Approximately 30% of the world’s total land area and over 50% of the world’s potential arable lands are acidic. Furthermore, the acidity of the soils is gradually increasing as a result of the environmental problems including some farming practices and acid rain. Soil pH decreased significantly from the 1980s to the 2000s in the major Chinese crop-production areas [2]. Aluminium (Al) is the most abundant metal and the third most abundant element in the earth’s crust after oxygen (O) and silicon (Si), comprising approximately 7% of its mass [3]. At mildly acidic or neutral soils, it occurs primarily as insoluble deposits and is essentially biologically inactive. However, in many acidic soils throughout the tropics and subtropics, Al toxicity is a major factor limiting crop productivity. The Al-induced secretion of organic acid (OA) anions, mainly citrate, oxalate, and malate, from roots is the best documented mechanism of Al tolerance in higher plants. Increasing evidence shows that the Al-induced secretion of OA anions may be related to the following several factors, including (a) anion channels or transporters, (b) internal concentrations of OA anions in plant tissues, (d) temperature, (c) root plasma membrane (PM) H+ -ATPase, (f) magnesium (Mg), and (e) phosphorus (P). Genetically modified plants and cells with higher Al tolerance by overexpressing genes for the secretion and the biosynthesis of OA anions have been obtained. In addition, some aspects needed to be further studied are also discussed.

1. Introduction

Approximately 30% of the world’s total land area and over 50% of the world’s potential arable lands are acidic [1]. Furthermore, the acidity of the soils is gradually increasing as a result of the environmental problems including some farming practices and acid rain. Soil pH decreased significantly from the 1980s to the 2000s in the major Chinese crop-production areas [2]. Aluminium (Al) is the most abundant metal and the third most abundant element in the earth’s crust after oxygen (O) and silicon (Si), comprising approximately 7% of its mass [3]. At mildly acidic or neutral soils, it occurs primarily as insoluble deposits and is essentially biologically inactive. In acidic solutions (pH < 5.0), Al becomes soluble and available to plants in the Al$^{3+}$ and Al(OH)$^{2+}$ forms [4]. Micromolar concentration of Al$^{3+}$ can rapidly inhibit root growth. The subsequent impairments on water and nutrient uptake lead to poor growth and productivity [5]. Therefore, in many acidic soils throughout the tropics and subtropics, Al toxicity is a major factor limiting crop productivity [6]. Many plants have evolved different mechanisms for detoxifying Al externally, including secretion of Al-chelating substances (e.g., organic acid (OA) anions, phosphate (Pi), and phenolic compounds) from the roots, increased pH in the rhizosphere, modified cell wall, redistribution of Al, and efflux of Al [6–9]. Increasing evidence shows that the Al-induced secretion of OA anions from roots is a major mechanism leading to Al tolerance in higher plants [6, 9–15]. In this paper, we review the roles of the Al-induced secretion of OA anions from roots in Al tolerance of higher plants.
2. Aluminium-Induced Secretion of Organic Acid Anions from Roots

The Al-induced secretion of OA anions, mainly citrate, oxalate, and malate, from roots is the best documented mechanism of Al tolerance in higher plants. Plants differ in the species of OA anions secreted, secretion patterns, temperature sensitivity, response to inhibitors, and dose response to Al [9, 13]. Since the first report on the Al-induced secretion of malate from wheat (Triticum aestivum) roots [16], increasing evidence shows that many Al-tolerant species or cultivars are able to secrete high levels of citrate, malate, and/or oxalate from roots when exposed to Al, including barley (Hordeum vulgare) [17], maize (Zea mays) [18], buckwheat (Fagopyrum esculentum) [19, 20], rye (Secale cereale) [21], soybean (Glycine max) [22, 23], Citrus junos [24], sorghum (Sorghum bicolor) [25], triticale (Triticosecale Wittmark) [26], Polygonum spp. [27], Paraserianthes falcataria [28], Lespedeza bicolor [29], Citrus grandis, and Citrus sinensis [30, 31]. All these OA anions (citrate, oxalate, and malate) secreted from plant roots can form stable, nontoxic complexes with Al in the rhizosphere, thereby preventing the binding of Al to cellular components, resulting in detoxification of Al [9, 12]. Of the three OA anions, citrate has the highest chelating activity for Al followed by oxalate and malate [9]. The Al-induced secretion of OA anions is localized to the root apex, which is in agreement with the targeting site for Al toxicity [20, 32, 33] and their secretion is highly specific to Al, neither phosphorus (P) deficiency nor other polyvalent cations result in the secretion of OA anions [20, 30, 34–38]. Based on the timing of secretion, two patterns of Al-induced OA anion secretion have been proposed [10, 11]. In Pattern I plants, no discernible delay is observed between the addition of Al and the onset of OA anion secretion such as buckwheat [39], tobacco (Nicotiana tabacum) [40], and wheat [37]. In this case, Al may simply activate a transporter in the plasma membrane (PM) to initiate OA anion secretion, and the induction of genes is not required [9, 11]. In Pattern II plants, OA anion secretion is delayed for several hours after exposure to Al such as in rye [22], Cassia tora [39], C. junos [24], soybean [41], L. bicolor [29], and triticale [26]. In this case, Al may induce the expression of genes and the synthesis of proteins involved in OA metabolism or in the transport of OA anions [12]. Yang et al. investigated the effects of a protein-synthesis inhibitor (cycloheximide, CHM) on the Al-induced secretion of OA anions from the roots of buckwheat, a typical Pattern I plant, and C. tora, a typical Pattern II plant, suggesting that both de novo synthesis and activation of an anion channel are needed for the Al-activated secretion of citrate in C. tora, but in buckwheat the PM protein responsible for oxalate secretion preexisted [39]. Although the Al-induced secretion of OA anions has been well documented, there is a lack of correlation between OA anion secretion and Al tolerance in some plant species. For example, the Al-induced secretion of OA anions (citrate and oxalate) cannot account for the genotypic differences in Al tolerance in maize, soybean, and buckwheat cultivars [42–44]. Wenzl et al. observed that the secretion of OA anions from Al-treated signalgrass (Brachiaria decumbens) apices was three- to 30-times smaller than that from Al-treated apices of buckwheat, maize, and wheat (all much more sensitive to Al than signalgrass) [45]. Ishikawa et al. investigated the amount of malate and citrate in Al media of seven plant species (Al tolerance order: Brachiaria brizantha, rice (Oryza sativa), and tea (Camellia sinensis) > maize > pea (Pisum sativum) and C. tora > barley) and of two cultivars with differential Al tolerance each in five plant species (rice, maize, wheat, pea, and sorghum). They did not observe any correlation of Al tolerance among some plant species or between two cultivars in some plant species with the amount of citrate and malate in Al media [46]. Yang et al. showed that eight oxalate accumulator cultivars from four species including Amaranthus spp., buckwheat, spinach (Spinacia oleracea), and tomato (Lycopersicon esculentum) secreted oxalate rapidly under Al stress, but oxalate secretion was not related to their Al tolerance [47]. Therefore, it is reasonable to assume that some plant species may contain other (stronger) mechanisms, which mask the effect of OA anions and/or that the Al-induced secretion of OA anions is too low to be an effective mechanism [44, 48–50]. In this section, we will discuss several aspects that have been implicated in the regulation of the Al-induced OA anion secretion.

2.1. Anion Channels or Transporters. From the experiments with anion channel and carrier inhibitors, the Al-activated secretion of OA anions is mediated through anion channels and/or carriers [9, 20, 37, 69]. As early as 1995, Ryan et al. observed that inhibitors of anion channels inhibited the Al-activated secretion of malate from wheat roots, providing evidence that Al might activate malate secretion via a channel in the PM in the apical cells of Al-tolerant wheat cells [37]. Increasing evidence shows that the influence of anion channel inhibitors on the Al-activated secretion of OA anions depends on the species of OA anions secreted, plant species, inhibitor concentration, and species (see [13, 30, 37, 62], Table 1). Li et al. observed that two citrate carrier inhibitors (pyridoxal 5′-phosphate (PP) and phenylisothiocyanate (PITC)) effectively inhibited citrate secretion, meaning that the Al-activated citrate from rye roots is mediated by citrate carrier [21]. Yang et al. [36] and Li et al. [63] showed that the Al-activated secretion of citrate from rice bean (Vigna umbellata) and Stylosanthes spp. roots was inhibited by both anion channel and carrier inhibitors, indicating the possible involvement of both the citrate carrier and anion channel in the Al-activated citrate secretion. Although the use of inhibitors can be indicative of the type of transport protein involved in OA anion secretion, they do not provide definitive evidence because most inhibitors will eventually affect transport processes that can happen nonspecifically depending on the concentration and period of application. The use of patch clamp technique, which directly measures the transport activity, provides a much stronger evidence that anion channels are involved in the secretion of OA anions from roots under Al stress [69–72]. To date, two families of membrane transporters, the Al-activated malate transporter (ALMT) and the multidrug
| Plant species                  | OA anions secreted | Secretion pattern | Dose response | Temperature sensitivity | Effective inhibitors | References |
|-------------------------------|--------------------|-------------------|---------------|-------------------------|----------------------|------------|
| Acacia mangium               | Citrate            | NA                | NA            | NA                      | NA                   | [28]       |
| Acacia auriculiformis         | Oxalate, citrate   | NA                | P             | NA                      | NA                   | [51]       |
| Arabidopsis thaliana          | Citrate, malate    | NA                | NA            | NA                      | NA                   | [52, 53]   |
| Barley (Hordeum vulgare)      | Citrate            | I                 | A             | P                       | NIF, A9C             | [17]       |
| Buckwheat (Fagopyrum esculentum) | Oxalate          | I                 | P             | NA                      | PG                   | [19, 20, 39, 54] |
| Cassia tora                   | Citrate            | II                | P             | NA                      | CHM                  | [34, 39, 46] |
| Citrus grandis and Citrus sinensis | Citrate, malate | I                 | P             | P                       | CHM (malate), DIDS(1), A9C | [30, 31] |
| CitrusJunos                   | Citrate            | II                | P             | NA                      | NA                   | [24]       |
| Deschampsia flexuosa          | Malate             | NA                | NA            | NA                      | NA                   | [55]       |
| Eucalyptus camaldulensis      | Oxalate, citrate   | NA                | P             | NA                      | NA                   | [51]       |
| Galium saxatile               | Citrate            | NA                | P             | NA                      | NA                   | [55]       |
| Lespeaeza bicolor             | Citrate, malate    | II                | P (malate), A (citrate) | NA                  | A9C, CHM             | [29]       |
| Leucanea leucophala           | Citrate            | NA                | NA            | NA                      | NA                   | [28]       |
| Maize (Zea mays)              | Oxalate            | NA                | P             | NA                      | NIF, DIDS(2)         | [18, 56]   |
| Melaleuca cajuputi            | Oxalate, citrate   | NA                | P             | NA                      | NA                   | [51]       |
| Melaleuca leucadendra         | Oxalate, citrate   | NA                | P             | NA                      | NA                   | [51]       |
| Oat (Avena sativa)            | Citrate, malate    | NA                | NA            | NA                      | NA                   | [19]       |
| Oryza glaberrima              | Citrate            | NA                | NA            | NA                      | NA                   | [46]       |
| Pusserianthes fakataria       | Citrate            | NA                | NA            | NA                      | NA                   | [28]       |
| Pea (Pisum sativum)           | Citrate            | NA                | NA            | NA                      | NA                   | [46]       |
| Polygonum aviculare and Polygonum lapathifolium | Oxalate | I                 | NA            | NA                      | PG                   | [35]       |
| Poplar (Populus tremula)      | Oxalate, citrate   | NA                | P             | NA                      | NA                   | [57]       |
| Radish (Raphanus sativus)     | Citrate, malate    | NA                | NA            | NA                      | NA                   | [19]       |
| Rape (Brassica napus)         | Citrate, malate    | NA                | NA            | NA                      | PG                   | [19, 58, 59] |
| Rice (Oryza sativa)           | Citrate            | NA                | NA            | NA                      | NA                   | [46]       |
| Rice bean (Viga umbellata)    | Citrate            | II                | NA            | NA                      | A9C, NIF, MA, PITC, CHM | [36]       |
| Rye (Secale cereale)          | Citrate, malate    | II                | P             | P                       | PP, PITC             | [21]       |
| Rye                           | Citrate, malate    | I (malate), II (citrate) | P             | P (citrate) | A (malate) | NA | [60] |
| Rumex acetosella              | Oxalate            | NA                | P             | NA                      | NA                   | [55]       |
| Snapheana (Phaseolus vulgaris)| Citrate            | NA                | NA            | NA                      | NA                   | [61]       |
| Soybean (Glycine max)         | Citrate, malate    | II                | P             | NA                      | NA                   | [22, 23, 41] |
| Soybean                       | Citrate            | II                | P             | NA                      | A9C, CHM, MA         | [62]       |
| Sorghum (Sorghum bicolor)     | Citrate            | NA                | NA            | NA                      | NA                   | [53]       |
| Plant species            | OA anions secreted | Secretion pattern | Dose response | Temperature sensitivity | Effective inhibitors                                      | References            |
|-------------------------|--------------------|-------------------|---------------|-------------------------|----------------------------------------------------------|-----------------------|
| Spinach (*Spinacia oleracea*) | Oxalate           | I                 | P             | NA                      | NA                                                       | [35]                  |
| Stylosanthes spp.       | Citrate            | II                | P             | NA                      | A9C, PITC, PG, NIF, DIDS(1), CHM                         | [63]                  |
| Sunflower (*Helianthus annuus*) | Citrate, malate   | NA                | NA            | NA                      | NA                                                       | [64]                  |
| Taro (*Colocasia esculenta*) | Oxalate           | NA                | P             | NA                      | NA                                                       | [65]                  |
| Tobacco                 | Citrate            | I                 | P             | NA                      | NA                                                       | [40]                  |
| Tomato (*Lycopersicon esculentum*) | Oxalate         | I                 | P             | NA                      | PG                                                       | [66]                  |
| Triticale (*×Triticosecale Wittmack*) | Citrate, malate | II                | P             | NA                      | NA                                                       | [26]                  |
| Veronica officinalis    | Citrate            | NA                | P             | NA                      | NA                                                       | [55]                  |
| Viscaria vulgaris       | Oxalate            | NA                | P             | NA                      | NA                                                       | [55]                  |
| Wheat (*Triticum aestivum*) | Malate            | I                 | P             | A                       | NIF, DPC, EA, A9C, NPPB, IAA-94                          | [21, 37, 67, 68]      |

A: absent; A9C: anthracene-9-carboxylic acid; CHM: cycloheximide; DIDS(1): 4,4′-diiothiocyanatostilbene-2,2′-disulfonic acid; DIDS(2): 4,4′-dinitrostilbene-2,2′-disulfonic acid; DPC: diphenylamine-2-carboxylic acid; EA: ethacrynic acid; IAA-94: 6,7-dichloro-2-cyclopentyl-3,3-dihydro-2-methyl-oxo-1H-indene-5-yl (6,7-dichloro-2-cyclopentyl-3,3-dihydro-2-methyl-oxo-1H-indene-5-yloxy) acetic acid; NA: not applicable; MA: mersalyl acid; NIF: nifluimic acid; NPPB: 5-nitro-2-(3-phenylpropylamino)-benzoic acid; P: present; PG: phenylglyoxal; PITC: phenylisothiocyanate; PP: pyridoxal 5'-phosphate; anion channel inhibitors: A9C, NIF, PG; Citrate carrier inhibitors: MA: PITC, PP; protein synthesis inhibitor: CHM. Two patterns of Al-induced OA anion secretion can be identified on the basis of the timing of secretion. In Pattern I plants, no discernible delay is observed between the addition of Al and the onset of OA anion secretion. In Pattern II AN plants, OA anion secretion is delayed for several hours after exposure to Al.
and toxin compounds extrusion (MATE) families, have been implicated in the secretion of OA anions from plant roots in response to Al. In 2004, Sasaki et al. first isolated the Al-activated OA anion secretion transporter from wheat (i.e., Al-activated malate transporter 1, TaALMT1) [73]. Electrophysiological studies show that TaALMT1 functions as a ligand-activated and voltage-dependent anion channel to facilitate malate secretion across the PM of root cells [67, 74, 75]. Following the cloning of the first Al-activated OA anion secretion transporter, TaALMT1 homologs have been cloned from rape (Brassica napus; BnALMT1 and BnALMT2) [76], Arabidopsis thaliana (AtMATE1) [77], and rye (ScMATE1) [78]. Osawa and Matsumoto proposed that protein phosphorylation was associated with the Al-activated malate secretion from wheat root apex and that the OA anion-specific channel was possibly a terminal target that responded to Al signal mediated by phosphorylation [79]. Kobayashi et al. observed that the activation of AtALMT1 by Al was inhibited by staurosporine (kinase inhibitor) and calyculin A (phosphatase inhibitor), and that K252a (serine/threonine protein kinase inhibitor) inhibited the Al-dependent malate secretion without reducing gene expression [80]. Ligaba et al. provided evidence indicating that TaALMT1 activity was regulated by protein kinase C-mediated phosphorylation. They observed that TaALMT1 activity was disrupted when the serine residue at position 384 was replaced with an alanine, and concluded that the serine residue needed to be phosphorylated before TaALMT1 was activated by Al. These results suggest that the activation of ALMT1 by Al may involve reversible protein phosphorylation [80]. However, not all ALMT1-type transporters mediate Al-activated OA responses. For example, ZmALMT1 isolated from maize was suggested to play a role in anion homeostasis and mineral nutrition, and the activity of this protein was independent of extracellular Al [81]. ZmALMT2 isolated from maize is a root anion transporter that mediates constitutive root malate secretion and may play a role in mineral nutrient acquisition and transport but not Al tolerance [82]. Three ALMT-type transporters isolated from A. thaliana were expressed in leaf mesophyll (AtALMT9) or guard cells (AtALMT6 and AtALMT12), implicating a primary role in malate homeostasis and guard cell function [83–85]. Recently, Gruber et al. demonstrated that HvMATE1 from barley likely contributed to the homeostasis of OA anions in the cytosol of guard cells and root cells by transporting them out of the cell or into cytosolic vesicles [86, 87].

In 2007, genes encoding citrate transporters that are members of a different transporter family, the MATE family, were isolated from barley (HvMATE1, also designated HvVATE1) [88, 89] and sorghum (SbMATE) [53]. The MATE family of transporter proteins is a large and diverse group present widely in bacteria, fungi, plants, and mammals. Evidence shows that MATE proteins function as H⁺ or Na⁺ coupled antiporters for numerous substances such as flavonoid, anthocyanins, norfluracoxin, ethidium bromide, berberine, acriflavine, nicotine, citrate, and Cd²⁺ [88, 90–92]. Plant MATEs can transport substrates other than citrate, which may also play a role in Al tolerance [88, 90–94]. Recently, MATE homologs involved in Al-activated citrate secretion were isolated from A. thaliana (AtMATE) [95], rye (ScFRDL2) [92], maize (ZmMATE1) [96], rice (OsFRDL4) [97], and rice bean (VuMATE) [98]. All these citrate transporters exhibit varying degrees of constitutive expression (i.e., in the absence of Al) except for VuMATE, and their expressions are upregulated by Al treatment except for HvMATE. Evidence shows that OsFRDL4 isolated from rice and AtMATE isolated from A. thaliana are regulated by a C2H2-type zinc finger transcription factor ART1 and STOP1, respectively [95, 97].

In buckwheat, evidence shows that ABA is involved in the secretion of oxalate [99]. ABA activates the anion channel in stomatal guard cells and may play a similar role in the roots [9]. However, no oxalate transporter has been isolated from plants so far.

### 2.2. Internal Concentrations of Organic Acid Anions in Plant Tissues

The effects of Al on OA metabolism have been investigated in some plant species. In an Al tolerant maize single cross, exposure to increasing level of Al led to a strong (over 3-fold) increase in root tip citrate concentration and a significant activation of citrate secretion, which saturated at a rate close to 0.5 nmol citrate h⁻¹ root⁻¹ occurring at 80 μM Al³⁺ activity, with the half-maximal rate of citrate secretion occurring at about 20 μM Al³⁺ activity [72]. Ligaba et al. demonstrated that Al-treated rape roots had increased in vitro activities of citrate synthase (CS, EC 4.1.3.7), malate dehydrogenase (MDH, EC 1.1.1.37) and phosphoenolpyruvate carboxylase (PEPC, EC 4.1.1.31), and concentrations of citrate and malate, together with decreased respiration rate, concluding that the Al-induced accumulation and subsequent secretion of citrate and malate were associated with both increased biosynthesis and reduced catabolism [59]. In an Al tolerant tree species, P. falcata, the Al-induced increases in both secretion and accumulation of citrate were accompanied by increased mitochondrial CS (mCS) activity and enhanced mCS expression, indicating that the increased amount of citrate is produced in response to Al [28]. Aluminium treatments resulted in an increase in CS activity and a decrease in aconitase (ACO, EC 4.2.1.3) activity in the root tips of C. tora, accompanied by an increase in citrate concentration. However, the activities of NADP-isocitrate dehydrogenase (NADP-IDH, EC 1.1.1.42), MDH, and PEPC were unaffected by Al. It was suggested that Al-regulation of both CS and ACO activities might be responsible for the Al-induced increase in both secretion and accumulation of citrate [100]. Yang et al. reported that CS activity in soybean root apex was increased by 16% when exposed to Al, but the activities of PEPC and NADP-IDH and the concentration of citrate were unaffected. They suggested that the Al-induced increase in CS activity resulted in the increased secretion of citrate [41]. The unchanged concentration of citrate in the Al-treated roots likely reflected the balance between citrate synthesis and secretion in the root apex. In rye, the activity of CS in the root tip increased by 30% when exposed to Al, and the Al-induced increase in the synthesis of citrate appeared to be responsible for the enhanced
secretion of citrate from roots [21]. In an Al-tolerant soybean cultivar, mitochondrial MDH and CS activities increased and ACO activity decreased with the increasing of Al concentration and duration of Al treatment. The Al-induced citrate secretion was inhibited by the CS inhibitor suramin and enhanced by the ACO inhibitor fluorocitric acid. Transcript level of the mitochondrial CS increased in soybean roots in response to Al, whereas the expression of ACO showed no significant difference. These results indicate that Al triggers OA metabolic responses in mitochondria of soybean roots, which support the sustained secretion of citrate [101]. Based on the above results, it is reasonable to believe that altered OA metabolism is involved in the Al-induced secretion of OA anions. However, it is not immediately obvious that simply increasing internal OA will lead to increased secretion, because in any case some transport processes must somewhat be involved in the Al-induced secretion of OA anions. For example, Gaume et al. showed that the Al-tolerant maize cultivar had higher root concentrations and higher root secretion of citrate, malate, and succinate compared with the Al-sensitive one. Increased PEPC activity in root apices after Al exposure partially explained the differences of OA anion concentrations in the roots. However, the increased secretion was not proportional to the OA anion concentrations in the roots. The concentrations of citrate, malate, and succinate in the roots of both cultivars increased by a factor of 2 to 4, whereas the secretion of these anions increased by 2 to 20. They suggested that the secretion of OA anions might be mediated by transporters that are either activated or induced by Al [102]. In a study with two lines of triticale differing in the Al-induced secretion of malate and citrate and in Al tolerance, the concentrations of citrate (root apices and mature root segments) and malate (mature segments only) in roots increased in response to Al, but similar changes were observed in the two lines. The Al-induced changes in in vitro activities of CS, PEPC, NAD-MDH, and NADP-IDH were similar in the sensitive and resistant lines in both root apices and mature root segments. These results suggest that the Al-induced secretion of malate and citrate from triticale roots is not regulated by their internal levels in the roots or by the capacity of root tissues to synthesize them [103]. Yang et al. reported that the root concentration of oxalate was poorly related with its secretion among some oxalate accumulators such as Amaranth spp., buckwheat, spinach, and tomato [47]. Recently, we observed that Al decreased or did not affect the concentrations of malate and citrate in roots of two citrus species having different tolerance to Al, indicating that the Al-induced secretion of citrate and malate is poorly related to their internal levels in roots [30, 31, 104–106].

Transgenic plants and cells have provided additional evidence that OA metabolism can contribute to the Al-induced secretion of OA anions and Al tolerance [6, 107]. Modulation of OA metabolism enhanced Al tolerance and secretion of citrate and/or malate in transgenic tobacco and papaya (Carica papaya) plants overexpressing a Pseudomonas aeruginosa CS [108], rape plants [58], and carrot (Daucus carota) cells [109] overexpressing a mitochondrial CS (mCS) from A. thaliana, Nicotiana benthamiana plants overexpressing an mCS from C. junos [24], tobacco plants overexpressing a cytosolic MDH from A. thaliana, an MDH from Escherichia coli [110] and a CS from rice mitochondria [111], alfalfa (Medicago sativa) plants overexpressing a alfalfa nodule-enhanced form of MDH (neMDH) [112], and tobacco plants overexpressing pyruvate phosphate dikinase (PPDK, EC 2.7.9.1) gene from Mesembryanthemum crystallinum [113]. However, Delhaize et al. showed that the expression of a P. aeruginosa CS in tobacco did not result in enhanced citrate accumulation or secretion, despite generating transgenic tobacco lines that expressed the CS protein at up to a 100-fold greater level than the previously described CSb lines [40, 108]. They concluded that the activity of the P. aeruginosa CS in transgenic tobacco is either sensitive to environmental conditions or that the improvements in Al tolerance and P nutrition observed previously are due to some other variable [40].

In an Al-tolerant soybean cultivar, the Al-induced root secretion of citrate increased steadily when exposed to continuous light, and only low citrate secretion was observed under 24 h in the continuous dark. The rate of Al-induced citrate secretion decreased at 6 h after the shoots were excised. The rate of citrate secretion by shoot-excised roots was 3-times lower than that of their respective controls (Al treatment in plants with shoots) during the 6–9 h after 50 μM treatment and 6-times lower during the 9–12 h. These results indicate that the shoots play a role in the Al-induced citrate secretion through providing the carbon source and/or energy for citrate synthesis in the roots [41]. Neumann and Römheld reported that P deficiency strongly increased the concentrations of carboxylic acids in chickpea (Cicer arietinum) and white lupin (Lupinus albus) roots, but only had small effects on the accumulation of carboxylates in shoots, and suggested that the ability to accumulate carboxylic acids in roots depended on the partitioning of carboxylic acids or related precursors between roots and shoots [114]. Quantification of soybean root enzymes involved in OA metabolism displayed only a 16% increase in CS activity 6 h after Al treatment with no differences in other enzymes; hence citrate may be transported from the shoots to the roots [41].

2.3. Temperature. Yang et al. observed that the Al-induced secretion of citrate and malate by the roots of C. grandis and C. sinensis seedlings was inhibited by low temperature, indicating that an energy dependent process may be involved in the Al-induced secretion of OA anions [30]. A similar result has been obtained in Al-tolerant barley [17]. However, the Al-induced secretion of citrate in rye (Pattern II) was decreased by low temperature, but the Al-induced secretion of malate in wheat (Pattern I) was unaffected by low temperature [21]. Recently, Li et al. reported that, in rye, the Al-induced secretion of malate belonged to Pattern I and was not inhibited, while the Al-induced secretion of citrate belonged to Pattern II and was affected by low temperature [60]. Further research is needed to elucidate the mechanism.

2.4. Root Plasma Membrane H⁺-ATPase. Since PM H⁺-ATPase plays a critical role in energizing and regulating an array of secondary transporters [115, 116], the modulation
of PM $\text{H}^+$-ATPase activity may be involved in the Al-induced secretion of OA anions. In two soybean cultivars, the Al-induced activity of root PM $\text{H}^+$-ATPase paralleled the secretion of citrate. The Al-induced increase in PM $\text{H}^+$-ATPase activity was caused by a transcriptional and translational regulation. Both activity and expression of root PM $\text{H}^+$-ATPase were higher in the Al-tolerant than in the Al-sensitive cultivar. Aluminum activated the threonine-oriented phosphorylation of PM $\text{H}^+$-ATPase in a dose- and time-dependent manner. The relationship between the Al-induced secretion of citrate and the activity of PM $\text{H}^+$-ATPase was further demonstrated by an analysis of PM $\text{H}^+$-ATPase transgenic $A. \text{thaliana}$. When grown on Murashige and Skoog medium containing 30 $\mu$M Al, transgenic plants of $A. \text{thaliana}$ overpressing PM $\text{H}^+$-ATPase secreted more citrate compared with wild-type $A. \text{thaliana}$ [117]. Ahn et al. showed that after 4 h in vivo treatment with 2.6 $\mu$M Al, PM $\text{H}^+$-ATPase activity and $\text{H}^+$-transport rate were decreased and $\zeta$ potential was depolarized in PM vesicles from root tips of Al-sensitive wheat cultivar (ES8) but not of Al-tolerant ET8. They concluded that the Al-induced secretion of malate from wheat roots was accompanied by changes in PM surface potential and activation of $\text{H}^+$-ATPase [118]. However, the Al-induced changes of root PM $\text{H}^+$-ATPase activity were not associated with oxalate secretion in two tomato cultivars differing in the ability to secrete oxalate under Al stress [66]. Other studies showed Al inhibited root PM $\text{H}^+$-ATPase activity in barley [119], squash ($Cucurbita \text{pepo}$) [120], and rice bean [121].

### 2.5. Magnesium

Magnesium (Mg) can ameliorate Al toxicity, but the mechanism by which Al alleviates it remains obscure [122, 123]. Long-term secretion of OA anions requires continuous biosynthesis of OAs inside the root cells. In this regard, cytoplasmic Mg$^{2+}$ is pivotal for the activation of many enzymes (e.g., CS, PEPC, IDH, malic enzyme (ME, EC 1.1.1.40), and MDH) involved in OA biosynthesis and degradation [122]. In soybean, micromolar concentration of Mg in the treatment solution alleviated Al toxicity by enhancing citrate biosynthesis and secretion by roots. Increased production and secretion by soybean roots in response to Mg might promote both external and internal detoxification by formation of Al-citrate complexes [123]. In rice bean, Mg could stimulate the Al-induced secretion of citrate from roots thus alleviating the inhibition of root growth by Al. The stimulation of citrate secretion by Mg might result from the restoration of root PM $\text{H}^+$-ATPase activity by Mg [121].

### 2.6. Phosphorus

Phosphorus deficiency is another major factor limiting plant growth in acidic soils [6]. Evidence has shown that Al toxicity can be alleviated by P supply in some plants, including $C. \text{grandis}$ [30, 31], sorghum [124], maize [102], and $L. \text{bicolor}$ [125]. There are several authors investigating the effects of P on the Al-induced secretion of OA anions from roots, but the results are somewhat different. Yang et al. showed that the Al-induced secretion of citrate and malate by excised roots from Al-treated $C. \text{grandis}$ and $C. \text{sinensis}$ seedlings decreased with increasing P supply, whereas P supply increased or had no effect on the concentrations of both citrate and malate in Al-treated roots [30, 31]. The decreased secretion of OA anions due to P application can be due to the amelioration of Al toxicity by P rather than due to decreased root accumulation of OA anions. In two maize cultivars, the Al-induced increases in root activity of PEPC, root concentrations, and secretion of OA anions were decreased in plants pretreated with higher P concentrations during the 21 days prior to Al treatment [102]. In two cowpea genotypes of contrasting Al tolerance, Al enhanced malate secretion from root apices of both genotypes. Phosphorus deficiency increased the Al-induced secretion of malate by roots only in the Al-tolerant genotype ITB9KD-391 [126]. In an Al-tolerant leguminous shrub, $L. \text{bicolor}$, the Al-induced secretion of citrate and malate under P deficiency was less than that under P sufficiency [125]. The above results indicate that the enhancement of Al tolerance by P is not associated with an increased secretion of OA anions from roots. However, P-sufficient rape plants displayed more pronounced Al-induced accumulation and secretion of citrate and malate in roots than P-deficient plants. Interestingly, the degree of inhibition of Al-induced root elongation was more or less the same in both P-sufficient and P-deficient plants. It was suggested that the severity of Al toxicity in P-deficient plants was masked by the stimulating effect of P deficiency on root elongation [59]. Using four soybean genotypes differing in P efficiency, Liao et al. investigated the effects of Al and P interactions on OA anion secretion by roots grown in homogeneous and heterogeneous nutrient solutions. In the homogeneous solution experiments, P enhanced Al tolerance in four soybean genotypes, but greatly decreased the Al-induced citrate and malate secretion by roots. The two P-efficient genotypes displayed more Al tolerance than the two P-inefficient genotypes under high-P condition, but no significant genotypic difference was found in the secretion of OA anions under both low- and high-P conditions. The secretion of OA anions in a homogenous solution may not reflect the ability of soybean plants to detoxify exogenous Al. At the early stages of the heterogeneous nutrient solution experiment, P greatly increased the rates of the Al-activated citrate and malate secretion from the taproot tips of the four genotypes and the Al tolerance for the two P-efficient genotypes, and the two P-efficient genotypes secreted more malate from the taproot apices under high-P condition. They concluded that, at the early stage of heterogeneous nutrient solution experiment, P might increase the Al-activated secretion of OA anions, thus enhancing Al tolerance [23]. In two soybean cultivars and one rye cultivar, P deficiency did not increase the Al-induced secretion of citrate by roots [60, 127]. In soybean, short-term P deficiency (4 days) followed by Al treatment led to 50% increase in the Al-induced citrate secretion, while longer-term (10 days) P deficiency followed by Al treatment reduced the Al-induced citrate secretion to trace amounts [128]. However, in another study with soybean, Yang et al. showed that application of Al induced a greater citrate secretion rate in the Al-tolerant cultivar than in the Al-sensitive cultivar independently of the P status of the plants [22]. Dong et al. showed that long-term (14 days...
P deficiency followed by Al stress (7 h) had no effect on the Al-induced secretion of citrate from soybean roots [127]. This disagreement was attributed to the differences in the plant materials and experimental methods used [128]. Thus, it appears that the influence of P on the Al-induced secretion of OA anions depends on the time of exposure to Al, growth conditions, and plant species or cultivar.

2.7. Other Factors. Yang et al. showed that sodium nitro-prusside (SNP, a nitric oxide (NO) donor) increased the Al-induced secretion of malate and citrate by excised roots from Al-treated C. grandis seedlings and that the stimulatory effects of SNP on the Al-induced secretion of malate and citrate might be involved in the SNP-induced amelioration of Al toxicity [105]. There are several papers reporting that NO regulates K⁺ and Ca²⁺ channels in plants [129, 130]. The stimulation of OA anion secretion by SNP might result from its direct effect on anion channels, because SNP did not enhance the accumulation of malate and citrate in the roots [105]. Chen et al. demonstrated that H₂S played an ameliorative role in protecting soybean plants against Al toxicity by increasing citrate secretion and citrate transporter gene expression and enhancing the expression of PM H⁺-ATPase [131].

3. Genetic Engineering Technology for the Secretion and Biosynthesis of Organic Acid Anions

A common agricultural practice for acidic soils is to apply lime to raise soil pH. However, the option is not economically feasible for poor farmers, nor is it an effective strategy for alleviating subsoil acidity [132]. A complementary approach to liming practice is to tailor plants to suit acidic soils by alleviating subsoil acidity [132]. A complementary approach is to produce Al tolerant plants. The two main approaches for increasing OA anion secretion are to increase OA synthesis and to increase OA anion transport across the PM [107]. Table 2 summarizes the attempts to obtain transgenic plants or cells with improved tolerance to Al in acidic soils. The best documented mechanism for decreasing Al toxicity by increasing citrate secretion and citrate transporter expression is that OA metabolism may not be a limiting factor for Al-induced secretion of OA anions in some plant species because only a small portion of internal OAs is secreted in response to Al [9]. In addition, the Al-induced secretion of OA anions must be associated with some transport processes [9, 107]. Therefore, the effect that modifying internal OA concentrations has on the level of plant Al tolerance may be small or not observed in some plant species.

Transgenic plants overexpressing genes encoding transporters for OA anions have been widely studied since the first major gene (TaALMT1) was cloned from wheat [73]. TaALMT1 expression in rice, cultured tobacco cells, barley, and A. thaliana led to increased Al-activated malate secretion and enhanced Al tolerance for all except for rice [73, 136, 137]. Overexpression of TaALMT1 in wheat conferred greater Al-activated malate secretion from the roots and improved Al tolerance, which was kept in the T1 and T2 generations [138]. This is the first report of a major food crop being stably transformed for greater Al tolerance. Homologs of TaALMT1 cloned from A. thaliana, rape, barley, and rye [76–78, 87] could also be utilized to increase plant Al tolerance. For example, expression of BnALMT1 and BnALMT2 in tobacco cultured cells [76], HvALMT1 in barley [87], and AtALMT1 in A. thaliana [107] resulted in increased malate secretion and enhanced Al tolerance. Increases in Al tolerance have been achieved by overexpressing citrate transporters. Expression of SbMATE1 [53], FRD3 [94], and ZmMATE1 [96] in A. thaliana, HvAACT1 in tobacco [88], and VuMATE in tomato [98] enhanced the secretion of citrate and Al tolerance.

*Arabidopsis thaliana* has one gene encoding for a type I H⁺-pyrophosphatase (AVP1, *Arabidopsis* Vacular Pyrophosphatase 1) and another gene encoding for a type II H⁺-pyrophosphatase (AVP2) [139, 142]. Yang et al. reported
Table 2: Transgenic plants or cells with higher aluminum- (Al-) tolerance overexpressing genes for the biosynthesis and the secretion of organic acid (OA) anions.

| Genes                              | Origins                          | Transgenic plants or cells | Increased secretion of OA anions | Al tolerance | References |
|------------------------------------|----------------------------------|----------------------------|----------------------------------|--------------|------------|
| **Pseudomonas aeruginosa**         | Tobacco                          | Tobacco                    | Citrate                          | +            | [108]      |
|                                    | Tobacco                          |                            | No                               | No           | [40]       |
| Citrate synthase (CS)              | Tobacco                          |                            | No                               | No           | [40]       |
| Citrate synthase (CS)              | A. thaliana                      | Tobacco                    | Citrate                          | +            | [133]      |
| Carrot                             | A. thaliana                      | Tobacco                    | Citrate                          | +            | [109]      |
| Citrate synthase (CS)              | C. junos                         | Tobacco                    | Citrate                          | +            | [24]       |
| Malate dehydrogenase (MDH)         | A. thaliana, Escherichia coli    | Tobacco                    | Citrate, oxalate, malate, succinate, acetate | +            | [112]      |
| Nodule-enhanced form of MDH (nMDH) | Alfalfa                          | Tobacco                    | Citrate                          | +            | [110]      |
| Phosphoenolpyruvate carboxylase (PEPC) | Alfalfa                         | Tobacco                    | Citrate                          | +            | [112]      |
| Pyruvate phosphate dikinase (PPDK) | Mesembryanthemum crystallinum    | Tobacco                    | Citrate, malate                  | +            | [113]      |
| TaALMT1                            | Wheat (Triticum aestivum)        | Tobacco cells              | Malate                           | +            | [73]       |
|                                    | A. thaliana                      | Malate                     | +                                | [138]        |
| AtALMT1                            | A. thaliana                      | Malate                     | +                                | [107]        |
| BnALMT1 and BnALMT1                | Rake                             | Tobacco cells              | Malate                           | +            | [76]       |
| HvALMT1                            | Barley                           | Barley                     | Malate                           | +            | [87]       |
| HvAACT1                            | Barley                           | Tobacco                    | Citrate                          | +            | [88]       |
| SbMATE                             | Sorghum (Sorghum bicolor)        | A. thaliana                | Citrate                          | +            | [53]       |
| FRD3                               | A. thaliana                      | A. thaliana                | Citrate                          | +            | [94]       |
| ZmMATE1                            | Maize                            | A. thaliana                | Citrate                          | +            | [96]       |
| VnMATE                             | Vigna umbellata                  | Tomato                     | Citrate                          | +            | [98]       |
| Plasma membrane H+-ATPase           | A. thaliana                      | Tomato                     | Citrate                          | NA           | [117]      |
| Type 1 H+-pyrophosphatase (AVP1)    | A. thaliana                      | A. thaliana, tomato, and rice | Malate                           | +            | [139]      |

NA: not applicable; No: no change in secretion of OA anions or Al tolerance.
that overexpression of AVP1 in A. thaliana, tomato, and rice exhibited greater tolerance to Al and higher level of citrate and malate secretion compared with controls and that increased AVP1-dependent $H^+$ extrusion appeared to be charge balanced by the enhancement of K uptake and the release of OA from roots [139].

4. Concluding Remark

Aluminium toxicity is one of the most deleterious factors for plant growth in acidic soils, which comprise approximately 30% of the world’s total land area and over 50% of the world’s potential arable lands [1]. In recent years, there has been significant progress in our understanding of the physiological and molecular mechanisms of Al tolerance in higher plants. In particular, the Al-induced secretion of OA anions from roots has been widely studied by many researchers in different plants because it is a major mechanism leading to Al tolerance in higher plants, but the mechanisms which lead to the accumulation and secretion of OA anions are not fully understood (Figure 1). Modulation of OA metabolism and activation of anion channels have been suggested to be involved in the Al-activated secretion of OA anions and transgenic plants or cells overexpressing genes for biosynthesis and secretion of OA anions have displayed increased secretion of OA anions and enhanced Al tolerance (Table 2). It is clear that both ALMT1 proteins from wheat, rye, A. thaliana, and rape and MATE proteins from barley and sorghum require Al to activate their function [107]. However, the mechanisms of this activation remain unclear, although evidence shows that the induction of ALMT1 expression by Al may involve reversible phosphorylation [79, 80, 107] and that OsFRDL4 and AtMATE are regulated by a C2H2-type zinc finger transcription factor ART1 and STOP1, respectively [95, 97]. Although anion channels may play an important role in the Al-induced secretion of oxalate in some plants [47], no oxalate transporter has been isolated from plants so far. Organic acid anions secreted from the roots of P-deficient plants have been shown to mainly result from increased PEPC activity in the shoots [143], but relatively few studies have investigated the roles of shoots in the Al-induced secretion of OA anions. Although some transgenic plants

Figure 1: A diagram showing the reactions and processes involved in the accumulation and secretion of organic acid (OA) anions in aluminium- (Al-) treated plants. Ac-CoA: acetyl-CoA; ALMT, Al-activated malate transporter; CS: citrate synthase; DPi: diphosphate; MATE, multidrug and toxin compounds extrusion; NAD-MDH: NAD-malate dehydrogenase; NADP-ME: NADP-malic enzyme; OAA: oxaloacetate; PDH: pyruvate dehydrogenase; PEP: phosphoenolpyruvate; PEPC: PEP carboxylase; Pi: phosphate; PK: pyruvate kinase; PPDK: pyruvate Pi dikinase; PPi: pyrophosphate; TCAC: tricarboxylic acid cycle; V-ATPase: tonoplast adenosine triphosphatase; V-PPiase, tonoplast pyrophosphatase; 1, aconitase (ACO); 2, NAD-isocitrate dehydrogenase (NAD-IDH); 3, α-ketoglutarate dehydrogenase; 4, succinate thiokinase; 5, succinate dehydrogenase; 6, fumarase; 7, NAD-MDH; 8, NADP-malic enzyme (NAD-ME); 9, NADP-IDH (redrawn from Delhaize et al. [14], Anoop et al. [58], Bose et al. [122], Lin et al. [140], and Mariano et al. [141]).
overexpressing PEPC or CS did not show enhanced accumulation and secretion of OA anions [40, 112], genetically modified plants with higher Al tolerance by overexpressing genes for the secretion and the biosynthesis of OA anions may still be a potentially rewarding area of research in the future. Recent work showed that the Al-activated malate and citrate transporters from the MATE and ALMT families functioned independently to confer Al tolerance of *A. thaliana* [95] and that overexpression of *TatAMT1* in barley, which is very sensitive to Al and does not possess an Al-activated secretion of malate, had an Al-activated secretion of malate with properties similar to those of Al-tolerant wheat and that overexpression of *TatAMT1* in barley, which is very sensitive to Al and does not possess an Al-activated secretion of malate, had an Al-activated secretion of malate very sensitive to Al and does not possess an Al-activated secretion of malate.

### References

[1] H. R. von Uexküll E and Mutert, “Global extent, development and economic impact of acid soils,” in *Plant-Soil Interactions at Low PH: Principles and Management*, R. A. Date, N. J. Grundon, and G. E. Raymet, Eds., pp. 5–19, Kluwer Academic, Dordrecht, The Netherlands, 1995.

[2] J. H. Guo, X. J. Liu, Y. Zhang et al., “Significant acidification in major chinese croplands,” *Science*, vol. 327, no. 5968, pp. 1008–1010, 2010.

[3] C. D. Foy, R. L. Chaney, and M. C. White, “The physiology of metal toxicity in plants,” *Annual Review of Plant Physiology*, vol. 29, pp. 511–566, 1978.

[4] T. B. Kinraide, “Identity of the rhizotoxic aluminium species,” *Plant and Soil*, vol. 134, no. 1, pp. 167–178, 1991.

[5] L. V. Kochian, “Cellular mechanisms of aluminium toxicity and resistance in plants,” *Annual Review of Plant Physiology and Plant Molecular Biology*, vol. 46, pp. 237–260, 1995.

[6] L. V. Kochian, O. A. Hoekenga, and M. A. Piñeros, “How do crop plants tolerate acid soils? Mechanisms of aluminium tolerance and phosphorous efficiency,” *Annual Review of Plant Biology*, vol. 55, pp. 459–493, 2004.

[7] D. M. Pellet, L. A. Papernik, and L. V. Kochian, “Multiple aluminium-resistance mechanisms in wheat roots of root apical phosphate and malate exudation,” *Plant Physiology*, vol. 112, no. 2, pp. 591–597, 1996.

[8] P. S. Kidd, M. Llugany, C. Poschenrieder, B. Gunsé, and J. Barceló, “The role of root exudates in aluminium resistance and silicon-induced amelioration of aluminium toxicity in three varieties of maize (*Zea mays L.*),” *Journal of Experimental Botany*, vol. 52, no. 359, pp. 1339–1352, 2001.

[9] J. F. Ma, “Syndrome of aluminum toxicity and diversity of aluminum resistance in higher plants,” *International Review of Cytology*, vol. 264, pp. 225–252, 2007.

[10] J. F. Ma, “Role of organic acids in detoxification of aluminum in higher plants,” *Plant and Cell Physiology*, vol. 41, no. 4, pp. 383–390, 2000.

[11] J. F. Ma, “Physiological mechanisms of Al resistance in higher plants,” *Soil Science and Plant Nutrition*, vol. 51, no. 5, pp. 609–612, 2005.

[12] J. F. Ma, P. R. Ryan, and E. Delhaize, “Aluminium tolerance in plants and the complex role of organic acids,” *Trends in Plant Science*, vol. 6, no. 6, pp. 273–278, 2001.

[13] J. F. Ma and J. Furuwaka, “Recent progress in the research of external Al detoxification in higher plants: a minireview,” *Journal of Inorganic Biochemistry*, vol. 97, no. 1, pp. 46–51, 2003.

[14] E. Delhaize, J. F. Ma, and P. R. Ryan, “Transcriptional regulation of aluminium tolerance genes,” *Trends in Plant Science*, vol. 17, no. 6, pp. 341–348, 2012.

[15] C. Inostroza-Blanchetue, Z. Rengel, M. Alberdi et al., “Molecular and physiological strategies to increase aluminum resistance in plants,” *Molecular Biology Reports*, vol. 39, no. 3, pp. 2069–2079, 2012.

[16] T. Kitagawa, T. Morishita, Y. Tachibana, H. Namai, and Y. Ohta, “Differential aluminum resistance of wheat varieties and organic acid secretion,” *Japanese Journal of Soil Science and Plant Nutrition*, vol. 57, no. 4, pp. 352–358, 1986.

[17] Z. Zhao, J. F. Ma, K. Sato, and K. Takeda, “Differential Al resistance and citrate secretion in barley (*Hordeum vulgare L.*),” *Planta*, vol. 217, no. 5, pp. 794–800, 2003.

[18] D. M. Pellet, D. L. Grunes, and L. V. Kochian, “Organic acid exudation as an aluminum-tolerance mechanism in maize (*Zea mays L.*),” *Planta*, vol. 196, no. 4, pp. 788–795, 1995.

[19] S. J. Zheng, J. F. Ma, and H. Matsumoto, “Continuous secretion of organic acids is related to aluminium resistance during relatively long-term exposure to aluminium stress,” *Physiologia Plantarum*, vol. 103, no. 2, pp. 209–214, 1998.

[20] S. J. Zheng, J. F. Ma, and H. Matsumoto, “High aluminium resistance in buckwheat: I. Al-induced specific secretion of oxalic acid from root tips,” *Plant Physiology*, vol. 117, no. 3, pp. 745–751, 1998.

[21] X. F. Li, J. F. Ma, and H. Matsumoto, “Pattern of aluminum-induced secretion of organic acids differs between rye and wheat,” *Plant Physiology*, vol. 123, no. 4, pp. 1537–1544, 2000.

[22] Z. M. Yang, M. Sivaguru, W. J. Horst, and H. Matsumoto, “Aluminium tolerance is achieved by exudation of citric acid from roots of soybean (*Glycine max*),” *Physiologia Plantarum*, vol. 110, no. 1, pp. 72–77, 2000.

[23] H. Liao, H. Wan, J. Shaff, X. Wang, X. Yan, and L. V. Kochian, “Phosphorus and aluminium interactions in soybean in relation to aluminium tolerance. Exudation of specific organic acids from different regions of the intact root system,” *Plant Physiology*, vol. 141, no. 2, pp. 674–684, 2006.

[24] W. Deng, K. Luo, Z. Li, Y. Yang, N. Hu, and Y. Wu, “Overexpression of c mitochondrial citrate synthase gene in *Nicotiana benthamiana* confers aluminium tolerance,” *Planta*, vol. 230, no. 2, pp. 355–365, 2009.

[25] L. V. Kochian, M. A. Piñeros, and O. A. Hoekenga, “The physiology, genetics and molecular biology of plant aluminum resistance and toxicity,” *Plant and Soil*, vol. 274, no. 1–2, pp. 175–195, 2005.
[26] J. F. Ma, S. Taketa, and Z. M. Yang, “Aluminum tolerance genes on the short arm of chromosome 3R are linked to organic acid release in triticale,” Plant Physiology, vol. 122, no. 3, pp. 687–694, 2000.

[27] J. F. You, Y. F. He, J. L. Yang, and S. J. Zheng, “A comparison of aluminum resistance among Polygonum species originating on strongly acidic and neutral soils,” Plant and Soil, vol. 276, no. 1-2, pp. 143–151, 2005.

[28] H. Osawa and K. Kojima, “Citrate-release-mediated aluminum resistance is coupled to the inducible expression of mitochondrial citrate synthase gene in Paraserianthus falcatoria,” Tree Physiology, vol. 26, no. 5, pp. 565–574, 2006.

[29] X. Y. Dong, R. F. Shen, R. F. Chen, Z. L. Zhu, and J. F. Ma, “Secretion of malate and citrate from roots is related to high Al-resistance in Lespedeza bicolor,” Plant and Soil, vol. 306, no. 1-2, pp. 139–147, 2008.

[30] L. T. Yang, H. X. Jiang, N. Tang, and L. S. Chen, “Mechanisms of aluminum-tolerance in two species of citrus: secretion of organic acid anions and immobilization of aluminum by phosphorus in roots,” Plant Science, vol. 180, no. 3, pp. 521–530, 2011.

[31] L. T. Yang, H. X. Jiang, Y. P. Qi, and L. S. Chen, “Differential expression of genes involved in alternative glycolytic pathways, phosphorus scavenging and recycling in response to aluminum and phosphorus interactions in citrus roots,” Molecular Biology Reports, vol. 39, no. 5, pp. 6353–6366, 2012.

[32] P. R. Ryan, J. M. Ditomaso, and L. V. Kochian, “Aluminum toxicity in roots: an investigation of spatial sensitivity and the role of the root cap,” Journal of Experimental Botany, vol. 44, no. 2, pp. 437–446, 1993.

[33] M. Sivaguru and W. J. Horst, “The distal part of the transition zone is the most aluminum-sensitive apical root zone of maize,” Plant Physiology, vol. 116, no. 1, pp. 155–163, 1998.

[34] J. F. Ma, S. J. Zheng, and H. Matsumoto, “Speciﬁc secretion of citric acid induced by Al stress in Cassia tora L.,” Plant and Cell Physiology, vol. 38, no. 9, pp. 1019–1025, 1997.

[35] J. L. Yang, S. J. Zheng, Y. F. He, and H. Matsumoto, “Aluminum resistance requires resistance to acid stress: a case study with spinach that exudes oxalate rapidly when exposed to Al stress,” Journal of Experimental Botany, vol. 56, no. 414, pp. 1197–1203, 2005.

[36] J. L. Yang, L. Zhang, Y. Y. Li, J. F. You, P. Wu, and S. J. Zheng, “Citrate transporters play a critical role in aluminum-stimulated citrate efflux in rice bean (Vigna umbellata) roots,” Annals of Botany, vol. 97, no. 4, pp. 579–584, 2006.

[37] P. R. Ryan, E. Delhaize, and P. J. Randall, “Characterisation of Al-stimulated efflux of malate from the apices of Al-tolerant wheat roots,” Planta, vol. 196, no. 1, pp. 103–110, 1995.

[38] Y. Kobayashi, O. A. Hoekenga, H. Ioh et al., “Characterization of AtALMT1 expression in aluminum-inducible malate release and its role for rhizotoxic stress tolerance in Arabidopsis,” Plant Physiology, vol. 145, no. 3, pp. 843–852, 2007.

[39] J. L. Yang, S. J. Zheng, Y. F. He, J. F. You, L. Zhang, and X. H. Yu, “Comparative studies on the effect of a protein-synthesis inhibitor on aluminum-induced secretion of organic acids from Fagopyrum esculentum Moench and Cassia tora L. roots,” Plant, Cell and Environment, vol. 29, no. 2, pp. 240–246, 2006.

[40] E. Delhaize, D. M. Hebb, and P. R. Ryan, “Expression of a Pseudomonas aeruginosa citrate synthase gene in tobacco is not associated with either enhanced citrate accumulation or efflux,” Plant Physiology, vol. 125, no. 4, pp. 2059–2067, 2001.

[41] Z. M. Yang, H. Nian, M. Sivaguru, S. Tanakamaru, and H. Matsumoto, “Characterization of aluminum-induced citrate secretion in aluminum-tolerant soybean (Glycine max) plants,” Physiologia Plantarum, vol. 113, no. 1, pp. 64–71, 2001.

[42] H. Nian, Z. Yang, H. Huang, X. Yan, and H. Matsumoto, “Citrate secretion induced by aluminum stress may not be a key mechanism responsible for differential aluminum tolerance of some soybean genotypes,” Journal of Plant Nutrition, vol. 27, no. 11, pp. 2047–2066, 2004.

[43] M. A. Piñeros, J. E. Shaff, H. S. Manslank, V. M. Carvalho Alves, and L. V. Kochian, “Aluminum resistance in maize cannot be solely explained by root organic acid exudation. A comparative physiological study,” Plant Physiology, vol. 137, no. 1, pp. 231–241, 2005.

[44] S. J. Zheng, J. L. Yang, Y. F. Yun et al., “Immobilization of aluminum with phosphorus in roots is associated with high aluminum resistance in buckwheat,” Plant Physiology, vol. 138, no. 1, pp. 297–303, 2005.

[45] P. Wenzl, G. M. Patiño, A. L. Chaves, J. E. Mayer, and I. M. Rao, “The high level of aluminum resistance in signalgrass is not associated with known mechanisms of external aluminum detoxification in root apices,” Plant Physiology, vol. 125, no. 3, pp. 1473–1484, 2001.

[46] S. Ishikawa, T. Wagatsuma, S. Sasaki, and P. Ofeli-Manu, “Comparison of the amount of citric and malic acids in Al media of seven plant species and two cultivars each in five plant species,” Soil Science and Plant Nutrition, vol. 46, no. 3, pp. 751–758, 2000.

[47] J. L. Yang, L. Zhang, and S. J. Zheng, “Aluminum-activated oxalate secretion does not associate with internal content among some oxalate accumulators,” Journal of Integrative Plant Biology, vol. 50, no. 9, pp. 1103–1107, 2008.

[48] A. N. Famoso, R. T. Clark, J. E. Shaff, E. Craft, S. R. McCouch, and L. V. Kochian, “Development of a novel aluminum tolerance phenotyping platform used for comparisons of cereal aluminum tolerance and investigations into rice aluminum tolerance mechanisms,” Plant Physiology, vol. 153, no. 4, pp. 1678–1691, 2010.

[49] J. L. Yang, X. F. Zhu, C. Zheng, Y. J. Zhang, and S. J. Zheng, “Genotypic differences in Al resistance and the role of cell-wall pectin in Al exclusion from the root apex in Fagopyrum tataricum,” Annals of Botany, vol. 107, no. 3, pp. 371–378, 2011.

[50] J. L. Yang, Y. Y. Li, Y. J. Zhang et al., “Cell wall polysaccharides are specifically involved in the exclusion of aluminum from the rice root apex,” Plant Physiology, vol. 146, no. 2, pp. 602–611, 2008.

[51] N. T. Nguyen, K. Nakabayashi, J. Thompson, and K. Fujita, “Role of exudation of organic acids and phosphate in aluminum tolerance of four tropical woody species,” Tree Physiology, vol. 23, no. 15, pp. 1041–1050, 2003.

[52] O. A. Hoekenga, T. J. Vision, J. E. Shaff et al., “Identification and characterization of aluminum tolerance loci in Arabidopsis (Landsberg erecta x Columbia) by quantitative trait locus mapping. A physiologically simple but genetically complex trait,” Plant Physiology, vol. 132, no. 2, pp. 936–948, 2003.

[53] J. V. Magalhaes, J. Liu, C. T. Guimarães et al., “A gene in the multidrug and toxic compound extrusion (MATE) family confers aluminum tolerance in sorghum,” Nature Genetics, vol. 39, no. 9, pp. 1156–1161, 2007.

[54] J. F. Ma, S. J. Zheng, H. Matsumoto, and S. Hiradate, “Detoxifying aluminum with buckwheat,” Nature, vol. 390, no. 6660, pp. 569–570, 1997.
Arabidopsis guard cells,” *Plant Journal*, vol. 63, no. 6, pp. 1054–1062, 2010.

[85] S. Meyer, J. Scholz-Starke, A. De Angeli et al., “Malate transport by the vacuolar AtALMT6 channel in guard cells is subject to multiple regulation,” *Plant Journal*, vol. 67, no. 2, pp. 247–257, 2011.

[86] B. D. Gruber, P. R. Ryan, A. E. Richardson et al., “HvALMT1 from barley is involved in the transport of organic anions,” *Journal of Experimental Botany*, vol. 61, no. 5, pp. 1455–1467, 2010.

[87] B. D. Gruber, E. Delhaize, A. E. Richardson et al., “Characterisation of HvALMT1 function in transgenic barley plants,” *Functional Plant Biology*, vol. 38, no. 2, pp. 163–175, 2011.

[88] J. Furukawa, N. Yamaji, H. Wang et al., “An aluminum-activated citrate transporter in barley,” *Plant and Cell Physiology*, vol. 48, no. 8, pp. 1081–1091, 2007.

[89] J. Wang, H. Raman, M. Zhou et al., “High-resolution mapping of the Alp locus and identification of a candidate gene HvMATE controlling aluminium tolerance in barley (*Hordeum vulgare L.*),” *Theoretical and Applied Genetics*, vol. 115, no. 2, pp. 265–276, 2007.

[90] H. Omote, M. Hiasa, T. Matsumoto, M. Otsuka, and Y. Moriyama, “The MATE proteins as fundamental transporters of metabolic and xenobiotic organic cations,” *Trends in Pharmacological Sciences*, vol. 27, no. 11, pp. 587–593, 2006.

[91] M. Morita, N. Shitan, K. Sawada et al., “Vacuolar transport of nicotine is mediated by a multidrug and toxic compound extrusion (MATE) transporter in *Nicotiana tabacum*,” *Proceedings of the National Academy of Sciences of the United States of America*, vol. 106, no. 7, pp. 2447–2452, 2009.

[92] K. Yokosho, N. Yamaji, and J. F. Ma, “Isolation and characterisation of two MATE genes in rye,” *Functional Plant Biology*, vol. 37, no. 4, pp. 296–303, 2010.

[93] J. V. Magalhaes, “How a microbial drug transporter became essential for crop cultivation on acid soils: aluminium tolerance conferred by the multidrug and toxic compound extrusion (MATE) family,” *Annals of Botany*, vol. 106, no. 1, pp. 199–203, 2010.

[94] T. P. Durrett, W. Gassmann, and E. E. Rogers, “The FRD3-mediated efflux of citrate into the root vasculature is necessary for efficient iron translocation,” *Plant Physiology*, vol. 144, no. 1, pp. 197–205, 2007.

[95] J. Liu, J. V. Magalhaes, J. Shaff, and L. V. Kochian, “Aluminum-activated citrate and malate transporters from the MATE and ALMT families function independently to confer *Arabidopsis* aluminum tolerance,” *Plant Journal*, vol. 57, no. 3, pp. 389–399, 2009.

[96] L. G. Maron, M. A. Piñeros, C. T. Guimarães et al., “Two functionally distinct members of the MATE (multi-drug and toxic compound extrusion) family of transporters potentially underlie two major aluminum tolerance QTLs in maize,” *Plant Journal*, vol. 61, no. 5, pp. 728–740, 2010.

[97] K. Yokosho, N. Yamaji, and J. F. Ma, “An Al-inducible MATE gene is involved in external detoxification of Al in rice,” *The Plant Journal*, vol. 68, no. 6, pp. 1061–1069, 2011.

[98] X. Y. Yang, J. L. Yang, Y. A. Zhou et al., “A de novo synthesis citrate transporter, *Vigna unguiculata* multidrug and toxic compound extrusion, implicates in Al-activated citrate efflux in rice *Vigna unguiculata* (root apex),” *Plant Cell & Environment*, vol. 34, no. 12, pp. 2138–2148, 2011.

[99] J. F. Ma, W. Zhang, and Z. Zhao, “Regulatory mechanism of Al-induced secretion of organic acids anions-involvement of ABA in the Al-induced secretion of oxalate in buckwheat,” in *Plant Nutrition-Food Security and Sustainability of Agro-Ecosystems Through Basis and Applied Research*, W. J. Hortst, H. Flessa, B. Sattelmacher et al., Eds., pp. 486–487, Kluwer Academic, Dordrecht, The Netherlands, 2001.

[100] Z. M. Yang, H. Yang, J. Wang, and Y. S. Wang, “Aluminum regulation of citrate metabolism for Al-induced citrate efflux in the roots of *Cassia tora L.*,” *Plant Science*, vol. 166, no. 6, pp. 1589–1594, 2004.

[101] M. Xu, J. You, N. Hou, H. Zhang, G. Chen, and Z. Yang, “Mitochondrial enzymes and citrate transporter contribute to the aluminium-induced citrate secretion from soybean (*Glycine max*) roots,” *Functional Plant Biology*, vol. 37, no. 4, pp. 285–295, 2010.

[102] A. Gaume, F. Mächler, and E. Frossard, “Aluminum resistance in two cultivars of *Zea mays L.*: root exudation of organic acids and influence of phosphorus nutrition,” *Plant and Soil*, vol. 234, no. 1, pp. 73–81, 2001.

[103] J. E. Hayes and J. F. Ma, “Al-induced efflux of organic acid anions is poorly associated with internal organic acid metabolism in triticate roots,” *Journal of Experimental Botany*, vol. 54, no. 388, pp. 1753–1759, 2003.

[104] L. S. Chen, N. Tang, H. X. Jiang, L. T. Yang, Q. Li, and B. R. Smith, “Changes in organic acid metabolism differ between roots and leaves of *Citrus grandis* in response to phosphorus and aluminum interactions,” *Journal of Plant Physiology*, vol. 166, no. 18, pp. 2023–2034, 2009.

[105] L. T. Yang, Y. P. Qi, L. S. Chen et al., “Nitric oxide protects sour pummelo (*Citrus grandis*) seedlings against aluminum-induced inhibition of growth and photosynthesis,” *Environmental and Experimental Botany*, vol. 83, pp. 1–13, 2012.

[106] L. T. Yang, L. S. Chen, H. Y. Peng, P. Guo, P. Wang, and C. L. Ma, “Organic acid metabolism in *Citrus grandis* leaves and roots is differently affected by nitric oxide and aluminum interactions,” *Sciento Horticulturae*, vol. 133, no. 1, pp. 40–46, 2012.

[107] P. R. Ryan, S. D. Tyerman, T. Sasaki et al., “The identification of aluminum-resistance genes provides opportunities for enhancing crop production on acid soils,” *Journal of Experimental Botany*, vol. 62, no. 1, pp. 9–20, 2011.

[108] J. M. De La Fuente, V. Ramirez-Rodriguez, J. L. Cabrera-Ponce, and L. Herrera-Estrella, “Aluminum tolerance in transgenic plants by alteration of citrate synthesis,” *Science*, vol. 276, no. 5318, pp. 1566–1568, 1997.

[109] H. Koyama, E. Takita, A. Kawamura, T. Hara, and D. Shibata, “Over expression of mitochondrial citrate synthase gene improves the growth of carrot cells in Al-phosphate medium,” *Plant and Cell Physiology*, vol. 40, no. 5, pp. 482–488, 1999.

[110] Q. F. Wang, Y. Zhao, Q. Yi, K. Z. Li, Y. X. Yu, and L. M. Chen, “Overexpression of malate dehydrogenase in transgenic tobacco leaves: enhanced malate synthesis and augmented Al-resistance,” *Acta Physiologiae Plantarum*, vol. 32, no. 6, pp. 1209–1220, 2010.

[111] Y. Han, W. Zhang, B. Zhang, S. Zhang, W. Wang, and F. Ming, “One novel mitochondrial citrate synthase from *Oryza sativa* L. can enhance aluminum tolerance in transgenic tobacco,” *Molecular Biotechnology*, vol. 42, no. 3, pp. 299–305, 2009.

[112] M. Tesfaye, S. J. Temple, D. L. Allan, C. P. Vance, and D. A. Samac, “Overexpression of malate dehydrogenase in transgenic alfalfa enhances organic acid synthesis and confers tolerance to aluminum,” *Plant Physiology*, vol. 127, no. 4, pp. 1836–1844, 2001.
[113] L. I. Trejo-Téllez, R. Stenzel, F. C. Gómez-Merino, and J. M. Schmitt, "Transgenic tobacco plants overexpressing pyruvate phosphate dikinase increase exudation of organic acids and decrease accumulation of aluminum in the roots," *Plant and Soil*, vol. 326, no. 1, pp. 187–198, 2010.

[114] G. Neumann and V. Römhild, "Root excretion of carboxylic acids and protons in phosphorus-deficient plants," *Plant and Soil*, vol. 211, no. 1, pp. 121–130, 1999.

[115] M. Arango, F. Gévaudant, M. Oufattole, and M. Boutry, "The plasma membrane proton pump ATPase: the significance of gene subfamilies," *Planta*, vol. 216, no. 3, pp. 355–365, 2003.

[116] T. E. Sondergaard, A. Schulz, and M. G. Palmgren, "Ener- gization of transport processes in plants. Roles of the plasma membrane H^+-ATPase," *Plant Physiology*, vol. 136, no. 1, pp. 2475–2482, 2004.

[117] H. Shen, L. F. He, T. Sasaki et al., "Citrate secretion coupled with the modulation of soybean root tip under aluminum stress. Up-regulation of transcription, translation, and threonine-oriented phosphorylation of plasma membrane H^+-ATPase," *Plant Physiology*, vol. 138, no. 1, pp. 287–296, 2005.

[118] S. J. Ahn, Z. Rengel, and H. Matsumoto, "Aluminum-induced plasma membrane surface potential and H^+-ATPase activity in near-isogenic wheat lines differing in tolerance to aluminum," *New Phytologist*, vol. 162, no. 1, pp. 71–79, 2004.

[119] H. Matsumoto, "Inhibition of proton transport activity of microsomal membrane vesicles of barley roots by aluminum," *Soil Science and Plant Nutrition*, vol. 34, no. 4, pp. 499–506, 1988.

[120] S. J. Ahn, M. Sivaguru, H. Osawa, G. C. Chung, and H. Matsumoto, "Aluminum inhibits the H^+-ATPase activity by permanently altering the plasma membrane surface potentials in squash roots," *Plant Physiology*, vol. 126, no. 4, pp. 1381–1390, 2001.

[121] J. L. Yang, J. F. You, Y. Y. Li, P. Wu, and S. J. Zheng, "Magnesium enhances aluminum-induced citrate secretion in rice bean roots (Vigna umbellata) by restoring plasma membrane H^+-ATPase activity," *Plant and Cell Physiology*, vol. 48, no. 1, pp. 66–73, 2007.

[122] J. Bose, O. Babourina, and Z. Rengel, "Role of magnesium in alleviation of aluminum toxicity in plants," *Journal of Experimental Botany*, vol. 62, no. 7, pp. 2251–2264, 2011.

[123] I. R. Silva, T. J. Smyth, D. W. Israel, C. D. Raper, and T. W. Rufty, "Magnesium ameliorates aluminum rhizotoxicity in soybean by increasing citric acid production and exudation by roots," *Plant and Cell Physiology*, vol. 42, no. 5, pp. 546–554, 2001.

[124] K. Tan and W. G. Keltjens, "Interaction between aluminum and phosphorus in sorghum plants—I. Studies with the aluminum sensitive sorghum genotype TAM4287," *Plant and Soil*, vol. 124, no. 1, pp. 15–23, 1990.

[125] Q. B. Sun, R. F. Shen, X. Q. Zhao, R. F. Chen, and X. Y. Dong, "Phosphorus enhances Al resistance in Al-resistant Lepidium sativum but not in Al-sensitive L. cuneata under relatively high Al stress," *Annals of Botany*, vol. 102, no. 5, pp. 795–804, 2008.

[126] M. Jem, R. C. Abaidoo, C. Nolte, and W. J. Horst, "Aluminum resistance of cowpea as affected by phosphorus-deficiency stress," *Journal of Plant Physiology*, vol. 164, no. 4, pp. 442–451, 2007.

[127] D. Dong, X. Peng, and X. Yan, "Organic acid exudation induced by phosphorus deficiency and/or aluminum toxicity in two contrasting soybean genotypes," *Physiologia Plantarum*, vol. 122, no. 2, pp. 190–199, 2004.

[128] H. Nian, S. J. Ahn, Z. M. Yang, and H. Matsumoto, "Effect of phosphorus deficiency on aluminum-induced citrate exudation in soybean (Glycine max)," *Physiologia Plantarum*, vol. 117, no. 2, pp. 229–236, 2003.

[129] V. Casolo, E. Petruccia, J. Krašňáková, F. Macri, and A. Vianello, "Involvement of the mitochondrial K^+ ATP channel in H_2O_2 or NO-induced programmed death of soybean suspension cell cultures," *Journal of Experimental Botany*, vol. 56, no. 413, pp. 997–1006, 2005.

[130] S. Sokolovski, A. Hills, R. Gay, C. Garcia-Mata, L. Lamattina, and M. R. Blatt, "Protein phosphorylation is a prerequisite for intracellular Ca^{2+} release and ion channel control by nitric oxide and abscisic acid in guard cells," *Plant Journal*, vol. 43, no. 4, pp. 520–529, 2005.

[131] J. Chen, W. H. Wang, F. H. Wu et al., "Hydrogen sulfide alleviates aluminum toxicity in barley seedlings," *Plant and Soil*. In press.

[132] I. M. Rao, R. S. Zeigler, R. Vera, and S. Sarkarung, "Selection and breeding for acid-soil tolerance in crops," *Bioclone*, vol. 43, no. 7, pp. 454–465, 1993.

[133] P. Barone, D. Rosellini, P. LaFayette, J. Bouton, F. Veronesi, and W. Parrott, "Bacterial citrate synthase expression and soil aluminum tolerance in transgenic alfalfa," *Plant Cell Reports*, vol. 27, no. 5, pp. 893–901, 2008.

[134] H. Koyama, A. Kawamura, T. Kihara, T. Hara, E. Takita, and D. Shibata, "Overexpression of mitochondrial citrate synthase in Arabidopsis thaliana improved growth on a phosphorus-limited soil," *Plant and Cell Physiology*, vol. 41, no. 9, pp. 1030–1037, 2000.

[135] M. Zhang, X. Y. Luo, W. Q. Bai et al., "Characterization of malate dehydrogenase gene from Citrus junos and its transgenic tobacco's tolerance to aluminium toxicity," *Acta Horticulturae Sinica*, vol. 35, no. 12, pp. 1751–1758, 2008.

[136] E. Delhaize, P. R. Ryan, D. M. Hebb, Y. Yamamoto, T. Sasaki, and H. Matsumoto, "Engineering high-level aluminum tolerance in barley with the ALMT1 gene," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 101, no. 42, pp. 15249–15254, 2004.

[137] E. Delhaize, P. Taylor, P. J. Hocking, R. J. Simpson, P. R. Ryan, and A. E. Richardson, "Transgenic barley (Hordeum vulgare L.) expressing the wheat aluminium resistance gene (TaALMT1) shows enhanced phosphorus nutrition and grain production when grown on an acid soil," *Plant Biotechnology Journal*, vol. 7, no. 5, pp. 391–400, 2009.

[138] J. F. Pereira, G. Zhou, E. Delhaize, T. Richardson, M. Zhou, and P. R. Ryan, "Engineering greater aluminum resistance in wheat by over-expressing TaALMT1," *Annals of Botany*, vol. 106, no. 1, pp. 205–214, 2010.

[139] H. Yang, J. Knapp, P. Koirala et al., "Enhanced phosphorus nutrition in monocots and dicots over-expressing the wheat aluminium resistance gene (TaALMT1) when grown on an acid soil," *Plant Biotechnology Journal*, vol. 5, no. 6, pp. 735–745, 2007.

[140] Z. H. Lin, L. S. Chen, R. B. Chen et al., "Root release and metabolism of organic acids in tea plants in response to phosphorus supply," *Journal of Plant Physiology*, vol. 168, no. 7, pp. 644–652, 2011.

[141] E. D. Mariano, R. A. Jorge, W. G. Keltjens, and M. Menossi, "Metabolism and root exudation of organic acid anions under aluminium stress," *Brazilian Journal of Plant Physiology*, vol. 17, pp. 205–214, 2005.

[142] Y. M. Drozdowicz, J. C. Kissinger, and P. A. Rea, "AVP2, a sequence-divergent, K^+-insensitive H^+-translocating inorganic
pyrophosphatase from Arabidopsis,” *Plant Physiology*, vol. 123, no. 1, pp. 353–362, 2000.

[143] E. Hoffland, R. van den Boogaard, J. Nelemans, and G. Findenegg, “Biosynthesis and root exudation of citric and malic acids in phosphate-starved rape plants,” *New Phytologist*, vol. 122, no. 4, pp. 675–680, 1992.