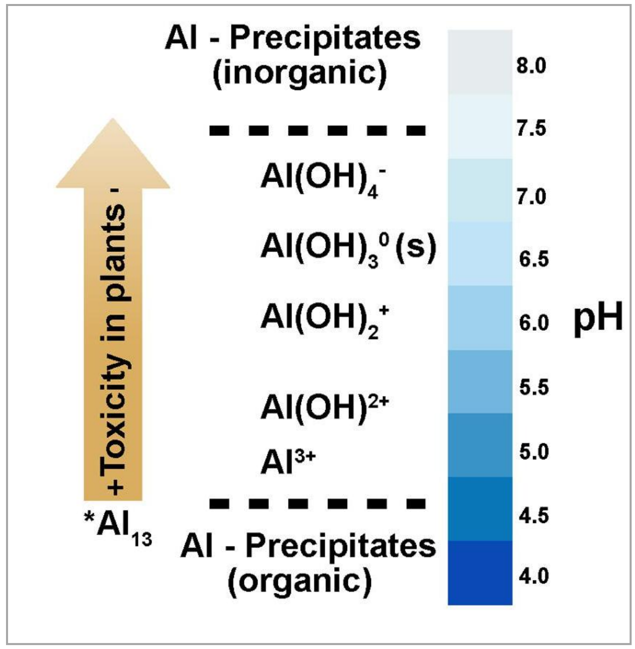

Figure 1. Chemistry of Aluminium with changing soil pH
(Source: Quintal et al 2017)

The coordination chemistry of Al plays a responsible role for its behavior in the environment. The reactions of Al in soil differ from other soluble metals due to the smaller ionic radius and high ionic charge. In fact Al concentration and the speciation of Al depend mainly on the pH and the chemical environment of the soil solution. As the pH increases above 4.0, $Al3^{+}$ forms mono nuclear species and soluble complexes with inorganic ligands like $(SO_4)^{2-}$, $(OH)^-$, phosphates, silicates and F^- and also with many organic compounds. Molecular aluminum (mononuclear) exists as hydroxyaluminum: $Al/Al(H_2O)_6^{3+}$, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$ and $Al(OH)_4^-$. Trivalent aluminum (Al^{3+}) is the most prevailing form and has the highest impact on plant growth at pH < 5. At pH 5–6.2, the dominant species are $Al(OH)^{2+}$ and $Al(OH)_2^+$, which are toxic to dicotyledonous plants but not as toxic as Al^{3+}. Gibbsite ($Al(OH)_3$)forms at a neutral pH, which is relatively insoluble and non-toxic Aluminate, $Al(OH)_4^-$ is the dominant species when the pH is alkaline (pH >7) (Kisnieriené and Lapeikaite, 2015). A very toxic polynuclear (Al_{13}) form of Al known as triskaidekaaluminium ($AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$) can form at near neutral solutions, but its natural occurrence and contribution towards soil toxicity are not known. The highest mobility of Al occurs between pH 4.0 and 4.5

FACTORS AFFECTING ALUMINIUM TOXICITY IN SOIL

Al Speciation: In soil there are three types of Al species : 1) aquo/ hydroxo-Al complexes, 2) inorganic-Al complexes, and 3) organic-Al complexes. Aluminium may exist as monomeric or polymeric forms in these complexes. In case of aquo/ hydroxo-Al complexes, monomeric Al forms complexes with OH and/or OH_2 groups, like $Al(HP)_6^{3+}$, Al- $(HPMOH)^{2+}$, $Al(HP)_4(OH)_2{}^+$, $Al(HPMOH)_3^{\circ}$, and $Al(OH)_4^-$. Aluminium forms combine with ligands such as fluoride, sulphate, phosphate *etc* leading to the formation of other inorganic Al complexes. It also forms complexes with organic ligands such as oxalate, citrate, carboxylate *etc* leading to the formation of organic- Al complexes. The aquo/hydroxo-Al complexes are more toxic to plant growth compared to other inorganic and organic –Al complexes.

Soil Acidification: Generally, acidification results in an increase in mobility for monomeric forms of aluminium. Because of the increased Al mobility in soil at low pH, the occurrence of acid rain and the release of acid mine drainage are bringing more amount of soluble Al in soil.

pH: Mechanisms controlling the solubility and speciation of Al are highly pH-dependent (Lundstrom and Giesler, 1995). The fraction of total Al present as inorganic Al will be increased by acid deposition due to a lowering of soil pH (Johnson and McBride, 1991).

Weathering of soil: Aluminium containing rocks on weathering releases Al and gibbsite ($Al(OH)_3$) occurs more in highly weathered soils which imparts a strong pH dependent Al^{3+} activity that decreases 1000 fold for each unit increase in soil pH.

Human activity: Aluminum concentrations in soil can be increased directly or indirectly by human activity through industrial and municipal discharges, surface run-off, tributary inflow, groundwater seepage, and wet and dry atmospheric deposition. Many wastes such as solid wastes from coal combustion, Al reduction, mining wastes and other metal processing operations release Al to soil.

Low basic cations: Low basic cations in the soil are found to be one of the major reasons of Al toxicity to plants. Among the basic cations, which are plant nutrients, Ca^{2+} and Mg^{2+} are important as the uptake of K^+ is not affected by Al toxicity.

ALUMINIUM TOXICITY SYMPTOMS IN PLANTS

The symptoms of Al toxicity are not easily identifiable. Generally, young seedlings are more prone to Al toxicity than older plants. It is generally known that plants grown in acid soils due to Al solubility at low pH have reduced root systems and exhibit a variety of nutrient-deficiency symptoms, with a consequent decrease in yield. Translocation of Al to upper plant parts is very slow and have a very less concentration (0.2 mg Al g^{-1} dry mass) except in Al hyper accumulating plants like tea (30 mg Al g^{-1} dry mass in old leaves). Aluminium toxicity inhibits the root growth by hindering the cell division and elongation even with a brief exposure to Al. Aluminum-injured roots turn into stubby and frequently obtain a brownish colouration (figure 2 a). Root hairs and fine branching are reduced and the root system often shows a "coralloid" appearance. In the root apex, cracks can easily be observed in the epidermis. Cells of the cortex showing uneven and radial expansion which results in root thickening and mechanical stress on the epidermis (Ciamporova, 2002).

Foliar symptoms resemble those of phosphorous (P) deficiency *i.e.* overall stunting, small, dark green leaves and late maturity, purpling of stems, leaves, and leaf veins, yellowing and death of leaf tips (figure 2 b). In some cases, Al toxicity appears as induced calcium (Ca) deficiency or reduced Ca transport problem *i.e.* curling or rolling of young leaves and collapse of growing points or petioles.

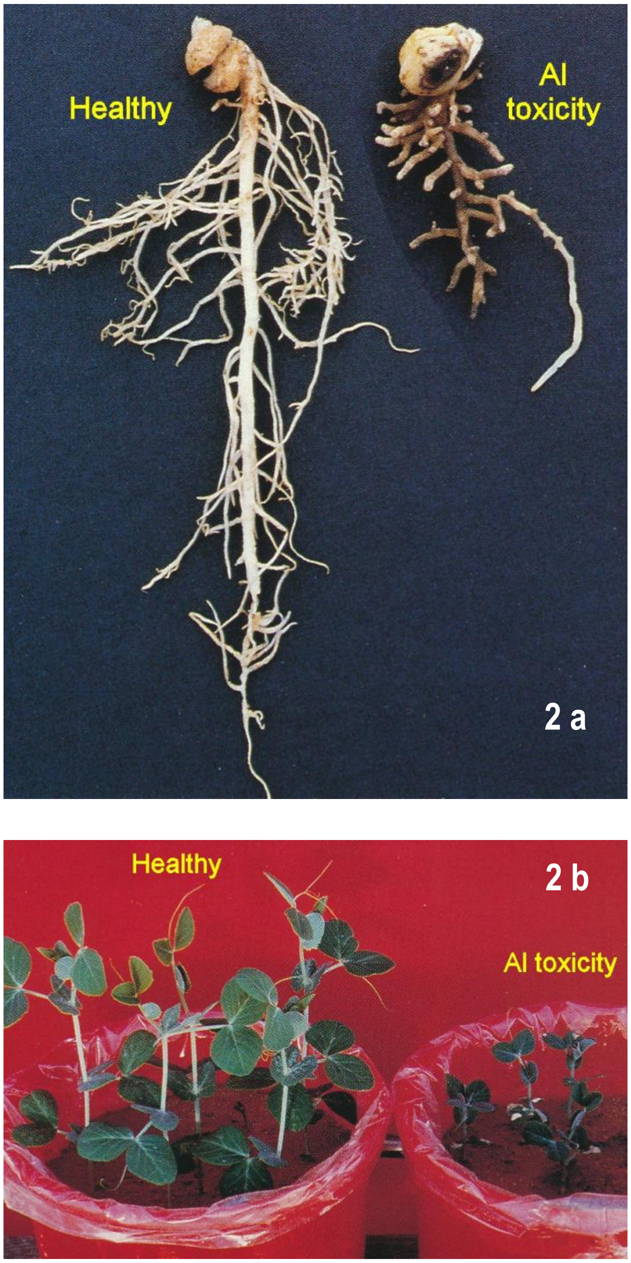

Figure 2. Aluminium toxicity symptoms in field pea (a) plant roots (b) foliage

(Source: https://www.agric.wa.gov.au/mycrop/diagnosing-soil-acidity-field-peas)

Sometimes excess Al even induces iron (Fe) deficiency symptoms in rice, sorghum and wheat. Aluminium toxicity also results in suppression of photosynthetic capacity of shoots in many plants. These results in cellular and ultrastructural modifications in leaves, reduced stomatal movements and CO_2 assimilation, reduction in chlorophyll concentration, chlorosis and necrosis of leaf tissues etc.

ALUMINIUM TOLERANT CROP PLANTS

Differential tolerance has been reported in rice, soybeans, corn, sorghum, wheat, potatoes, alfalfa, tomato, sunflower and other species. Al tolerant plants have different mechanisms to alleviate Al toxicity. In cereals Al exclusion is the most common mechanism to avoid Al toxicity. Organic acid exudation and forming strong chelating compounds with Al in the roots are the exclusion mechanisms existing in these crops. Tolerance mechanism allows plants to safely take up and accumulate Al in their cells. Tea is an important plant which is having the capacity to tolerate high concentration of soil Al. Hydrangea is a flowering plant in which Al ions are bound in the vacuoles by citrate.

TOLERANT MECHANISMS IN PLANTS

There are two types of tolerance mechanisms namely internal and external mechanisms. Among these, internal tolerance would be the compartmentalization of Al in vacuoles such as organelles after being absorbed, reducing its toxic effect. Outer or external tolerance is related to the ability of plants to check absorption and transportation of aluminium into the plant. In cereals and grasses, exclusion of Al from root apex and detoxification of Al in the root and shoot system are the two important mechanisms of Al tolerance. In higher plants like tea both the mechanisms help to prevent Al toxicity.

More than 10 Al-tolerant plant species are known to secrete organic acids from their roots in response to Al. Citrate, malate, carboxylate, oxalate are some of the organic ligands secreted by plants to prevent Al toxicity. The Al tolerant genotypes exude organic acids from first few millimeters of root apices and the amount depends on the external Al concentration. Other mechanisms like exudation of other inorganic ligands like phosphate and exclusion of Al from entering the system have been reported as alternate mechanisms of Al tolerance in different crop species. It is also proved that phosphate plays an important role in complexing with Al, and alkalinisation of the rhizosphere pH by binding proton.

There are reports that reasons out exudation of aromatic secondary plant metabolites called phenolic compounds are involved in Al toxicity tolerance. In maize, Kidd et al. (2001) reported the presence of high concentration of catechin and quercetin in the Al- sensitive area of the root and stable Al complex with pentahydroxy-flavones and flavanpentols strongly supported the role of the flavonoid type phenolics in Al-chelating activity and potentially detoxify Al. De novo synthesised polypeptides exudation in response to Al exposure is reported in wheat. Another tolerance mechanism is binding of Al to root tip mucilage that protect root tip from toxic Al. In wheat this mechanism helps to minimize Al injury.

INTERNAL DETOXIFICATION

The possible internal tolerant mechanisms *i.e.* after it has entered the cytoplasm are formation of aluminum chelates by organic acids, proteins, or other organic ligands; compartmentalization of aluminum in the vacuole; the synthesis of aluminum tolerant proteins; and elevated enzyme activity (Taylor, 1991; Kochian, 1995). In tea plant, a major portion of Al is bound to catechins and a small portion to organic acids and phenolics. The non toxic Al-citrate is formed in Hydrangea plants to prevent Al toxicity. In buckwheat, oxalic acid formation helps to bind the Al. In Al hyperaccumulator Melastoma also, oxalic acid strongly bind Al and detoxifies the Al. Silicon accumulating plants can release the silicon to bind Al so as to detoxify aluminium by forming aluminosilicate compounds in root apoplast (Cocker et al., 1998). In wheat suicidal death of cells affected by Al is also reported as detoxification mechanism. Sequestration of Al in vacuole and organelles detoxifies the Al effect in the cytoplasm (Miyasaka et al., 2007).

AL HYPER-ACCUMULATOR PLANTS

Hyper-accumulator plants show high metal concentrations in their aboveground tissues relative to external soil concentrations. There are some plants which have the capacity to hyperaccumulate Al (more than 1000 ppm) in the dried leaf tissue without any toxic effect in the system. Such plants are known as Al hyperaccumulator plants. Al hyper accumulators mainly belong to families like Anisophylleaceae, Hydrangeaceae, Melastomataceae, Memecylaceae, Rubiaceae, Theaceae, Symplocaceae, Vochysiaceae. Examples are given in Table 1.

Table1. Al hyperaccumulator plants

Family	Scientific Name
Melastomataceae	*Miconia ferruginata, M. pohliana*
Hydrangeaceae	*Hydrangia macrophylla*
Memecylaceae	*Lijndenia laurina*
Theaceae	*Camellia sinensis*
Symplocaceae	*Arbor aluminosa, Symplocos odoratissima, S. ambangensis*
Rubiaceae	*Palicourea rigida*
Vochysiaceae	*Qualea grandiflora, Q.parviflora, Q.multiflora, Vochysia thyrsoidea, V.elliptica, V.hondurensis, Callisthene fasciculata*

AMELIORATIVE MEASURES

Applications of lime, organic manure/compost, silicon and use of tolerant crop species or varieties are the most common methods used to overcome the impact of Al-toxicity. Liming encourages organic carbon mineralization by increasing soil pH and detoxification of Al and thereby increases microbial survivability by C use efficiency. Calcium present in the liming material will compete with Al for binding sites in the cell membrane and helps to alleviate the Al toxicity. Organic manure or compost application also helps to alleviate Al toxicity to plants. Organic compounds released during the decomposition of organic material by microbes will combine with active Al ion and form complexes which are non toxic to plants. Application of silicon to plants is another useful method to alleviate Al toxicity. Here Si will combine with Al forming hydroxyaluminosilicate complexes and thus reduces the Al toxicity in soil. The use of tolerant crop varieties is considered to be the best match to non-genetic management choice for combating Al-toxicity problem

(Abebe, 2007). Hence developing transgenic crop varieties with Al tolerant genes is the best cost effective solution to alleviate aluminium toxicity in plants.

REFERENCES

Abebe, M. 2007. Nature and Management of Acid Soils in Ethiopia. Ethiopian Institute of Agricultural Research, Addis Ababa, Ethiopia.

Ciamporova, M. 2000. Diverse responses of root cell structure to aluminium stress. Plant Soil 226:113-116.

Cocker, K.M., Evans, D.E. & Hodson, M.J. 1998.The amelioration of aluminium toxicity by silicon in higher plants: Solution chemistry or an in planta mechanism? Physiol. Plant. 104(4): 608-614.

Cotton, F.A., Wilkinson, G., Murillo, C.A.1999. The group 13 elements: Al, Ga, In, Tl. Advanced inorganic chemistry. 6th ed. John Wiley & Sons, Inc., 175-207.

Johnson, M.G. and McBride, M.B. 1991. Solubility of aluminium and silicon in acidified spodosols: evidence for soluble aluminosilicate. In: Wright, R.J. et al. (Eds.) Plant–Soil Interactions at Low pH. Kluwer, Dordrecht, pp. 19–24.

Kidd, P. S., Llugany, M., Poschenrieder, C., Gunse, B., and Barcelo, J. 2001. The role of root exudates in aluminium resistance and silicon-induced amelioration of aluminium toxicity in three varieties of maize (*Zea mays* L.). J. Exp. Bot. 52: 1339–1352.

Kisnieriene, V. and Lapeikaite, I. 2015. When chemistry meets biology: the case of aluminium- a review. Chemija. 26:148–158.

Kochian, L.V. 1995. Cellular mechanism of aluminum toxicity and resistance in plants. Annu. Rev. Plant Boil. 46: 237-260.

Lindsay, W.L. 1979. Chemical Equilibria in Soils. John Wiley & Sons, New York.

Lundstrom, U.S. and Giesler, R. 1995. Use of aluminium species composition in soil solution as an indicator of acidification. Ecol. Bull. 44:114–122.

Miyasaka, S.C., Hue, N.V., Dunn, M.A. 2007. Aluminum. In: Barker AV, Pilbeam DJ (eds) Handbook of Plant Nutrition. Tayler and Francis Group, Boca Raton, pp. 439-497.

Quintal, B.E., Magana, E.C., Machado, E., Estevez, M.M. Aluminum, a Friend or Foe of Higher Plants in Acid Soils. Front. Plant Sci. 2017,8:1-18.

Taylor, G.J. 1991. Current views of the aluminum stress response: the physiological basis **of** tolerance. Curr Top Plant

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