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Aluminum Toxicity in Plants: Present and Future

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Abstract

Toxic aluminum ions (Al^{3+}) found in acidic soils are absorbed by plants and interact with multiple sites during plant development, affecting especially the root growth. The mechanisms by which plants cope with Al^{3+} stress are variable, and Al^{3+} can be excluded or accumulated internally. The molecular and physiological mechanisms associated with Al^{3+} response have been substantially studied. Thus, reviewing the findings about these mechanisms is important to portrait the state-of-the-art of Al^{3+} response in plants, highlight key results, identify research gaps, and ask new questions. In this paper, we discuss the current knowledge about DNA damage response induced by Al^{3+}, as well as membrane transporters that avoid Al^{3+} toxicity in the apoplast, Al^{3+} exclusion mechanisms, how Al^{3+} influences plant nutrition, signaling pathways evoked by Al^{3+} affecting gene expression, changes in plant growth regulators concentrations caused by Al^{3+} toxicity, and beneficial effects of microorganisms on plants exposed to Al^{3+} stress. The future research on these topics is also discussed. The current and future knowledge of how plants cope with Al^{3+} stress is important to comprehend the inter- and intraspecies variability of Al^{3+} response and to pave the way for new molecular breeding targets that can improve plant performance under Al^{3+} stress.

Keywords Abiotic stress · Acidic soil · Organic anions · Plant nutrition · Root growth · Signal pathways

Introduction

Aluminum is the third most abundant metal in the Earth crust where it is usually found in soil minerals as aluminosilicates, and it is not readily available to plants. However, under acidic soil conditions (pH < 5.5), the aluminosilicates in the soil undergo dissociation leading to the release of soluble Al ions where toxic $Al(H_20)_6{}^{3+}$, or simply Al^{3+}, becomes the prevalent ion below pH 5.0. Al^{3+} is easily taken up by plants and causes toxicity (Chandra and Keshavkant 2021). Al^{3+} toxicity has been considered the second most important abiotic stress factor responsible for lowering crop production, after drought (Von Uexküll and Mutert 1995). This is because acidic soils occupy approximately 30% of the world's ice-free land area and 50% of potentially arable lands. In addition, increasing human activities, farming practices, leaching basic cations from soils, and acid rains have led to considerable acceleration of soil acidification in recent years.

Toxic Al^{3+} interacts with both extra- and intracellular sites in the plant cell leading to injuries in several cellular components including root cell wall, plasma membrane, cytoskeleton, and nucleus. Al^{3+} toxicity disturbs DNA replication and cell division, causes nutrients imbalances and modifies the concentration of phytohormones and other signaling molecules (Singh et al. 2017). Understanding the plant mechanisms to cope with Al^{3+} toxicity is critical to comprehend the diversity of Al^{3+} response among plant species and genotypes as well as help improving the productivity of susceptible species grown on acidic soils.

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As the knowledge about plant response to Al^{3+} stress grows rapidly, the current state-of-the-art requires a highlight. In this paper we summarize studies related to Al^{3+} toxicity on root meristems, Al^{3+} distribution within the plant cells, expression of genes responsible for Al^{3+} transport, Al^{3+} signaling and Al^{3+}-mediated changes in the patterns of gene expression in plants. Additionally, we review the impact of Al^{3+} on plant mineral nutrition, growth regulators that modify the response to Al^{3+} toxicity, the beneficial microorganisms helping plants to cope with Al^{3+} stress, and the results of studies about alleviation mechanisms for enhancing plant Al^{3+} tolerance. We also discuss the future research perspectives of these topics. This paper can help research groups interested in understanding the Al^{3+} effects on plants, eventually leading to sustainable improvements in the performance of plants growing on acidic soils.

Plants Use Two Distinct Strategies to Cope with Al^{3+} Toxicity

Plants have evolved two strategies to survive under Al^{3+} stress. One is the exclusion of Al^{3+} from the root symplast and the another is the internal sequestration and detoxification (Ryan and Delhaize 2010). Keeping in mind that the binding of Al^{3+} with pectic nets in the cell wall decreases the wall functions and inhibits root elongation (Horst et al. 2010; Silva et al. 2019), the exclusion mechanism could not be effective in protecting plant roots from Al^{3+} toxicity unless is associated with Al^{3+} chelation by organic molecules and formation of stable and non-toxic complexes to prevent Al^{3+} binding with the cell wall. In accordance with these strategies, the term 'Al^{3+} resistance' is defined as traits enabling plants to grow without or with little injury under toxic Al^{3+} concentrations in the medium. The mechanisms responsible for Al^{3+} resistance is divided into 'Al^{3+} exclusion' and 'Al^{3+} tolerance' mechanisms. Exclusion mechanisms prevent Al^{3+} from entering into the root symplast while internal tolerance enables Al accumulation in the symplast (Ryan and Delhaize 2010).

Physiological and molecular genetic studies suggest that both strategies are expressed in every species to some extent and, thus, plants benefit from both exclusion and sequestration mechanisms for minimizing the toxic effects of Al^{3+} in soil. However, different species have different ability for employment of these mechanisms leading to distinct degrees of Al^{3+} resistance in each species.

Role of DNA Damage Response (DDR) in the Effect of Al^{3+} Toxicity on Root Meristems

The primary site of Al^{3+} toxicity is the root apex, which leads to inhibition of root elongation and results in stunted root system. Rhizotoxic Al^{3+} is capable of destructing the root meristems and in-turn restricts the proliferation of the cells and elongation as well (Doncheva et al. 2005). Study of the spatial distribution of Al^{3+} toxicity events within root apex revealed that the transition zone, i.e., the zone located between the active cell division zone and the fast cell elongation zone, is the most Al^{3+} sensitive part in the root apex (Sivaguru and Horst 1998; Poschenrieder et al. 2008). Some morphological changes are also associated with the Al^{3+} effect on root apex, including initiation of lateral roots, disturbance in the peripheral tissues, thickening or bulging of the root apices. Noticeable swelling in the root tissues in the elongation zone and meristem and thickening of the root caused by radial expansion of cortical cells along with vacuolation are marked in the inner cortex (Čiamporová 2002).

It is well-documented that the exposure to Al^{3+} induces DNA damage in plant roots (Nisa et al. 2019; Pedroza-Garcia et al. 2022). Two *ALS* (*Al-Sensitive*) mutants, including *als1* and *als3* have been identified in *Arabidopsis* using molecular genetic approach. Both mutants show extreme sensitivity to Al^{3+} and a severe inhibition of root growth under very low Al^{3+} concentration (Larsen et al. 1996). Screening for suppressors of *als3-1*, revealed involvement of the plant DNA damage pathway in the root response to Al^{3+} (Rounds and Larsen 2008; Tsutsui et al. 2011). In all living organisms, including plants, exposure to DNA damaging factors activates repair mechanisms in order to maintain the genome stability. The DNA Damage Response (DDR) is a pathway that activates repairing mechanisms and stops cell division until DNA repair is complete (Gimenez and Manzano-Agugliaro 2017).

Two DNA damage signaling proteins, ATM (Ataxia-Telangiectasia Mutated) and ATR (Ataxia-Telangiectasia Mutated and RAD3-Related) have kinase activities and are required for monitoring DNA integrity (Culligan et al. 2006). Despite some common downstream pathways, ATM and ATR have different response thresholds for DNA damage and have different capacities. ATM contributes to the response to double-stranded DNA breaks, while ATR responds to a wide range of DNA damaging events, including those that interfere with DNA replication (Yoshiyama et al. 2013). Another cell cycle checkpoint factor, Aluminum Tolerant2 (ALT2), has been identified as an *als3-1* suppressor mutant (*alt2-1*) and monitors DNA crosslinks and responds to DNA damage (Nezames et al. 2012). Finally, SOG1 (Suppressor of Gamma Response1), that is a transcription factor regulating numerous genes in response to DNA damage, is known to activate cell cycle arrest, DNA repair and endoreduplication (Sjogren et al. 2015). Phosphorylation of one specific motif in SOG1 by ATR or ATM is required to activate downstream pathways. The extent of

phosphorylation of this specific motif in SOG1 regulates the expression level of genes and the extent of DNA damage responses (Yoshiyama et al. 2017).

Although loss-of-function mutants of ATR, ALT2 and SOG1 have expectedly higher sensitivity to DNA crosslinking agents, they show increased Al^{3+} tolerance and the retention of root growth is not observed in the mutants (Sjogren et al. 2015). These unexpected results suggest that Al^{3+}-mediated inhibition of root growth results from detection of DNA damage and induction of repair mechanisms by ATR, ALT2 and SOG1 that ultimately stop cell cycle progression (Zhang et al. 2018). A loss-of-function mutation in the *SUV2* (*Sensitive to UV 2*) gene, which encodes a component of the ATR-dependent pathway, was found to have a similar role in Al^{3+}-dependent stoppage of root growth (Sjogren and Larsen 2017).

In contrast to the effect of low Al^{3+} concentrations applied in the above-mentioned studies, under severe Al^{3+} stress, *atm* and *sog1* mutants rather show Al^{3+} hypersensitivity confirmed by a complete stoppage of root growth (Chen et al. 2019b). These two contrasting behaviors possibly suggest a two-level response to DNA damage in plants. At low Al^{3+} concentrations causing a mild DNA damage, the DDR pathway can be activated in the absence of functional ATR and SOG1 without compromising plant survival because of the function of an alternative DNA repair pathway (Chen et al. 2019b), likely RBR1, Retinoblastoma-Related 1 (Biedermann et al. 2017). Under severe DNA damage induced by higher concentrations of Al^{3+}, ATM-dependent SOG1 pathway leads to the full activation of the DDR. This pathway is crucial for plant survival as confirmed by the Al^{3+} hypersensitivity phenotype of *atm* and *sog1* mutants (Chen et al. 2019b). An illustration on the effect of Al on root growth via DNA Damage Response pathway mediated by SOG1 is shown in Fig. 1.

Contrary to the evidence on the role of DNA damage in the root response to Al^{3+}, a recent study on tea (*Camellia sinensis*) as an Al accumulator species, reported an unexpected response of root growth to Al^{3+} (Sun et al. 2020). The beneficial effect of Al^{3+} on root growth of this species has been well documented (Hajiboland et al. 2013b); however, a rather essential role of Al^{3+} for root growth of tea plants has been reported (Sun et al. 2020). These authors showed that in the absence of Al^{3+}, the length of the root meristematic zone decreased, cells in this zone stopped dividing, showing its involvement in the maintenance of DNA integrity in meristematic cells. Such controversial data suggest that the special interaction between Al^{3+} and DNA need to be reevaluated and more cytological and biochemical analyses are needed for interpretation of these data and the reason for different responses obtained between species.

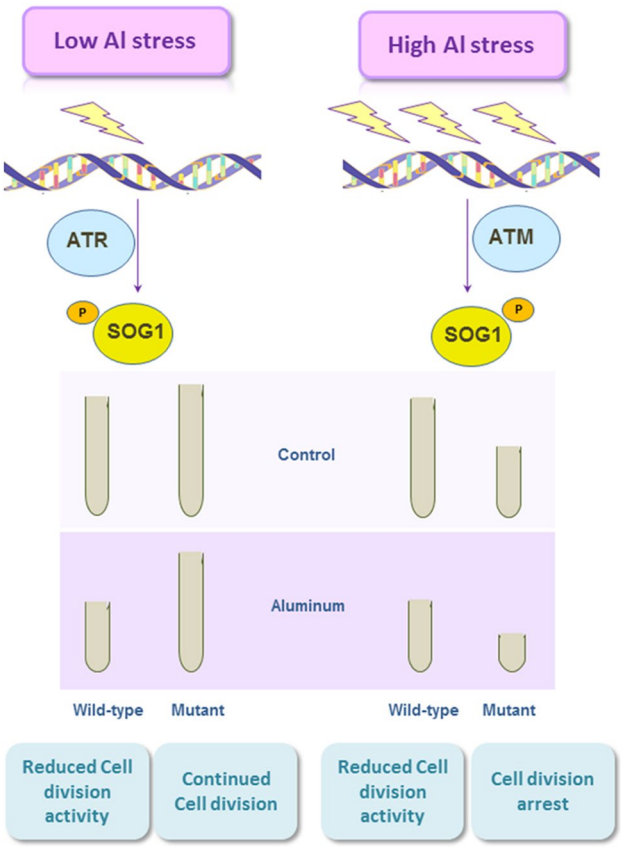

Fig. 1 Schematic illustration on the effect of Al^{3+} on root growth via DNA Damage Response pathway mediated by SOG1. Under low level of Al^{3+} stress, SOG1 pathway is mediated by ATR, which involve in DNA repair mechanism but its inactivation in the mutants results in Al^{3+}-insensitivity suggesting that this pathway could be inactivated without compromising root growth. Under sever Al^{3+} stress, DNA damage is mediated by ATM that is essential for root growth and survival so the mutants show Al^{3+}-hypersensitivity

Al^{3+} Binding with the Root Cell Wall is a Major Determinant in the Response of Plants to Al^{3+}

Cell walls (CWs) are very important for the perception and expression of Al^{3+} toxicity in plants (Horst et al. 2010). The primary CW of plants consists of cellulose, hemicellulose, pectins and structural proteins (Cosgrove 2005). Under toxic concentrations of Al^{3+}, CW is the major site for Al accumulation and about 90% of cellular Al is associated with the CW (Horst et al. 2010).

Among CW components, cellulose shows no interaction with Al^{3+}, while the branched structures and negatively charged carboxyl groups, make hemicelluloses and pectins suitable for binding with Al^{3+} (Horst et al. 2010). The accumulation of Al in root tips is a two-phase process (Zhang and Taylor 1990). The first rapid phase reflects Al^{3+} binding with the root apoplast (Horst et al. 2010). The root apoplast that is

defined as the compartment beyond the plasma membranes, including the interfibrillar and intermicellar space of the CWs and the outer root surface (Sattelmacher 2001; Farvardin et al. 2020) is the site of the primary lesion of Al^{3+} (Kopittke et al. 2015). It has been demonstrated that the primary lesion of Al^{3+} occurs five minutes after Al^{3+} exposure upon binding with the CW of outer cells leading to a direct inhibition of wall loosening in the elongation zone. Modification of biosynthesis and distribution of phytohormones (ethylene and auxin) is the second effect that results in a long-term reduction of root growth in the elongation zone (Kopittke et al. 2015; Silva et al. 2019).

The carboxylic groups in the pectic matrix have specifically high affinity for Al^{3+} and are the important Al^{3+}-binding sites (Horst et al. 2010). Strong binding of Al^{3+} to the pectin fraction of the CW is a major cause of Al^{3+} toxicity (Rangel et al. 2009) because higher density of carboxylic groups belonging to the polygalacturonic acids in the CW results in higher Al accumulation in the root tips (Yang and Horst 2015). In the process of CW biogenesis, pectin is first methylesterified in the endomembrane system and released into the wall where it is subjected to a partial demethylesterification processes through pectin methyesterase (PME) (Cosgrove 2005). Activity of PME, thus, results in the exposure of free carboxylic groups to Al^{3+} and serve as its binding sites in the CW. It has been observed that methylation of pectin minimizes its negative charge and confers Al^{3+} tolerance, while demethylation by PME leads to more Al^{3+} binding to pectin (Eticha et al. 2005a; Yang et al. 2008, 2011b, 2013). Transgenic potato (*Solanum tuberosum*) plants with higher PME expression show higher Al accumulation in the roots and more severe inhibition of root growth than the wild type when exposed to Al^{3+} (Schmohl et al. 2000). Similarly, in the Al^{3+}-sensitive rice and maize cultivars, PME activity is higher and are more severely damaged by Al^{3+} compared with the Al^{3+}-resistant cultivars (Eticha et al. 2005a; Yang et al. 2008, 2013).

In addition to pectin, the contribution of hemicellulose to the Al^{3+}-binding capacity of CW and thus Al^{3+} toxicity has been demonstrated (Yang and Horst 2015). In *Arabidopsis*, 75% of the Al localized in the CW is bound with the hemicellulose compared to only 20% found in the pectin fraction (Yang et al. 2011a). Xyloglucan (XyG) is the major component of hemicellulose or the primary wall in nonpoalean monocotyledons and dicotyledons (Cosgrove 2005), and it is the principal binding site for Al^{3+}. The importance of Al^{3+} binding with XyG, has been observed using mutants of hemicellulose-modifying enzymes. Modifications of the CW matrix are catalyzed by several enzymes, including the xyloglucan endotransglucosylase/hydrolase (XTH) family (Cosgrove 2005). It has been observed that mutants affected in *XTH* (*xth31* and *xth17*) have shorter roots than wild type plants, showing their essential function for growth and particularly cell expansion. However, these mutant roots accumulate less Al^{3+} than wild-type plants and show no significant Al^{3+}-dependent growth inhibition (Zhu et al. 2012b).

Considering that the hydroxyl groups in XyG could bind with Al^{3+}, the amount of nonacetylated hydroxyl groups is important to determine the Al^{3+} binding capacity of XyG. In accordance with this, mutants in an O-acetyltransferase responsible for O-acetylation of XyG, *TRICHOME BIREFRINGENCE-LIKE27* (*TBL27*/*AXY4*) has lower O-acetylation level and shows more Al^{3+} accumulation in the CW, and, thus, is more Al^{3+}-sensitive (Zhu et al. 2014). In addition to pectin and hemicellulose, a direct interaction of Al^{3+} with structural CW proteins, thus, a direct effect on CW extensibility cannot be ruled out (Yang and Horst 2015).

Regarding decisive role of the pectin and XyG structures in their Al^{3+} binding capacity, the effect of Al^{3+} on the enzymes responsible for their modifications is also important. Transcriptional analysis in maize revealed that Al^{3+} up-regulates the expression of the *PME* gene thus, increases Al^{3+} binding possibility with the CW (Maron et al. 2008). An opposite effect of Al^{3+} treatment was observed on the expression of *TBL27*, encoding a Golgi-localized O-acetyltransferase. This effect of Al^{3+} treatment, however, similarly increases the Al^{3+} binding with the CW because reduction of O-acetylation level of XyG upon Al^{3+} treatment leads to higher Al^{3+} binding with the hemicellulose fraction (Zhu et al. 2014). In contrast, the expression of *XTH* genes (*XTH14*, *15*, and *31*) are down-regulated upon Al^{3+} treatment even within 30 min, leading to lower Al^{3+} binding (Yang et al. 2011a). Different patterns of response to Al^{3+} observed on the CW-modifying enzymes, likely reveal different strategies to cope with Al^{3+} effect on the cell expansion and suggest that the plant's response to Al^{3+} binding in the apoplast is, indeed, a complex response.

A crucial role of Al^{3+} binding with the CW for Al^{3+} toxicity is supported by the studies showing that rice mutations of *Nrat1* (*Nramp aluminum transporter 1*), whose protein specifically transports Al^{3+} ion through the plasma membrane (see section 'Transporters of Plasma Membrane'), show higher Al^{3+} sensitivity. This indicates that Al transport from the apoplast to the symplast leading to reduction of the Al concentration in the root CW, significantly contributes to the remarkably high Al^{3+} tolerance observed in rice plants (Xia et al. 2010; Li et al. 2014).

Irrespective of the nature of Al^{3+} binding site in the CW, its binding affects CW extension directly or indirectly. The replacement of Ca^{2+} by Al^{3+} in the CW pectic matrix, makes the CW rigid and interferes with cell division and extension (Cosgrove 2005; Boyer 2009), or decreases the expression and activity of CW-loosening enzymes, such as XTHs (as described above) (Tabuchi and Matsumoto 2001; Ma et al. 2004), and of CW structural proteins such

as expansin (Yang and Horst 2015). Al^{3+} binding with the CW may affect cell extension through modifications in the CW-plasma membrane-cytoskeleton continuum (Sivaguru et al. 2000). The CW-associated receptor kinases (WAKs) that are involved in the interaction between CW and plasma membrane (Kohorn and Kohorn 2012), may contribute to the Al^{3+}-induced inhibition of root growth in *Arabidopsis* (Sivaguru et al. 2003).

Considering the pivotal role of CW components in the determination of Al^{3+} tolerance, several genes involved in the synthesis and metabolism of CW components have been identified to modify the plants Al^{3+} response. Two leucine zipper transcription factors, AtHB7 and AtHB12 participate in Al^{3+} resistance due to the effects on the CW properties and influencing its Al^{3+} binding properties (Liu et al. 2020). AtHB12 increases expression of CW-related genes such as *EXPANSINA10* and *DWARF4* (Liu et al. 2020). AtHB7 and AtHB12 stimulate root growth through increasing the cell number and cell length under normal conditions, but play an opposite role under Al^{3+} toxicity by regulating the Al^{3+} binding capacity of CW (Liu et al. 2020). AtHB7 and AtHB12 are likely to interact with different components in Al^{3+}-response pathways and are also able to form heterodimers leading to the inhibition of activities of each other under Al^{3+} stress (Liu et al. 2020).

In barley, a homeobox-leucine zipper transcription factor HvHOX9 is up-regulated by Al^{3+} stress in root tips and plays an important role in Al^{3+} tolerance through reduction of Al^{3+} binding capacity of root CW. Silencing *HvHOX9* increased Al accumulation in root CW and significantly increased sensitivity to Al^{3+} (Feng et al. 2020). In rice bean (*Vigna umbellate*), the expression of a transcription activator *VuNAR1* is specifically up-regulated by Al^{3+} in roots. VuNAR1 directly activates transcription of *WAK1* (*Wall-Associated Receptor Kinase 1*) independent of the function of known Al-resistance genes. *VuNAR1* overexpressing plants show higher *WAK1* expression, lower pectin content and exhibit improved Al^{3+} resistance (via Al^{3+} exclusion) compared to wild-type *Arabidopsis* plants (Lou et al. 2020).

In contrast to the experimental data suggesting that less Al in the CW helps to maintain root growth and higher Al^{3+} tolerance, there is also evidence showing that reduction of CW Al binding capacity leads to higher Al in the symplast and reduces Al^{3+} tolerance. A WRKY transcription factor (containing a conserved WRKYGQK motif), WRKY47, that is required for root growth under normal conditions also regulates Al^{3+} distribution between the apoplast and symplast (Li et al. 2020). WRKY47 directly regulates the expression of *Extensin-Like Protein* (*ELP*) and *Xyloglucan Endotransglucosylase-Hydrolases17* (*XTH17*) responsible for CW modification (Li et al. 2020). In wild-type plants, an adequate expression of *ELP* and *XTH17* confers a proper Al^{3+} binding with CW and, thus, less entry into the symplast. In the *wrky47-1* mutant, however, Al content decreases in apoplast but increases in symplast, following reduction of Al-binding capacity of CW. An Al^{3+}-sensitive phenotype of *wrky47-1* mutant and higher Al^{3+} tolerance in the *WRKY47* overexpressing line (Li et al. 2020), could likely be related to a limited capacity for internal Al^{3+} detoxification in *Arabidopsis*.

The knockdown mutations of *CDT3* (*Cadmium Tolerant 3*), encoding a small cysteine-rich peptide that directly bind Al^{3+} in the plasma membrane, results in decreased tolerance to Al, probably due to reduction of Al^{3+} content in the CW and plasma membrane of the roots, but its increase in the root cell sap (Xia et al. 2013). These results suggest that a balance between both external and internal detoxification is necessary for achievement of higher Al^{3+} resistance.

Nitric Oxide Acts as a Player in the Modification of CW and Changes Al^{3+} Binding

Nitric oxide (NO) is a signaling molecule that contributes to the response of plants to various biotic and abiotic stress factors (Domingos et al. 2015). Nitric oxide is also involved in CW metabolism (Pacoda et al. 2004).

Results of the studies on the effect of NO application (applied as sodium nitroprusside, SNP) on the Al^{3+} accumulation in the root tip and Al^{3+} binding with the CW are contradictory. In rice bean, SNP pretreatment caused greater induction of PME activity leading to increased Al accumulation and exacerbation of Al^{3+}-induced inhibition of root growth (Zhou et al. 2012). In contrast, NO application reduces Al^{3+} toxicity in rice and improves root elongation by decreasing the concentration of pectin and hemicellulose, accompanied by reduction of PME activity that leads to less Al^{3+} accumulation in CW (Zhang et al. 2011; Lan et al. 2021). In peanut (*Arachis hypogaea*), similarly, NO application relieved Al^{3+}-induced inhibition of root elongation, decreased PME activity and Al^{3+} adsorption in CW and up-regulated the xyloglucan endotransglucosylase/hydrolase (*XTH-32*) gene (Pan et al. 2017). Data on the effect of Al^{3+} on the endogenous concentration of NO were also divergent, where both no effect (Zhou et al. 2012) or accumulation of NO upon Al^{3+} treatment (Sun et al. 2016; Pan et al. 2017; Zhang et al. 2019a; Lan et al. 2021) have been reported. Application of NO scavenger, cPTIO have led also to contradictory results. While no effect of cPTIO was observed on the root growth, Al^{3+} accumulation in root tip, Al^{3+} binding with the CW and PME activity in rice (Lan et al. 2021), in wheat, these parameters were decreased after elimination of endogenous NO production with cPTIO and, thus, Al^{3+}-induced inhibition of root growth was significantly alleviated (Sun et al. 2016; Zhang et al. 2019a). Although these contradictory results could be primarily attributed to a species-specific role of NO in

plants Al^{3+} response, this seems to be unlikely because the experimental plants are all crop species without considerable difference in their Al^{3+} susceptibility, and experimental data are missing on Al accumulators native to acidic soils. A probable explanation for these discrepancies is a difference in the constitutive and/or Al^{3+}-induced concentration of NO among the studied species leading in turn, to different outcomes after NO application donors and scavengers. Similar to other signaling molecules, different effects on the downstream pathways could be emerged by low versus high concentrations of NO. In addition, the spatial and temporal patterns of NO concentrations in tissues are also critical for the downstream pathways but remained unexplored. Mutants with modified NO production will likely help to explore the contribution of endogenous NO to plant Al^{3+} response, and will shed more light on the mechanisms for NO-mediated CW modification under Al^{3+} stress.

Al^{3+} is Internalized and Distributed Within the Plant Cells Through Specific Transporters

The uptake of Al into the cytoplasm is mediated by transporters present on the root plasma membrane and those localized on the tonoplast sequester Al into the vacuole. Recent studies provided evidence on the contribution of these transporters to the decreasing apoplastic toxicity of Al^{3+}. The internalization into the symplast prevents Al^{3+} effects on root elongation and acts as a prior step for final Al^{3+} detoxification within cells through chelation with organic molecules and compartmentalization into vacuoles mediated by the related transporters. Figure 2 shows an illustration on the function of various transporters in the plasma membrane and tonoplast for Al^{3+} exclusion, internalization and vacuolar sequestration.

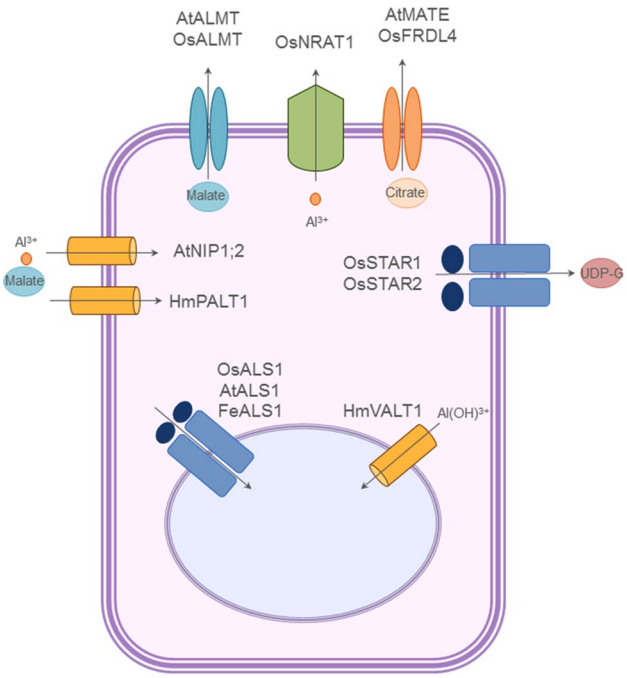

Fig. 2 Schematic illustration on the function of various transporters in the plasma membrane and tonoplast for Al^{3+} exclusion, internalization and vacuolar sequestration. ALMT: Al-Activated Malate Transporter; MATE: Multidrug and Toxic compound Extrusion; FRDL4: Ferric Reductase Defective 3-Like 4; NRAT1: Nramp Aluminum Transporter 1; NIP1; 2: Nodulin 26-like Intrinsic Proteins, PALT1: Plasma Membrane Al Transporter 1; STAR1 and STAR2: Sensitive to Al Rhizotoxicity 1; ALS1: Al-Sensitive 1; VALT1: Vacuolar Al Transporter 1

Transporters of Plasma Membrane

Nrat1

The Natural resistance-associated macrophage protein (Nramp) family is conserved throughout all organisms and involved in the acquiring and trafficking of transition metal ions across cellular membranes (Bozzi and Gaudet 2021). A member of Nramp family of transporters, Nrat1 (Nramp Aluminum Transporter 1) shares < 60% similarity with other members and is located in the plasma membrane of root apex cells, except the epidermal cells (Xia et al. 2010). Unlike other Nramp members, Nrat1 is a transporter of trivalent Al ion (Al^{3+}) but not of divalent metals such as Fe^{2+}, Mn^{2+} and Cd^{2+} and Al-citrate complex (Xia et al. 2010). A detailed functional analysis of Nrat1 showed that knockout mutation of *Nrat1* is associated with decreased Al^{3+} uptake and results in its binding with CW and enhanced Al^{3+} sensitivity while over-expression of *Nrat1* in rice and *Arabidopsis* increases Al^{3+} uptake and enhances Al^{3+} tolerance (Xia et al. 2010). Expression of *Nrat1* is positively regulated by a C_2H_2 zinc finger transcription factor responsive to Al^{3+}, ART1 in rice (Xia et al. 2010). For more details, see section 'Candidate Signaling Molecules Acting Upstream of Gene Expression Pathway'.

NIP1;2

Aquaporins (AQPs) that facilitate selective transport of water and many others molecules are present in eukaryotes and prokaryotes. Plant AQPs are categorized into five major sub-families: plasma membrane intrinsic proteins (PIP), tonoplast intrinsic proteins (TIPs), nodulin 26-like intrinsic proteins (NIPs), small intrinsic proteins (SIPs), and uncharacterized intrinsic proteins (XIPs) (Deshmukh et al. 2016). A member of NIP subfamily, NIP1;2 is localized in plasma membrane of the root tips and mediates Al^{3+} transport into the cell in the form of Al-malate (Wang et al. 2017). Interestingly, the function of NIP1;2 is dependent

on a functional ALMT1-mediated malate release system suggesting a close relationship between Al^{3+} exclusion and detoxification mechanisms (Wang et al. 2020). The hypersensitive phenotype of *nip1;2* to Al^{3+} associated with Al hyperaccumulation in the CWs of the root tip cells in this mutant confirms the important function of NIP1;2 in the removal of Al^{3+} from root CW (Wang et al. 2017). *In planta* studies in *Arabidopsis* suggest that NIP1;2 is also responsible for xylem loading and root-to-shoot translocation of Al^{3+}. *NIP1;2* is up-regulated by external Al^{3+} but not with any other metal (Wang et al. 2017).

Another member of the AQPs family, Plasma Membrane Al Transporter1 (PALT1) was identified in Hydrangea (*Hydrangea macrophylla*) an Al hyperaccumulating species (Negishi et al. 2012). *PALT1* is highly expressed in the sepals and mediates Al^{3+} influx and accumulation in this organ (Negishi et al. 2012). Interestingly, overexpression of *HmPALT1* in *Arabidopsis* increased Al^{3+} sensitivity due to higher Al accumulation (Negishi et al. 2012), likely because such high Al^{3+} concentration was beyond detoxification capacity for this species. In addition to the role in the Al^{3+} transport, PIP1-1 and PIP2 are down-regulated in 'Rangpur' lime (*Citrus limonia* L.) exposed to 1480 µM Al^{3+}) in nutrient solution, suggesting that the Al^{3+} not only reduces the root growth, important for water absorption, but also compromises AQPs responsible for water transport (Cavalheiro et al. 2020).

STAR1 and STAR2

ATP-binding cassette (ABC) proteins are involved in the transmembrane transport of a wide range of unrelated molecules. ABC proteins have been classified into eight subfamilies, ABCA to ABCI. Nevertheless, plants lack ABCH group. Some of these subfamilies include the half-size transporters along with the full-size ones. Functional ABC transporters consist of two transmembrane domains (TMD) and two nucleotide-binding domains (NBD) (Lefèvre and Boutry 2018). Genetic studies have identified two genes that are responsible for Al^{3+} tolerance in rice, *STAR1* (*Sensitive to* Al^{3+} *Rhizotoxicity1*) encoding an NBD and *STAR2* encoding a TMD. STAR1 interacts with STAR2 to form a complex that acts as a functional ABC transporter responsible for efflux of UDP-glucose (Huang et al. 2009). Both *STAR1* and *STAR2* are expressed in all root cells, except the epidermal layer of mature root zone and are specifically induced by Al^{3+} exposure. UDP-glucose may be used to modify the CW and mask the sites for Al^{3+} binding as the UDP-glucose application restored root growth in the *star1* mutant exposed to Al^{3+} (Huang et al. 2009). Homologous genes in *Arabidopsis* (*AtSTAR1*) (Huang et al. 2010) and Al-accumulator species, buckwheat (*Fagopyrum esculentum*) (*FeSTAR1, FeSTAR2*) (Che et al. 2018b; Xu et al. 2018) have also been identified. Interestingly, the Al^{3+}-mediated up-regulation of *FeSTAR1* and *FeSTAR2* expression in buckwheat was up to 10 times higher than that in their homologous genes in rice and *Arabidopsis* (Che et al. 2018b).

ALS3

This transporter has been identified in the screening for Al^{3+}-hypersensitive phenotype in the mutants of *Arabidopsis*. ALS3 contains seven putative membrane spanning domains, represents an atypical ABC transporter structure and is responsible for movement of an unidentified substrate into or out of a cell. In contrast to some authors who suggested the ALS3 to be localized in the tonoplast (Chandra and Keshavkant 2021; Kar et al. 2021b), immunolocalization analysis indicated that ALS3 accumulates on the plasma membrane (Larsen et al. 2005). ALS3 is situated on the plasma membrane of epidermal cells in the root cortex and in cells of the phloem and it is necessary for Al^{3+} tolerance likely because of its involvement in the long-distance movement away from the root tip for storage or exudation through hydathodes (Larsen 2009). Homologs of *ALS3* have been found in both monocots and dicots, suggesting that ALS3-mediated mechanism for Al^{3+} tolerance is rather common in higher plants (Larsen 2009).

H^+-ATPases

Solute flux across the plasma membrane depends largely on the function of plasma membrane H^+-ATPases that belongs to a superfamily of pumps classified as P-type ATPase (Gaxiola et al. 2007). It has been observed that, the function of H^+-ATPases is correlated with plant Al^{3+} tolerance due to higher release of organic acid anions (also referred to as organic acids). In the roots exposed to toxic Al^{3+} concentration, the activation of plasma membrane H^+-ATPase occurs in parallel with citrate exudation (Shen et al. 2005). Furthermore, activators (e.g., fusicoccin) and inhibitors (e.g., vandate) of plasma membrane H^+-ATPase, causes activation and repression of Al^{3+}-induced citrate exudation, respectively (Shen et al. 2005). In Al^{3+}-tolerant species, such as tea (*Camellia sinensis*), Al^{3+} treatment results in higher H^+-ATPase activity in roots leading to enhanced rate of H^+ release to the rhizosphere (Wan et al. 2018). In Al^{3+}-sensitive species, in contrast, Al^{3+} inhibits the activity of H^+-ATPase in a concentration-dependent manner (Ahn et al. 2002).

ALMT and MATE

A family of transporters, Aluminum-activated Malate Transporter (ALMT) family is responsible for malate efflux and the Multidrug and Toxic Compound Extrusion (MATE) family mediates citrate exudation from the root apex. These

transporters are discussed with more details in the section 'Aluminum Exclusion Strategy is Relied on the Root Release of Organic Acid Anions' of this review. The function of these transporters contributes indeed to both Al^{3+} exclusion and Al^{3+} resistance mechanisms.

Transporters of Tonoplast

Vacuoles are the main storage compartment for the majority of ions and metabolites in the cytoplasm and are crucial for detoxification of metal ions (Schumacher and Krebs 2010). Vacuolar compartmentalization of Al is the final step of internal detoxification and mediated by various transporters located on tonoplast.

VALT1

In hydrangea (*Hydrangea macrophylla*), VALT1 (Vacuolar Al Transporter 1), a TIP-family protein located in the tonoplast is involved in the Al^{3+} tolerance. *VALT1* is highly expressed in sepal tissues and is responsible for the transport of Al into vacuoles that causes a blue sepal color due to the formation of Al complex with anthocyanin (Negishi et al. 2012). Since AQPs are known to mediate the transport of non-ionic substrates, the chemical form of Al^{3+} subjected to the transport across the tonoplast is likely $Al(OH)_3$ because of a relatively high pH (7.5) in the cytosol (Negishi et al. 2012). The overexpression of *VALT* in *Arabidopsis* confers Al^{3+}-tolerance in this species. Cooperation between HmPALT1 that transports Al^{3+} into the cytosol and HmVALT that sequesters Al^{3+} into vacuoles is the main mechanism for Al^{3+} hyperaccumulation in hydrangea (Negishi et al. 2012).

ALS1

ALS1 in *Arabidopsis* (*AtALS1*) and rice (*OsALS1*) encode a tonoplast-localized half-size ABC transporter and is required for internal detoxification of Al^{3+}. *OsALS1* is regulated by a C_2H_2-type zinc finger transcription factor, ART1 (see section 'Candidate Signaling Molecules Acting Upstream of Gene Expression Pathway') and the mutants accumulate more Al^{3+} in the cytoplasm and nucleus than the wild-type plants, indicating its role in Al^{3+} detoxification (Huang et al. 2012). Expression of *OsALS1* is specifically induced by Al^{3+} in the roots, while other metals or low pH show no effect. The expression of the homologue genes in buckwheat (*FeALS1.1* and *FeALS1.2*), similar to that observed for *FeSTAR1* and *FeSTAR2* (see section 'Transporters of Plasma Membrane'), was much higher than *AtALS1* in *Arabidopsis* that may contribute to high Al^{3+} tolerance in buckwheat (Che et al. 2018b).

V-ATPases

The H^+ electrochemical gradient across the tonoplast is relied on the vacuolar H^+ pumps (V-ATPases) that is another player in the regulation of plants response to Al^{3+} toxicity. Since malate and citrate are involved in both external Al^{3+} detoxification and vacuolar sequestration, tonoplast- and plasma membrane-localized organic acid anions (OAs) transport systems may antagonistically regulate external and internal Al^{3+} detoxification. Phenotypes of mutants affected in the V-ATPAse subunits (*VHA-a2* and *VHA-a3*) proposed a model in which interaction of V-ATPase with AHAs, ALMT1, and MATE regulates the allocation of OAs to efflux into vacuole lumen or apoplastic space. According to this model, transcription of *AHAs*, *ALMT1*, and *MATE* is preferentially activated in response to Al^{3+} stress while expression of *VHA-a2* and *VHA-a3* is suppressed leading to promoting cytosol OAs efflux into the apoplastic space to detoxify external Al^{3+}. When this transport is inhibited, VHA-a2 and VHA-a3 are reversibly activated to release OAs from the cytosol into the vacuole lumen, leading to internal Al^{3+} detoxification (Zhang et al. 2019c).

Al^{3+} Evokes Signaling Pathways and Affects the Expression of Several Genes

The molecular components of regulatory network related to Al^{3+} tolerance have been identified in recent years. An illustration on the Al-signaling pathway leading to the expression of Al-responsive genes is shown in Fig. 3.

The best characterized gene is *STOP1* (*Sensitive to Proton Rhizotoxicity 1*) that is involved in both proton (acidic environment in the rhizosphere) and Al^{3+} tolerance (Iuchi et al. 2007, 2008). AtSTOP1 is a C_2H_2-type zinc finger transcription factor that regulates the expression of multiple downstream Al^{3+} resistance genes, among them *AtALS3*, *AtMATE* and *AtALMT1* (Iuchi et al. 2007). *STOP2*, a *STOP1* homolog, has also been identified in *Arabidopsis*. STOP2 is localized in the nucleus and activates expression of some genes regulated by STOP1. However, the expression level of STOP2 is much lower than that of STOP1 (Kobayashi et al. 2014). In rice, OsART1 (Al^{3+} Resistance Transcription Factor 1), an ortholog of AtSTOP1, regulates the expression of numerous genes linked with Al^{3+} tolerance, such as *OsSTAR1* and *OsSTAR2* (rice homolog of *AtALS3*), *OsNrat1*, *OsALS1*, *OsFRDL4* (rice homolog of *AtMATE*) (Yamaji et al. 2009). A homolog of *OsART1* (*OsART2*), plays a supplementary role independent of the *OsART1*-regulated pathway in Al^{3+} tolerance of rice (Che et al. 2018a). In the species other than *Arabidopsis*, the functions of STOP1-like proteins, including CcSTOP1 (*Cajanus cajan*), GhSTOP1 (*Gossypium hirsutum*), GmSTOP1 (*Glycine max*), NtSTOP1

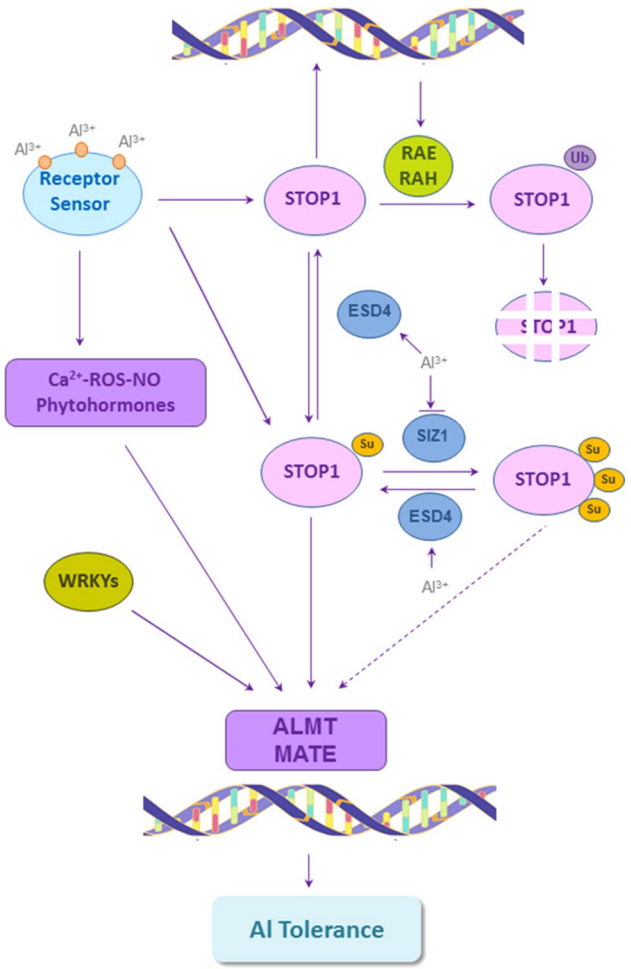

Fig. 3 Schematic illustration on the Al^{3+}-signaling pathway leading to the expression of Al^{3+}-responsive genes, ALMT (malate transporter) and MATE (citrate transporters) and increases Al^{3+} tolerance. Al^{3+} indirectly, or after binding to an unknown receptor or sensor, directly activates STOP1. STOP1 is constitutively expressed but is regulated through post-translation modifications. RAE is a F-box protein which contributes to ubiquitination (Ub) and degradation of STOP1 while transcription of RAE is stimulated by STOP1 providing a feed-back loop. Sumoylation of STOP1 through SIZ1-dependent or SIZ1-independent pathways, influence its stability and transcriptional activity depending on the level of sumoylation. SIZ1 a SUMO E3 ligase, is down-regulated by Al^{3+} while ESD4 a SUMO protease is up-regulated by Al^{3+} providing a complex network for STOP1 regulation. Other signaling events mediated by Ca^{2+}, reactive oxygen species (ROS), (NO) and phytohormones and other transcription factors (e.g., WRKYs) are also involved in the regulation of key genes (ALMT and MATE) and Al^{3+} response

(*Nicotiana tabacum*), SbSTOP1 (*Sorghum bicolor*), and ScSTOP1 (*Secale cereale* L.), have also been identified and shown to be necessary for the expression of some important genes for Al^{3+} tolerance in these species (Silva-Navas et al. 2021; Wei et al. 2021b). In barley, a homolog of *AtSTOP1* and *OsART1*, *HvATF1* (*Al-Tolerant Transcription Factor 1*) contributes to Al^{3+} tolerance through regulating some Al^{3+}-tolerance-related genes (Wu et al. 2020).

The regulation of STOP1 as the key player in the expressional control of Al^{3+}-induced genes has been extensively investigated. It has been demonstrated that the expression of *AtSTOP1* is unaffected by Al^{3+} stress, while its transcripts undergo posttranscriptional and posttranslational modulations. It has been demonstrated that, a dynamic regulation of STOP1 is critical for the balance between Al^{3+} resistance and plant growth (Zhang et al. 2019b). The level of STOP1 is regulated by a F-box protein encoded by *RAE1* (*Regulation of AtALMT1 Expression 1*) involved in degradation of STOP1 via ubiquitin-26S proteasome pathway, in *Arabidopsis* (Zhang et al. 2019b). There is a negative feedback loop between STOP1 and RAE1. STOP1 binds with the RAE1 promoter and up-regulates its expression leading to degradation of over-accumulated STOP1 and, thus, attenuates Al^{3+}-resistance responses (Zhang et al. 2019b). A homolog of *RAE1*, *RAH1* (*RAE1 Homolog 1*), is expressed in root caps and vascular tissues and directly interacts with STOP1 and catalyzes its ubiquitination. The expression of *RAH1* is induced by Al^{3+} suggesting that RAH1 plays also a role in the feedback regulation of STOP1 level (Fang et al. 2021b). The nucleocytoplasmic export of STOP1 mRNA is carried out by HPR1/RAE3 (Hyperrecombination Protein 1), a subunit of the *Arabidopsis* THO/TREX complex (Guo et al. 2020; Zhu et al. 2021).

The mono-SUMO (Small Ubiquitin-Like Modifier)-ylation of STOP1 at K40, K212, or K395 sites increases its stability, while blocking STOP1 SUMOylation increases Al^{3+} sensitivity through reduction of expression of STOP1-regulated genes (Fang et al. 2020). A SUMO protease, ESD4 (Early in Short Days 4) is responsible for deSUMOylation of STOP1 since mutation of *ESD4* enhances the SUMOylation level of STOP1 and consequently increases the expression of *AtALMT1*, which ultimately increases Al^{3+} resistance in the *esd4* mutants (Fang et al. 2020). However, there is a complex effect of SUMOylation on STOP1 activity and distinctive functions occur when STOP1 is SUMOylated at different sites. In contrast to single substitution of K212R/K40R, simultaneous substitutions of K40R and K212R mediated by SIZ1, a SUMO E3 ligase, attenuates the transactivation and DNA-binding activity of STOP1 (Xu et al. 2021). Interestingly, the protein level of SIZ1 is down-regulated by Al^{3+}, which decreases the SUMOylation of STOP1 at K40 and K212 residues to up-regulate the expression of *ALMT1* for Al^{3+} detoxification (Xu et al. 2021). However, STOP1 SUMOylation is dependent on two pathways, SIZ1-dependent and -independent pathways (Fang et al. 2021a). In addition, since mutation of *ESD4* increases *AtALMT1* expression while simultaneously reduces the expression of *AtMATE* and *RAE1*, it has been speculated that increased SUMOylation level of STOP1 has different effects on its association with the promoters of different target genes (Fang et al. 2020).

In addition to *STOP1* and *ART1*, there are also other Al^{3+}-responsive factors involved in the regulation of Al^{3+}

resistance genes (Iuchi et al. 2007; Yamaji et al. 2009). The plant-specific WRKY domain-containing proteins are transcription factor with 74 members in *Arabidopsis* (Rushton et al. 2010). AtWRKY46 was reported to act as a repressor of *AtALMT1* through direct binding with its promoter (Ding et al. 2013). Mutation of *AtWRKY46* show higher *AtALMT1* expression leading to increased malate exudation and higher Al^{3+} resistance compared with wild type *Arabidopsis* plants (Ding et al. 2013). Another WRKY protein, AtWRKY47 also indirectly influences the expression of *AtALMT1*, *AtMATE* and *AtALS3*. Since AtWRKY47 is involved in the balance of Al^{3+} distribution between apoplast and symplast (see section 'Al^{3+} binding with the root cell wall is a major determinant in the response of plants to Al^{3+}'), loss of WRKY47 function elevates leads to the increased cytosolic Al^{3+} and, thus, higher expression of *AtALMT1*, *AtMATE* and *AtALS3* (Li et al. 2020). OsWRKY22 as transcription factor, activates the expression of *OsFRDL4* (rice homolog of *AtMATE*) that enhances the citrate release from the roots in rice (Li et al. 2018). In addition to *OsART1/AtSTOP1* and *WRKY*, two *ASR* (*ABA Stress and Ripening*) genes, *OsASR1* and *OsASR5* encoding transcription factors, are involved in Al^{3+} tolerance in rice (Arenhart et al. 2013).

Candidate Signaling Molecules Acting Upstream of Gene Expression Pathway

As extensively described above, exposure of roots to Al^{3+} triggers the expression of many Al^{3+} resistance genes or contributes to post-transcriptional and post-translational activation or inactivation of Al^{3+}-responsive proteins. Al^{3+} may trigger these events directly or indirectly by binding with some proteins or with an unknown Al^{3+} sensor on the plasma membrane or in the cytosol. Due to an extraordinarily high charge-to-size ratio, Al^{3+} forms extremely strong covalent bonds with oxygen in the hydroxyl, carboxyl and phosphate groups (Poschenrieder et al. 2019). Such a high binding ability not only has severe consequences for the functioning of CWs, cell membranes and cell division described above, but may also trigger specific pathways if Al^{3+} binds with a specific receptor protein. Regardless the nature of Al^{3+} sensor or receptor, the pathways triggered by Al^{3+} involve some intermediate molecules that propagate the Al^{3+} signaling and lead to increased resistance or even alter or disrupt a number of cytosolic processes.

Cytoplasmic Ca^{2+} is a candidate that may mediate Al^{3+}-signaling. Al^{3+} entering the root cell via voltage-dependent cation channels is normally involved in Ca^{2+} influx that could trigger signaling or regulatory pathways in the cytosol (Kawano et al. 2004). Al^{3+} exposure is often associated with changes in cytosolic Ca^{2+} in roots and root hairs. Although reports on the Al^{3+}-mediated changes in the cytosolic Ca^{2+} include both increase (Rengel 1992) and decrease (Jones et al. 1998), Al^{3+}-induced changes in cytosolic Ca^{2+} has been suggested as a part of signaling pathways leading to enhanced resistance (Rengel and Zhang 2003; Liu et al. 2014).

The second candidate acting in Al^{3+} signaling pathways is the reactive oxygen species (ROS). The production of ROS by Al^{3+} is well-documented and it is not only associated with root cell damage (Yamamoto et al. 2003; Ranjan et al. 2021) but may also contribute to Al^{3+} signaling and regulatory pathways. Evidence supporting the signaling role of ROS in Al^{3+}-mediated induction of resistance include the temporal coincidence of ROS accumulation and induction of Al^{3+} resistance genes and related physiological processes, i.e., release of organic acid anions (Magalhaes et al. 2007; Sivaguru et al. 2013). In addition, Al^{3+}-induced ROS generation is specifically localized to the epidermal and outer cortical cell layers of the distal transition zone and was precisely coincident with the Al^{3+}-induced gene expression and the onset of the recovery from Al^{3+}-induced lesion (Sivaguru et al. 2013).

Effect of exogenous or endogenous NO on the alteration of Al^{3+}-induced modifications in the CW and the expression of CW modifying enzymes has been mentioned above. A signaling role for NO particularly as a downstream component of ROS has been proposed for several cellular events in Al^{3+} response pathway (He et al. 2012a; Sun et al. 2018). Plant hormones that are also important for plant Al^{3+} response (Kong et al. 2017) may have a cross-talk with NO signaling. NO may act as a regulator of plant hormones signaling (He et al. 2012b).

The possible involvement of these Al^{3+}-mediated changes in the cytosolic Ca^{2+}, ROS, NO and phytohormones, as putative signaling molecules that indirectly link Al^{3+} to activation of plant stress tolerance may help to establish some models for plant Al^{3+} response pathways. However, such models are not complete without convincing evidence on the Al^{3+} sensors and receptors and more information on the components of the pathways linking Al^{3+} sensing to the gene expression and consequent Al^{3+} resistance is needed.

MicroRNA are Also Involved in Plant Al^{3+} Tolerance

MicroRNAs (miRNA) are small non-coding RNAs acting in translational repression of target genes and play regulatory roles in plant stress response (Sunkar et al. 2012). There is evidence showing that miRNAs are involved in the plant response to Al^{3+} stress. In rice, *miRNA168*, *miRNA528*, and *miRNA399* are up-regulated under Al^{3+} stress, while *miRNA395* is down-regulated (Lima et al. 2011). In wild soybean, 30 Al^{3+}-responsive miRNAs were identified (Zeng et al. 2012). In barley, 50 Al^{3+}-responsive miRNAs were identified, among them *miR160*, *miR393*, and *PC-miR1* are

exclusively expressed in wild barley plants and involved in Al^{3+} tolerance (Wu et al. 2018b). The target genes of these miRNAs contribute to different processes including response to auxin, ROS scavenging, CW modification and carbon metabolism (He et al. 2014).

Al^{3+} Influences Plant Mineral Nutrition

Low pH and excess Al^{3+} in the soil solution may affect acquisition of water, macro- and micronutrients by plants. Al^{3+} interferes with the activity of ion channels and carriers, changes the overall rate of ion uptake in the root and disturbs cellular ion homeostasis (Bose et al. 2010). Thus, an imbalanced mineral nutrition and disturbances in the plant ion homeostasis is another mechanism through which plant growth and metabolism is affected under toxic Al^{3+} conditions. Accordingly, Al^{3+} tolerance may be also due to an ability to maintain adequate concentrations of macro- and micro-nutrients in roots and leaves.

Al^{3+} Reduces Nutrient Uptake and Interacts with the Function of Alkaline and Soil Alkaline Elements

In the tropics, abundant rainfall results in leaching anions, but also cations (K^+, Ca^{2+} and Mg^{2+}) from soil first layers, including rhizosphere, and causes acidification and higher soil Al^{3+} saturation. The most prevalent interference of Al^{3+} occurs with the uptake or transport of K^+, Ca^{2+} and Mg^{2+} (Schroth et al. 2003; George et al. 2012).

The binding of Al^{3+} with the pectin in the CW competitively hinders the apoplastic movement of Mg^{2+} (Rengel and Robinson 1989). In addition, Mg^{2+} uptake is inhibited by Al^{3+} through reduction in the activity of Mg^{2+} Transporter (MGT), a plasma membrane-localized transporter for Mg^{2+} (Kar et al. 2021b). Mutation in this transporter results in higher sensitivity to Al^{3+}, while its overexpression or excess Mg^{2+} alleviates Al^{3+} toxicity (Deng et al. 2006; Chen et al. 2012). It is also likely that, Mg^{2+} competes with Al^{3+} at the potential cellular Al^{3+} targets, such as DNA, ATP, proteins and cell organelles (Bose et al. 2011; Chen et al. 2012; Chen and Ma 2013).

Al^{3+} blocks the voltage-gated Ca^{2+} channels on the root plasma membrane (Rengel and Zhang 2003). There is also an interaction between Ca^{2+} and Al^{3+} in the binding sites at the PM and CW level. The competition between two ions at the root apoplast is likely the underlying mechanism for Al^{3+}-mediated disruption of cell Ca^{2+} homeostasis. Ca^{2+} bound with the phosphate residues of phospholipids stabilizes the PM (Shoemaker and Vanderlick 2003), while Al^{3+} replaces it and tightly binds with phosphatidylcholine on the membrane bilayers (MacKinnon et al. 2004). Using electrostatic interactions data at the root PM surface and molecular analyses in *Arabidopsis*, it has been demonstrated that Ca^{2+} alleviates root toxicity caused by Al^{3+} through reduction of PM negativity and stabilization of the CW (Kobayashi et al. 2013).

In addition to the structural roles, Ca^{2+} plays microdynamic roles in plants, including the participation in the cell signaling. Al^{3+} treatment affects free cytoplasmic Ca^{2+} concentrations in the Al^{3+}-sensitive but not in the Al^{3+}-tolerant maize genotypes (Garzón et al. 2011). In wheat, the Al^{3+}-mediated increase of cytosolic Ca^{2+} was higher in the Al^{3+} susceptible than in the Al^{3+} resistant genotype (Zhang and Rengel 1999). This evidence confirmed modification of Ca^{2+} signaling as an early event under Al^{3+} toxicity conditions. Al depolarizes membranes in the Al^{3+}-susceptible wheat (Ahn et al. 2004) and tobacco cells (Sivaguru et al. 2005). The time-course of PM depolarization co-occurred with the increase of cytosolic Ca^{2+} concentration and accumulation of callose (Sivaguru et al. 2005). In contrast to the above-mentioned observations, however, a significant depolarization in root tips was observed in the Al^{3+}-tolerant but not in the Al^{3+}-sensitive wheat genotypes (Wherrett et al. 2005).

It has been reported that maize genotypes with higher Al^{3+} tolerance retained higher K^+, Ca^{2+} and Mg^{2+} concentrations under Al^{3+} stress (Giannakoula et al. 2007). This could be explained by a direct effect of Al^{3+} on the uptake of these nutrients and/or by higher root elongation rates in the tolerant genotypes enabling them to explore a larger volume of soil (Silva et al. 2010). Mg^{2+} and Ca^{2+} deficiencies may also result from low soil pH that acts synergistically with Al^{3+}, impairs root elongation and reduces the uptake of these nutrients (Poschenrieder et al. 1995). Mg^{2+} supplementation alleviates the root growth inhibition caused by Al^{3+} in rice and bean probably through enhancement of citrate efflux (Yang et al. 2007). In hydroponically grown tea plants, the maintenance of Ca^{2+} and Mg^{2+} homeostasis in young leaves (Tolra et al. 2020) or even higher uptake of these nutrients found in Al^{3+}-supplemented plants (Fung et al. 2008) suggest that Ca^{2+} and Mg^{2+} homeostasis is a characteristic of Al^{3+} hyperaccumulators (Tolra et al. 2020).

Potassium plays important roles in the osmoregulation, cell elongation and growth. The more growth inhibitory effects in Al^{3+}-sensitive genotypes of wheat suggest higher disturbance in the osmotic balance and, consequently, lower cell elongation in these genotypes compared with tolerant ones (Silva et al. 2010). Al^{3+} toxicity causes significant reduction of K^+ uptake following Al^{3+}-mediated blockage of Shaker voltage-dependent K^+ channels in root hairs (Gassmann and Schroeder 1994). Al^{3+} alters the activation kinetics of K^+ channel KAT1 in *Arabidopsis* (Liu and Luan 2001).

It has been suggested that Al^{3+}-induced depolarization of membranes causes enhanced K^+ efflux in sensitive plants (Ahn et al. 2004). Furthermore, K^+ efflux accompanies

the exudation of organic acid anions (Samac and Tesfaye 2003; Gonçalves et al. 2005), suggesting that reduction of K^+ counterbalances the extrusion of organic acid anions. However, short-term exposure to Al^{3+} that induces reduction of K^+ concentration is not accompanied by malic acid extrusion in the roots of Al^{3+}-susceptible plants (Silva et al. 2010), implying that the mechanisms involved in Al^{3+}–K^+ interaction need to be further studied. Another hypothesis for the low concentration of K^+, Ca^{2+} and Mg^{2+} found in Al^{3+}-stressed plants is that the efflux these cations from the roots is a mechanism for maintaining the root surface pH above 5.0 (Silva et al. 2010).

Al^{3+} Influences Nitrogen Uptake and Assimilation

Nitrogen (N) is available for plants mainly in the form of ammonium (NH_4^+) and nitrate (NO_3^-) in soil solution. Plant species differ in their N form preference. In general, Al^{3+}-tolerant species adapted to acidic soils, prefer NH_4^+ while Al^{3+}-sensitive species adapted to neutral, calcareous and alkaline soils prefer NO_3^- as N form (Marschner 1995). In Al^{3+}-sensitive species, the uptake of NO_3^- is inhibited while much less effect of Al^{3+} is observed on NH_4^+ uptake (Zhao and Shen 2018). In contrast, *Amaranthus blitoides*, an Al-accumulating species that grows as weed in tea gardens, has considerably higher N and protein concentrations and nitrate reductase activity under Al^{3+} treatment (Roghieh Hajiboland, unpublished data).

Al^{3+} Toxicity Influences Fe Homeostasis of Plants

In acidic soils, concentrations of not only Al^{3+} but also Fe^{2+} can be raised to toxic concentrations in the soil solution leading to Fe^{2+} toxicity. Excess Fe^{2+} accumulation in plant tops results in oxidative stress and is associated with leaf symptoms including necrotic spots (George et al. 2012).

In tea plants grown hydroponically in the absence of Al^{3+}, Fe^{2+} concentration in young leaves reached to the Fe^{2+}-toxicity threshold while Al^{3+} supplementation reduces its uptake and transport (Hajiboland et al. 2013a). Hematoxylin staining of tea roots showed that Al^{3+} inhibits the accumulation of Fe^{2+} in the roots and less Fe^{2+} is bound with root surfaces (Hajiboland et al. 2013a). Considering the root hair and epidermal cells are the main targets for both Al^{3+} and Fe^{2+} in tea, competition between these two elements is likely the explanation of how Al^{3+}-induced reduction of Fe^{2+} accumulation in the leaves and roots of this species occur (Hajiboland et al. 2013a). Competition between Al^{3+} and Fe^{2+} for citrate as a ligand in xylem loading and in the long-distance transport is probably the mechanism for less leaf Fe^{2+} accumulation in Al^{3+}-supplemented tea plants (Hajiboland et al. 2013a). In *Eucalyptus,* Al^{3+} induces reduction in Fe^{2+} concentration of leaves and roots under both low and excess Fe supply (Nguyen et al. 2005). In addition, Al^{3+} treatment modifies Fe^{2+} distribution within the shoots, as reduction of Fe^{2+} concentration in the leaves but increasing its storage in the stems (Nguyen et al. 2005). In addition, Al^{3+} is likely involved in the precipitation of ferric phosphate and other ferric compounds in the leaves leading to reduction of Fe^{2+} in leaf cell sap and impairment of free Fe^{2+} accumulation and toxicity effects (Nguyen et al. 2005). *Tradescantia fluminensis* and *Commelina communis*, weed species of tea gardens, show high sensitivity to Fe^{2+} deficiency when grown in nutrient solution with Al^{3+} while plants not exposed to Al^{3+} remains green under low Fe^{2+} supply conditions (Fig. 4, unpublished data). Reduction of Fe^{2+} uptake and transport mediated by Al^{3+} may be an important strategy for plants grown in acidic soils and could be considered an adaptive mechanism for plants under these conditions. Soil acidity is associated not only with Al^{3+} toxicity but also with an enhanced availability of Fe^{2+} and Mn^{2+} (Fernando and Lynch 2015) that may lead to toxicity of both elements (Foy 1984). These results show that the Al^{3+}-induced growth improvement reported for Al-accumulators such as tea is at least partly related to the mitigation of a latent Fe^{2+} toxicity occurring in the absence of Al^{3+} (Hajiboland et al. 2013a). Iron is a Fenton metal and at excess concentrations causes oxidative damages to cellular structures (Broadley et al. 2012).

Toxic Effect of Al^{3+} is Related to Plant P Nutritional Status

Phosphorus (P)-deficiency is another nutritional limitation under acidic soil conditions (Kochian et al. 2004; Hawkesford et al. 2012). Thus, plants growing in acidic soils often suffer from both P deficiency and Al^{3+} toxicity. On the other hand, Al^{3+} is prone to form complexes with P and co-precipitate both in the rhizosphere soil, root surface and even within the plant cells that modifies the Al^{3+} activity and P availability for metabolic pathways. Thus, interaction between Al^{3+} and P in the soil and within plants is a factor of Al^{3+} tolerance.

Co-occurrence of Al^{3+} toxicity and P deficiency suggests that plants native to acidic soils employ mechanisms for higher utilization of sparingly soil P sources simultaneous with detoxification of Al^{3+}. In agreement with this, buckwheat (*Fygopyrum esculentum* Moench), which also accumulates Al^{3+} in their leaves (Zheng et al. 2005), shows higher P efficiency (Zhu et al. 2002). For tea plants grown hydroponically, the optimum growth is attained under P supply as low as 50 µM that is much lower than the required concentration range for macronutrients, including P (Salehi and Hajiboland 2008). Higher internal P use efficiency in tea could be partly attributed to a high rate of redistribution of

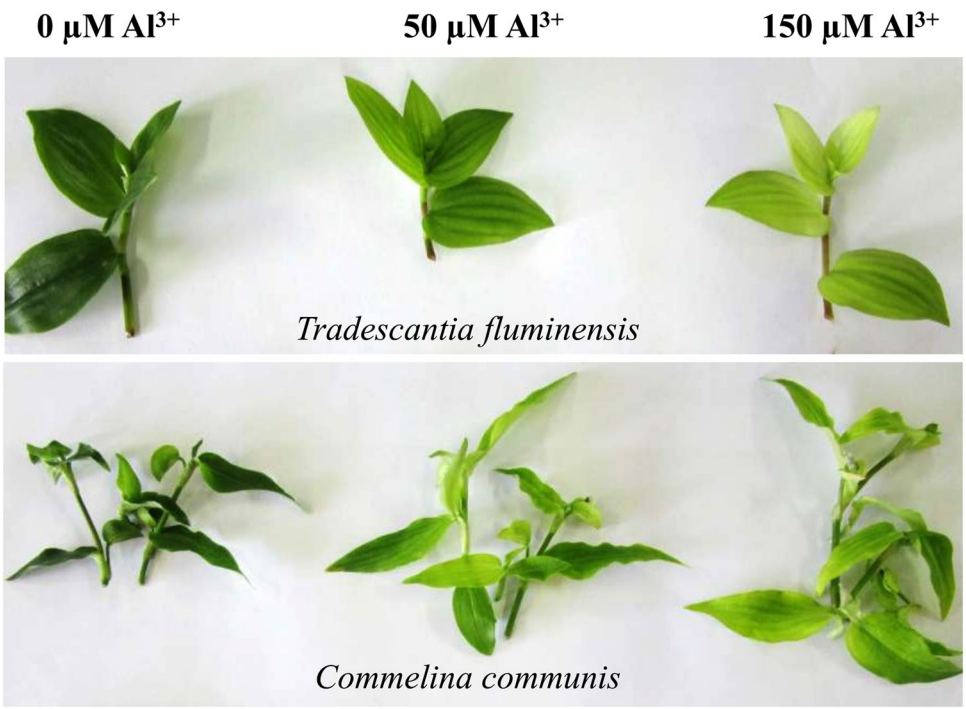

Fig. 4 Leaf chlorosis in two weed species of tea gardens grown hydroponically under low Fe supply and different Al^{3+} concentrations. Plants were grown for two weeks under three different Al^{3+} levels (0, 50 and 150 µM as $AlCl_3$) then Fe was completely omitted from the nutrient solution. Two weeks after Fe deprivation, leaf symptoms were detected in the young leaves of Al-treated plants

P from mature to young leaves in this species (Hajiboland and Salehi 2014).

Considering the precipitation of Al^{3+}–P complexes in the soil, in the nutrient solutions and even at root surfaces, it is well expected that Al^{3+}-toxicity in sensitive species can be alleviated by application of P. This effect has been observed in sorghum (Tan and Keltjens 1990), maize (Gaume et al. 2001), *Lespedeza bicolor* (Sun et al. 2008), and *Citrus grandis* (Jiang et al. 2009b). Al forms insoluble complexes with P, like $Al_4(PO_4)_3$ that precipitate and accumulate on the root surface, thus reducing Al^{3+} toxicity (Pellet et al. 1997). The formation of insoluble and non-toxic Al-P complexes in the CW of the root surfaces, delays Al^{3+} entry into the cytosol. Significant correlations between Al^{3+} and P concentrations have been found in the CW of *Avena sativa* (Marienfeld and Stelzer 1993) and maize (Gaume et al. 2001).

The Al^{3+}-P complexes may also be formed within plant cells and, thus, species or genotypes with higher P uptake efficiency may be more successful in the internal detoxification of Al^{3+} than P-inefficient ones. It has been observed that P-efficient soybean genotypes have higher Al^{3+} tolerance than P-inefficient ones (Liao et al. 2006). Enhancement of Al tolerance with P application was observed in tolerant species *Lespedeza bicolor* but not in the sensitive species *L. cuneata* that was related to an efficient P uptake and transport to the shoot in the former species (Sun et al. 2008). Similarly, Al^{3+}-tolerant *Citrus sinensis* shows higher P uptake than the Al^{3+}-sensitive *C. grandis* (Yang et al. 2011c), suggesting, once more, an association between the ability for higher P uptake and Al^{3+} tolerance. Similar results were obtained in cowpea (*Vigna unguiculata*) (Jemo et al. 2007). An active transport of Al^{3+}-P complex to vacuoles has been demonstrated in Al^{3+} resistance maize genotypes (Vazquez et al. 1999). Since morin positively stains Al^{3+}-P complexes (Eticha et al. 2005b), higher signal from the root CW indicated that co-precipitation of P and Al^{3+} in CW is a mechanism for high Al^{3+} tolerance in buckwheat (Zheng et al. 2005).

Since both Al^{3+} toxicity and P deficiency induce the root exudation of organic acid anions (OAs) (Chen and Liao 2016; Wu et al. 2018a), an interaction is expected between Al^{3+} toxicity and P nutritional status at the level of external detoxification of Al^{3+}. In cowpea, malate is released in response to toxic concentrations of Al^{3+}, while P deficiency induces mainly citrate exudation (Jemo et al. 2007). When both Al^{3+} toxicity and P deficiency co-occur, higher malate and citrate exudation is detected in the Al^{3+}-resistant compared with Al^{3+}-sensitive genotypes of this species (Jemo et al. 2007). In soybean, the release of citrate is responsive to Al^{3+} and low P supply induces exudation of oxalate while the release of malate was triggered by both treatments (Liao et al. 2006). In addition to species-specific pattern, OAs secretion differs under P deficiency and Al^{3+} stresses depending on root zone, developmental stage, and the lag time after imposition of these stresses (Dong et al. 2004; Wang et al. 2007a). There is also a variation of organic P mobilization among OAs depending on the soil type and a concentration dependency of the amount of malate, citrate and oxalate where greater OAs concentrations leads to higher P mobilization (Richardson et al. 2022).

Despite the fact that, OAs release is induced under P deficiency conditions, under severe P deficiency that reduce provision of carbon skeletons or in plant species with inherently low organic acid release in response to P limitation, plants may not be able to sufficiently release OAs for Al^{3+} detoxification. In soybean cultivars with low ability for citrate release under P deficiency, the Al^{3+}-induced exudation of OAs was detectable only in the P-sufficient plants (Nian et al. 2003). When divided root system experimental approach is used for this species, it was observed that higher P nutritional status is associated with higher OAs exudation (Liao et al. 2006). As a result, the presence of Al^{3+} in acidic and low-P soils provide possibility for secretion of OAs and mobilization of P, and it is probably a mechanism against P deficiency.

Release of phosphate as inorganic P (Pi) from the root apical region is another mechanism in Al^{3+}-resistant species or genotypes. Inorganic phosphate release from the root tip leads to the formation of Al^{3+}–P complex in the apoplast, on the root surface or in the rhizosphere (Pellet et al. 1996). Phosphate released from the roots raises the rhizosphere pH because of its high affinity for H^+ that, in turn, leads to reduction of Al^{3+} activity in the rhizosphere (Pellet et al. 1996). Root release of Pi has been observed to be the Al resistance mechanism in wheat cultivars (Pellet et al. 1996) and in *A. auriculiformis* (Nguyen et al. 2003) but not in buckwheat, which is Al^{3+}-accumulator (Zheng et al. 2005).

Other aspect of the Al^{3+}-P interaction is found at the CW and plasma membrane. Under P deficiency conditions, the pectin concentration in the root cells decreases in *Arabidopsis* (Zhu et al. 2012a) and rice (Maejima et al. 2014) and that was associated with less Al^{3+} accumulation in the shoots and roots of P-deficient plants (Maejima et al. 2014). In agreement with this, less Al^{3+} accumulation in the P-deficient rice plants compared with P-sufficient ones was evidenced with histochemical reactions of hematoxylin at their root tips (Maejima et al. 2014).

Under P starvation, a PM remodeling process has been observed in root cells, as a replacement of phospholipids with galactolipids (Andersson et al. 2003; Russo et al. 2007; Tjellström et al. 2010). Since Al^{3+} is bound to PM phospholipids and induces reduction of its fluidity and increases its permeability (MacKinnon et al. 2004), it is expected that their replacement with non-P-containing galactolipids under P deficiency conditions leads to prevention of Al^{3+} binding with the PM and protection of root cells membranes from Al^{3+}. It has been demonstrated that double mutants of *Arabidopsis* for *PAH* (*pah1pah2*) that is unable to replace phospholipids with galactolipids is more sensitive to Al^{3+} than wild-type plants under P deficiency conditions (Kobayashi et al. 2013).

Molecular genetic studies revealed also a crosstalk between Al and P that is expressed under toxic Al^{3+} concentrations and P starvation. A casein kinase 2 (CK2) that is responsible for phosphorylation of SOG1 confers Al^{3+} tolerance and the inactivation of *CK2* and *SOG1* prevents meristem exhaustion under P deficiency, suggesting the involvement of a low P-induced cell cycle checkpoint that depends on the DNA damage activator ATM (Wei et al. 2021a). Furthermore, both STOP1 and ALMT1 contribute to low-P signaling as the primary root growth is insensitive to P deficiency in the mutants of either gene (Balzergue et al. 2017). HPR1/RAE3 that is responsible for the regulation of nucleocytoplasmic export of *STOP1* mRNA (see section 'Al^{3+} evokes signaling pathways and affects the expression of several genes'), along with RAE2/TEX1, another protein with the same function, are not only involved in Al^{3+} resistance but also contribute to plant response to Pi availability. Mutations in *RAE3* and *RAE2* impair plants response to P deficiency, and stronger effect in *rae2* mutants suggests that the role of *RAE2* is more important for plant response to Pi compared with *RAE3* because it also regulates the AtALMT1-independent pathway (Zhu et al. 2021). Not only Pi, but also Fe^{2+} (at excess concentrations) is involved in a complex signaling network involved with STOP1 (Godon et al. 2019; Mercier et al. 2021). Although all the components of such network have not yet been identified, it could be speculated that the soil chemical link between Al^{3+} and Fe^{2+} toxicity and low P availability may lead to selective pressures for pleiotropic mechanisms that ultimately enable plants to have a concurrent adaptation to tolerate Al^{3+} and Fe^{2+} toxicities and P deficiency (Chen et al. 2022).

An interaction Exists Between Al^{3+} and Boron in the Cell Wall

In acid soils found in areas with high rainfall, boric acid is washed out from the soils and boron (B) deficiency becomes a common nutritional problem (Shorrocks 1997). On the other hand, structural similarity of $B(OH)_3$ with $Al(OH)_3$ as the major Al species within plants (Kochian 1995), and considering the CW as the common target of both molecules, an interaction between these elements is plausible.

In Al^{3+}-sensitive species, B deficiency exacerbates Al^{3+} toxicity and supra-optimal concentration of B mitigates Al^{3+}-mediated reduction of root growth (Yang et al. 2004; Stass et al. 2007; Corrales et al. 2008; Jiang et al. 2009a; Yu et al. 2009). This effect results probably from the B-mediated modification in the Al^{3+} speciation and/or compartmentation in the roots and less Al accumulation in the leaves (Jiang et al. 2009a). In Al-accumulating species such as tea, growth of B-starved plants is resumed by Al^{3+} supply brought about by an increase in the B uptake and its long-distance transport into shoot in Al^{3+}-supplemented plants (Hajiboland et al. 2014).

There are also interactions between Al^{3+} and B at binding sites in the CW. However, the mechanisms for these

interactions are not well explored. In Al^{3+}-sensitive species, modifications in the CW properties occurring under B deficiency conditions affect Al^{3+} binding with the CW in the root apex and Al^{3+} toxicity (Yang et al. 2004; Stass et al. 2007; Yu et al. 2009). In B-deficient common bean, higher proportion of unmethylated pectin in the CW of root tips increases the apoplastic Al^{3+} binding in this species (Stass et al. 2007). Similarly, CW-bound Al^{3+} was significantly higher under B deficiency conditions in pea (Yu et al. 2009). Despite an alleviating effect of optimal concentrations of B on root elongation in cucumber under Al^{3+} stress, this was not linked with lower Al^{3+} accumulation suggesting that B may induce alterations in the Al^{3+} speciation and/or compartmentation in the root tips (Corrales et al. 2008). In agreement with the postulated effect of B through CW pectin, different concentrations of B supply did not influence root elongation or Al^{3+} accumulation in the root apoplast of maize, a monocot with low pectin in the CW (Corrales et al. 2008).

Al^{3+} Toxicity and Water Status

Because Al^{3+} stress inhibits root elongation, plants might show undersized root systems depending on the level of Al^{3+} resistance/tolerance. In contrast to deep roots, which are generally associated with improved water and nutrient uptake (Lynch and Wojciechowski 2015; Figueroa-Bustos et al. 2020), plants with short roots will explore a small fraction of soil lowering their chances to find water and nutrients. For instance, wheat cultivars with contrasting root system size shows different grain yield under terminal drought, with the performance related mainly to water use and with a strong association between root system size and phenology, leaf area, and shoot biomass (Figueroa-Bustos et al. 2020).

When focusing on Al^{3+} stressed soil, the growth and proliferation of the root system in an Al^{3+}-resistance durum wheat line improved terminal drought (Liu et al. 2022). It was reported that 12.9 cm increase in root length in the Al^{3+}-resistant durum wheat line resulted in 1 g of grain yield under terminal drought (Liu et al. 2022). Even in nutrient solution, where water is constantly available, exposure to Al^{3+} in *Citrus limonia* ('Rangpur' lime) reduced the stomatal capacity of plants to respond to oscillations in vapor pressure deficit (Silva et al. 2018). Similar response was observed for tomato growing under Al^{3+} stress in nutrient solution where Al^{3+} reduced root hydraulic conductance and decreased plant water transport capacity (Gavassi et al. 2020). 'Rangpur' lime in nutrient solution under the same Al^{3+} stress showed up-regulation of the gene encoding 9-cis-epoxycarotenoid dioxygenase (NCED), a key enzyme in abscisic acid (ABA) biosynthesis, and an increase in ABA in roots and leaves (Gavassi et al. 2021).Thus, better drought tolerance might be an additional benefit of a greater Al^{3+} resistance.

Aluminum Exclusion Strategy is Relied on the Root Release of Organic Acid Anions

Preventing the entrance of toxic Al^{3+} inside the cell, through an exclusion mechanism, is one of the strategies by which plants cope with Al toxicity. The exclusion mechanism relies on the ability of the plant root to exudate Al^{3+}-chelating compounds and the most studied Al^{3+} exclusion mechanism is the efflux of low molecular weight organic acids. At the near-neutral pH of the cytoplasm, most organic acids occur as anions, i.e., dissociated from their protons, and they are probably transported outside the cell as anions and not acids (Ma et al. 2001; Ryan et al. 2001). The organic acid anions (OAs) exuded by the roots are thought to chelate the toxic Al^{3+} both in the apoplast and rhizosphere, but the main location seems to be the apoplast (Kopittke et al. 2017). Once chelated by OAs, Al^{3+} becomes less available and a lower amount of Al^{3+} will bind with the negatively charged CW components leading to a lower impact on root elongation (Horst et al. 2010).

The concept that OAs were beneficial to plants under Al^{3+} stress was available long time ago when citrate added to the nutrient solution allowed greater root growth, nutrient concentration and yield in maize (Bartlett and Riego 1972). However, the evidence that Al^{3+}-resistant plants were able to exude OAs from the roots were published years later. In these studies, more malate was exuded by roots of an Al^{3+}-resistant wheat cultivar (Kitagawa et al. 1986) and more citrate was secreted by roots of an Al^{3+}-tolerant snapbean cultivar (Miyasaka et al. 1991) than from Al^{3+}-sensitive control plants. Nevertheless, the most detailed experiments about OA exudation by plant roots under Al^{3+} stress were performed with near-isogenic lines of wheat contrasting for Al^{3+}-resistance (Delhaize et al. 1993). That study stablished the main characteristics of the malate exudation by wheat plants as: (1) the efflux was specifically induced by Al^{3+}; (2) ten times more exudation occurred in Al^{3+}-resistant genotypes than in Al^{3+}-sensitive ones; and (3) the root apex was responsible for the greatest amount of malate exudation. Subsequently, a high correlation was found between wheat root length and malate efflux by the root apex (Ryan et al. 1995) and the Al^{3+}-stimulated malate efflux was considered the main contributor of Al^{3+} resistance in wheat. Years later, wheat was also found to exuded citrate although in a constitutive fashion and not induced by Al^{3+} (Ryan et al. 2009).

Malate and citrate are indeed the main OAs conferring Al^{3+} resistance in plants. The reason why these OAs are so widespread involved in Al^{3+} resistance may be because they are ubiquitous in living cells and metabolically 'cheap' to synthesize (Ryan and Delhaize 2010). Oxalate has also been detected in several woody plants (Brunner and Sperisen 2013) but it is rarely reported in herbaceous species, as in

Fagopyrum esculentum (Ma et al. 1997; Zheng et al. 1998) and *Colocasia esculenta* (Ma and Miyasaka 1998). Even *Styrax camporum*, a moderately Al-accumulating species from the Cerrado vegetation in South America, where soils are acidic and rich in Al^{3+}, was found to exude OAs in response to Al^{3+} concentrations in the root environment (Bittencourt et al. 2020).

Al resistance can be associated with one specific OA as, for example, in barley, maize, and sorghum where citrate efflux is closely associated with Al^{3+} resistance (Pellet et al. 1995; Piñeros et al. 2002; Zhao et al. 2003; Magalhaes et al. 2007). However, the strategy of exudating more than one Al^{3+}-chelating OA is also observed. For instance, besides wheat, plant species where both malate and citrate are exuded by the root apex and have been associated with Al^{3+} resistance include *Avena sativa*, *Brassica napus*, *Raphanus sativus* (Zheng et al. 1998), *Helianthus annuus* (Saber et al. 1999), *Secale cereale* (Collins et al. 2008; Silva-Navas et al. 2012; Santos et al. 2018), Triticosecale sp. (Stass et al. 2008), *Arabidopsis thaliana* (Liu et al. 2009), *Brachypodium distachyon* (Contreras et al. 2014), and some species of woody plants (Brunner and Sperisen 2013).

Besides differing in the type of OAs exuded by the roots, plants also differ in the time required for the efflux after the Al^{3+} exposure (Ma et al. 2001). Also, OA efflux is not necessarily constant as, for example, in rice bean where citrate efflux from the root apex is biphasic showing an early phase with low efflux and a later phase of large citrate exudation (Liu et al. 2018b). Additionally, there are differences in the strength in which each of these OA chelates the toxic Al where the formation constant is 9.6 for Al:citrate, 6.1 for Al:oxalate, and 5.7 for Al:malate is 5.7, meaning that the order of strength of Al^{3+} chelation is citrate > oxalate > malate (Ryan et al. 2001). The greater formation constant for Al:citrate has been used to explain why citrate is exuded by the root of so many plant species (Kochian et al. 2004). However, studies with bread wheat show that the exudation of citrate is not necessarily more beneficial to Al resistance than the efflux of malate. For example, near-isogenic lines obtained by crossing cultivars contrasting for malate and citrate efflux have shown that citrate efflux is less important in wheat plants already showing greater malate exudation (Han et al. 2016). Most of the wheat genotypes with alleles associated with greater efflux of both malate and citrate did not outperform the genotypes with alleles for greater malate efflux but lower citrate exudation (Pereira et al. 2015). Also, the frequency of the allele linked to greater citrate efflux did not increase over 90 years of wheat breeding in Brazil, which might indicate that citrate efflux in wheat has little selection pressure and, consequently, low adaptive power for Al^{3+} resistance (Aguilera et al. 2016). One explanation for the lower importance of citrate for Al^{3+} resistance in wheat is that around tenfold less citrate is secreted by the wheat root apex when compared to malate (Ryan et al. 2009, 2014). In contrast, durum wheat lines with the allele associated with greater citrate efflux performed better in acidic soil than lines with the allele for higher malate efflux (Han et al. 2016).

The molecular basis for the efflux of malate and citrate is currently known for several plant species. Clearly, OAs need to be synthesized in order to be exuded. In fact, an increased synthesis of citrate has been firstly associated with greater Al resistance in tobacco and papaya (de la Fuente et al. 1997). However, the synthesis and concentrations of OAs in the cell tend to be strictly regulated (Ryan et al. 2001). For instance, even though Al^{3+}-resistant wheat plants release malate from their roots, the activities of phosphoenolpyruvate carboxylase or NAD-malate dehydrogenase are not different between Al^{3+}-resistant and Al^{3+}-sensitive wheat genotypes (Ryan et al. 1995). Similarly, the production of malate and citrate by root cells do not regulate the efflux of OA in triticale (Hayes and Ma 2003). Thus, it is the ability to transport the OAs to the outside of the plant cell that is more associated with Al^{3+} resistance, and OAs channels and transporters are pivotal in this process.

The first anion channel associated with Al^{3+} resistance in plants was characterized in wheat and named as TaALMT1 (Sasaki et al. 2004). The characteristics of the *TaALMT1* gene that supports its role as membrane-bound protein that releases malate from the root apex include its role as membrane protein, higher expression in root apices of Al^{3+}-resistant genotypes, activation of an inward current by $AlCl_3$ when the *TaALMT1* cDNA and malate were injected in *Xenopus laevis* oocytes, and activation of malate efflux by Al^{3+} in transgenic rice and tobacco expressing *TaALMT1* (Sasaki et al. 2004). Because, at that time, TaALMT1 did not belong to any existing protein family, it became the founding member of the ALMT (aluminum-activated malate transporter) protein family. By similarity to *TaALMT1*, several other members of the ALMT family have been isolated in plants and associated to Al^{3+} resistance (Fig. 5). However, members of this family are not only linked to Al^{3+} resistance but involved in a number of physiological processes (Sharma et al. 2016) including being permeable to GABA (gamma-aminobutyric acid), which might explain why malate efflux is negatively correlated with endogenous GABA concentrations in wheat root apices (Ramesh et al. 2015, 2018).

Besides the ALMT family, other protein family that have been linked to OA efflux by the root apex of plants is the MATE (multidrug and toxic compound extrusion) family, which is known for a long time to facilitate the efflux of a variety of secondary compounds in prokaryotic cells (Takanashi et al. 2014). MATE transporters are also associated with a number of physiological functions in a plant cell (Takanashi et al. 2014; Kar et al. 2021a) and

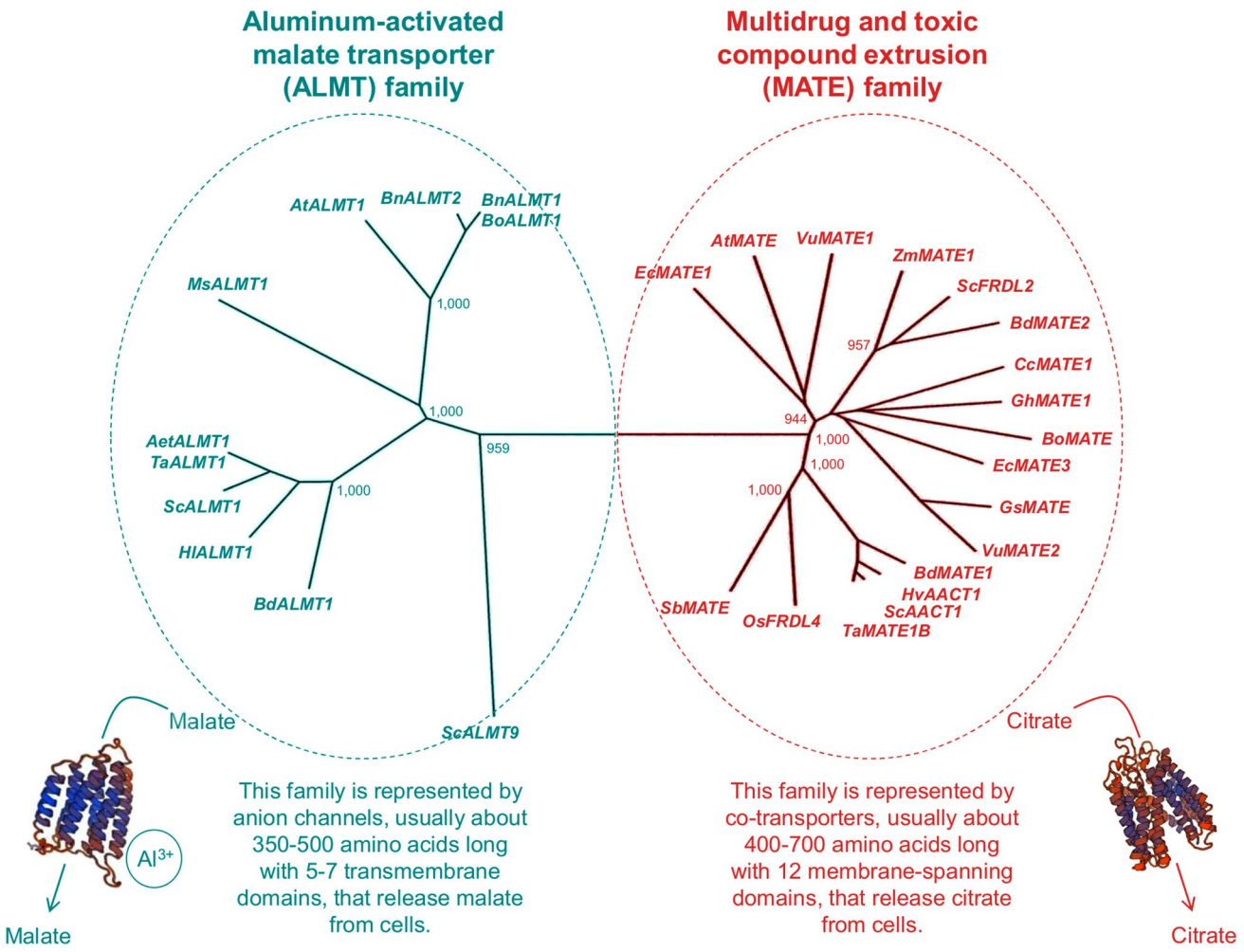

Fig. 5 Unrooted phylogenetic tree representing the relationship among ALMT and MATE transporters. Although members of these families are implicated in a number of functions, the proteins used to build this tree have all been associated with aluminum resistance in several plant species. Because the proteins from both families have the same function (OA efflux by the root apex associated with Al^{3+} resistance) but they share no common ancestral, they represent a case of convergent evolution. The phylogenetic tree was constructed using the neighbor-joining method (Saitou and Nei 1987). The numbers in the main branches indicate the bootstrap based on 1000 replicates. Three-dimensional structures for ALMT and MATE transporters were built by SWISS-MODEL (Biasini et al. 2014) based on sequences of *TaALMT1* and *HvAACT1*. GenBank accession numbers used here are *AetALMT1* (DQ072271), *AtALMT1* (AEE28289), *AtMATE* (AF448231), *BdALMT1* (XM_003579669), *BdMATE1* (XM_003558439), *BdMATE2* (XM_010236379), *BnALMT1* (BAE97280), *BnALMT2* (BAE97281), *BoALMT1* (XM_013745011), *BoMATE* (KF031944), *CcMATE1* (MF377547), *EcMATE1* (AB725912), *EcMATE3* (AB725914), *GhMATE1* (MG780413), *GsMATE* (XM_006575183), *HlALMT1* (AB792703), *HvAACT1* (AB302223), *MsALMT1* (GU550122), *OsFRDL4* (AB608020), *SbMATE* (EF611342), *ScAACT1* (EU399684), *ScALMT1* (DQ158087), *ScALMT9* (KY094467), *ScFRDL2* (AB571882), *TaALMT1* (AB081803), *TaMATE1B* (KC152454), *VuMATE1* (KM090855), *VuMATE2* (KR494281), and *ZmMATE1* (FJ015155)

their first implication in plant Al^{3+} resistance came from studies in barley and sorghum. Both these species have MATE transporters, SbMATE in sorghum and HvAACT1 (also known as HvMATE) in barley, that are responsible for Al^{3+} resistance through the efflux of citrate by the root apex (Furukawa et al. 2007; Magalhaes et al. 2007; Wang et al. 2007b). After these first studies, MATE transporters from a number of plant species have been associated with citrate efflux and Al^{3+} resistance (Fig. 5). A large number of members from both the *ALMT* and *MATE* gene families have been detected in plant genomes and the identification of which specific gene is responsible for the efflux of malate or citrate by the root apex is extremely important for assertive improvement of Al^{3+} resistance (Ma et al. 2020; Duan et al. 2022; Kar et al. 2021a). Up to this date, the transporter responsible for the efflux of oxalate, which may correspond to a different family of transporters, has not been identified.

Members of the ALMT and MATE families that are responsible for the OA efflux share no sequence homology (Fig. 5). Because they have a similar function (OA efflux)

but share no common ancestors, these protein families have convergently evolved (Ryan and Delhaize 2010). The evolution of these families likely arose from mutations that co-opted malate and citrate transport proteins from other functions (Ryan and Delhaize 2010). Transposable elements are responsible for a number of these mutations (Pereira and Ryan 2019) that are especially important if they happen in regulatory regions (promoters), which alter the level and/or location of the gene expression (Magalhaes et al. 2007; Fujii et al. 2012; Tovkach et al. 2013). The increased number of *cis*-elements associated with transcription factors from different families, like Cys_2His_2-type zinc-finger (STOP1 and ART1) and WRKY (OsWRKY22), have been proposed to improve interaction between the transcription factors and the promoter, which will increase the OA transporter expression and consequently the OA efflux (Yokosho et al. 2016; Arbelaez et al. 2017; Daspute et al. 2018; Li et al. 2018; Melo et al. 2019). Other changes in the promoter of genes responsible for OA efflux explain a large portion of the differences in plant performance under Al^{3+} stress (Delhaize et al. 2012). For example, blocks of repeats and insertions in the promoter regions of the genes *TaALMT1*, *SbMATE*, *HvAACT1*, and *TaMATE1B* are highly correlated with higher gene expression, larger efflux of malate or citrate and increased Al^{3+} resistance in wheat, sorghum, and barley (Sasaki et al. 2006; Magalhaes et al. 2007; Fujii et al. 2012; Tovkach et al. 2013).

Molecular markers based on these promoter regions have been used to characterize germplasm (Pereira et al. 2015; Aguilera et al. 2016; Ferreira et al. 2018) and track the introgression of a superior allele into a high yielding Al^{3+}-sensitive cultivar (Soto-Cerda et al. 2015). The introgression of superior alleles of OA transporter genes can led to advantages as 0.6 ton/ha increase in grain when sorghum plants expressing *SbMATE* were grown on acidic soil (Carvalho Jr et al. 2016) and 21 to 48% more yield in maize hybrids with the *ZmMATE1* superior allele growing in Al^{3+}-rich soil (Vasconcellos et al. 2021). These are interesting cases where the knowledge about physiology of plants growing under Al^{3+} stress can be applied in pre-breeding and breeding programs which can help to obtain plant cultivars with greater Al^{3+} resistance. Biotechnology can also be used as an alternative to increase plant growth under Al^{3+} stress as, for example, the over-expression of citrate and malate transporters (Pereira et al. 2010; Zhou et al. 2014). However, the strategy of over-expressing OA transporter has unanswered questions regarding their performance under field conditions (Pereira 2021) and also seems to impact the plant growth under some circumstances, as the *OsALMT4* expression disrupting mineral nutrition and compromising the growth of rice in low-light environments (Liu et al. 2017a, 2018a). Additionally, some OA transporters seem to transport GABA and other hormones (as discussed in the section below) and the impact of these findings on plants overexpressing OA transporters are still to be shown.

Other aspect that should also be considered when breeding Al^{3+} resistance in plants is the correlation between this phenotype and OA efflux. For some species, like wheat and barley, Al^{3+} resistance is highly correlated with OA efflux. For instance, OA efflux in wheat is 71% correlated with Al^{3+} resistance under field conditions (Aguilera et al., 2016). However, in species like rice, the correlation between OA efflux and Al^{3+} resistance is much lower because OA efflux is one among different mechanisms influencing Al^{3+} resistance. In this case, manipulating the efflux of citrate and/or malate, either conventionally or through biotechnology, in species as wheat and barley will probably result in greater Al^{3+} resistance than in species like rice.

Plant Response to Al^{3+} Toxicity is Modulated by Different Levels of Growth Regulators

As a rule, under the influence of adverse environmental conditions, the concentration of growth-stimulating hormones such as auxins, gibberellins, cytokinins decreases, while the concentration of growth inhibitors such as abscisic acid and ethylene increases in plant tissues (Kopittke 2016; Rhaman et al. 2021). These phytohormones along with three other growth-regulators, brassinosteroids, jasmonic acid and salicylic acid play a pivotal role in plant growth regulation, induction of resistance and tolerance against a wide range of biotic and abiotic stresses (Kopittke 2016; Sun et al. 2016; Emamverdian et al. 2020; Rhaman et al. 2021).

A large number of data showed that treatment of plants with phytohormones improves plant tolerance to almost any abiotic stresses including Al^{3+} (Kopittke 2016; Diego and Spíchal 2020; Emamverdian et al. 2020). Application of auxins, gibberellins and cytokinins help to 'soften' the oxidative stress, reducing lipid peroxidation and activating the antioxidant defense system (Emamverdian et al. 2020; Kollmeier et al. 2000). In this section, we summarized the effect of three plant growth regulators (brassinosteroids, jasmonic acid and salicylic acid), and two regulatory and signaling compounds (polyamines and γ-aminobutyric acid) in plant Al^{3+} response.

Brassinosteroids (BRs) and the most bioactive BR, brassinolide (BL), are known to be essential for plant growth and development and regarded as a new class of plant hormone. Most stable analogue of BR, 24-epibrassinolide (EBL) has the ability to enhance yield and stress tolerance (Bajguz and Hayat 2009; Ahanger et al. 2018; Anwar et al. 2018). Evidence shows that BRs maintain the cell redox state by regulating activities of antioxidative enzymes (Rajewska et al. 2016). Two genes associated with BR biosynthesis

and signaling were significantly up-regulated by Al^{3+} in maize, BR biosynthesis-like protein (Dark-Induced DWF-Like Protein 1, DDWF1) and BRI 1 (Brassinosteroid Insensitive 1)-associated receptor kinase 1 (BAK1) precursor (Matiello et al. 2014). Applied BRs can promote or stunt growth in plants, and this is concentration-, species- and stress intensity/duration-dependent (Ahanger et al. 2018). In mung bean (*Phaseolus aureus* Roxb.), BL promotes growth when the plants are exposed to Al^{3+} (Abdullahi et al. 2003). In another work, EBL causes increase in biomass of shoot and roots and chlorophyll (Chl) concentration in mung bean (*Vigna radiate* L. Wilczek) under Al^{3+} stress and significantly enhances the activities of superoxide dismutase (SOD), catalase (CAT) and peroxidase (POD) in leaves, as well as root and leaf proline concentrations (Ali et al. 2008). Application of EBL and 28-homobrassinolide (HBL) alleviates Al^{3+}-induced decreases in carbonic anhydrase activity, relative water content, water use efficiency, Chl concentration, stomatal conductance and CO_2 assimilation in leaves, and mitigates reduction of plant growth caused by Al^{3+} (Ali et al. 2008). Similarly, EBL alleviates Al^{3+}-induced decrease in CO_2 assimilation by increasing Chl concentration, photochemical efficiency, stomatal conductance, activity of carbonic anhydrase and Rubisco in soybean (*Glycine max* L.) (Dong et al. 2008). EBL also improves Al^{3+} tolerance in wheat (*Triticum aestivum* L.) through modulation of proline metabolism (Yusuf et al. 2017). BRs-driven Al^{3+} resistance is reflected in the improvement of plant growth and photosynthesis, and EBL seems to be more effective than HBL in mung bean (Fariduddin et al. 2014).

Jasmonic acid (JA) or methyl jasmonate (MeJA) are key regulators during plant development and are involved in various biotic and abiotic stress response pathways, generally acting cooperatively with other plant hormones, as ethylene and auxin (Wasternack and Hause 2013; Ahmad et al. 2017; Ulloa-Inostroza et al. 2017). It has been observed that, the expression of COI1 (the JA receptor) was up-regulated in response to Al^{3+} stress in the root tips of *Arabidopsis* (Yang et al. 2014). COI1 (Coronatine Insensitive 1)-mediated JA signaling is involved in the Al^{3+}-induced root-growth inhibition through regulation of polymerization of cortical micro-tubules in the root apex mediated by ethylene but independent from auxin signaling (Yang et al. 2014). In addition, ALMT-mediated malate exudation, and thus Al^{3+} exclusion from roots, was also regulated by the COI1-mediated JA signaling (Yang et al. 2017). In *Cassia tora*, a non-model species that is well adapted to acidic soils, JA application decreased Al^{3+} tolerance and increased the concentration of hydrogen peroxide (H_2O_2) and lignin in roots (Xue et al. 2008). Similarly, application of JA enhanced the Al^{3+}-induced root growth inhibition in *Arabidopsis* (Yang et al. 2017). However, the protective effects of JA on plants exposed to Al^{3+} cannot be ruled out. For instance, transiently high concentration of JA in an Al^{3+}-tolerant rice variety corresponds to the alarm phase required for the activation of inducible defense mechanisms (Roselló et al. 2015). MeJA shows a protective effect on photosynthetic responses in an Al^{3+}-sensitive and, to a much less extent, in an Al^{3+}-tolerant blueberry cultivar (Ulloa-Inostroza et al. 2019). In this case, MeJA seems to be involved in the reduction of Al^{3+} accumulation in the leaves, stimulation of the antioxidant response through phenolic compounds and enzymatic activity (SOD and CAT) and also protection of the photosystem II (PSII) by increasing the pool of xanthophyll pigments (Ulloa-Inostroza et al. 2019).

Salicylic acid (SA) is a signaling molecule that regulates metabolic and physiological processes involved in specific biotic and abiotic responses to stress in plants (Sinha et al. 2015; Arif et al. 2020; Sharma et al. 2020). The protective effects of SA application on Al^{3+}-toxicity by preventing Al^{3+}-induced oxidative stress have been described in various plant species, such as *Cassia tora* (Yang et al. 2003), *Herdeum vulgare* (Song et al. 2011), *Coffea arabica* (Muñoz-Sanchez et al. 2013), *Oryza sativa* (Pandey et al. 2013), *Solanum lycopersicum* (Surapu et al. 2014), *Brassica oleracea* (Sinha et al. 2015), *Glycine max* (Liu et al. 2017b), *Panax notoginseng* (Dai et al. 2019) and *Lupinus termis* (Hemada et al. 2020). The protective effects of exogenous SA are related to the activity of antioxidant enzymes such as SOD, CAT and ascorbate peroxidase (APX), reducing H_2O_2 and lipid peroxidation caused by Al^{3+} in mung bean (Ali 2017) and soybean (Liu et al. 2017b). In soybean, phenylalanine ammonia-lyase (PAL) and benzoic acid 2-hydroxylase (BA2H) enzymes were showed to be involved in Al^{3+}-induced SA production and Al^{3+} toxicity attenuation by modulating the cellular H_2O_2 concentration and the antioxidant enzymes in the root apex. Seed priming with SA attenuated Al^{3+} toxic effects on *Trifolium repens* shoots and *T. vesiculosum* roots, with antioxidant activity demonstrated in their seedlings (Bortolin et al. 2020). Some studies evidenced that SA enhances the exudation of OAs from the root under Al^{3+} stress (Liu et al. 2012; Yang et al. 2018). Ca^{2+} and SA act as primary signaling molecules in response to Al^{3+} stress, and regulate citrate exudation, root elongation, Al^{3+} content and oxidative stress (Lan et al. 2016). SA can mediate soybean's response to Al^{3+} stress by increasing cytosolic Ca^{2+} concentration and the expression of Ca^{2+}-related genes, such as calmodulin-like genes, that activates a series of other enzymes in the cell (Bender et al. 2014). SA application and Al^{3+} induce root exudation of some hydroxamic acids from an Al^{3+}-resistant maize cultivar, which can be responsible for Al^{3+} resistance and alleviation of Al^{3+} toxicity in maize (Zhao et al. 2019).

SA is also correlated with the maintenance of photosystems functions increasing photosynthetic capacity in plants that are tolerant to Al^{3+}. Application of SA

alleviates damaging effects of Al^{3+} on photosynthesis by increasing light capture efficiency, promoting electron transport in the electron transport chain and thylakoid lumen deacidification, and accelerating ATP and NADPH synthesis, as well as regulating carboxylation process in alfafa (*Medicago sativa*) (Cheng et al. 2020). In *P. notoginseng* leaves, SA decreased Al^{3+} accumulation, reduced the damage to the photosynthetic system, increased the utilization rate of light energy, and then accelerated the process of carbon assimilation, promoting root gain of dry biomass (Dai et al. 2019).

Polyamines (PAs) are a water-soluble group of polybasic aliphatic amines that act as important regulatory molecules. In plants, PAs putrescine (Put; diamine), spermidine (Spd; triamine) and spermine (Spm; tetramine) are recognized for their role as stabilizers of membrane, proteins, and nucleic acids, protectors of cellular integrity and the photosynthetic apparatus, direct and indirect signaling agents, and new members of the non-enzymatic antioxidant system. In addition, PAs function as key regulatory players in plants tolerance to stresses (including metal toxicity) (Chen et al. 2019a; Yu et al. 2019a, b; Spormann et al. 2021). Application of Spd enhanced the concentration of PAs, and regulated the concentration of proline and improved leaf water content, photosynthesis and growth in mung bean when exposed to Al^{3+} (Nahar et al. 2017). Transgenic European pear (*Pyrus communis* L. 'Ballad') overexpressing apple spermidine synthase (*MdSPDS1*) and subjected to long-term Al^{3+} exposure, showed higher survival status when compared to the wild type due to modified activities of SOD and glutathione reductase (GR) and differential accumulation of proline and malondialdehyde (MDA), in response to Al^{3+} (Wen et al. 2009). Spd and Spm application failed to alleviate impairment of root growth under Al^{3+}-stress in kidney bean (*Phaseolus vulgaris*), while application of Put was effective, suggesting that Put is likely involved in responses to Al^{3+} stress (Wang et al. 2013a). In wheat, the activity of the CW-bound polyamine oxidase (PAO) increased under Al^{3+} toxicity, leading to Spd oxidation and H_2O_2 production (Yu et al. 2018). By contrast, these authors showed inhibition of PAO activity by Put, and subsequent reduction of H_2O_2 accumulation in roots under Al^{3+} stress. Al^{3+} increases Put accumulation in the roots of wheat and it is accompanied by significant increase in the activity of arginine decarboxylase (ADC) (Yu et al. 2015), a Put producing enzyme, that contributes more to Al^{3+} induced endogenous Put accumulation than ornithine decarboxylase (ODC) (Wang et al. 2013b). Bound Put decreases ROS accumulation, and reduces Al^{3+}-induced oxidative damage in wheat roots (Yu et al. 2019a). In addition, Put seems to prevent root inhibition under Al^{3+}-stress reducing ACC (1-aminocyclopropane-1-carboxylic acid) synthase activity, and thus reduction of ethylene production (Yu et al. 2016).

In plants, γ-aminobutyric acid (GABA) is synthesized mainly from L-glutamate (Glu) catalyzed by glutamate decarboxylase (GAD) (Podlešáková et al. 2019). It has been proved that GABA metabolism system (GABA shunt) is involved in varied physiological responses such as cytosolic pH regulation, carbon and nitrogen balance, repelling herbivorous insects, protecting against oxidative stresses, osmoregulation, and signaling (Seifikalhor et al. 2020). The intracellular GABA concentration in plants are very low under normal growth conditions, however, it can be quickly and greatly increased under adverse environmental conditions of both biotic and abiotic nature (Long et al. 2020; Seifikalhor et al. 2020). Stress-induced increase in the cytosolic Ca^{2+} ions activates some isoforms of GAD thereby resulting in an increased GABA synthesis. The increased GABA is capable of regulating ALMT through an allosteric effect, reducing anion channel opening frequency (Long et al. 2020). However, GABA probably plays a role as a regulator of anion transport through ALMT family, which has numerous physiological roles beyond Al^{3+} tolerance. Stress-induced elevated level of cytosolic GABA negatively regulates anion transport by ALMT proteins in wheat plants (Long et al. 2020). Considering the role of ALMT in the regulation of guard cell movement (Medeiros et al. 2018), pollen tube and root growth (Ramesh et al. 2015), it could be proposed that GABA exerts diverse physiological effects in plants through ALMT, and can be considered as legitimate signaling molecule in the plant kingdom, that modulates plant growth, development, and stress response (Ramesh et al. 2015, 2017, 2018). These findings suggest that a GABA-ALMT interaction from the cytosolic face has the potential to form part of a novel plant signaling pathway (Long et al. 2020). Al^{3+} stress also leads to increased GABA biosynthesis in the woody plant hybrid Liriodendron (*Liriodendron chinense* × *Liriodendron tulipifera*), a genus of the magnolia family (Wang et al. 2021). Additional GABA induces the expression of antioxidant enzymes, the biosynthesis of proline and up-regulation of *LchMATE1* and *LchMATE2* promoting citrate efflux and amelioration of Al stress (Wang et al. 2021).

There is also some information in the literature that GABA application contributes to increased tolerance of plants against different stresses including Al^{3+} toxicity through modulating the expression of genes involved in plant signaling, transcription regulation, hormone biosynthesis, production of ROS, and polyamine metabolism (Song et al. 2010; Sita and Kumar 2020). Exogenous GABA significantly ameliorated damages caused by Al^{3+} stress in barley plants which manifested both in cellular and whole organism levels (Song et al. 2010). Treatment with GABA reduced Al^{3+}-caused

oxidative cell damages through activating antioxidant defense enzymes and decreasing the concentration of ROS, lipid peroxidation and carbonylated proteins (Song et al. 2010). Several enzymes involved in the GABA shunt are controlled by STOP1 (Sadhukhan et al. 2021) the transcription factor involved in plants Al^{3+} response and regulates ALMT expression (see section 'Al^{3+} evokes signaling pathways and affects the expression of several genes'). Nevertheless, the mechanisms underlying GABA-induced plant tolerance to Al^{3+} toxicity are still far from clear and further research should be carried out to provide more insights into the mechanism of GABA function in plant defense responses against Al^{3+} toxicity stress. However, the role of GABA in mitigating the effects of many other heavy metals in crop species such as chromium toxicity in *Brassica* (Mahmud et al. 2017), cadmium toxicity in maize (Seifikalhor et al. 2020) and microalgae (Zhao et al. 2020) and arsenite toxicity in rice (Kumar et al. 2019) have been reported.

Microorganisms Show Beneficial Effects on Plants Under Al Stress

The presence of soil microorganisms can increase or decrease bioavailability of Al^{3+} and heavy metals, increasing or decreasing the absorption of these compounds (Chaudhary and Khan 2018). Al^{3+} in soil affects plant–microbe associations and, in turn, the dynamics of reproduction, extinction and migration of microbial populations in ecological niches changes the root zone. As a result of root surface colonization under Al^{3+} and heavy metal stress, the survival of both components (plants and microorganisms) of plant-bacterial system increases (Pishchik et al. 2016). Plants form unique conditions in the plant–microbe systems mainly for those micropartners that can reduce the phytotoxicity of the soil contaminated with heavy metals (Jing et al. 2007; Qiu et al. 2014; Sungurtseva et al. 2015; Pishchik et al. 2016; Abou-Aly et al. 2021; Caracciolo and Terenzi 2021). A prerequisite for creating a stable plant–microbe system is the ability of an introduced microorganism to actively colonize plant roots and maintain a certain population size. Employment of molecular-genetic approaches for generation of transgenic plants with altered root microbiome structure, e.g., through higher expression of ALMT and MATE transporters (Kawasaki et al. 2021), may remarkably enhance the potential of crop plants to establish an efficient interaction with microorganism in the rhizosphere and improve plant growth under acidic soil conditions.

Plant Growth-Promoting Bacteria

Plant growth-promoting bacteria (PGPB), which are able to tolerate heavy metals, may be considered a new approach for improving growth of many crops, especially in areas containing heavy metal (Chaudhari and Khan 2018; Islam et al. 2021). PGPB possess various mechanisms of biological plant protection, manifested both at the cell and whole organism/population levels (Jing et al. 2007; Abou-Aly et al. 2021; Caracciolo and Terenzi 2021). Plants and bacteria can form non-specific associations in which plant metabolites stimulate the microbial community and reduces the number of contaminants in the soil (Jing et al. 2007). Several mechanisms of bacterial tolerance to heavy metals exist: extracellular barrier, active transport of metals from the cell, extracellular binding, intracellular binding, and restoration metal concentrations. The main defense mechanisms occur outside bacterial cells due to a change in the pH and redox potential of the medium, the mobilization of phosphates or production of polysaccharides, siderophores, and various antioxidant enzymes (SOD, CAT, POD, and proline) (Islam et al. 2021).

The ability of PGPB to synthesize phytohormones can play an important role in PGPB-mediated plant stress adaptation (Lastochkina et al. 2019; Abd El-Daim et al. 2019; Rashid et al. 2021). Most often, compounds exhibiting an indole ring are found in the liquid culture of PGPB, for example, indolyl-3-acetic acid (Sgroy et al. 2009). Some PGPB have also been shown to synthesize cytokinins, gibberellins, ABA, SA, and JA (Lastochkina et al. 2019). PGPB capable of synthesizing growth regulators can probably be considered potential sources of hormones to be applied in plants subjected to Al^{3+} toxicity. Nevertheless, studies about the effect of PGPB on plant hormones under Al^{3+} toxicity are limited. Most studies about the effect of microorganisms on the hormonal status of plants under Al^{3+} toxicity aim to find PGPBs capable of synthesizing ACC deaminase, which is able to decrease the concentration of ethylene, a plant hormone that triggers the cascade of nonspecific stress and adaptive reactions (Singh et al. 2013; Zafar-ul-Hye et al. 2019). These bacteria, which use ACC as a source of nitrogen, are able to metabolize it and, thereby, reduce the negative effects of ethylene on plant growth (Glick 2014).

Recently, phytohormones-producing endophytic bacteria, *Sphingomonas* sp. LK11 and endophytic fungus *Paecilomyces formosus* LHL10, showed significant plant growth stimulation and tolerance induction in soybean (*Glycine max* L.) under Al^{3+} toxicity (Bilal et al. 2018). LK11 + LHL10-inoculated and Al^{3+}-stressed plants demonstrated significantly higher plant growth and chlorophyll concentration in comparison with solely LK11 and LHL10 inoculated and especially non-inoculated control plants under Al^{3+} toxicity. A similar finding demonstrated that inoculation with *P. simiae* N3, *B. ginsengiterrae* N11-2, and *C. polytrichastri* N10 lead to higher biomass (especially leaf biomass) and chlorophyll concentration in Al^{3+}-stressed Korean ginseng seedlings (Farh et al. 2017). In addition, these microorganisms

resulted in higher expression of genes related to Al^{3+} toxicity (*AtAIP*, *AtALS3*, and *AtALMT1*) in *Arabidopsis* plants. Expression profiles of the genes reveal the induction of external mechanism of Al^{3+}-stress tolerance by *P. simiae* N3 and *B. ginsengiterrae* N11-2 and internal mechanism by *C. polytrichastri* N10 (Farh et al. 2017). Moreover, under metal stress, the combination of *Sphingomonas* sp. LK11 and *P. formosus* LHL10 exhibited lower metal uptake and inhibited metal transport in roots. Al^{3+}-induced oxidative stress was modulated in co-inoculated plants via reduction of H_2O_2, lipid peroxidation, and antioxidant enzymes (SOD and CAT) in comparison with non-inoculated soybean. In addition, endophytic co-inoculation increased uptake of macronutrient (N P, K, and S) and modulated soil enzymatic activities under stress conditions. These endophytic microorganisms also down-regulated the expression of heavy metal ATPase genes, *GmHMA13*, *GmHMA18*, *GmHMA19*, and *GmPHA1* and up-regulated the expression of an Ariadne (ARI)-like ubiquitin ligase gene, *GmARI1* in Al^{3+}-stressed plants. Furthermore, in response to co-inoculation with *P. formosus* LHL10 and *Sphingomonas sp.* LK11 significantly increased gibberellins and reduced abscisic acid and JA concentration thereby mitigating the adverse effect of Al stress in plants. Co-inoculation with bacteria LK11 and LHL10 actively contributed to the tripartite mutualistic symbiosis in soybean under Al^{3+} stress and, therefore, could be used an excellent strategy for sustainable agriculture in metal-contaminated fields (Bilal et al. 2018).

Arbuscular Mycorrhizal Fungi

Arbuscular mycorrhizal fungi (AMFs) are natural root symbionts and aid in the provision of macro and micronutrients to host plants, consequently improve plant biomass and nutritional status (Smith and Read 2008). Colonization by AMF enhances the ability of the root system to mine and acquire essential nutrients, especially P (Smith et al. 2003). AMF produces a glycoprotein (glomalin), which plays an important role in improving soil structure (Agnihotri et al. 2022). The extra radical mycelium of AMF has the potency to explore and extend a large volume of soil capable of improvising the uptake of nutrients and water from soil (Smith and Read 2008).

In the course of abiotic stress, AMF aids in improving plant growth and stress adaptation (Hajiboland 2013; Begum et al. 2019; Jajoo and Mathur 2021). It has been observed that AMF inoculation in plants builds up the oxidative stress tolerance by increasing antioxidant potential, decreasing lipid peroxidation, down-regulating lipoxygenase and regulating AQP genes and phytohormone biosynthesis pathways (Hajiboland et al. 2020; Kaur and Suseela 2020; Sharma et al. 2021). For heavy metal stress, AMF confers toxicity tolerance by immobilizing the metals in the fungal hyphae, fixing heavy metals in the CW and also enabling their chelation with other substances in the cytoplasm (Hildebrandt et al. 2007; Dhalaria et al. 2020; Riaz et al. 2021).

Under acidic soil conditions that P deficiency is the predominant constraint for growth, AMF associations may play an important role in plants adaptation and resistance (Kochian et al. 2004). AMF colonization leads to root architecture remodeling, such as increased root growth, enhanced number and length of lateral roots and more fine roots (Smith and Read 2008). AMF structures have the ability to produce and build an enlarged mycorrhizosphere in which Al is detoxified (Muthukumar et al. 2014). Root colonization by AMF up-regulates photosynthesis and carbon metabolism, induces the release of OAs into the rhizosphere, which chelates Al^{3+} leading to Al^{3+}-detoxification (Seguel et al. 2013). In addition, glomalin-related soil protein (GRSP) produced by AMF sequesters Al^{3+} in the rhizosphere (Etcheverría 2009).

The Al^{3+} tolerance that AMF colonization may provide to plants, however, is variable in terms of Al exclusion, nutrient acquisition or effects on plant growth. This is, at least, partly a consequence of a substantial genetic variation in the Al^{3+} tolerance among and within AMF species (Coughlan et al. 2000). In general, AMFs are found in soils from pH 2.7 to 9.2, but different species and isolates of the same species vary in tolerance to acidity. AMF species and isolates are adapted to soil conditions from which they were collected (Walker et al. 1998; An et al. 2008). Variation existing among ecotypes of potentially Al^{3+} tolerant AMF species is related to differences in sensitivity of life stage events, including spore germination, germ tube growth, hyphal growth, root colonization and persistence (Siqueira et al. 1990; Coughlan et al. 2000; Higo et al. 2011). Interestingly, different parameters show different Al^{3+} susceptibility, i.e., germ tube growth and spore germination are differentially affected by Al^{3+} exposure that may reflect the variation in genotypes among spores and subsequent selection and survival under Al^{3+} stress (Lambais and Cardoso 1989).

In studies of plants exposed to Al^{3+}, the colonization rate either remains unaffected, decreased or even increased by Al^{3+} exposure (Seguel et al. 2013). Nevertheless, growth and protection of the host plant from Al^{3+} toxicity by different AMF species is not associated with the AMF resistance traits, suggesting that the Al^{3+} resistance mechanisms in AMF may not be extrapolated to the life stage in host plants (Klugh-Stewart and Cumming 2009). Indeed, selection of AMFs with potential for Al^{3+} tolerance under acidic soil conditions may occur at the spore germination and hyphal growth stages but their response to Al^{3+} toxicity after colonization of plant roots depends on specific interactions between AMF species/ecotype and plant species/genotype. The same was observed for AMF-mediated amelioration of other stresses (Hajiboland 2013).

Future Research Perspectives

Most of physiological studies about Al^{3+} stress are performed with plants growing on hydroponics, which is a quite fast method to measure important traits. That means the knowledge regarding Al^{3+} stress on plants grows rapidly, although not necessarily reflecting the physiological response of plants growing on acidic soils in field conditions (Pereira 2021). The future research of plant Al^{3+} toxicity should still answer several questions. Hot topics as the relationship between Al^{3+} resistance/tolerance and climate change will eventually lead to the establishment of the mechanisms by which Al^{3+} stress may impact plants in the future, since elevated CO_2 seems not to decrease the Al^{3+} tolerance of Al^{3+} resistant wheat genotypes (Dong et al. 2018) and actually increase grain yield of wheat Al^{3+}-resistant lines (Dong et al. 2019). Based on the topics reviewed in this paper, we suggest the following questions to be addressed by future research on plant Al^{3+} toxicity:

- Does the interaction between Al^{3+} and DNA differs among Al^{3+}-sensitive, -resistant and -accumulating species?
- What genes and mechanisms mediate the nitric oxide modification of cell wall under Al^{3+} stress?
- Do other transcription factor families control the expression of Al^{3+} responsive genes besides STOP1/ART1, WRKY, and ASR?
- How is the interaction between families of transcription factors when the plants are growing under Al^{3+} stress?
- What are the sensors and receptors of Al^{3+} and how do they interfere with Al^{3+} sensing, gene expression and consequent Al^{3+} resistance?
- How is the level of involvement of miRNAs in regulating plant response to Al^{3+} stress between Al^{3+}-resistant and -accumulating species?
- Is greater Al^{3+} tolerance/resistance able to maintain high leaf hydration, root hydraulic conductivity, and plant production under drought conditions in the field?
- What are the impacts of plant Al^{3+} resistance for plant hormone transport (such as GABA) by organic acid anions (OAs) transporters?
- When using biotechnology to obtain greater Al^{3+} resistance, will the overexpression of OAs transporters significantly impact plant nutrition, growth and grain quality?
- Can the amino acid sequence of OAs transporters be changed so the efflux of OAs is more efficient?
- What is the impact for plant growth, development, and grain quality when both OAs synthesis and efflux are increased through biotechnology?
- Why oxalate seems to be more important for woody plants than for crop species?
- What is the transporter responsible for oxalate efflux by the roots of some plant species?
- Can we establish a model for the effects of plant hormones (brassinosteroids, jasmonic acid and salicylic acid) and signaling compounds (polyamines and γ-aminobutyric acid) in plant Al^{3+} response?
- What are the mechanisms underlying GABA-induced plant tolerance to Al^{3+} toxicity?
- What are the effects of plant growth-promoting bacteria on plant growth regulators, regulatory and signaling compounds under Al^{3+} stress?
- Can a product based on the mutualistic symbiosis between beneficial microorganism and a plant species be developed as a strategy for sustainable agricultural production in large field areas with Al^{3+} stress?
- What is the molecular basis for different stages (spore germination, hyphal growth and colonization) of the interaction between beneficial fungal species and plants growing under Al^{3+} stress?

The efforts helping answering these and other questions will help to mitigate the adverse effect of Al^{3+} stress on plant growth and development, and help to obtain biotechnological products and new targets for conventional breeding to improve yield and plant production under acid soils.

Conclusion

In recent years, our knowledge on the uptake and root-to-shoot translocation of Al and its intracellular movements has made significant progress. However, there are still several questions needing answers in order to have a better picture of the Al^{3+} toxicity and Al^{3+} stress response in plants. The Al^{3+}-evoked signaling pathways have also been widely discovered and the main players in plants response pathways to Al^{3+} have been identified. However, potential molecules involved in the sensing and/or perception of Al^{3+} have not yet been identified. Studies of the mechanisms for extracellular Al^{3+} chelation led us to draw a comprehensive physiological and molecular scenario for exclusion strategy in plants, while internal Al^{3+} detoxification have not been adequately addressed so far. Exploring the machinery for Al^{3+} sequestration in the intracellular compartments requires, probably, new model species with efficient internal detoxification mechanisms. New features of organic acid anions transporters, as the ability to transport GABA, adds interesting questions to be answered. Although the use of microorganisms to overcome the stress of acidic soils has been developed, their influence in plant physiology are largely unknown and their application is limited to special conditions such as growing high value horticultural crops. Development of suitable priming methods and introduction of low-cost and

environmentally friendly priming agents may greatly contribute to a sustainable crop production on acidic soils.

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