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REVIEW ARTICLE

Beneficial elements for agricultural crops and their functional relevance in defence against stresses

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ABSTRACT

The beneficial elements are not deemed essential for all crops but may be vital for particular plant taxa. The distinction between beneficial and essential is often difficult in the case of some trace elements. Elements such as aluminium (Al), cobalt (Co), sodium (Na), selenium (Se) and silicon (Si) are considered beneficial for plants. These elements are not critical for all plants but may improve plant growth and yield. Pertinently, beneficial elements reportedly enhance resistance to abiotic stresses (drought, salinity, high temperature, cold, UV stress, and nutrient toxicity or deficiency) and biotic stresses (pathogens and herbivores) at their low levels. However, the essential-to-lethal range for these elements is somewhat narrow. The effect of beneficial elements at low levels deserves more attention with regard to using them to fertilize crops to boost crop production under stress and to enhance plant nutritional value as a feed or food. A more holistic approach to plant nutrition would not only be restricted to nutrients essential to survival but would also include mineral elements at levels beneficial for best growth. Here, we describe the uptake mechanisms of various beneficial elements, their favourable aspects, and the role of these elements in conferring tolerance against abiotic and biotic stresses.

Introduction

There is rising awareness of the need to pay greater attention to the role of trace elements in plant nutrition as we seek to elucidate the adverse effects of deficiencies and toxicities, and avoid suboptimal concentrations that limit the attainment of optimum economic yields of crops, animal productivity and welfare. The most important role of these elements does not lie in its general acceptance of essentiality, but rather in its most striking and unique function in conferring tolerance in plants to various abiotic and/or biotic stresses. There are diverse opinions regarding the 'essentiality' of mineral nutrients in plants. Early classical reports on the essentiality of minerals came from Arnon and Stout (1939), who identified three criteria to consider an element as essential: 1) a plant cannot complete its life cycle in the absence of the mineral element, 2) the function of the element is not replaceable by another mineral element, and 3) the element is directly involved in plant metabolism. Other elements that promote growth in many plant species but are not needed to complete the plant life cycle, or fail to meet the Arnon and Stout criteria on other grounds, are termed beneficial elements. Of the 92 known elements, 17 are considered essential and are categorised into macro-elements such as C, H, O, Ca, K, Mg, N, S and P (requirement >1000 mg kg^{-1} dry weight – and micro-/trace elements such as B, Cl, Cu, Fe, Mn,

Mo, Ni and Zn (requirement <100 mg kg^{-1} dry weight). Certain other elements, such as Al, Si, Co, Na and Se, do not meet the 'essentiality' criteria for mineral nutrients but have a ubiquitous presence in both soil and water and can be widely taken up and used by plants. Such elements, which may enhance biomass and yield but may not be required for species to survive, are termed functional/beneficial elements (Marschner 2012). Not all metabolic functions need a unique element to function; there are a number of chemically different but physically similar elements that can substitute the functions of essential elements in various metabolic processes. For example, Na, Rb and K, Se and S, Co and Ni, and Si and C often replace each other in certain non-specific metabolic processes. Therefore, it can be opined that the element replacing the essential element may be more efficient than any other element.

Various approaches have been executed to analyze the growth-promoting effects of beneficial elements. For instance, plants have been grown in the presence or absence of beneficial elements with positive and negative effects at the plant tissue level determined. The beneficial elements were effective at their low concentrations and acted as co-factors for some specific enzymes. It is critical to study beneficial elements in the context of ecological processes to establish how valuable these elements are for alleviating abiotic stresses and how plants accumulating these elements interact with pathogens/herbivores (Pilon-Smits et al. 2009). Better nutrient cycling contributes towards an improved ecological environment, resulting in an ecologically sound and sustainable flow of these elements. Soil–plant system strategies that have been assumed to perk up human micronutrient nutrition mainly include: a) beneficial elements flow from soils to the edible parts of crops, and b) a better knowledge of the relationship between the content and bioavailability of beneficial elements in soils and those in edible crop products. The omission of beneficial nutrients in commercial production may mean that plants are not grown to their optimum genetic potential but are merely produced at a subsistence level. Here, we summarize our current knowledge about the abundance of the beneficial elements in soil, their uptake mechanisms, and roles in plant growth, especially under various types of abiotic and biotic stresses.

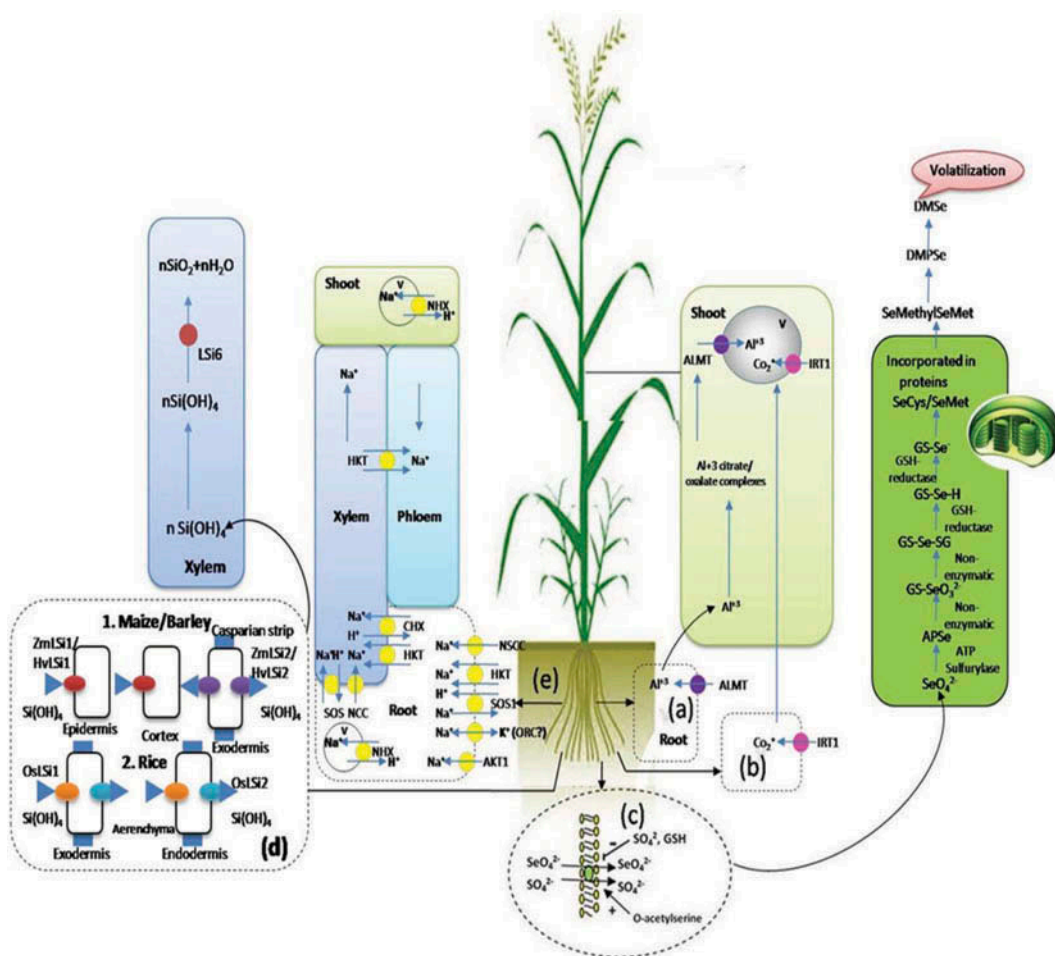## Uptake mechanisms of beneficial elements

To illustrate the beneficial role of these elements, it is fundamental to understand their uptake and transport mechanisms as well as their movement between different tissues and within cell compartments. This section describes the uptake mechanisms of various beneficial elements, which are summarized in Figure 1.

Aluminium

Aluminium is present in acidic soils (pH<5.5) and released in the form of Al^{3+}, $Al(OH)_2^+$, and $Al(OH)^{2+}$. However, Al^{3+} uptake, whether symplastic (storing Al^{3+} in the less toxic forms complexed with organic acids) or apoplastic (Al^{3+} binding to cell walls and obstructing its transport to symplasm), is under debate. There is evidence that a high shoot aluminium level in soluble form is transported through the xylem to accumulate in leaf vacuoles or the apoplast (Hodson & Evans 1995). Al^{3+} sensing involves a specific receptor – ALMT (aluminium-activated malate transporter) – which encodes the Al^{3+}-activated anion channel that facilitates malate efflux from root apices (Figure 1a).

Cobalt

Soil pH is the most important factor for cobalt uptake in roots, which increases with decreasing pH. Korshunova et al. (1999) found that IRT1, an *Arabidopsis thaliana* iron transporter, assisted in the uptake of cobalt into plant cells. Consequently, Co^{2+} uptake occurs in roots via IRT1 transporters (Figure 1b), which seems to have eight membrane-spanning domains and a putative histidine-rich, metal-binding domain. Cobalt transport occurs in the form of the cobalt ion (Co^{2+}) through cortical cells via passive diffusion and active transport. Upward transport in the xylem tissue chiefly takes place by transpirational flow (Jarosick et al. 1988; Figure 1b).

Figure 1. Uptake mechanisms of beneficial elements (a) Al^{3+}-activated organic anion influx takes place via ALMT (aluminium-activated malate transporter) transporters in root apices, and then interacts with the protein to form Al^{3+} citrate/oxalate-complexes.(b) For cobalt, Co^{2+}ion uptake takes place in roots via IRT1 (iron transporter 1) transporters. Transport of cobalt occurs via passive diffusion and active transport. (c) Selenate (SeO_4^{2-}) uptake takes place across the root plasma membrane by high-affinity sulphate transporters whose expression is regulated positively by O-acetylserine and negatively by sulphate and glutathione. Selenate is then transported to chloroplast where it is finally reduced to GS-Se-(glutathione conjugated selenide) via various enzymatic and non-enzymatic reactions (Terry et al. 2000). (d) Si uptake occurs in the form of silicic acid [$Si(OH)_4$] through roots via silicon transporters Lsi1 (low silicon 1), which is then transported through xylem sap to the leaf cells via Lsi6 transporter as reported in rice (Ma et al. 2006). 1 and 2 shows the Si uptake in maize/barley and rice, respectively, via specific transporters attributed to their root structure. OsLsi1, 2: *Oryza sativa* Low Silicon transporter1, 2; ZmLsi1, 2: *Zea mays* Low Silicon transporter1, 2; HvLsi1, 2: *Hordeum vulgare* Low Silicon transporter1, 2 (e) Na^+ uptake, efflux and distribution occur through transport proteins. Transport functions are shown for Na^+ uptake, efflux, long-distance transport, and cellular partitioning in roots and shoots. Abbreviations: AKT1, inward rectifying K^+ channel; CHX, cation: H^+ exch nger; HKT, high affinity K^+ transporter; NHX, vacuolar Na^+:H^+ exchanger; NSCC, non-selective cation channel; ORC; outward rectifying K^+ channel; SOS1, plasma membrane Na^+:H^+ antiport (Maathuis 2014).

Selenium

Se is present in different forms (elemental selenium, selenite, selenate, thioselenate, and selenide) in the soil. However, plants can absorb and sequester Se in the form of selenite and selenate. Selenate readily competes with sulphate uptake and is taken up via sulphur transporters in the root plasma membrane. Genes encoding sulphate transporters – SHST1, SHST2, and SHST3 (*Stylosanthes hamata* transporters 1, 2, and 3) – have been isolated from the tropical legume *Stylosanthes hamata* (Smith et al. 1995) and one gene HVST1 (*Hordeum vulgare* sulphate transporter 1) from

barley (*Hordeum vulgare* L.; Smith et al. 1997). The expression of these transporter genes is positively and negatively regulated by special regulators such as glutathione (GSH), O-acetylserine, and S (sulfur) (Davidian et al. 2000; Figure 1c).

Silicon

Plants take up silicon in the form of monosilicic acid, $Si(OH)_4$, through roots via silicon transporters Lsi1 and Lsi2 (low silicons 1 and 2; Figure 1d), discovered from rice plants (Ma et al. 2006). A second Si transporter, Lsi2, reportedly involves Lsi1 mutant approach, i.e. different from Lsi1, and acts as an efflux transporter in rice. Lsi2 expression and localization in tissues and cells is similar to Lsi1; however, Lsi2 is confined to the proximal side of the exodermis and endodermis cells (Ma et al. 2007). After the Si^{4+} uptake through roots via Lsi1 and Lsi2, more than 90% is transported to the shoots by transpirational flow in the xylem. From the stem xylem sap, silicic acid is transported to other leaf cells via Lsi6 transporter reported in rice (Ma et al. 2006). Similar to rice transporters (OsLsi1,2), HvLsi(1,2), ZmLsi(1,2), and CmLsi (1,2) silicon transporters have been discovered in barley (*Hordeum vulgare* L.), maize (*Zea mays* L.), respectively, that are localized at epidermal, hypodermal, and cortical cells (Chiba et al. 2009; Mitani et al. 2009; Figure 1d).

Sodium

Sodium (Na^+) at its low levels is beneficial in the presence of low potassium (K^+) levels. At high Na^+ levels, low-affinity fluxes catalyze Na^+ movement via K^+ selective ion channels such as AKT1 (inward rectifying K^+ channel), HKT (high-affinity K^+ channels), non-selective ion channels (NSCC), and outward rectifying K^+ channels (ORC) (Maathuis 2014; Figure 1e). However, in salt-sensitive plants, there is a Na^+-H^+ antiporter, SOS1 (salt overly sensitive), resulting in the efflux of Na^+ ions. Elevated Ca^{+2} levels are sensed by SOS3 (a Ca^{+2} binding protein), which stimulates SOS2 (a serine threonine protein kinase). The SOS3–SOS2 protein complex then phosphorylates SOS1 that induces the plasma membrane Na^+-H^+ antiporter (NHX1), leading to efflux of Na^+ ions. NHX1 antiport activity can be regulated by SOS2 independent of SOS3, probably by SOS3-like Ca^{2+} binding proteins (SCaBP). High Na^+ levels stimulate ABA production, which negatively regulates SOS2/SOS1 and NHX1 (Silva & Gerós 2009; Figure 1e).

Functional relevance against abiotic stresses

Aluminium

Aluminium (Al^{3+}) is the third most abundant element in the earth's crust. In soil, 7% of total aluminium is present in solubilized form under acidic conditions, increasing their availability to plants. No convincing evidence implies that aluminium is a vital nutrient for plants, while there are a few reports of its beneficial effects (Huang & Barchelard 1993; Figure 2). Soluble Al is released from acidic soils in the form of Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^+$. Among all soluble forms of Al in soil, inorganic aluminium in the form of ($Al (H_2O)_6^{3+}$) is considered the most phytotoxic. In contrast, Al-F, Al-SO$_4$, and Al-P forms are less toxic/non-toxic to plants. Aluminium-tolerant species store Al-organic acid complexes in the symplast (Ma et al. 2001b). Phosphorus treatments along with aluminium increase root and shoot growth and enhance phosphorous absorption in tea plants (Konishi 1992). Al induced the increase in the activities of antioxidant enzymes, such as superoxide dismutase (SOD), catalase (CAT), and ascorbate peroxidase (APX), resulting in increased membrane integrity and delayed lignification and ageing, thus stimulating the growth of tea (*Camelia sinensis* L.) plants (Ghanati et al. 2005; Table. 1). In non-accumulator plants such as turnip (*Brassica rapa* L. sub. sp. *Campestris*) and (*Glycine max* Merr.) increasing aluminium concentrations increased root length (Rufty et al. 1995). At low concentrations, Al^{3+} ameliorates H^+ ion toxicity in wheat (*Triticum aestivum* L.) (Kinraide et al. 1992). Considering the beneficial effects of Al on plant growth indicated by limited studies, its involvement in countering the effects of abiotic stress situations needs to be explored.
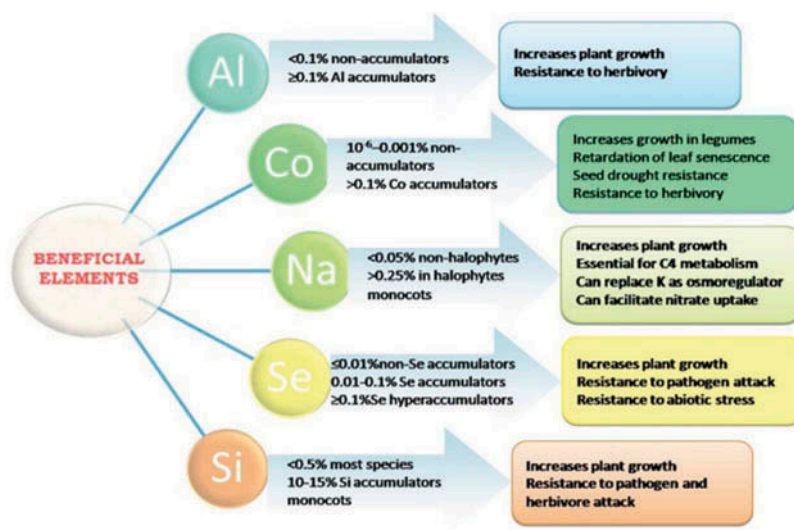
Figure 2. Overview of the functions of beneficial elements at various concentrations.

Cobalt

Cobalt (Co^{2+}) is a micronutrient in plants, and a constituent of vitamin B_{12}. Cobalt has similar chemical properties to nickel (Ni^{2+}), and enters plasma membrane through the same carriers. On the basis of plant dry weight, cobalt concentration ranges from 0.1 to 10 mg kg^{-1} with the exception of plants related to families like *Lamiaceae, Scrophulariaceae, Asteraceae,* and *Fabaceae*, which are co-hyperaccumulators containing >1000 mg cobalt per plant. Of these, *Haumaniastrum robertii* (Robyns) J. Duvign. & Plancke (a copper-tolerant plant) has a peculiarly highest cobalt concentration among phanerogams (about 4304 mg kg^{-1} dry weight) (Brooks 1977). Numerous studies on cobalt estimation in diverse plant species found the presence of cobalt in different plant parts, i.e. in the style and stigma of *Lilium longifolium* Thunb., leaves of green beans (*Phaseolus sativus* L.) and radish (*Raphanus sativus* L.), and in leafy plants such as lettuce (*Lactuca sativa* L.), cabbage (*Brassica oleracea* var. capitata L.), and spinach (*Spinacea oleracea* L.) (above 0.6 mg kg^{-1}) (Kloke 1980). Cereals contain 2.2 mg Co kg^{-1} and forage plants 0.6–3.5 mg Co kg^{-1}, rice (*Oryza sativa* L.) contains 0.02–0.150 mg Co kg^{-1} plant dry weight (Palit et al. 1994).

The essentiality of Co^{2+} has not been recorded in the literature, but is required as a constituent of vitamin B_{12} into methyl and adenosyl vitamin B_{12}, which function as coenzymes. Cobalt is not found at active sites of respiratory chain enzymes; however, there are two sites of action of cobalt discovered in mitochondrial respiration. It prompts different responses towards dissimilar substances like α-ketoglutarate and succinate. In higher plants, Co^{2+} plays a major physiological role, i.e. nitrogen fixation by leguminous crops. Cobalt is an essential component of cobalamine, which is needed for activities of several enzymes in nitrogen fixation by rhizobia bacteria and cyanobacteria that live in root nodules of leguminous plants. In pea (*Pisum sativum* L.), doses of 8 mg of cobalt to the soil increased growth, plant nutrient levels, nodule numbers and weight, and seed pod yield and quality (Gad 2006). In sweet potato (*Ipomea batatas* L.), 10 mg cobalt had a collegial effect on root growth, yield quality as starch, sugars, L-ascorbic acid, and contents of N^+, P^{+3}, K^+, Mn^{2+}, Zn^{2+} and Cu^{2+} compared to the control and other supplemented concentrations (Gad & Kandil 2008). Additionally, Gad (2012) found that supplementation of 8 mg cobalt to groundnut (*Arachis hypogaea* L.) plants significantly increased nitrogenase activity and subsequently enhanced growth and yield, leading to improved quality of pods and oil yield.

A study on peas (*Pisum sativum* L.) revealed that three cultivars varied in their horticultural characteristics when primed with a combination of ascorbic acid (2 mg L^{-1}) + $CoCl_2$ (150 mg L^{-1});

Table 1. Role of beneficial elements in activating antioxidant enzymes to counteract stress conditions.

Beneficial element	Plant species	Antioxidant enzymes	Stress type	Concentration	Reference
Aluminium	Tea (*Camelia sinensis* L.)	Activity of superoxide dismutase (SOD), catalase (CAT), and ascorbate peroxidase (APX) enzymes increases	Improves growth	50 μM as aluminium chloride	Ghanati et al. (2005)
Cobalt	Tomato (*Lycopersicon esculentum* Mill.)	Activity of superoxide dismutase (SOD) and catalase (CAT) enzymes increases	Improves growth	20 mM as cobaltous sulphate	Zhu et al. (2000)
Selenium	Clover (*Trifolium repens* L.)	Alleviates ascorbate peroxidase (APOX) and glutathione reductase (GR) activity	Drought stress	5 μMSe as sodium selenate	Wang (2011)
	Rapeseed (*Brassica napus* L.)	Increase the activity of dehydroascorbate reductase (DHAR), glutathione S-transferase (GST), glutathione peroxidase (GPX), and glyoxalase I (Gly I)	Drought stress	25 μM Se as sodium selenate	Hasanuzzaman and Fujita (2011)
	Rapeseed Seedlings (*Brassica napus* L.)	Enhances antioxidative defence and MG detoxification systems	Salt stress	25 μM Se as sodium selenate	Hasanuzzaman et al. (2011)
	Ryegrass roots (*Lolium* L.)	Enhancing spontaneous dismutation of superoxide radicals and the subsequent activation of POD enzyme	Salt + Heavy metal stress (Al)	0–10 μM Se as sodium selenite	Cartes et al. (2010)
	Spring barley (*Hordeum vulgare* L. cv. Rihane-03)	Increases CAT and GSH-Px activities and lowers lipid peroxidation	Drought stress	30 g ha⁻¹ Se as sodium selenate	Habibi (2013)
	Sorghum seeds (*Sorghum bicolor* L.)	Improves ascorbic acid peroxidase and guaiacol peroxidases activity	Chilling stress	0, 3, 6 & 12 mgL⁻¹Se as sodium selenate	Abbas (2012)
	Sorghum leaves (*Sorghum bicolor* (L.)Moench)	Enhancing antioxidant defence	High temperature stress	75 mgL⁻¹Se as sodium selenate	Djanaguiraman et al. (2010)
	Wheat (*Triticum aestivum* L.)	Enhancing antioxidant defence	Chilling stress	5 mgL⁻¹Se	Akladious (2012)
	Wheat (*Triticum aestivum* L.)	Enhances anthocyanin, phenolic compounds, flavonoids, peroxidases and catalase activity	Chilling stress	1.0 mg kg⁻¹ Se	Chu et al. (2010)
Silicon	Barley (*Hordeum vulgare* L.) cultivars, i.e. Kepin No. 7 (salt sensitive) and Jian 4 (salt tolerant),	Higher activity of superoxide dismutase (SOD), peroxidase (POD), catalase (CAT) and glutathione reductase (GR).	Salt stress	1 mM L⁻¹ Si as potassium silicate (K₂SiO₃)	Liang et al. (2003)
	Cotton (*Gossypium hirsutum* L.)	Si lowers Ni uptake and enhance antioxidant enzymes activities	Nickel toxicity	1.0 mM Si as sodium silicate (Na₂SiO₃)	Khaliq et al. (2015)
	Okra (*Abelmoschus esculentus* L.)	Enhance the activity of superoxide dismutase, peroxidase and catalase	Salt stress	150 mgL⁻¹ Si as silicic acid (Si(OH)₄)	Abbas et al. (2015)
	Rice (*Oryza sativa* L.)	Enzymatic antioxidant (catalase, peroxidase and polyphenol oxidase) increased	Salt stress	1mMSi as sodium silicate (Na₂SiO₃·5H₂O)	Kim et al. (2014)
	Tomato (*Lycopersicon esculentum* Mill c.v.)	Raising SOD and CAT activities	Salt stress	2.5 mM Si as sodium silicate (Na₂SiO₃)	Al-aghabary et al. (2005)
	Wheat (*Triticum aestivum* L.)	Improved leaf membrane stability index, epicuticular wax, relative water content and proline level	Drought stress	Silicic acid (Si(OH)4; 29.16% Si), sodium silicate (Na₂SiO₃; 22.95% Si) and silica gel (SiO(OH)₂; 45.16% Si)	Ahmed et al. (2015)

with desirable significant increases in N and protein content when compared to non-treated plants (Gheeth et al. 2013). A high concentration of cobalt might be attributed to catalase and peroxidase activities that increase catabolism rather than anabolism in tomatoes (Zhu et al. 2000; Table. 1). Cobalt helps to delay senescence in apples and keeps the fruit fresh (Bulantseva et al. 2001). Co^{2+} delays ageing in marigold (*Tagetes patula* L.) and chrysanthemum (*Chrysanthemum* spp.), maidenhair fern (*Adiantum* spp.), common vetch (*Vicia* spp.), and rose (*Rosa* spp.) thereby extending vase and shelf life (Mitra 2015; Figure 2). Cobalt at high doses suppresses Cd^{2+} uptake by roots; moreover, cobalt acts synergistically with Zn^{2+} and Cr^{2+} (Palit et al. 1994). The interaction of cobalt with other metals mainly depends on the concentration of other metal ions. More studies are required to test the role of Co^{2+} in plants growing in stressed environments.

Selenium

Selenium (Se) is a group VIA metalloid in the periodic table whose properties are intermediate between those of sulphur and tellurium. In cultivated soils, selenate and selenite are the most prevalent forms. Selenite is more toxic than selenate, due to its faster incorporation. Depending on the geographical area, Se content ranges from 0.1 to 2.0 mg kg^{-1}. The minimal nutritional level of Se for animals is about 0.05–0.10 mg kg^{-1} dry forage feed, while 2–5 mg kg^{-1} is toxic (Dhillon & Dhillon 2003).

Se is a beneficial micronutrient for animals and humans, yet its essentiality in higher plants is ambiguous and unresolved. Se is essential for growth of some algae (*Chlamydomonas reinhardtii* P. A.Dang) and bacteria but not for higher plants. It is also a structural component of some specific selenoproteins and seleno-tRNAs. Selenocystiene acts as an opal stop codon in selenoproteins when present in a specific secondary mRNA structure (SeCys insertion sequence) (Lee et al. 1989). However, in higher plants, SeCys insertion sequences have not been identified, rather glutathione peroxidase (GPX) (a plant homologous of selenoproteins) replaced Cys with SeCys at their active sites (Lobanov et al. 2007).

Se may be an essential micronutrient for plants endemic to seleniferous soils. *Astragalus* and *Stanleya* are major hyperaccumulators of Se. However, the beneficial effects of Se on Se-hyperaccumulators is much less when plants were grown under lower phosphate levels, which suggests that Se may antagonize phosphate toxicity in Se hyperaccumulator plants (Terry et al. 2000).

In Se non-accumulator plants, Se essentiality is questionable (Marschner 2012). Despite this, Se has not been validated as an essential element; numerous studies have demonstrated that Se may exert beneficial effects at their low concentration, including increased growth in ryegrass, lettuce, potato, and buckweed (Hartikainen 2005). Se has diverse biological roles at different concentrations: trace amounts are needed for normal growth and development; moderate concentrations maintain homeostatic functions, while elevated concentrations have toxic effects on plants. The sensitivity of each plant species to Se concentrations in the soil varies, agriculturally important plant species when exposed to varied Se levels may respond accordingly.

Protective effects of selenium in counteracting various abiotic stresses. Selenium helps to ameliorate various abiotic stress injuries induced in plants by cold, drought, high temperature, water, salinity, heavy metals, UV-B stress, senescence, and desiccation stress. Selenium protects plants against abiotic stresses by (1) helping to maintain ion balance and structural integrity of cells, hence regulating the uptake and redistribution of elements essential in the antioxidative system (Table1), and (2) interfering with the electron transport complex (ETC) of the photosynthetic system (Kaur et al. 2014; Figure 2).

Se affects plants by (1) stimulating plant growth and protecting plants against abiotic stresses and heavy metal stresses at low dosage, and (2) acting as a pro-oxidant, which is toxic to plants at high doses. Hence, the concentrations of Se are either beneficial or toxic depending on the crop type. In ryegrass (*Lolium perenne* L.), 1 mg kg^{-1} Se (H_2SeO_4) added to soil was marginally toxic, while a similar level (0.8 mg L^{-1} Se as Na_2SeO_3) was more toxic in paddy-rice in a hydroponic

system (Feng et al. 2013). Se application as a foliar spray or base fertilizer increased Se content in the edible portion of crops, thus helping to combat injuries generated by four different abiotic stresses (Pezzarossa et al. 2012).

Silicon

Silicon does not qualify as an essential element but provides substantial benefits to many crops particularly those growing in greenhouse. Silicon mimics carbon on the basis of chemical properties, and can make four bonds with molecule/molecules. Silicon is available to plants as monosilicic $(Si(OH)_4)$ acid with 0.1–0.6 mM in soil and water (Epstein & Bloom 2005), and is supplied to agricultural crops in the form of potassium silicate (K_2SiO_4) or sodium silicate (Na_2SiO_4). In plants, silicon is deposited in cell walls in the form of amorphous silica $(SiO_2\text{-}nH_2O)$ and enhances cell wall rigidity and strength interacting with pectins and polyphenols. Monocotyledonous plants (10–15%) contain more Si^{4+} levels compared with dicotyledonous plants (0.5% or less), especially members of the commelinids clade orders *Arecales* and *Poales* (Hodson et al. 2005). As Si^{4+} deficiency affects plant growth, development, and reproduction, it may be classified as a 'quasi essential' element.

Marschner (2012) demonstrated that Si^{4+} is deposited in epidermal cells of leaves, hence improving leaf exposure to light by keeping leaves more erect; in roots, it increases cell elongation thus enhancing cell wall elasticity. Si^{4+} helps to alleviate various abiotic stresses such as metal toxicity, drought, high temperature, salt, radiation damage, freezing, and chilling. The reduction in dry weight of 30-day-old rice seedlings when exposed to different doses of X-rays was less in those treated with Si^{4+} than those without Si^{4+} (Ma 2004). Likewise, when Si^{4+} was supplied, subsequent radiation exposure restored plant growth.

Si^{4+} mitigates water scarcity by lowering the transpiration rate, since Si^{4+} is deposited under the cuticle of leaves. Si^{4+}-supplemented rice seedlings had 30% lower transpiration rates than controls, which has a thin cuticle. Substantial Si^{4+} was deposited on epidermal cells in cell walls and caused partial hindrance to transpiration bypass flow. The effect of Si^{4+} is more evident under water-stressed conditions (low humidity) than non-water-stressed conditions (high humidity) (Ma et al. 2001a). Si^{4+} thermally stabilizes lipids in cell membranes and helps to prevent heat stress. Si^{4+}-supplemented leaves had less electrolyte leakage at high temperature (42.5°C) than those without Si^{4+}. The effect of salt stress in rice, wheat, and barley was mitigated by silicon application (Ma 2004). NaCl (100mM) applications for 3 weeks suppressed root and shoot growth by 60%, but Si^{4+} addition nullified the salt-induced injury in rice plants (Yeo et al. 1999). In barley, Si^{4+} may assist changes in structural integrity and function of plasma membranes by suppressing lipid peroxidation caused by salt stress and stimulating root H^+-ATPases in membranes and antioxidant machinery (Liang et al. 2002; Rizwan et al. 2015; Figure 2; Table. 1).

Sodium

Sodium (Na^+) nutrition remains an alluring and evasive topic. While most research has been conducted on sodium toxicity; there are various deliberations and controversies, which suggest that Na^+ is a beneficial element at low concentrations. As K^+ is the principal electrolyte for plants, Na^+ and K^+ are similar both chemically and structurally. In addition, pervasive use of Na^+ by numerous salt-tolerant species suggests that Na^+ can replace K^+ via non-selective cation transporters. The role of Na^+ in plant nutrition is based upon a plant's ability to accumulate or eliminate this ion in tissues of glycophytic plant species. However, in halophytic plants, specifically, sodium transporters exclude Na^+ ions out of roots, into the vacuole or shoot phloem to counteract high sodium levels in the soil. Non-halophytes can use Na^+ to some extent under K^+ inadequacy (Subbarao et al. 2000; Figure 2). In C_4/CAM plants, Na^+ acts as an essential element for regeneration of PEP (phosphoenolpyruvate) from pyruvate to fix carbon for photosynthesis. Sodium acts as a beneficial element in some natrophilic species by replacing potassium ions as co-factors for certain enzymes and also acts as an osmoregulator in stomatal movement and cell expansion, which is particularly beneficial under K^+-limiting levels. Na^+ application to plants of family poaceae,

brassicaceae, apiaceae, asteraceae, malvaceae, fabaceae, and solanaceae enhanced growth in potassium-deficient soils (Flowers & Lauchli 1983; Figure 2). Moreover, the estimated extent to which Na^+ replaced K^+ in edible portions of wheat (*Triticum aestivum* L.) and rice (*Oryza sativa* L.) was by 1% and in red beet (*Beta vulgaris* L.) by 90% (Subbarao et al. 2000).

According to the Arnon and Stout (1939) criteria, for C_4 plant species such as saltbrush (*Atriplex vesicaria* Heward. and *A. tricolor* Heward.), Bassia (*Kochia childsii*), millet (*Panicum miliaceum* L.), and saltgrass (*Distichlis spicata* L.), Na^+ is essential. Indeed, in Na^+-lacking soils, C_4 plants (*Amaranthaceae, Chenopodiaceae,* and *Cyperaceae*) show visual deficiency symptoms like chlorosis and necrosis, grow poorly, and have impaired flower formation; nonetheless, supplementation of 100 µM Na^+ enhanced growth and alleviated visual deficiency symptoms (Johnston et al. 1988). Maathuis (2014) opined that sodium is beneficial but not essential for halophytes and is required at micronutrient levels. Halophytes, particularly succulent halophytes from the *Chenopodiaceae* family, respond to moderate-to-high salinity and reach maximum biomass. Conversely, in other halophytic plant species, growth is stimulated at low sodium levels, which imply that the overall nutritional requirement of the plant is fulfilled.

Some aquatic halophytes use Na^+ to facilitate nitrate uptake via Na/NO_3 co-transporters. Sodium may also interfere in the nitrate and ammonium uptake from soil, thereby impairing nitrogen metabolism (Ullrich 2002). Nitrate is a significant vacuolar solute in many plant species, especially those in the *Chenopodiaceae* and *Graminae* families, under non-saline conditions. Sodium assists in maintaining osmotic balance in plants by synthesizing large amounts of nitrogen-containing compatible solutes like glycinebetaine and proline (to some extent) that leads to the accumulation of amides and polyamines (Pilon-Smits et al. 2009). Although there is considerable influential evidence on the role of Na^+ in plant metabolism and growth stimulation, the essentiality of Na^+ in glycophytic plants is under debate.

Functional relevance against biotic stresses

Plants are the easy targets of regular attempts of attack by biotic stress factors such as fungi, viruses, and herbivores. In response, diverse defence strategies are activated by plants against various invaders, which require the interaction of a susceptible host and a virulent pathogen. In relation to availability of diverse levels of beneficial elements, a range of complex interactions can be expected, taking into account that pathogens, herbivores, and plants also differ in deficiency and toxicity thresholds for such elements. Beneficial metal ions are capable of protecting plants from biotic stresses in various ways: a) 'metal defence' in metal ion-hyperaccumulators by acting either as antifeedants or as plant-systemic pesticides, b) 'trade-off' of organic defences, c) 'metal therapy' by switching a defective signalling system, or d) 'metal-induced fortification' of plants against pathogen attack (Poschenrieder et al. 2006).

Exogenous application of beneficial elements can generate defence reactions in response to pathogen attack in non-accumulator plants. Protection is only possible if the metal is not as much toxic to the plant than to the parasite, i.e. the plant is more resistant to the metal than the pathogen/herbivore. Moreover, a fundamental difference in the relevance of stress signalling between biotic and ion toxicity stress depends on the effectiveness of inducible defence responses. In biotic stress resistance, pathogen elicitor-induced ion fluxes and reactive oxygen species (ROS) are essential for triggering activation of genes responsible for the synthesis of compounds such as phytoalexins that proficiently stop the pathogen, which is the origin of the signal. In the first line of defence, beneficial elements (in low concentration) also act as scavengers for excess of ROS, which lower cell injury induced by the plant pathogen. Secondly, ROS species can result in cell wall lignification that serves as a barrier for pathogen invasion. ROS may also trigger defence signals and defence-related secondary metabolites (Walters et al. 2005). Signal transduction pathways of biotic stress present multiple spots of interaction with metal ion stress signalling (Figure 3). Biotic stress leads to increased
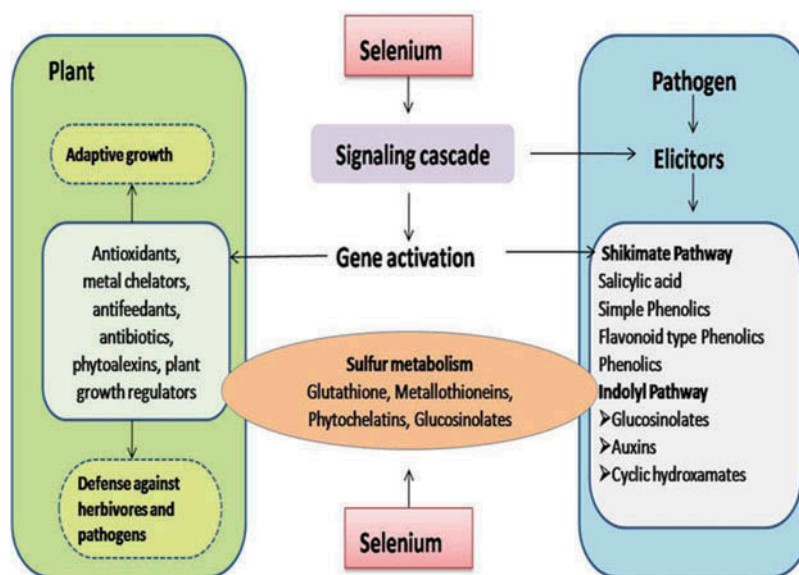
Figure 3. The role of beneficial metal ions in plant–pathogen interactions at a metabolic level (Poschenrieder et al. 2006). The shikimate pathway and sulphur metabolism produce compounds that assist in both biotic stress defence and metal binding. An increased level of reduced glutathione is required for stress resistance over a broad range. A shikimate pathway-derivative growth regulator (auxin) makes a connection between stress metabolism and adaptive growth.

cytoplasmic Ca^{2+}, ROS production, nitric oxide (NO), salicylate, thioredoxin and mitogen-activated protein kinase (MAPK) interactions between pathogen-elicited reactions and those activated by metal ions (Glazebrook 2005). In biotic stress resistance, pathogen elicitors result in ion fluxes and oxidative burst, which are crucial for prompt activation of genes responsible for the synthesis of compounds like phytoalexins that competently stop the pathogen, which is the origin of the signal (Walters et al. 2005). However, metal ion-induced ROS activates antioxidant production, which assists to limit ROS-derived injury, but does not abolish the stress factor.

Biotic stresses and metal ions can interact at a metabolic level. High levels of reduced glutathione and production of phytochelatins is the key route for interactions between the metal ion and biotic stresses in sulphur metabolism (Figure 3). The shikimate pathway occurring in the host cell is another significant way for interactions between biotic stress and beneficial elements (Figure 3). In this pathway, beneficial ions trigger the production of some defence-related molecules such as essential amino acids; phenolics such as salicylic acid directly concerned in stress signalling; catechin (high-affinity ligand for metal ion) under neutral pH conditions; and flavonoid-type phenolics are released into the rhizosphere, which act as plant signals to N_2-fixing symbiotic microorganisms (Barceló & Poschenrieder 2002). In shikimate pathway, benzoic acid 2-hydroxylase (BA2H) is synthesized in leaf vacuoles of cereals, which catalyzes the hydroxylation of benzoic acid to salicylic acid, a mediator of plant responses to pathogens and wounding, which require iron and aluminium for binding. Benzoxazinoids like DIMBOA (2,4-dihydroxy-7-methoxy-1,4-ben -zoxazin-3-one) have a high affinity for iron. Moreover, aluminium bound to DIMBOA is not toxic. Upon Al application to the host plant (*Zea mays* L.), enhanced levels of DIMBOA were observed in root tips of an Al-resistant maize variety, while a drastic Al-induced decrease of DIMBOA levels was found in tips of a sensitive variety (Poschenrieder et al. 2005). The indolyl pathway (Figure 3) functional in the host cells presents an extraordinary metabolic range that reflects interactions between plants and insects, predominantly in the case of reactions catalyzed by cytochrome P_{450}-type monooxygenase (Chapple 1998). It produces glucosinolates, cyclic hyroxamates, which may be responsible for regulation of interactions among biotic stress and metal ions.

Pathogen stimulates the elicitors such as salicylic acid, benzothiadiazole, benzoic acid, glucosinolates, auxins, cyclic hydroxamates and so forth, which affect production of phenolic compounds and activation of various defence-related enzymes in host cell (Figure 3). In plants, beneficial elements at their low concentrations trigger the antioxidants, metal chelators, antifeedants, antibiotics, phytoalexins, and various growth regulators through a signalling cascade, which impart resistance against biotic stresses (Poschenrieder et al. 2006). Additionally, in response to metal ions, a variety of S-containing secondary metabolites such as thionins and defensins, glucosinolates, and phytoalexins are synthesized, having a key role in defence against pathogen and herbivore attack. Also, the low-molecular-weight thiol glutathione (GSH), evoked by beneficial elements, plays a significant role in response to biotic stresses as part of the glutathione cycle in detoxification of reactive oxygen species (Figure 3).

Limited work has been done regarding the role in beneficial elements in biotic stresses; some case studies are presented further:

Aluminium

Aluminium helps in disease control because it can be toxic to pathogenic microorganisms. It inhibits spore germination and vegetative growth in the blast rot pathogen (*Thielaviopsis basicola* Ferraris.) (Meyer et al. 1994), and consequently, mycelial growth and sporangial germination of late blight in potato (*Phytophthora infestans*), thus saving it from the disease (Andrivon 1995; Table. 2).

Table 2. Beneficial elements which help to suppress insect/pathogen attack in various crop plants.

Beneficial element	Plant species	Insect/Pathogen	Reference
Aluminium	Potato (*Solanum tuberosum* L.)	*Phytophthora infestans* (Late blight of potato)	Andrivon (1995)
		Thielaviopsis basicola. Ferraris (Blast rot)	Meyer et al. (1994)
Selenium	Desert princes plume (*Stanleya pinnata* Pursh.)	*Plutella xylostella* (Diamond back moth)	Freeman et al. (2006)
	Indian mustard (*Brassica juncea* L.)	*Pieris rapae* (Caterpillar), *Mesodon ferrissi* (Snail), *Fusarium sp.* (Root stem pathogen) *Alternaria brassicicola* (Leaf pathogen) *Myzus persicae* (Green peach aphid)	Hanson et al. (2003, 2004)
Silicon	Cucumber (*Cucumis sativus* L.)	*Didymella bryoniae Botrytis cineria* (Stem rotting &Stem lesions)	O'Neill (1991)
		Pythium ultimum Pythium aphanidermatum (Root disease)	Cherif et al. (1994)
	Grape (*Vitis vinifera* L.)	*Uncinula necator Oidium tuckeri* (Powdery mildew)	Bowen et al. (1992)
		Oscinella frit (Fruit fly)	Sang-Young et al. (1996)
	Italian ryegrass (*Lolium multiforum* Lam.)	*Oscinella frit* (Fruit fly)	Moore (1984)
	Maize (*Zea mays* L.)	*Sesamia calamistis* (Pink stalk borer)	Setamou et al. (1993)
	Pea (*Pisum sativum* L.)	*Mycosphaerella pinodes* (Leaf spot)	Dann and Muir (2002)
	Rice (*Oryza sativa* L.)	*Magnaportha grisea* (Leaf and neck blast)	Seebold et al. (2001)
		Xanthomonas oryzae pv. oryzae (Xoo) (Bacterial blight)	Chang et al. (2002)
		B. graminis f.sp. *tritici. M. grisea* (Blast disease)	Liang et al. (2005)
		Rhizoctonia solani (Sheath blight pathogen)	Zhang et al. (2006)
	Sorghum (*Sorghum bicolor* Moench.)	*Striga asiatica* Kuntze (Witch weed)	Hodson and Sangster (1989)
	Sugarcane (*Saccharum officinarum* L.)	*Leptosphaeria sacchari* (Sugarcane ring spot)	Raid et al. (1992)
		Eldana saccharira (Sugarcane borer)	Meyer and Keeping (2001)
	Wheat (*Triticum aestivum* L.)	*Tribotium castaneum* (Flour beetle)	Setamou et al. (1993)
	Wild rice (*Zizania aquatica* L.)	*Bipolaris oryzae* (Fungal brown spot)	Malvick and Percich (1993)

Selenium

Selenium (Se)-hyperaccumulating plants such as *Stanleya pinnata* Pursh. (*Brassicaceae*) accumulate more than 1000 mg Se kg^{-1} DW from soils that contain 10 mg Se kg^{-1} DW or less (Feist & Parker 2001). Se protects *S. pinnata* from caterpillar herbivory (a newly discovered variety of the invasive diamondback moth (*Plutella xylostella*) through deterrence and toxicity). More interestingly, a Se-tolerant wasp (*Diadegma insulare*) can parasitize the tolerant moth (*Plutella xylostella*) (Freeman et al. 2006; Table. 2). In *Brassica juncea* L., Se accumulation defends plants from the *Brassica*-specific herbivore *Pieris rapae* (caterpiller), *Mesodon ferrissi* (snail), *Myzus persicae* (green peach aphids), and fungal infection (Hanson et al. 2003, 2004; Table. 2).

Silicon

Silicon (Si^{4+}) acts as a signal and renders the natural defence from herbivores by instigating enzyme activity such as peroxidases, chitinases, and polyphenoloxidases, or by enhancing the release of phenolic compounds, phytoalexins, antimicrobial compounds, and systemic stress signals (salicylic acid, jasmonic acid, and ethylene). Si^{4+} is polymerized in cell walls providing sturdiness, which obstructs fungal germ tubes from penetrating the epidermis and therefore prevents infection (Hayasaka et al. 2008). Si^{4+} bioactivity has been correlated with the secondary messengers of systemic acquired resistance (SAR), i.e. analogous to a plant's immune system, reported in cucumber (Kauss et al. 2003). Si^{4+} has an equivalent saturable effect and can modulate the activity of the post-lecitation intracellular signalling system comprising mitogen-activated protein (MAP) kinases. Fauteux et al. (2005) reported that when Si^{4+} invariably accumulates in plants, it is only the soluble forms of Si^{4+} within plants that can provide the SAR defence response, while the polymerized form of Si^{4+} is almost inert. Furthermore, Si^{4+} is an obstacle for insect pests like stem borer, brown plant hopper, rice green leaf hopper, and white-backed plant hopper, and non-insect pests such as leaf spider and mites (Savant et al. 1997; Table. 2).

Conclusions

We conclude that adequate intracellular concentrations of beneficial metal ions (in traces) are not only required for optimal growth and development of plants and their enemies, but also for pathogen virulence and plant defences. Hyperaccumulators of beneficial elements are the principal basis for the metal defence hypothesis against plant pathogens. Cross-talk in stress signalling and metal ions is related to plant responses against both abiotic and biotic stress factors and is an upcoming research area in metal-hyperaccumulator and non-hyperaccumulator plants. Elements such as aluminium (Al), cobalt (Co), sodium (Na), selenium (Se) and silicon (Si) are considered beneficial for plants. Na and Si are vital for certain plant groups, while Al and Se are recommended as crucial for some hyperaccumulator species. Co is essential for the microbial partners of some plants rather than the plants themselves. In this era of research, the effects of beneficial elements at low levels deserve more awareness in order to fertilize crops with these nutrients to boost crop production under stressed environments as well as enhance plant nutritional value as feed or food. The mechanisms following the beneficial effects (at low levels) to the plants have not been fully explored, unlike the toxic effects (at high levels). How these elements impart protection from pathogens and abiotic stress factors need to be probed further, especially at a molecular level. Whether these elements have synergistic or antagonistic effects on plants growing under unstressed and stressed situations requires to be investigated. Foliar application of these elements needs to be tested in plants growing under stressed environment. It is noteworthy that elements other than those discussed here may also be beneficial for plants, but more validation is needed to support these results.

Disclosure statement

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