Importance of Mineral Nutrition for Mitigating Aluminum Toxicity in Plants on Acidic Soils: Current Status and Opportunities

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Abstract: Aluminum (Al) toxicity is one of the major limitations that inhibit plant growth and development in acidic soils. In acidic soils (pH < 5.0), phototoxic-aluminum (Al³⁺) rapidly inhibits root growth, and subsequently affects water and nutrient uptake in plants. This review updates the existing knowledge concerning the role of mineral nutrition for alleviating Al toxicity in plants to acid soils. Here, we explored phosphorus (P) is more beneficial in plants under P-deficient, and Al toxic conditions. Exogenous P addition increased root respiration, plant growth, chlorophyll content, and dry matter yield. Calcium (Ca) amendment (liming) is effective for correcting soil acidity, and for alleviating Al toxicity. Magnesium (Mg) is able to prevent Al migration through the cytosolic plasma membrane in root tips. Sulfur (S) is recognized as a versatile element that alleviates several metals toxicity including Al. Moreover, silicon (Si), and other components such as industrial byproducts, hormones, organic acids, polyamines, biofertilizers, and biochars played promising roles for mitigating Al toxicity in plants. Furthermore, this review provides a comprehensive understanding of several new methods and low-cost effective strategies relevant to the exogenous application of mineral nutrition on Al toxicity mitigation. This information would be effective for further improvement of crop plants in acid soils.

Keywords: mineral nutrient; aluminum; toxicity; alleviation; plant; acidic soil

1. Introduction

Aluminum (Al) toxicity represents a serious limitation to plant production in acid soils worldwide, as approximately 40–50% of the world’s total potential arable land consists of acidic soils [1]. Acid soils (pH 5.5 or lower) are globally distributed and comprise approximately 30% of the total area of the earth [2]. Hence, soil acidification is a natural process which occurs mostly in tropical and subtropical regions. Several natural and/or anthropogenic inputs are responsible for accelerating soil acidification [3]. The important causes of soil acidification on agricultural land are acidic precipitation (H⁺ ions in precipitation), input of acidifying gases or particles (i.e., SO₂; NO₃), contribution of nitric and hydrochloric acids (i.e., HNO₃; HCl) from the atmosphere, application of elemental sulfur (S), ammonium-based fertilizer (NH₄⁺), nutrient uptake by leguminous crops, and mineralization of organic matter [4–6].
Impacts of soil acidification have been critically recorded on agricultural soil as well as pH level. The replacement of exchangeable base cations such as calcium (Ca$^{2+}$), magnesium (Mg$^{2+}$) and potassium (K$^+$) by H$^+$ and Al$^{3+}$, and the dissolution of Al-bearing and Mn minerals, and the dissolution of Fe-bearing minerals are the most significant consequences of soil acidifications. These three processes buffer the soil pH at approximately 5–6, 4, and 3, respectively [5]. Consequently, metal toxicity (i.e., Mn, Fe, and Al) and nutrient imbalance (i.e., P) are found to occur in acid soils, wherein Al toxicity is the most significant threat to plant survival in acid soils [3].

Al is the most abundant metal on earth; it is ubiquitously distributed as the third most abundant element in the earth’s crust that comprising 7–8% of its mass after oxygen and silicon [3,6]. However, the specific biological function of Al is still to be disclosed. The presence of Al could be marked easily in all forms of life as it is an integral component of mineral soil. Country specific soil acidity and concentration of Al in soils has been widely distribution worldwide (Table 1). Al in the soil is mainly found incorporated in the form of minerals such as aluminum oxides or harmless aluminosilicates [7]. However, solubilization and speciation of Al depend on the chemical environment and the pH of the soil solution [8]. In acid soil at low pH (4.3), Al is solubilized into $[\text{Al(H}_2\text{O)}_6]^{3+}$ that usually referred as to Al$^{3+}$. Al also formulates other species such as Al(OH)$_2^{2+}$, Al(OH)$_4^{-}$, and Al(OH)$_6^{3-}$, wherein Al$^{3+}$ is considered as the most toxic form that has a huge impact on plant growth and development [6,7,9]. One of the major consequences and the most obvious symptom of Al toxicity is the root growth inhibition in plants [10]. Excessive Al inhibits roots cell division–elongation, root hair formation, and enhances the development of swollen roots apices [11]. Concurrently, toxic Al inhibits the uptake of water and nutrients by plants [3]. Several reports have provided indications that toxic Al$^{3+}$ alters nutrient levels such as N, K, Ca, Mg, and P, and reduces the photosynthetic rate ($P_N$), stomatal conductance (gs), and leaf transpiration ($E$) rate in plants [7,12,13]. Surprisingly, the initial response to Al toxicity marked to be induced within a few minutes even at micro-molar ($\mu$M) concentrations of toxic Al in plant cells [14]. The phytotoxic Al leads to generate excess reactive oxygen species (ROS) such as H$_2$O$_2$ and O$_2$, as those ROS were detected in the root tips of Glycine max [15], the leaves of Oryza sativa [16], and cells of Nicotiana tabacum [17]. Other phytotoxic effects of Al have been described in different cellular organelles; such as toxic Al-induced disruption of free cytosolic Ca$^{2+}$ [18], callose deposition at the plasmodesmata [19], and respiration inhibition in mitochondria [20].

Several studies have shown the impact of Al toxicity on crop plants based on their sensitivity threshold to acid soils; wherein most of them mainly focused on roots and their growth [21–23]. Other issues are included like Al protection, tolerance, and/or resistance mechanisms [13,24–26], Al effects on plant metabolism [7], Al speciation and detoxification in plants [9], the role of mitochondria in the Al response [27], the link between Al chemistry and biology [8], inhibition of auxins synthesis, and transportation inhibition by Al toxicity [23], have been extensively studied in plants. Recently, it has been elucidated both toxic and beneficial impacts of Al in plants [3], also clarified the accumulation, localization, and impacts of Al on various levels of the plant organs [6], and identified the Al-induced genes in the root apex of buckwheat [26]. Molecular and physiological mechanisms related to Al resistance and/or tolerance are extremely complex phenomena. As a part of natural selection, plants have evolved some specific mechanism to cope with Al toxicity. Exclusion was extensively mentioned as it the key approach to detoxifying Al toxicity in plants [25]. Exudation chelating ligands, speciation of pH barriers at the root apoplasm or at the rhizosphere, immobilization of cell walls, selective permeability of the plasma membrane (PM), and Al efflux have been widely suggested as the mechanisms of Al-exclusion [13,21,24,25]. However, these resistance and tolerance mechanisms in plants are not mutually exclusive; rice (Oryza sativa) and buckwheat (Fagopyrum esculentum) for example benefit from both mechanisms [28]. Al is a non-biodegradable metal that widely distributed in soil environment globally [29]. Al is able to be transmitted through the food cycle. The impact of Al toxicity has been manifested not only in plants but also in animals and humans; thus, Al represents a critical threat to the whole system. For example, Al toxicity was reported to be involved in poor quality forage and fodder production, consequently it negatively impacts on grazing animals, cow milk and...
overall livestock production [30]. Chaney suggested that 1000 mg Al·kg$^{-1}$ should be the maximum in animal diet, although no results have been given for the time course analysis [31]. At the beginning of the 21st century, soil acidity along with Al-toxicity related damage in crops resulted in huge economic losses of more than 600 million USD in the agricultural sector in Australia [32]. Al is also recognized as a risk factor for human health. For instance, tea leaves appear to accumulate substantial amounts of Al [33], and one-third of total Al is able to be transferred easily during the tea leaf infusion process, this Al can cause potential health problems for humans [34]. Although, a trace amount of Al is reported to be available for absorption across the gastro-intestinal tract [35], tea-drinkers should be warned about this health risk. In contrast, high levels of Al can induce chronic renal failure in humans [36]. Based on several investigations, it has been hypothesized that high levels of Al in the human body are related to several diseases including osteomalacia fractures, encephalopathy, Parkinsonism dementia, and Alzheimer’s disease [37–39].

Several conventional strategies for farmers have been proposed to ameliorate Al toxicity and/or decrease Al-accumulation through liming, P fertilizer, and the production of low Al-accumulating cultivars through genetic manipulation [13]. In addition, developing a variety with new traits may take 5–10 years, and the entire process involves in a considerable amount of time and expense [40]. Moreover, continuous application of P fertilizer and lime in soil is not only expensive but also environmentally risky [41]. Therefore, low-cost effective and environmentally friendly approaches are in high demand. In this regard, the application of mineral nutrition would be a suitable strategy for minimizing Al toxicity in plants to acid soils.

Many crop plants have a range of susceptibility to acidic soils, and overall their performance is highly influenced by Al toxicity [42]. Therefore, Al toxicity has emerged as the major limitation to agronomic performance in acidic soils. We updated here the information of several literature reviews provide the evidence on the exogenous application of mineral nutrients mitigating Al toxicity in plants. Consequently, the application of mineral nutrients to mitigate Al toxicity in plants exposed to acid soils is now the most recent and important research topic in this field.

The application of mineral nutrition provides several benefits such as (i) a cost-effective approach relative to other organic and inorganic amendments, (ii) little or low environmental risk of application, (iii) high availability of nutrients, (iv) few skills are needed to sustain crop yield, and (v) crop plants can easily take up mineral nutrition throughout the entire year. Therefore, more attention has been given to study plant–nutrient–soil interactions as well as to minimize Al toxicity in plants exposed to acid soil by nutritional amendments. The main objectives of this review were to: (a) present a comprehensive discussion of several factors affecting soil acidification, Al toxicity, and Al accumulation in plants; (b) understated how plant nutrition can be an effective strategy to minimize Al toxicity; (c) analyze how plants develop suitable strategies to enhance Al toxicity tolerance in the presence of mineral nutrition; and (d) explore the best nutrition management practice for minimizing Al toxicity in plants. This review updates the knowledge concerning the influence and distribution of Al toxicity in crop plants grown in acidic conditions, factors affecting Al toxicity and nutritional imbalance and homeostasis, and overall mechanisms related to the efficiency of different mineral nutrition strategies to mitigate Al toxicity in plants. Captivating materials have been distributed in the current literature pinning down Al toxicity at various levels of plant cells and organisms, the application of mineral nutrition would be an effective strategy to counteract Al toxicity. These updated findings might disclose new avenues for minerals leading to physiological, molecular and agricultural inquiries into Al toxicity that markedly advances our understanding.
| Country          | Area/Region/Location                                                                 | Nature/Type of Soil                                      | Soil Depth (cm) | Range of pH  | No. of Samples | Range of Al Concentration (g/kg) | Mean    | References |
|------------------|--------------------------------------------------------------------------------------------|----------------------------------------------------------|-----------------|--------------|----------------|----------------------------------|---------|------------|
| Bangladesh       | Dinajpur, Rangpur, Bangladesh                                                              | Paddy soil; sandy loam, non-calcareous, acidic-siluval   | 0–15, 15–30     | 4.8–5.4      | 04             | 0.024–0.059                     | 0.043   | [43]       |
|                  | Hill of Chittagong University, Bangladesh                                                  | Hill topsoil; surface, subsurface                        | 0–12            | 4.4–5.5      | 45             | 0.036–0.058                     | 0.048   | [44]       |
| Brazil           | Cantareira State Park, Brazil                                                              | Forest back-ground                                      | 0–20,20–40      | 3.3–5.7      | 11             | 17.1–71.8                      | 41.1    | [45]       |
| China            | Guizhou province, China                                                                    | Yellow-brown                                            | 0–30            | 3.5–4.8      | 13             | 65.2–128.5                     | 106.4   | [46]       |
|                  | Sichuan, Zhejiang, and Jiangsu, Southeast China                                           | Original, bulk and rhizosphere soil                     | 0–20            | 3.4–5.9      | 18             | 0.18–0.58                      | 0.37    | [47]       |
|                  | Central and Southwest China                                                               | Yellow sandstone, red earth, and Pleistocene deposits    | 0–20            | 3.5–5.7      | 12             | 75.5–108.3                    | 89.2    | [48]       |
| Canada           | Northwestern Alberta, eastern and western Canada                                          | Podzolic, luvisoli, gleysolic, subsoil                  | – –             | 3.5–5.4      | 35             | 0.015–0.027                    | 0.069   | [49]       |
| Czech Republic   | Jizera Mountains area, Czech Republic                                                     | Horizon; Organic-fragmented organic-humified organic-mineral mineral | 0–12.2         | 3.8–4.2      | 491            | 0.0057–0.017                   | 0.0097  | [50]       |
| France           | Vosges Mountains area, North Eastern France                                               | Acid brown, podzolic                                    | 0–220           | 3.7–4.6      | 8              | 0.0003–0.047                   | 0.0173  | [51]       |
| India            | Bihar, India                                                                              | Fine mixed, fine loamy, sandy mixed                     | 0–150           | 4.4–7.0      | 13             | 0.0003–0.0051                  | 0.0023  | [52]       |
| Ireland Republic | South-eastern region, Ireland                                                             | Grassland, tillage, forest, peat                        | 0–10            | 5.3–5.9      | 295            | 0.0–89.1                      | 45.6    | [53]       |
| Japan            | Hokkaido, Tohoku, Kanto, Kinki, Hokuriku-Chubu, Chugoku, Shikoku, Kyushu, and Okinawa    | Agricultural soil; paddy/upland field                   | 0–15            | – –          | 180            | 33.0–117.0                    | 79.0    | [54]       |
| Korea Republic   | Osan, Korea                                                                               | Sandy clay loam                                         | – –             | 4.0–7.1      | – –            | 0.384–1.825                   | 0.836   | [55]       |
|                  | Seoul, Ulsan, Hongchon, Korea                                                             | Forest; urban and industrial areas                      | 0–15            | 4.1–4.3      | – –            | – –                           | – –     | [56]       |
| New Zealand      | North Canterbury, Central Canterbury, Central Ohio                                         | Stony brown, brown, dense brown hill soil               | 0–15            | 4.9–6.7      | 14             | 0.0005–0.0174                 | 0.0057  | [57]       |
| USA              | Palouse Conservation Field Station (PCFSS) located near Pullman, WA, USA                   | Agricultural soils; silt loam                           | 0–30            | 4.7–6.3      | 80             | 0.034–0.055                   | 0.0196  | [58]       |
|                  | Crawford County, OH, USA                                                                  | Subsoil, acid soil                                      | 0–110           | 4.5–7.5      | 99             | 0–0.25                        | – –     | [59]       |
2. Multiple Forms of Aluminum in the Soil Environment Relevant to Toxicity

Al represents approximately 7–8% of the total solid matter in the earth’s crusts, it ubiquitously distributed as different forms in soil environments [3,6]. Different forms of Al may exist in the soil such as inorganic, soluble, and/or organic forms. Inorganic forms of Al are exchangeable and are primarily bound to silicate clays, hydrous oxides, phosphates, and sulfates [60]. A significant correlation has been found between soil pH and phytotoxicity of Al species. Hence, these multiple forms of Al, their concentrations, speciation, and toxicity in the soil environment depend on pH level and the chemistry of the soil solution [8].

Several soluble forms of Al species such as $\text{Al}^{3+}$, $\text{Al(OH)}_2^{2+}$, $\text{Al(OH)}_2^{3+}$, and $\text{Al(OH)}_4^{-}$ have been shown to occur when the soil pH drops below 5 [8,61]. In acidic soil (pH < 5), Al is solubilized into $[\text{Al(H}_2\text{O)}_6]^{3+}$, usually referred to as $\text{Al}^{3+}$. The solubilization of Al occurs due to the inception of soil acidification which leads to the release of phytotoxic $\text{Al}^{3+}$ [6]. This trivalent $\text{Al}^{3+}$, which is the most abundant form and very toxic, has the greatest impact on plant growth at pH < 4.3. In contrast, solution pH level increases and reduces the $\text{Al}^{3+}$ concentration by repeated deprotonation [8]. At pH > 5–6, mononuclear species are reported to be formed, including $\text{Al(OH)}_2^{2+}$ and $\text{Al(OH)}_2^{3+}$, which are toxic to dicotyledonous plants but not toxic as $\text{Al}^{3+}$ is initiated [3]. At pH 7, the formation of gibbsite $[\text{Al(OH)}_3]$, occurs; however, it is non-toxic in nature and relatively insoluble [62]. At alkaline pH (>7), aluminate $[\text{Al(OH)}_4^{-}]$ was reported to be formed [63]. $\text{Al(OH)}_4^{-}$ is not always toxic; for example, at a concentration of 25 micromolar it was shown to be non-toxic in red clover whereas in wheat it showed at pH 8–8.9 [64]. Despite the above-mentioned speciation of Al, a highly toxic polynuclear Al species that is identified as “$\text{Al}_{13}$”, is reported to be toxic ten-fold higher than $\text{Al}^{3+}$ [61]. Surprisingly, the soluble or exchangeable aluminum (Al$^{3+}$) is able to associate with a variety of organic and inorganic ligands. However, organic Al is formed when Al$^{3+}$ binds to several ligands (i.e., $\text{SO}_4^{2-}$, $\text{PO}_4^{3-}$, $\text{F}^-$ etc.) in the soil solution to generate stable complexes [62]. Exchangeable Al$^{3+}$ cations and assimilable Al can participate in the formation of the above types of complexes. Briefly, the above-mentioned facts suggest that Al speciation, level of Al toxicity, availability of Al in the soil, alteration of pH level, and complexation of ligands are influenced by the chemistry of soil environment.

3. Aluminum Uptake, Accumulation, and Toxicity Responses in Plants

The uptake of Al from the soil by vascular plants is a complex process that is highly influenced by the soil pH, and the chemical environment of the rhizosphere. Due to the lack of conclusive evidence on precise mechanisms regarding Al uptake, some questions about this issue have still to be answered. For example, in which form and process Al are taken up? Which is the most active cellular site for Al uptake? Where is the location of Al-loading into the xylem, and how the process is mediated? Al ions are taken up by plants mostly through the root system, and only to a limited extent do they penetrate the leaves. A body of knowledge indicates that Al is taken up as Al$^{3+}$ by an active process wherein root apices play a vital role in Al toxicity perception and response [9,62]. Though it is still a matter of debate whether Al uptake at the root surface occurs symplastically or apoplastically? Lazof et al. [29] elucidated that a sizable amount of Al efficiently enters the root symplasm, but later it can affect the growth of the membrane on the cytosolic side. Surprisingly, the highest ratio of symplastic Al to total Al has been found at the root apex in buckwheat [22]. Rengel [65] suggested that the entrance pathway of Al$^{3+}$ is the root apoplast, as he found that approximately 30–90% of the total Al that is present in the root apoplasm could be acquired by a plant. Recently, an apoplasmic lesion caused by Al, wherein it is primarily bound to the outer cell wall after immediate exposure has been explored [66].

Based on the Al concentration and organic acid exudation in root systems, several researchers have tried to determine the most active site for Al uptake in plants [9]. The mature elongation zone above the root apex has been suggested as the Al uptake site in buckwheat, as the highest level of oxalic acid exudated from the apex [67]. Klug et al. [22] detected a high proportion of total Al at the root apex, thus, they suggested that the root apex was the most active site of Al uptake in plants.
Transporters are often associated with the uptake and transport of metal into the plant system. Broadly, aquaporin (AQP) family members are responsible for Al transport in plants [68].

Plants are capable of accumulating Al in above-ground tissues. Chenery, [69,70] classified plants as Al accumulators or non-accumulators after an investigation of 1000 plant species, plants that accumulate Al greater than 1000 mg Al kg\(^{-1}\) in their leaves or roots were marked as Al accumulators and those with less than 1000 mg Al kg\(^{-1}\) were Al non-accumulators. Moreover, the author found that high Al accumulators were mostly woody plant species, wherein cereals were marked as lesser Al accumulators. For example, *Oriza sativa*, *Glycine max*, and *Zia mays* were found to accumulate less than 500 mg Al kg\(^{-1}\) in the leaves. Rice accumulates less than 200 mg Al kg\(^{-1}\) in shoots and is reported as a potential Al excluder [71]. In contrast, *Camellia sinensis* was recognized as the highest accumulator species that accumulated 13,500 mg Al kg\(^{-1}\) in the leaves. This result suggests that woody plants that normally thrive in soil with high concentrations of free Al have evolved internal mechanisms to cope with Al toxicity.

Al toxicity has dramatic impacts on plant growth and development that lead to significant yield reductions [9]. One of the clearest signs of Al toxicity is the inhibition of root growth in plants. Direct impacts of Al toxicity can be estimated by the evaluation of plant parameters based short and long term responses. Based on the result of several investigations, a variety of physiological, molecular, and economical occurrences resulting from Al toxicity have been detected in plants (Table 2). Moreover, it has been shown that the toxic Al tends to fix phosphorus (P) in a less available form which leads to a severe limitation of P availability for plant growth [13]. Toxic Al leads to the production of ROS in the root apex, decreases root respiration, reduces polysaccharide deposition in the cell wall, reduces DNA replication by enhancing the rigidity of the double helix, induces programmed cell death, and results in a decline in photosynthetic efficiency [7,25]. These impacts of Al toxicity in plants can be induced within a few minutes to hours [14]. Rengel, [65] demonstrated that the first 15 min is the shortest critical time for the detection of measurable symptoms of Al-toxicity in intact root cells. The first symptoms of Al toxicity resulting in root growth inhibition were detected in wheat after 1 h of Al exposure [72]. Additionally, Al toxicity-induced disturbance of Ca\(^{2+}\) ion passing across the plasma membrane has been recognized as one of the earliest responses in wheat root apical cells.

The responses of plants to Al toxicity can vary across the species, variation can also be found among the different genotypes of the same species. Cereals along with other cultivated crop plants which diversely responded under Al stress can be classified as sensitive or moderate sensitive to Al toxicity. According to several investigations, the responses of various plants to Al exposure have been presented in Table 3. Among cereals, *Hordeum vulgare* and *Triticum durum* are considered the most sensitive crops to Al toxicity while *Oryza sativa* is reported as a potential Al excluder that significantly prevents Al toxicity compared to other cereals [71]. Notably, *Fagopyrum esculentum* and *Camellia sinensis* were able to store Al in above-ground tissue without symptoms of Al toxicity [9].

Al tolerance has been reported in a number of plants species enabling them to grow on acid soil. These tolerance mechanisms are mainly involved with the chelation strategy in roots by means of organic acids, such as citrate, malate, etc. Among the members, *ALMT1* located in root plasma membrane, was associated with Al tolerance through the exudation of malate into the rhizosphere in few plant species [73]. In addition, *NIP1;2* assists the Al-malate in *Arabidopsis* [68]. Yokosho et al. [74] demonstrated that *FRDL4* gene responsible for citrate efflux, was involved in citrate secretion from rice roots. Further, Al toxicity was alleviated in transgenic *Arabidopsis* roots while *Brassica oleracea* MATE (*BoMATE*) gene expression was more abundant in roots compared with wild-type plants. This gene was related to the of citrate exudation that confers Al tolerance in *Arabidopsis* [75].
Table 2. Impacts of aluminum toxicity in plants.

| Index of Toxicity               | Sensitivity/Time of Al Exposure | Impacts of Al Toxicity                                                                 | Conditions of Experiment | Aim of Assessment | References |
|--------------------------------|--------------------------------|---------------------------------------------------------------------------------------|--------------------------|-------------------|------------|
| Grain yield                    | Low/LD                         | Al-induced delay flowering; significantly reduced grain yield in sensitive cultivar     | NS                      | FS                | [76]       |
| Biomass production             | Moderate/LD                    | Reduced dry matter yield                                                               | NS                      | FS                | [77]       |
| Nutrient imbalance             | Moderate/SD                    | Resulted imbalance of macronutrients including Mg, K and P                            | NS                      | TS                | [78]       |
| Survival                       | Low/LD                         | Resulted dry weight is the most sensitive tolerance index while survival is considered as the most cost-effective indicator of tolerance | SC                      | TS                | [79]       |
| Root growth                    | High/SD                        | Root growth was significantly inhibited by toxic Al ions in acid soil                   | SC                      | TA                | [80]       |
| Change of root system          | High/SD                        | Indicated potential toxicity problem; root tips and lateral roots become more stubby, turned brown, and inhibited fine branching | SC                      | TA                | [81]       |
| Rapture/cracks of root         | High/SD                        | Induced rhizodermal cracks on roots after exposures to Al (11 µM)                     | NS                      | TA                | [82]       |
| Plasma membrane (PM)           | High/SD                        | Al$^{3+}$ ion attached to PM; cells become more leaky and rigid                       | NS                      | TS                | [83]       |
| Cell division and elongation   | High/SD                        | Al resulted the disordered the arrangement of the cells, deformed cell shapes, altered cell structure, and the shorter of the meristematic zone of the root tips | NS                      | FS, AR            | [23]       |
| Interference with enzymes      | Moderate/SD                    | Down regulated peroxidase and chitinase isoforms in root tips                          | NS                      | FS, TS            | [84]       |
| Organic acid exudation         | Low/LD                         | Organic acids (oxalate, citrate) enhanced plant growth and adaptation following Al stress to acid soil | SC                      | FS, AR            | [85]       |
| Callose formation              | High/SD                        | Resulted a link between callose formation and Al-induced inhibition of root growth     | NS                      | TA, TS            | [86]       |
| Auxin transport                | High/SD                        | Al toxicity inhibited (IAA) transportation from the shoot base to root tip; though exogenous application of IAA alleviated Al stress | NS                      | FS, AR            | [23]       |
| Al content in pectin           | High/SD                        | Aggravated Al$^{3+}$ toxicity due to accumulation of more Al in pectin                | NS                      | TA                | [87]       |

Plant-based indices for assessment of the impacts of Al-toxicity (LD, long-duration; SD, short-duration; FS, fundamental study; AR, applied research; TA, toxicity assessment; TS, tolerance screening; NS, nutrient solution; SC, soil condition).
Table 3. Sensitivity of plants to aluminum toxicity, modified from [3,25,60,82,88–92].

| Sensitivity Threshold                              | High Sensitive (Indicator Plants) | Moderate Sensitive | Low Sensitive (Resistant/Tolerant Plants) |
|---------------------------------------------------|-----------------------------------|--------------------|------------------------------------------|
|                                                   | Hordeum vulgare L. (barley)       | Raphanus sativus L. (radish) | Fagopyrum esculentum Moench (buckwheat)  |
|                                                   | Triticum aestivum L. (wheat)      | Sorghum bicolor L. Moench (sorghum) |                                               |
|                                                   | Triticum durum Desf. (durum wheat)|                   |                                           |
|                                                   | Lactuca sativa L. (lettuce)       | Capitata var. alba L. (cabbage) |                                          |
|                                                   | Beta vulgaris L. (beet)           |                     |                                          |
|                                                   | Phleum pretense L. (timothy-grass)| Avena sativa L. (oat) | Zea mays L. (maize)                       |
|                                                   | Glycine max Merr. (soybean)       |                     |                                           |
|                                                   | Pisum sativum L. (pea)            | Medicago sativa L. (alfalfa) | Brassica rapa L. (turnip)                |
|                                                   | Phaseolus vulgaris L. (common bean)|                     |                                           |
|                                                   | Pachyrhizus ahipa Wedd. (Parodi) | Secale cereale L. (rye) | Agrostis gigantean Roth. (redtop)         |

Several reports have provided indications regarding the level of Al sensitivity in plants. It has been found that the inhibition of root growth occurs within a few minutes to hours with a low concentration (µM) of toxic Al$^{3+}$ [14]. Though in some cases low doses of Al have been reported to stimulate root and shoot growth of plants [3]. This might be due to Al enhancing capability of meristematic regions. Concentration-dependent Al toxicity and its effects have been widely manifested in various plants. For example, Al toxicity-induced rhizodermal cracks were observed in ahipa roots following exposure of roots to Al (11 µM) stress. In cowpea (Vigna unguiculata) the sensitivity threshold was observed at 0.1 µM Al wherein complete growth inhibition occurred at 40 µM Al [93]. Several sensitive and tolerant cereals and legumes with their responses to Al toxicity have been explored whereas the rice was marked as tolerant compared to other cereals [25]. Recently, nodulated legumes including common bean (Phaseolus vulgaris), soybean (Glycine max), and pea (Pisum sativum) has been reported to be sensitive to Al toxicity wherein their sensitivity doses were greater than 25 µM, 4.7 µM, and 50 µM, respectively, though soybean growth was inhibited at 10 µM Al [60].

4. Factors Affecting Aluminum Toxicity and Nutrient Imbalance

Soil acidification is an important factor that influences Al toxicity on agricultural land. The acidification of soil is caused by a number of natural and/or anthropogenic processes (Figure 1). Deposition of atmospheric gases or particles such as SO$_2$, NH$_3$, HNO$_3$, and HCl; and application of acidifying fertilizer including elemental sulfur (S) or ammonium (NH$_4$) salt accelerated the soil acidification process that led to increased soluble Al$^{3+}$ concentrations in the soil solution [5]. Moreover, the imbalance of N, S, and C cycles, uptake of N by legumes, and intensified leaching of base cations (BC) were responsible for increasing H$^+$ ions and decreasing soil pH level [94]. Over 100 years ago, it was noted for the first time that the concentration of soluble Al$^{3+}$ increased in soils [95], this Al$^{3+}$ was able to create phytotoxicity in the rhizosphere when the pH was below 5, and the most prominent sign of Al toxicity was considered the inhibition of root growth [62].
nutrients. Soil toxicity is known to be induced by the excess cations such as Mn\(^{2+}\), Fe\(^{3+}\), H\(^+\) and Al\(^{3+}\) [3]. Among these, Al\(^{3+}\) is the most critical cation that leads to rhizotoxicity and severely impairs plant growth in acid soil. A ratio of BC/Al\(^{3+}\) less than 1 in soil solution was considered as a potential index for the adverse effect of soluble Al\(^{3+}\) and nutrient imbalance for plant growth [97]. Hence, the availability of BC and toxic Al\(^{3+}\) in acid soil depends on acid rain pH, soil properties, cation exchange capacity (CEC), soil texture and initial base content in soil [98].

Acid rain/deposition has dramatic impacts on leachability of essential nutrient cations, mobility of toxic element (Al\(^{3+}\)), and acidity development in soil [96]. Basic and acidic cations are available at soil exchange sites or in the soil solution. Cation exchange sites that hold cations in the soil are negatively charged. Soil is buffered during acidification by a series of chemical processes resulting in the replacement of exchangeable base cations (Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), and Na\(^+\)) by H\(^+\) and Al\(^{3+}\) at the cation exchange sites [5]. Concurrently, the proportion of acidic cations such as H\(^+\) and Al\(^{3+}\) in the soil solution increases. Often, acid rain stimulates the leaching of base cations such as Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), and Na\(^+\) from soil. As a consequence, the essential nutrient cations such as Ca\(^{2+}\), Mg\(^{2+}\), and K\(^+\) are leached resulting in the depletion of base cations (BC) from the soil. The significant losses of these nutrient cations from soil solution or soil exchange sites result in nutrient imbalance in the soil. However, acid soils contain high amounts of Al\(^{3+}\) and a low amount of BC that are linked to deficiencies of important plant nutrients. Soil toxicity is known to be induced by the excess cations such as Mn\(^{2+}\), Fe\(^{3+}\), H\(^+\) and Al\(^{3+}\) [3]. Among these, Al\(^{3+}\) is the most critical cation that leads to rhizotoxicity and severely impairs plant growth in acid soil. A ratio of BC/Al\(^{3+}\) less than 1 in soil solution was considered as
a potential index for the adverse effect of soluble $\text{Al}^{3+}$ and nutrient imbalance for plant growth [97]. Hence, the availability of BC and toxic $\text{Al}^{3+}$ in acid soil depends on acid rain pH, soil properties, cation exchange capacity (CEC), soil texture and initial base content in soil [98].

Soil pH is often considered a master variable as it controls solubility, bioavailability, mobility, ionic speciation, and ultimately toxicity of any metal in the soil [99]. Ion availability in soil solution is influenced by low-pH. For example, Mn oxide solubilizes at soil pH below 5.5, and releases $\text{Mn}^{2+}$ ions; at pH 4.3 a large amount of soluble $\text{Al}^{3+}$ is released; at pH $< 3.8$ Fe becomes the most exchangeable ion in the soil solution [13,62]. The pH-dependent metal toxicity is quite complex; acid deposition to soil promotes soil acidity wherein more soluble ions are released into the soil solution. Consequently, potential phytotoxicity of metal ions was found to be enhanced due to their increased availability and concentration in soil solution [99]. The $\text{Al}^{3+}$ and $\text{Al(OH)}_4^-$ are often described as the major rhizotoxic Al species at low and high-pH levels, respectively. At low pH (about 4.3) soluble ionic aluminum ($\text{Al}^{3+}$) is the most dominant form that is toxic for plant growth [3]. Surprisingly, it appears that toxic Al species not only inhibit root growth at pH 4.3 but also at pH 8.0, though the concentration of Al species at pH 8.0 was lower compared to at pH 4.3 [100]. Conversely, Al acquisition of root apices was higher at pH 8.0 compared to at pH 4.3. Callose (1,3-glucan) formation is often considered as the most perceptible indicator for Al toxicity that induced at pH 8.0, whereas the mobilization of callose was highly induced at pH 4.3 in the cortical region [100,101]. In addition, several nutrients such as P, K, Ca, Mg, Mo, and B contents were altered at low pH with Al toxicity [6,42]. So, the important note is that plants adapting to grow on low pH acid soils are threatened by the combination of Al toxicity and nutrient imbalance and/or deficiency.

The solubility of Al is an important factor that influences Al-availability, mobility, and toxicity in the environment [102]. Al was reported to highly soluble at more acidic (pH < 6.0) and at more alkaline (pH > 8.0) conditions but relatively insoluble at pH 6.0–8.0 [gibbsite; $\text{Al(OH)}_3$] [103]. This insoluble form of Al is considered less toxic compared to soluble $\text{Al}^{3+}$ [104]. Hence, Al species existing in clay fractions are mainly in a less toxic form such as alumino-silicate or aluminium oxide. Soil acidification promotes the process of its solubilization and mobilization which lead to potential phytotoxicity [105]. In acidic soil, when the pH drops (about 4.3) a large number of soluble Al ions (mostly $\text{Al}^{3+}$) are released, this toxic $\text{Al}^{3+}$ rapidly inhibits root elongation [62,100]. At neutral pH (7.0), Al hydroxide species (e.g., $\text{Al(OH)}_3$) are relatively insoluble but at pH above 7.5, Al species are formed as $\text{Al(OH)}_4^-$ and solubilized again [61]. However, a relationship has been observed between pH and Al solubility, wherein the Al solubility increases when pH is below 4.5 in acid soil [3]. In addition, Al toxicity is also known to be stimulated by the pH-dependent hydrolysis intensity of several Al species in soil solution [6]. Hydrolysis of ions occurred when the charge/radius ($z/r$) ratio is large enough to break down the bond (H–O), and releases $\text{H}^+$ into the soil solution. pH-dependent hydrolysis of mononuclear Al species are presented by simple equations (Figure 1), wherein each chemical reaction indicated the production of $\text{H}^+$ that leads to the generation of more soluble $\text{Al}^{3+}$. Hence, the hydrolysis of these Al species occurs at low pH (<5.0).

Toxic-Al interferes in the acquisition, accumulation, localization, and utilization of most of the mineral elements. For instance, the uptake of mineral nutrients such as $\text{Ca}^{2+}$ (69%), $\text{Mg}^{2+}$, $\text{K}^+$ (13%), and $\text{NH}_4^+$ (40%) were inhibited by Al toxicity, and Al was known to be enhanced influx of the specific anions such as $\text{HN}_3^-$ (44%), and $\text{PO}_4^{3-}$ [42]. Al toxicity-induced nutritional imbalances have been widely manifested in several plant species. For instance, a distinct Al accumulating pattern with nutritional imbalance (e.g., Ca, Mg, P, and K) has been detected in eleven pteridophytes families [106]. Al toxicity generally inhibits to uptake up macro-and micro elements plants, whereas tolerant cultivars found to be exhibited several macro elements including Ca and Mg [12]. In wheat, both sensitive and tolerant genotypes manifested a marked reduction of K and Mg content whereas the concentration of Ca, Al and Si increased in roots [78]. Hence, the sensitive genotypes exhibited higher Al accumulation and nutritional imbalance in both roots and shoots than the tolerant one.
Al-toxicity reduced K, Mg, Ca, and P accumulation in two contrasting rice cultivars, whereas the utilization of P, Ca and Mg increased more in tolerant cultivar than a sensitive plant [107]. Simon et al. [108] reported that Al exposure was involved in the reduction of Ca, K, Mg, Mn, Fe and Zn contents in tomato. Zobel et al. [109] observed that the changes in fine root diameter with changes in nutrient such as N, P, and Al in plants. Additionally, the specific absorption rate of B (SAR_{B}) was significantly influenced by Al-toxicity. Poschenrieder et al. [110] detected a correlation between the Al-induced reduction of B absorption and the root growth inhibition in maize. From the above-mentioned literature it appears that Al toxicity induces the imbalance of nutrient uptake and acquisition in plants.

5. Role of Mineral Nutrition for Mitigating Aluminum Toxicity in Plants

A large number of strategies have been explored to mitigate the Al toxicity in plants to acid soils. Most of the strategies can be divided into two classes: inorganic amendments such as exogenous application of mineral elements including Ca, Mg, P, S, B, and Si and ground oxide/hydroxide [111–117] (Tables 4 and 5) and organic amendments such as organo-mineral fertilizers, plant growth promoting bacteria (PGPB), green waste compost, plant-derived biochars, and their combination with other minerals [118,119] which played a pivotal role in Al toxicity alleviation in plants to acid soils. Conversely, we did not observe considerable existing literatures concerning the role of K, Mn, Zn, and Mo in Al toxicity alleviation in plants though these are essential minerals. The following sections clarify the role of major nutrients based amendments to mitigate Al toxicity in plants to acid soils.

5.1. Calcium (Ca)

Ca alleviates Al-induced rhizotoxicity in different crops growing in acid soils [111]. Ca was reported to alleviate Al toxicity through several mechanisms: (i) displacement of Al from the cell membrane surface (CMS) by an electrostatic effect; (ii) restoration of Ca^{2+} on the CMS; and (iii) ionic interaction between Ca^{2+} and Al^{3+} that occurred at cell surface and at Donnan free space (DFS) of root cells [120,121]. Kinraide, [121] reported that 1 mmol·L^{-1} concentration of Ca is capable to inhibit the effect of 1 µmol·L^{-1} Al. Ca nutrient was known to be applied as different practical alternatives such as liming oxide (CaO), hydroxide [Ca(OH)_{2}], calcites (CaCO_{3}), dolomites [CaMg(CO_{3})_{2}], and gypsum (CaSO_{4}) including its bio-products. Application of these Ca-amendments greatly influences the effectiveness of Ca for mitigating Al toxicity. Moreover, the application of Cd before Al stress is more effective to mitigate Al-induced damage than that of Cd supplementation during Al treatment [122]. In the following sections, we discuss the beneficial effects of several Ca-amendments such as lime (e.g., calcite, dolomite), phosphogypsum (PG), and gypsum (G) with various application doses on different crop plants to acid soils.
Table 4. Calcareous amendments-induced alleviation of Al toxicity in plants to acid soils.

| Amendments      | Plant Species                                      | Dose (t·ha⁻¹) and Duration | Outcomes                                                                                           | References |
|-----------------|----------------------------------------------------|-----------------------------|----------------------------------------------------------------------------------------------------|------------|
| Phosphogypsum (PG) |                                                   |                             |                                                    |            |
|                  | *Zea mays* L., *Triticum aestivum* L., *Glycine max* L. | 12.0, (0–8.0 cm), 180 days   | Increased Ca concentrations in all crops; enhanced root growth; provided nutrients to the soil and reduce Al³⁺ activity. | [123]      |
|                  | *Medicago sativa* L. cv. Hunter River and *Glycine max* L. Merr. cv. Lee | 2.0, (60–80 cm); 50 days    | Ameliorated subsoil acidity; Increased Ca in soil solution; Reduced exchangeable Al, and increased in crop growth. | [124]      |
|                  | *Malus domestica* Borkh. cv. Gala/MM 106           | 2.0, (40–60 cm), 90 days    | Decreased exchangeable Al; increased Ca in topsoil as well as plant leaf; increase root density. | [125]      |
|                  | *Trifolium* spp.                                   | 2.5, (0–25 cm), 1.5 years   | Reduced toxic Al concentration in soil solution and exchange site in subterranean clover-based pasture. | [126]      |
|                  | *Zea mays* L.                                      | 34.9% PG; (5 × 7 × 5 cm)    | Reduced soil acidity; decreased Al activity of in the soil solution; increased root development. | [127]      |
| Gypsum (G)       |                                                   |                             |                                                    |            |
|                  | *Lolium perenne* L. cv. Nui                        | 2.0, (0–20 cm)              | Balanced nutrient elements; increased forage quality and yield; reduced exchangeable Al; increased soil pH. | [128]      |
|                  | *Vaccinium corymbosum* L.                          | 4.4, 60 days                | Enhanced Ca and S contents; reduced Al concentration and lipid peroxidation in roots and leaves; Ameliorated Al toxicity in plant by gypsum. | [129]      |
|                  | *Arachis hypogaea* L.                              | 1.0, 60 days                | Reduced Al phytotoxicity; increased nodules, pods, and yield of groundnut. | [130]      |
|                  | *Medicago sativa* L.                               | 22.2, (0–75 cm), 12 years   | Provided Ca and S benefits as a source in nutrient-limiting soils; enhanced soil fertility and alfalfa growth. | [131]      |
|                  | *Zea mays* L.                                       | 11.0, (40–60 cm), 1 year    | Improved root density; Increased Ca, Mg, and SO₄²⁻-S; declined the level of exchangeable Al. | [132]      |
| Plant Species                          | Dose and Duration of Al Exposure | Mineral Treatment | Plant Responses                                                                                                                                                                                                 | References |
|---------------------------------------|-----------------------------------|-------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| *Glycine max* (L.) Merr.              | 2 µM Al, 24 h                     | 500–2000 µM Ca, 3 days | Mitigated the inhibition of root growth and root hair formation during Al toxicity; enhanced protection against the deleterious effect of toxic Al in soybean.                                                      | [111]      |
| *Triticum aestivum* L.                | 20 µM Al, 28 days                 | 1600 µM Ca; 800 µM Mg, 7 days | Ca and Mg alleviated Al toxicity in wheat, respectively; decreased Al$^{3+}$ activity at PM surface in root cell.                                                                                              | [112,133]  |
| *Glycine max* (L.) Merr.              | 100 mM Al, 72 h                   | 25 µM Mg, 3 days    | Increased root growth; Alleviated Al rhizotoxicity during lateral root elongation.                                                                                                                                | [113]      |
| *Eucalyptus grandis* × *E. urophylla* clones “G9” and “DH32-29” | 5 mM Al, 20 weeks | 200 µM P; 140 days | Al resistant G9 clone, enhanced more malate, oxalate, and citrate secretion in roots; P was involved in elemental Al fixation in roots, and restricted Al transport to the stems and leaves; Increased the activities of PEPC, CS enzymes. | [117]      |
| *Citrus grandis*                      | 1 mM Al, 16 days                  | 0.5 mM S, 126 days  | Reduced Al transport in roots, shoots and leaves; Decreased H$_2$O$_2$ production; Increased, P, Mg, Ca and RWC; Enhanced OAs in roots.                                                                          | [116]      |
| *Citrus grandis*                      | 1.2 mM Al, 18 weeks               | 20 µM B, 126 days   | Over 100 genes including GSTZ1, TRX-M4, CLM 19, *IAA-amino acid hydrolase* ILR1-4, GAG-POL were associated with B-induced alleviation of Al-toxicity.                                                     | [115]      |
| *Pisum sativum* cv Zhongwan           | 50 µM Al, 24 h                    | 50 µM B, 2 days     | Increased chlorophyll and biomass; reduced chlorosis; reduced Al concentration in shoots; inhibited Al-binding in cell wall; reduced toxicity effect in roots and shoots.                                                  | [114]      |
| *Vigna unguicula* L.                  | 10 mM Al, 16 days                 | 2.50 mM Si, 26 days | Increased SOD, CAT, APX and POX activities; Reduced Al contents of all tissues; Mitigated toxic effects of Al.                                                                                              | [134]      |
| *Oriza sativa* L.                     | 50 µM Al, 7 days                  | 10 µM Si, 7 days    | Restricted the uptake and transport of toxic Al in roots and leaves; maintained Mg and Zn at optimum levels; reduced cellular injury from Al toxicity.                                                         | [135]      |
5.1.1. Liming

Liming is an important and well-known approach for correcting acid soil, along with restoring Ca availability, and alleviating Al toxicity in plants [5,136]. Application of Ca or Ca-Mg containing minerals [calcites, CaCO$_3$; dolomites, CaMg(CO$_3$)$_2$] to acid soil increases the pH level and reduces toxic Al concentration [137]. Consequently, enhances the cation exchange capacity (CEC), and P availability by inactivation Al and Fe of soils. Several factors such as neutralizing value (NV) or purity of lime, particle fitness (PF), and lime distribution (LD) indicate the effectiveness of lime [136]. NV of agricultural lime materials is determined by a percentage (%) relative to the neutralizing value of standard CaCO$_3$, and is known as calcium carbonate equivalent (CCE). It has been marked that calcites and dolomites consist of 70–100% and 70–109% CCE, respectively [136]. PF is important for lime effectiveness because large particles (>1.7 mm) can remain unreacted in the soil for many years. Moreover, limes are known to be extended about 3 mm after placing, and takes more time to soluble, and subsequent neutralization of soil acidity. Therefore, it should be distributed by the following incorporation at least two months before planting.

5.1.2. Phosphogypsum (PG)

PG is primarily calcium sulfate hydrate formed as a by-product from the industry of phosphate fertilizer [138]. It is mainly composed of Ca$^{2+}$, SO$_4^{2-}$ and a small amount of phosphorus (P), silicon (Si), and fluoride (F) [139]. PG was known to be involved in Al toxicity alleviation by complexing with F at low pH. Several reports have provided indications regarding the use of PG as an alternative to Ca and SO$_4^{2-}$, applied for balancing acidity and alleviating Al toxicity in acid soils [140,141] (Table 4). Mays and Mortvedt, [142] suggested a dose range from 500–1000 kg ha$^{-1}$ for a single PG application. Conversely, a combined PG with CaCO$_3$ amendment, and/or gypsum (2500 kg ha$^{-1}$) treatment was found to reduce Al$^{3+}$ concentration at a depth of up to 5 cm in soil, also increased root density and decrease Al$^{3+}$ concentration in apple trees [125].

5.1.3. Gypsum (G)

G is known as a soft sulfate mineral composed of a calcium sulfate dihydrate (CaSO$_4$·2H$_2$O), widely used as an amendment in soils under acidic conditions. The solubility of G (2.5 g L$^{-1}$) was reported approximately 5-fold higher than calcite lime (0.5 g L$^{-1}$) [143]. G is an important source of Ca and S which improves mineral (N, P, K, Mn, and Zn) profiles in plants [144]. Several calcareous amendments would offer a suitable option for decreasing Al toxicity and soil acidity [145] (Table 4). To reduce Al toxicity the role of SO$_4$ is important in acid sub-soils, wherein Al complexes organic ligands (OL). Complexing OL after G application has been detected in Malaysian acid soils resulting in increased AlSO$_4^{3+}$ and decreased Al activity that led to enhanced corn yield [146]. Interestingly, the toxic effects of Al species [Al$^{3+}$, Al(OH)$_2^{2+}$, and Al(OH)$_2^{3+}$] have been alleviated by G whereas soybean roots were elongated at 500 mM G application [111]. G not only alleviates Al toxicity but also provides nutritional benefits in plants grown in acid soils. For instance, N, P, K, S, Mn and Ca levels increased in blueberry leaves after a combined G (4.0 t ha$^{-1}$) and NPK fertilizer (0.3 t ha$^{-1}$) application to acid soil, and enhanced stem elongation, bud survival, and blossom quantity [147]. Korcak [148] found that soil pH and Ca levels were increased after G (0.60 t ha$^{-1}$) application for five years, whereas Ca levels were inconsistent in leaves and fruits. Recently, Tirado-Corbalá et al. [131] declared that G is able to provide Ca and S benefits to nutrient-limiting soils that led to enhance soil fertility and alfalfa growth. Moreover, the authors undertook a long term (12 years) study on alfalfa with G (22.2 t ha$^{-1}$) application (Table 4).

5.2. Magnesium (Mg)

Mg is an essential nutrient that plays the vital role in phloem loading of sucrose, also alleviates soil-borne Al toxicity [149]. Unfortunately, Al toxicity induces Mg deficiency that leads partitioning
of dry matter and carbohydrates between roots and shoots [150]. Consequently, observed that plant growth and yield were severely impaired in Mg-deficient plants. Therefore, exogenous application of Mg would be a suitable approach to alleviate Al toxicity in plants. Exogenous application of Mg found to be alleviated Al toxicity through (i) increasing ionic strength of the solution [120]; (ii) reducing Al saturation at the space outside of plasma membrane (PM), declining Al activity at PM of root cells [151]. Bose et al. [152] also elucidated that several mechanisms relevant to Mg mediated alleviation of Al toxicity in plants. For example, intercellular Mg-dependent regulation of organic acid anions (OAs) exudation, stimulation of H$^{+}$-ATPase activity, modulation of free cytosolic Ca$^{2+}$ spikes, and regulation of ROS homeostasis under Al toxicity in plants.

Exudation of OAs one of the best strategies for phytotoxic Al exclusion in several plant species to acid soils [13]. Exogenous application of Mg (50 µM) to medium ameliorated Al toxicity by enhancing citrate exudation in soybean [113]. Interestingly, Mg pre-treated soybean seedlings led to induce citrate secretion within 1 h following Al exposure. H$^{+}$-ATPase is a key protein known to be involved in nutrient acquisition [153], auxin transport and cell elongation [155]. It has been reported that H$^{+}$-ATPase activity inhibited by Al toxicity in Vigna umbellata roots, surprisingly H$^{+}$-ATPase activity was marked to be rebound and induced citrate exudation while added 10 mM Mg to the same nutrient solution [156]. Similarly, exogenous application of 20 mM Mg treatment following Al exposure stimulated H$^{+}$-ATPase activity, along with enhanced citrate exudation that alleviated Al toxicity in Vicia faba [157]. In a plant cell, free cytosolic Ca$^{2+}$ found to increase during Al stress, and free cytosolic Ca$^{2+}$ activity usually maintained 100–200 nM range, over this dose might be induced cytotoxicity in the cell, also observed free cytosolic Ca$^{2+}$ level significantly increased in yeast cells due to exclusion of Mg nutrition [158]. Additionally, it has been reported that elevated Mg modulates intracellular Ca$^{2+}$ permeable channels, and along with lead to release free Ca$^{2+}$ from the internal organelles [159]. Therefore, it is hypothesized that the Al exposure in plants enhanced Mg content that leads to prevent Ca$^{2+}$ cytotoxicity.

Several studies have provided indications regarding the Mg nutrition not only alleviates Al toxicity but also enhances root growth in diverse plant species. Root growth was found to be enhanced by Mg nutrition (10–200 µM treatment) in several legumes such as soybean (Glycine max) [113], rice bean (Vigna umbellata) [156] and broad bean (Vicia faba) [157]. Moreover, Mg transporter genes were associated to ameliorate Al toxicity in plants. Overexpression of an Mg transporter gene (AtMGT1) alleviated Al toxicity by enhancing Mg acquisition in N. benthamiana [160]. Al treatment (50 µM AlCl$_3$, at pH 4.2) in nutrient solution showed an increased Mg uptake and free Mg concentration in the cytoplasm of Al-tolerant Arabidopsis (Col-0 and alr104) than sensitive one (als-5 and als3) [152]. Such elevation of cytosolic Mg nutrition might be a key indication of a tolerant plant to alleviate Al toxicity.

5.3. Phosphorus (P)

P is an essential macro-mineral that plays an important role in plant growth and development under normal and/or stress conditions [161,162]. In acidic soils, inorganic phosphate (Pi) is fixed by Al/Fe, it becomes critical when the pH drops; the result is a severe limitation of Pi in acid soils [13]. Consequently, plants surviving in acid soils have to face both Al toxicity and P deficiency. Exogenous application of P alleviates Al toxicity in a number of plants such as sorghum [163], buckwheat [164], and wheat [165] on acid soils. Tan and Keltjens, [163] found that plant biomass production was not influenced by a low concentration of Al (0.4 mg·L$^{-1}$), but plant growth and dry matter yield (DMY) were severely inhibited at a high Al concentration (1.6 mg·L$^{-1}$) in sorghum. In this regard, the addition of P alleviated Al toxicity by increasing root respiration and nutrient uptake that led to enhanced DMY. Iqbal [165] observed that P content in wheat seedlings was largely reduced by Al stress (150 mg AlCl$_3$ kg$^{-1}$ soil), conversely pH level was found to be balanced and increased P level after addition of exogenous P (160 mg P kg$^{-1}$ soil) to soil. Chen et al. [166] provided a threshold of P alleviating Al toxicity based on tested plants, and mentioned if the value of P/Al molar ratio exceeds 5 in the root cells, that plant can alleviate Al toxicity. Recently, P application (8 g·plant$^{-1}$) in nursery conditions
was reported to enhance plant growth, height, root collar diameter, and chlorophyll content in maple tree [161].

Several effective strategies have been explored for plant production under Al toxicity and P deficiency in acidic soils. Ch’ng et al. [167] suggested to increase P availability by adding organic amendments (e.g., biochar, compost etc.) as he observed the total P and Pi were increased by organic amendments that effectively fixed toxic Al and/or Fe in acid soil. In addition, several molecular breeding related strategies have been explored in plant response to Al toxicity and P deficiency. Sasaki et al. (2004) cloned malate transporter TaALMT1 gene from wheat and transferred them into Al-sensitive barley that obtained the trait of Al-resistance. Wang et al. [168] suggested a ‘root breeding’ approach to developing P-efficient plants based on those that have the ability to utilize native and exogenous P from acidic soils. Recently, Chen and Liao [13] highlighted the opportunity for organic acid synthesis in crop production for sustainable agriculture though genetic manipulation as the application of P-fertilizers are costly and can be seen to be environmentally risky.

5.4. Sulfur (S)

Until the 1970’s, S was mainly regarded as a neglected element in soil science, though it has a pivotal role in the production of protein, vitamins, chlorophyll, and glucoside oil in plants [169]. Recently, S has received more attention due to its capacity to modify metal toxicity as well as having a vital role in plant growth and development [116,170,171]. Several studies have provided evidence that S-containing components alleviate Al toxicity in wheat [172], barley [173], oilseed rape [174] and citrus trees [116]. In the above studies S exerts protective functions against Al toxicity through: (i) increasing antioxidant activity, and decreasing ROS and lipid peroxidation levels; (ii) decreasing uptake of Al in roots and shoots; (iii) increasing uptake of several nutrients viz phosphorus (P), magnesium (Mg), and calcium (Ca); and (iv) enhancing Al-induced secretion of organic acid anions (OAs) from plant roots. The toxicity induced by several heavy metals was alleviated in plants by exogenous S addition, though the efficiency of alleviation mostly depends on the S-application strategies, doses, and sources. Generally, high doses of S are recommended to abate arsenic (As) uptake in plants. For example, S treatment (120 mg S·kg⁻¹ soil; Na₂S₂O₃·5H₂O) was applied to As (20 mg As·kg⁻¹ soil; Na₂HAsO₄·12H₂O) contaminated soil, and it was found that As concentrations reduced in rice grains by 44% compared to grains from the treatment without S application [175]. Recently, S addition (0.5 mM S; MgSO₄ and/or 0.5 mM Na₂SO₄) was shown to be alleviated Al toxicity by increasing minerals (P, Mg and Ca) and relative water contents; decreasing Al and H₂O₂ contents, and involving S-metabolism and antioxidant enzymes in citrus [116]. Additionally, several studies have reported that S increased mineral components that supported to alleviate several metal toxicities, along with Al toxicity in plants [116,170], and better increased NO₃⁻ and NH₄⁺ levels in the soil compared to an NPK fertilizer treatment [176].

5.5. Boron (B)

B is an essential micronutrient which was reported to decrease the accumulation of toxic Al in several plants [114]. Hossain et al. [177] conducted a nutrient culture to assess the impact of B application (200 µM) on Al toxicity (50 µM Al; pH 4.5), B deficiency, and growth of 15 wheat cultivars. Subsequently, they found that malate exudation level increased in the roots of all cultivars under Al toxicity (100 µM Al; pH 4.5). Among the 15 cultivars, the most tolerant cultivar exuded approximately 6-fold higher malate content than a sensitive one. Additionally, vigorous seedling growth was observed at 40 µM B application, and 200 µM B alleviated Al toxicity in a sensitive wheat cultivar. Recently, Riaz et al. [178] found that B treatment (25 µM B as H₃BO₃) alleviated Al toxicity by: (i) improving the activities of antioxidant enzymes such as peroxidase, catalase, and ascorbate peroxidase, and; (ii) reducing mobilization of toxic Al in roots and shoots of rapeseed. Gupta et al. [179] demonstrated that B concentrations (20–100 µg B·g⁻¹ DW, DW = dry weight; 20–100 µg boron present in per gram
dry weighted sample. Either root or shoot sample.) were adequate for growth, but an excess level of B (200 µg B·g⁻¹ DW) was associated to induce toxicity in plant cells.

5.6. Silicon (Si)

Si is the second most abundant metal in the earth’s crust [180]. In soil medium, plants take up and accumulate Si ranging from (1–100 g Si·kg⁻¹ DW) through different modes, uptake, and transport processes [181]. Si is taken up in plants as orthosilicic acid (H₄SiO₄), and rice is considered as typical Si accumulator (100 g Si·kg⁻¹ DW) [182]. Si is still to be considered as an essential element, although the beneficial impact of Si concerning multiple stress tolerances in plants has been wildly recognized [183]. Several studies have demonstrated the effectiveness of Si application towards decreasing Al uptake by plants grown hydroponically or in pot experiments [135,184]. Singh et al. [135] demonstrated that exogenous Si addition alleviated Al toxicity by reducing Al accumulation, and preventing the Mg and Zn deficiency in rice during Al stress. Interestingly, Si showed efficiency by forming Al-Si complexes in sorghum mucigel and outer cellular tissues. Consequently, this Al-Si complex inhibited the binding of toxic Al to the cell wall [185]. Recently, a novel approach has been applied to alleviate Al phytotoxicity in wheat through silicon (Si)-rich biochar amendment in soil [184]. In the same study, the authors suggested this cost-effective approach as it ameliorated the acidic soil, subsequently alleviated phytotoxicity by a mechanism wherein Al involves the chelation of metal with Si-biochar (Al-Si). Additionally, Si-particle reduced the amount of soil exchangeable Al and prevented the migration of toxic Al in different plant tissue.

5.7. Miscellaneous

Several low-cost effective and available ameliorants such as alkaline slag (AS) coal fly ash (CFA), and red mud (RM), are known to be involved in correcting soil acidity, and subsequent alleviation of Al toxicity under tea plantation [186]. In addition, it was found to be increased soil pH and cation exchange capacity (CEC%), and decreased exchangeable Al by RM, AS, and CFA. A mechanism by which these amendments were involved in “formation and retention of hydroxyl-Al-polymers” that alleviated Al phytotoxicity. The important note is that constitutes of these byproducts used in agriculture with limited environmental hazard. These industrial byproducts provided a good source of base cations (Ca²⁺, Mg²⁺, K⁺, and Na⁺) and anions (P and S). Therefore, use of these industrial byproducts would be effective as an alternative source for balancing soil acidity, and alleviating Al phytotoxicity instead of the traditional use of lime and gypsum.

Hormones, organic acids, and polyamines participated in favor of alleviation of Al toxicity in different plants [3,13,187]. The foliar application of indole acetic acid (IAA; 25 µM) reduced the accumulation of Al in the root apex in wheat [188], and IAA (6 mg·L⁻¹) alleviated Al-induced damage of cell structure in alfalfa [189]. IAA stimulated the plasma membrane H⁺-ATPase activity and reduced Al contents in root tip, cell wall, and pectin fractions. This process participated in Al-toxicity alleviation by decreasing toxic-Al binding ability in pectin through enhancing H⁺ secretion in rhizosphere. Polyamines (PAs), and salicylic acids (SAs) are involved in organic acids (OAs) secretion, osmolyte biosynthesis, and activation of the antioxidant system in plants [3,190,191]. Putrescine (Put) is an important signaling molecule; Al toxicity-induced root inhibition was alleviated by Put through reducing ethylene synthesis [192]. It has been observed that Al-exclusion and internal Al toxicity alleviation mechanisms rely on Al-induced secretion of organic acids anions and phenolic compounds in root apex [193]. SA alleviated Al toxicity by positive modulation of the citrate efflux in Cassia tora roots [194]. In addition, Al toxicity was alleviated in tomato [195], and soybean [191] by SA (<20 µM) through activation of the antioxidant system.

Biofertilizers (e.g., micorrhizal fungi (MF), plant growth promoting bacteria) and biochars (e.g., agricultural wastes, organic wastes) application provide several advantages to overcome Al³⁺ toxicity in plants to acidic soils. In acidic soil (pH 3.5) with Al stress (1.0 mM; AlCl₃·6H₂O), following the inoculation of arbuscular mycorrhizal species: *Rhizophagus irregularis* (formerly *Glomus*...
intraradices) and Funneliformis mosseae (formerly Glomus mosseae) supported to enhance plant yield, total biomass, and better nutritional (N, P, K, Ca, Mg, Fe, Zn and B) status in Cucurbita pepo compared to non-inoculated plants [196]. In addition, application of arbuscular mycorrhizal inoculum Glomus intraradices alleviated Al toxicity by decreasing toxic Al accumulation, and enhancing Ca, Mg and P accumulations in banana roots [197].

Plant growth promoting bacteria (PGPB) played an important role against Al$^{3+}$ toxicity and soil acidity. In field condition, 4 t·ha$^{-1}$ biofertilizer (a consortium of PGPB: Bacillus sp., Stenotrophomonas maltophilia, Burkholderia thailandensis, and Burkholderia seminalis; 5 × 10$^9$ CFU·g$^{-1}$ bacterial cells) combined with ground magnesium limestone (GML) application ameliorated Al$^{3+}$ toxicity in rice to acid sulfate soil [119]. A mechanism was involved wherein PGPB-mediated Al toxicity amelioration occurred by chelation of Al-organic acids (Al-OAs). Concurrently, PGPB-led to the production of phytohormones which were associated with enhancing better growth and yield in rice [118,119]. Recently, the promising role of rice straw derived Si-rich biochars has been explored toward the alleviation of Al-toxicity, and soil acidity [184]. Moreover, an alleviation mechanism of Al phytotoxicity was involved in wheat wherein biological sourced-Si coordinated simultaneously with Al to form Al-Si complex for toxicity alleviation, on other hand Si-particles prevented the migration of toxic Al through root tips cell.

6. Conclusions and Prospects

This extensive review clarified that Al toxicity can be effectively mitigated in plants by the application of nutrient elements in optimum quantities. Exogenous phosphorus (P) application is more beneficial during plants were found to be affected rigorously by soil acidification, Al toxicity and P deficiency. P was able to repair P-deficiency in acid soil, increased root respiration, plant growth, chlorophyll content, and dry matter yield. Ca amendment (liming) is more effective for correcting soil acidity and alleviating Al toxicity, but it takes more time to solubilize, and neutralize soil acidity. Moreover, continuous input of P-fertilizer, and lime in soil is expensive and environmentally risky. Gypsum (G) is attributed with better solubility (approximately 5-fold higher than lime), supplied dual benefits simultaneously as an alleviator of Al toxicity, and inducer of nutrients content. Magnesium (Mg) is effective for decreasing Al-activity at plasma membrane of root apex, and able to prevent Al toxicity-induced Ca cytotoxicity. Sulfur (S) can be used as several metals (Al, As) toxicity alleviator. The beneficial impact of exogenous Si-application has been widely recognized against Al toxicity in plants though it is still to be reconsidered as an essential element. Despite these above-mentioned facts, less attention has been given to clarify the potential roles of exogenous application of K, Mg, Zn, and Mo toward Al toxicity alleviation in plants to acidic soils.

Some other promising approaches have been applied considering miscellaneous mineral elements to ameliorate Al toxicity in plants to acid soils. For example, exogenous application of several low cost effective industrial byproducts (alkaline slag, coal fly ash, and red mud), hormones (auxin; IAA), organic acids (OAs; citrate, oxalate, and malate), polyamines (putrescine), biofertilizers (e.g., micorrhizal fungi, growth promoting bacteria), biochars (e.g., agricultural wastes, organic wastes) mitigated Al toxicity in plants to acidic soils. However, this review presents existing knowledge concerning the application of mineral nutrition on Al toxicity mitigation in plants that could be a potential approach for further crop plants improvement under Al toxicity and soil acidity worldwide.

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Abbreviations

Al Aluminum
ALMT1 Aluminum-activated malate transporter 1
AtMGT1 Arabidopsis magnesium transport gene 1
BC Base cation
Ca Calcium
PG Phosphogypsum
G Gypsum
Mg Magnesium
P Phosphorus
S Sulfur
B Boron
Mg Manganese
Zn Zinc
Mo Molybdenum
Si Silicon
OAs Organic acids
IAA Indole acetic acid
PA Polyamine
SA Salicylic acid
Put Putrescine
MF Micorrhizal fungi
PGPB Plant growth promoting bacteria

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