





# Non-Essential Elements and Their Role in Sustainable Agriculture

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**Abstract:** Agricultural systems are constantly under environmental pressure, and the continuous rise of the global population requires an increasingly intensification of agronomical productivity. To meet the current global food demand, particularly in depleted ecosystems under adverse climate conditions, the development of novel agronomical practices, which ensure crop productivity while safeguarding minimal impact to the environment, must be encouraged. Since aluminium (Al), cobalt (Co), selenium (Se), silicon (Si) and sodium (Na) are not essential to plant metabolism, their benefits are often neglected or underestimated in agriculture; however, several studies support their advantages in sustainable agriculture when properly employed. The agronomical uses of these elements have been studied in the last decades, delivering important cues for the improvement of food and feed production worldwide due to beneficial effects in plant growth and productivity, nutrient balance, pest and pathogen resistance, water stress management, heavy-metal toxicity alleviation, and postharvest performance. However, their application has not been addressed as part of a holistic conservation strategy that supports the sustainability of agroecosystems. Here, we discuss the potential use of these elements in sustainable agriculture, and the knowledge gaps that hinder their effective integration into agronomical practices, which result in equally profitable applications while supporting environmental sustainability.

**Keywords:** climate change; ecosystem services; plant nutrition; plant protection; sustainability



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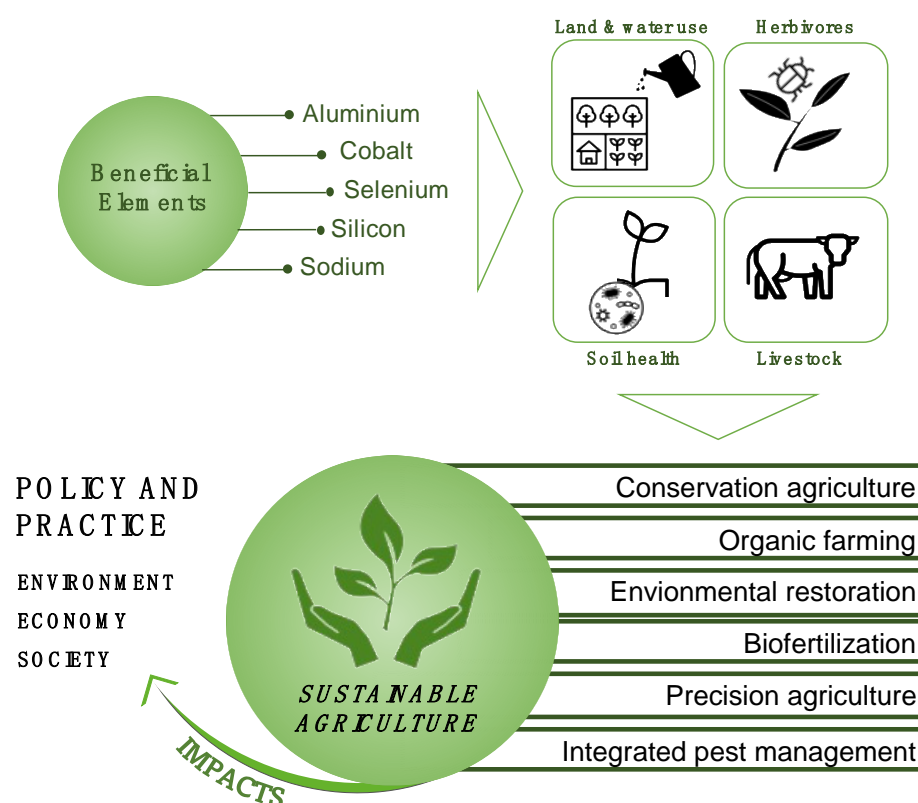
## 1. Introduction

Current environmental changes combined with the rise of the global population have resulted in extreme pressure over the current agricultural systems. In order to respond to the increasing demand for food, the use of intensive agricultural practices has resulted in increased greenhouse gases emissions, biodiversity loss, and soil erosion [1]. Furthermore, several studies show that the predicted increase in temperature and elevated atmospheric carbon dioxide (CO<sub>2</sub>) can reduce pesticides' efficacy [2,3], which may lead to an exacerbated use of these compounds, decreasing soil quality and impacting the existent beneficial microbial communities. Notwithstanding, it has been demonstrated that the productivity and profitability of farms and orchards are not necessarily dependent on the use of pesticides [4].

Agriculture provides economic, cultural, social, and nutritional benefits to the global population [5], and it continues to transform in response to climate variances such as CO<sub>2</sub> levels, water and air temperature, sea levels, and rainfall [6]. All these conditions directly influence agricultural yields and crop resilience, creating an increasing need to take actions that can mitigate or at least delay the effects of this phenomenon [7].

Due to the deeply negative impact that these climatic and environmental factors impose on crops' productivity and nutritional value, alternative agricultural systems have

been promoted during the last decades [8]. However, the greatest challenge of these alternatives is to maintain yield and comply with the sustainable agriculture definition [9]. This definition integrates the animal and plant production systems, under an efficient management to respond to human food and fibre needs that improve environmental conditions, balance the use of natural and non-renewable resources, support the economic farm revenue, and increase general life quality. Examples of sustainable agricultural practices include conservation agriculture, organic farming, biofertilization, precision agriculture, and integrated pest management (Figure 1). Ideally, these techniques should contribute to the sustainability of the farming systems' ecosystem in light of their environmental, economic, and social impacts [10].



**Figure 1.** The role of beneficial elements in sustainable agriculture, plus the main contributions and impacts. As beneficial elements impact land and water use, herbivores' life cycle, soil health, and livestock feed and management, they can contribute to different practices related to sustainable agriculture. Hence, their optimised use can contribute to the environment, economy, and society.

Although these interventions must be able to support the need to increase food production, they must also be pursued with low pressure on the natural environment. In order to accomplish this, crop rotation [11], biofertilization [12], and precision agriculture have been used to decrease these inputs while improving crop productivity and soil fertility (Figure 1). Within organic agriculture and integrated pest management, a minimum or no input is considered, specifically in the case of pesticides or veterinary medicines [13].

However, maintaining optimal plant nutrition with no or very low inputs is challenging, since different climatic and environmental conditions alter nutrients bioavailability, hindering their uptake. This is particularly relevant when managing beneficial elements in agriculture. Aluminium (Al), cobalt (Co), selenium (Se), silicon (Si), and sodium (Na), when supplied to plants in low or limited concentrations (such as the ones promoted within sustainable agriculture), can bring beneficial outcomes in certain crops, such as growth-promoting effects [14]. Hence, they are not considered essential elements for species to survive but have an important role in plant biology, including the ability to balance the

toxicity and the beneficial effect of one another, as is the case of Al and Si or Na [15]. This interaction between different beneficial elements can regulate ion uptake and accumulation, enhancing the antioxidant defence system of the plant [16].

Additional members of the ecosystem such as herbivores, soil microbiota, and livestock are also impacted by the effects of these beneficial elements. For example, the elements play a role in defence against pathogens and herbivores, particularly by priming the plants to enhance and shorten the response to insect herbivory [17]. Soil microbiota, on the other hand, benefits from the presence of beneficial elements such as Se, since these elements enhance microbiome diversity and beneficial rhizobacteria abundance, while decreasing the abundance of pathogenic fungi [18,19]. As for livestock, by incorporating the beneficial elements in the plant's edible parts that serve as cattle feed, depending on their bioavailability, they can impact feed efficiency, ensuring an efficient transformation of feed into animal protein [20].

In contempt of all the positive outcomes that sustainable measures have on plant nutrition, farming yield, and land use, European policy strategies to support farmers and repel biodiversity loss and climate change, have failed to ensure an increased sustainable production [21]. Political commitment in combination with a strong participation of all stakeholders into decision-making continues to be pointed out as one of the most possible effective strategies in order to successfully establish sustainable agricultural practices and to make them profitable and competitive in the long-run [22]. The use of beneficial elements can be an important tool to support these policies and enable the adoption of new strategies, which can result in equally profitable production and more sustainable consumption.

## 2. Aluminium

Aluminium utilization in agricultural context is oftentimes limited, since its toxicity is one of the primary factors impairing crop yield on highly acidic soils [23]. At pH values lower than 5,  $\text{Al}^{3+}$  ions dissolve from clay minerals, potentially being toxic to plants by hampering root growth and functioning as well as leading to reduced plant yield due to drought and/or mineral deficiencies [24]. In fact, as much as 40–50% of arable lands worldwide are acidic, with approximately 60% of acid soils being located in developing countries, where Al toxicity limits crop production further threatening food security [25]. Since Al has been considered a major toxic factor for agriculture in these soils, most research has focused on unravelling Al toxicity mechanisms in plants. Nevertheless, when supplied at low concentrations through soil application, Al has been shown to be beneficial to some plant species, having been classified as a beneficial element [7,26].

For example, Al-based biochar and nanoparticles could become an alternative to synthetic chemicals in enhancing plant growth and productivity as well as in the control of noxious pests and pathogens. Moreover, Al fluorides, sulphates, or phosphates have also been proven to be less toxic or even non-toxic to plants, when applied in adequate concentrations adapted to each type of crop [27]. Stimulatory effects have been reported in several plant species supplemented with Al, ranging from increased mineral uptake, including calcium (Ca), potassium (K), boron (B), and phosphorous (P), mitigation of pests and pathogens, and alleviation of unfavourable environmental conditions, such as high  $\text{H}^+$  concentration in acid mineral soils, drought, high and low temperatures, soil salinity, and manganese (Mn) and copper (Cu) toxicity [28–31].

Due to its proposed roles in signal transduction within plant tissues [32], Al-based compounds could represent an additional option for crop valorisation and protection, either by complementing other chemicals and fertilization regimens to promote plant growth and productivity, or to enhance plant protection by inhibiting pests and pathogens, particularly in situations of acquired resistance to currently used control compounds.

### 2.1. Plant Growth and Productivity

Although Al is generally linked to toxicity and impaired growth in most plants, a beneficial effect has been observed in several economically important crops. In Al-tolerant

rice (*Oryza sativa*) varieties, increased root growth was reported following supply of 160 and 200 mM of this element [30,33]. Similarly, Bertrand and Wolf [34] showed that increasing Al concentration from 2.2 to 7.4  $\mu\text{M}$  increased the yield of corn (*Zea mays*) plants by four-fold. More recently, Wang et al. [35] observed that supply of corn plants with a low dose of Al inhibited root growth, while increasing leaf growth. Nevertheless, increased root elongation and activity was reported in soybean (*Glycine max*) and coffee (*Coffea arabica*) supplied with up to 41  $\mu\text{M}$  and 300  $\mu\text{M}$  of Al, respectively [28,36]. In the tea plant (*Camellia sinensis*), Al generally stimulates root growth in concentrations as high as 6.4 mM, with reported delayed plant growth when Al is absent [37–39]. In fact, it has been shown that Al supply alleviates Fe toxicity in tea plants, thus improving plant growth [40]. In silver birch (*Betula pendula*) and jolcham oak (*Quercus serrata*), long-term Al supply increased root and shoot growth [41,42], possibly due to stimulation of the nitrate reductase enzyme in roots and to IAA-induced nitrate synthesis [43]. Nevertheless, it has been demonstrated that Al promotes plant growth under ammonium supply, but it was inhibiting the nitrate supply [44], clearly demonstrating an interaction between Al and other minerals during plant growth.

## 2.2. Nutrient Balance

It has been hypothesised that Al induces the activity of transport proteins and changes in membrane potential and proton flux, thus promoting nutrient fluxes into plant tissues [45]. The uptake of several macronutrients, such as N, P, and K, was found to be stimulated following Al application to several agronomically interesting plant species, such as rice, wheat (*Triticum aestivum*), cranberry (*Vaccinium macrocarpon*), Japanese bamboo (*Polygonum sachalinense*), and buckwheat (*Fagopyrum esculentum*) [46]. Nevertheless, the outcomes of Al supply seem to vary greatly depending on the form, concentration applied, and plant species (Table 1).

In tea plants, for example, root growth stimulation by Al [44] probably results from increased uptake of macronutrients such as P, most likely resulting from the precipitation of Al–P complexes on the root surface and/or apoplast [38,42,46]. However, Konishi et al. [37] showed that in these plants Al significantly decreased Ca content and, to a lesser extent, Mg content, while nitrogen (N) and K contents increased. Most importantly, Al was also shown to alleviate P-toxicity, suggesting a regulatory role in its absorption and utilization [37]. In jolcham oak, stimulation of root growth by Al was not only associated with P uptake, but also with the activation of the enzyme nitrate reductase and the increase in nitrate uptake [43,47]. Additionally, bananas (*Musa* spp.) growing with 78.5  $\mu\text{M}$  of Al also showed increased K and P contents, although the authors also reported reduced Ca and Mg contents [48]. Similarly, in barley (*Hordeum vulgare*) plants, Al (100  $\mu\text{M}$ ) inhibited the influx of Ca, P, and ammonium, but enhanced the influx of nitrate and phosphate [49].

In coffee plants, a supply of 100  $\mu\text{M}$  of Al increased K and Ca concentrations in roots [31]. In maize, ammonium enables Al-induced stimulation of N assimilation, leading to increased nitrate accumulation in roots [55]. In addition, in tea plants submitted to B deficiency, Al positively regulated N and carbon (C) metabolism as well as antioxidant activity, increasing the uptake and transport of B into upper plant tissues [29,56].

It is clear that the interplay between Al and plant nutrient balance is extremely dependent on the plant species, plant growth condition, and regimen of Al supply. However, further studies could consolidate the potential of Al in the formulation of novel fertilizers. In fact, nanoparticles of potassium aluminium silicate (Leucite) occluded by calcium ammonium nitrate have already been proposed as green fertilizers, allowing the slow release of nitrate for up to 16 days [57]. An Al-rich biochar from sugarcane cake has also been proposed as an adsorbent and fertilizer, by increasing P availability in sandy soils [58], which supports the use of agricultural by-product resulting from biomass pyrolysis and other plant residues to improve nutrient use efficiency (NUE).

**Table 1.** Impact of aluminium (Al) root supply to plant mineral contents and physiological traits in several food and feed agronomical crops.

Plant Species	Al Supply	Al Concentration Tested	Effects	Reference
<i>Brachiaria ruziziensis</i>	AlCl <sub>3</sub>	15 ppm	↑N, P and K and ↓ Ca in L; ↑ K and ↓ Ca in St	[46]
<i>Camellia sinensis</i>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	43 ppm, low P 345 ppm, high P	Low P: ↑ K in L, St and R and Mn in L; ↓Ca in L; ↑ DW High P: ↑ K and Mn in L, St and R and N in L; ↓Mg in L, St and R; ↑ DW	[37]
	AlCl <sub>3</sub>	200 µM	↑ Ca and Fe and ↓ P, Mn, Mg and B in L; ↓ catechin and epicatechin	[50]
<i>Coffea arabica</i>	AlCl <sub>3</sub>	2.7 ppm	↑ K and Ca in R; ↑ root growth; ↑ phospholipase C activity	[28]
<i>Hordeum vulgare</i>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	100 µM	↑ NO <sub>3</sub> <sup>−</sup> and PO <sub>4</sub> in R; ↓P, Ca, and NH <sub>4</sub> <sup>+</sup> in R	[49]
		600 µM	↑ Zn in Sh and R and P in R; ↓ P in Sh and K, Ca, Mg, Fe and Mn in Sh and R	[51]
<i>Musa spp.</i>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	78.5 µM	↓ Ca, K, P, Mg, NO <sub>3</sub> -N and NH <sub>4</sub> -N; ↓ Water uptake	[48]
<i>Oryza sativa</i>	AlCl <sub>3</sub>	3 ppm	↑ N and P in L, P and K in St and P in R; ↑ DW	[46]
<i>Phaseolus vulgaris</i>	AlCl <sub>3</sub>	10 ppm	↓ Ca in R, St and L, and ↑ R length, DW and St length in cv. ‘Hilds Maxi’; ↓ Ca in R, L area, Sh DW in cv. ‘Seleccion F-15’; ↑ Ca in St and ↓ Ca in L, R and St length, L area, R and Sh DW in cv. ‘Eagle’	[52]
<i>Prunus persica</i>	NS	1000 µM	↑ N in St ↓ P, K, Ca, Mg, in R, St and L; ↓ Fe, Mo, in R and L; ↓ Mn in L; ↓ total growth, lateral Sh number and length, L number and area	[53]
<i>Secale cereale</i>	AlK(SO <sub>4</sub> ) <sub>2</sub>	10 ppm	↑ P and ↓ K, Ca, Mg and Mn in L; ↑ K and ↓ Ca and Mn in R; ↓ Chl. b and carotenoid	[54]
× <i>Triticosecale</i>	AlK(SO <sub>4</sub> ) <sub>2</sub>	10 ppm	↑ Mn in R; ↓K in L and R; ↓ Chl. a and Chl. b; ↑ carotenoid	[54]
<i>Triticum aestivum</i>	AlK(SO <sub>4</sub> ) <sub>2</sub>	5 ppm	↑ K and ↓ P and Mn in L; ↑ Ca and ↓ Mn in R; ↑ Chl. a	[54]
<i>Vaccinium macrocarpon</i>	AlCl <sub>3</sub>	3 ppm	↑ N, P and K in L, St and R; ↑ DW	[46]

↑ Increase; ↓ Decrease; (L) Leaves; (St) Stems; (Sh) Shoots; (R) Roots; (DW) Dry Weight; (NS) Not Specified; (Chl) Chlorophyll.

### 2.3. Environmental Stress-Mitigation

Another mechanism by which Al may benefit plant fitness is through the alleviation of toxicity caused by other elements when in potentially noxious concentrations [59]. In fact, root biomass increase has been associated for a long time with proton flux toxicity mitigation in several plant species under Al supply, including wheat, pea plants (*Pisum sativum*), and Japanese radish (*Raphanus sativus* var. *longipinnatus*) [45,60]. Copper toxicity in citrus (*Citrus* spp.) and wheat was also alleviated by low Al concentrations in the nutrient solution [61]. Similarly, in tea plants grown in acidic soils, Al was found to ameliorate iron (Fe) toxicity by preventing leaf bronzing due to toxicity and by reducing Fe content in roots and leaves [40]. In soybean and rice, Al may also prevent Mn toxicity [62,63]. Mitigation of Mn toxicity by Al in rice plants is possibly due either to reduced Mn accumulation in plant shoots, resulting from decreased Mn uptake in roots due to changes in cell membrane potential, or reduced Mn availability in roots, resulting in changes in the properties of cell wall junctions [63]. In peanut (*Arachis hypogaea*), shoot and root growth was promoted by adding Al to the nutrient solution (up to 20.4 µM), which was attributed to reduced zinc (Zn) uptake and concentration in shoots, found to be toxic in plants without Al supply [64]. Aluminium can also help to detoxify fluoride (F) through the formation of Al-F complexes, thus alleviating F stress [31,65]. This possibly occurs through the regulation of lipid peroxidation and antioxidant enzymes activity in leaves, or through the exudation of organic acids, which allow the regulation of root pH through the interaction of Al with F [31]. Recent works also highlight the possibility to exploit Al-rich corn stalk biochar to remove F and cadmium (Cd) from contaminated water bodies [66]. This evidence supports the use of Al-containing plant biomass, resulting from, e.g., the phytoremediation of industrial-contaminated soils [67], to promote plant resilience to environmental stresses while ensuring the sustainability of agroecosystems.



#### 2.4. Aluminium Potential in Plant Protection

Fosetyl-aluminium, a systemic organophosphorus fungicide, has also been used for a long time to promote plant health, acting directly on the pathogens and indirectly by activating disease resistance mechanisms, such as phytoalexin production [68–71]. This compound proved to be efficient in controlling a variety of diseases in several crops, including *Phytophthora* spp. in citrus, pineapple (*Ananas comosus*), avocado (*Persea americana*), black pepper (*Piper nigrum*), pepper (*Capsicum annuum*), tobacco (*Nicotiana tabacum*), and potato (*Solanum tuberosum*) [68–70,72,73], *Plasmopara viticola* in grapevines (*Vitis* spp.) [68], and, also, *Pseudoperonospora cubensis* in in vitro conditions [71]. Andreu et al. [70] demonstrated that Fosetyl-aluminium increased tolerance to *Phytophthora infestans* in moderately resistant and moderately susceptible potato cultivars, by increasing phytoalexin concentration in tubers, during plant growth, and after harvest, possibly as a consequence of downward mobility.

Despite the promising effects of fosetyl-aluminium to control several plant diseases, the increasing concerns related with the negative impact of organophosphorus fungicides in the environment and human health propelled the identification of, e.g., Al-containing salts and nanoparticles, which have been evaluated with varying degree of success as an alternative to synthetic fungicides [74–77]. Aluminium-based salts, such as aluminium chloride, aluminium sulphate, and aluminium lactate, have been applied to control diseases caused by, e.g., *P. infestans*, *Pythium sulcatum*, and *Thielaviopsis basicola*, in crops including potato and carrot (*Daucus carota*) [77]. Results suggest that Al may act as an elicitor of a pathogenesis-related transduction pathway, as most genes found to be overexpressed following Al supply are similar to the ones induced by pathogens [78]. Further research supported this evidence by showing that Al-protective role was linked to hydrogen peroxide accumulation in plant roots and to the activation of the acquired systemic response through nitric oxide- and salicylic acid-dependent pathways [79]. In tobacco plants, black root rot caused by *T. basicola* and black shank caused by *P. parasitica* were suppressed by aluminium sulphate [64,80]. Treatment of tobacco plants with aluminium hydroxide before *Ralstonia solanacearum* infection also reduced the extent of disease development and leaf injury, possibly due to increased antioxidant activity, particularly of NADPH oxidase and superoxide dismutase [75]. Similarly, pre-soaking of pigeon pea (*Cajanus cajan*) seeds in 50  $\mu\text{M}$  of Al for 24 h significantly decreased *Fusarium incarnatum-equiseti* infection, also resulting in decreased reactive oxygen species (ROS) generation and cell death [76]. The mycelial growth of other pathogens, such as *F. sambucinum*, *P. sulcatum*, *Alternaria solani*, *Botrytis cinerea*, and *Rhizopus stolonifera*, was also negatively affected by Al-containing salts [77]. Aside from Al-based salts, in recent years research efforts have focused on the potential of nanotechnology to promote sustainable agriculture through improved crop production and soil quality. Goswami et al. [74] explored novel applications of solid and liquid formulations of nanoparticles against rice weevil (*Sitophilus oryzae*) and observed that after only two days more than 90% mortality was obtained, with Al oxide nanoparticles at dosage rates of 2 g per  $\text{kg}^{-1}$  rice. However, Al oxide nanoparticles at concentration of up to 50,000 parts per million (ppm) have been found to be toxic to wheat, which showed reduced root elongation, cellular damage in root cortex cells, and lignin and callose accumulation [81]. Further research on the potential of Al in nanoparticle formulation could greatly benefit the development of green fertilizers that mitigate noxious pests and pathogens.

#### 2.5. Enhancing Postharvest Performance

Despite the great efforts employed by crop producers to grow and harvest healthy plants and food amenities, several diseases can lead to important losses when stored for long periods. Such losses have been successfully mitigated using pesticides, although these are frequently associated with negative impacts to consumers and the environment. Aluminium chloride at concentrations up to 5 mM showed high efficacy in controlling potato tubers' postharvest pathogens, such as *F. sambucinum*, *P. infestans*, *Helminthosporium solani*,

and *Rhizoctonia solani*, possibly by interfering with pathogen cell membrane integrity and permeability through the induction of lipid peroxidation [82,83].

Aluminium starch octenylsuccinate (ASOS), commonly used in the cosmetic industry as an anticaking agent, has been successfully combined with plant essential oils (from e.g., peppermint and spearmint) and plant terpenes (including l-menthone and S-carvone,) to inhibit several potato storage diseases caused by *F. coeruleum*, *F. sambucinum*, *F. avenaceum*, *F. oxysporum*, *A. solani*, *R. solani*, *H. solani*, *P. infestans*, *P. erythroseptica*, *Phoma exigua*, and *Pythium ultimum*. Mixtures of 10 g of ASOS and 4 g or 8 g of essential oils were the most effective in inhibiting these pathogens for periods over 13 or 20 days, respectively, particularly *R. solani* [84].

These results open the possibility to develop alternative tools for controlling storage diseases and improve the shelf-life of food and plant amenities, and further studies should be greatly encouraged for the development of novel affordable and sustainable conservation products that support the sustainability of food and feed value chains.

### 3. Cobalt

Cobalt, a heavy metal, is a known essential element for both prokaryotes and animals, particularly as a constituent of several enzymes and co-enzymes, i.e., vitamin B12. Although any crucial role in plant physiological functions is yet to be reported, Co is considered to be an important, although not essential, nutrient, which may affect, in different degrees, growth and plant metabolism [7,85].

Co is normally an environmental scarce element, appearing in normal concentration scopes between 15 and 25 ppm in soil, and 0.04 ppm in natural waters. Regarding the plant itself, on a dry weight basis, the range is around 0.1–10 ppm, apart from plant species including black bent (*Agrostis gigantea*, used as feed), and *Haumaniastrum robertii*, *H. katangense*, and *Aeollanthus subacaulis* (used as food commodities), which are Co-hyperaccumulators and may contain up to 1000 mg cobalt per plant [86]. Still, certain types of industrial activities, misuse of fertilizers, and sewage sludge spreading can easily contaminate the environment and adulterate the previously discussed Co concentrations [87], posing new challenges to the mechanisms by which plants are able to successfully deal with this element.

Co concentration limits are crucial, since Co can be noxious for plant health once present in large amount in soils [88]. Specifically, it can hinder plant growth, photosynthetic dynamics, seed germination, and metabolic functions [89,90]; therefore, most of the Co-related literature is vastly focused on a better comprehension of the mechanisms and molecular responses to cope with Co stress. Nevertheless, at lower concentrations, this element has noteworthy beneficial effects, which are usually overlooked due to the toxic effects. Providing the concentration is optimal, Co is capable of promoting overall plant growth and it is even essential for specific taxa, as is the case for leguminous plants. With food security goals and improvements on crop productivity in need to feed a growing human population, an in-depth understanding of the beneficial effects of Co on plants may very well be an important tool.

#### 3.1. Cobalt Uptake and Stimulatory Effects on Plant Growth

As a transition element, Co is considered a divalent cation ( $\text{Co}^{2+}$ ), with a similar chemical structure to nickel (Ni), whose uptake is entirely species-dependent, as it could be transported along cortical cells by a various broad range transporters, both by passive diffusion and active transport [91].

This element distribution within the plant depends on the stage of development, while normally plant tissues contain Co in the subsequent increasing order: roots, leaves, seeds, and stems. Soil pH variations impact Co uptake, which increases in acidic conditions, and interactions between elements may also influence its bioavailability for root uptake, i.e., high Mn levels in soil lead to the formation of complexing compounds with Co, thus inhibiting its uptake from the soil to the plant [88].

Even though the mechanisms and even the effects of Co on plants are still under investigation, there are a wide variety of advantageous effects described [92,93]. It has beneficial effects not only on legumes, where it plays an essential role, but it is also capable of promoting overall plant growth and functions [88,94]. These effects include hindrance of leaf senescence, probably through inhibition of the biosynthesis of ethylene [95], and enhanced seed drought resistance as cobalt treatments significantly increasing the growth, yield, and mineral content under different water regime levels [96]. It may also stimulate the regulation of alkaloid accumulation in medicinal plants, which could be hypothesised to have an indirect effect on biotic stress resistance, although further confirmation is needed [26]. Furthermore, in hyperaccumulators plants, that usually concentrate potentially phytotoxic elements to relatively extreme levels, high Co levels can offer direct protection from herbivores or pathogens [97], thus leveraging the productivity of commercially important but susceptible cultivars used for food and feed production.

### 3.2. Cobalt in Plant Nutrition

In legume crops, Co is crucial for N fixation by *Rhizobium*, thus being indirectly required by these species. An indispensable component of cobalamine, required for the activity of various enzymes regarding N fixation by rhizobia bacteria in root nodules of leguminous plants, Co supplementation was reported to increase the root nodules formation and atmospheric N fixation, which consequently increased the N content in leguminous plants [18]. Another study, with pea plants, also emphasised the beneficial effects of Co incorporation in the soil (8 ppm in 10 kg pots), which resulted in increased growth, plant nutrient levels, seed yield, and quality [98], likely due to the role of Co as a co-factor for bacterial nitrogenase. There are few on-field examples of Co contribution to plant nutrition and sustainable agriculture, but one promising study conducted a soil–crop system management experiment, where, through application of combined treatments of Co and organic fertilizers, improvements were achieved in overall productivity, yield, nutritional status, and chemical constituents of moringa crops (*Moringa* spp.) [99]. Additionally, Co supplementation on soybean plants lead to increased yield, oil, and protein contents in seeds [93], and these results are in harmony with those reported for fava bean (*Vicia faba*) and wheat [100,101]. Despite these positive effects, the interaction between Co and other microelements in plant physiology and productivity still lacks sufficient attention, limiting the possibilities to deliver comprehensive and well-thought Co biofortification strategies that support sustainable agroecosystem management, NUE, and food safety.

### 3.3. Cobalt and Increased Shelf-Life

Several processes, such as humidity management and ethylene concentration control, are essential in increasing a product's shelf-life, and improving these processes is necessary to meet the markets demand. Cobalt may play a key role in the latter, as demonstrated by Prasetyo et al. [102], who developed an adsorbent analogous for ethylene removal, during storage of fruit, based on Co-oxide-impregnated nanoporous carbon with substantial ethylene adsorption capacity, leading to an extended shelf life of these products. Nevertheless, although postharvest storage of horticultural products, especially fruits, is of crucial significance, the use of Co to promote product's shelf-life and availability to the public has still to be optimised and validated for larger-scale application.

## 4. Selenium

Different forms of Se can be found in the soil, including elemental selenium, selenite, selenate, thioselenate, and selenide. However, only selenite and selenate can be absorbed and retained by plants [27]. This mineral is essential for many species of plants as well as for humans, but becomes toxic at higher levels, with the gap between deficiency and toxicity being quite small [103,104]. Until today, it has not been proven that plants require Se for their growth; however, it has been determined that there are beneficial effects of its application in plant species with the particular capability to accumulate high quantities of this



element [7,105]. Despite the fact that Se uptake can negatively affect plants by stunting their growth or promoting chlorosis, the addition of this mineral in low quantities has proven to increase plant resistance to oxidative stress and, even, hinder senescence while promoting plant growth [106]. It has also been found that Se is capable of improving plant resilience to abiotic and biotic stress injuries, generally resulting from cold, drought, senescence, salinity, and pathogenic attacks. In fact, Se-protective mechanisms against pathogenic fungi attacks in agricultural crops indirectly contribute to the reduction in the amount of fungicides necessary to maintain healthy crops [107]. Moreover, Se can be used as a green fertilizer and for crop biofortification, and it can intervene in phytoremediation (Table 2).

**Table 2.** Selenium (Se) contribution towards sustainable agriculture interventions.

	Plant Species	Se Supply	Se Amount Supplemented/Se Amount Present *	Application Method	Effects	Reference
Green Fertilizer	<i>Triticum aestivum</i> , <i>Secale cereale</i>		10 ppm	Soil fertilization	↑ bioavailability of Se in the final yield	[108]
	<i>Pisum sativum</i> L.		3 ppm	Foliar fertilization	↑ photosynthetic ability; ↓ lipid peroxidation rate	[109]
	<i>Camellia sinensis</i>	Na <sub>2</sub> SeO <sub>3</sub>	150 ppm	Foliar fertilization	↑ Vit C and plant antioxidant activity	[110]
	<i>Phaseolus vulgaris</i> <i>Zea mays</i>		10 and 31 g ha <sup>-1</sup>	Foliar fertilization	↑ bioavailability of Se in the final yield	[111]
	<i>Ocimum basilicum</i> L.		8 ppm	Foliar fertilization	↑ number of germinated seeds and longer roots	[112]
Biofortification	<i>Triticum durum</i>	Na <sub>2</sub> SeO <sub>4</sub>	40 g ha <sup>-1</sup>	Foliar fertilization	Uptake avg: 1.540–5.532 ppm DW (SeMet)	[113]
	<i>Lens culinaris</i> L.	SeO <sub>3</sub> and SeO <sub>4</sub>	0.037 to 0.301 ppm *	Natural soil Se concentration	Uptake avg: 0.425–0.673 ppm DW (SeMet)	[114]
	<i>Allium porrum</i>	SeO <sub>3</sub>	3.8 ppm	Soil fertilization	Uptake avg: 0.167 ppm DW (SeMet) and 0.068 ppm DW (MeSeCys)	[115]
	<i>Triticum aestivum</i>	SeO <sub>4</sub>	10 g ha <sup>-1</sup>	Soil fertilization	Uptake avg: >0.100 ppm DW (SeMet)	[116]
	<i>Ocimum basilicum</i> L.	SeO <sub>3</sub>	8 ppm	Foliar fertilization	Uptake avg: 0.203 ppm DW (SeMet)	[112]
Phytoremediation	<i>Oryza sativa</i>	SeO <sub>4</sub>	0.25–4.55 ppm *	Soil fertilization	↑ water pH from 29 to 92%	[117]
	<i>Oryza sativa</i> , <i>Brassica oleracea</i>		20 µM	Volatilization	↑ volatilization of SeO <sub>4</sub> and SeO <sub>3</sub> by rhizosphere bacteria	[118]
	<i>Lolium perenne</i>	Na <sub>2</sub> SeO <sub>3</sub>	150 ppm	Soil fertilization	↑ aerial part weight and plant development by 59% and 27% respectively	[119]
	<i>Olea europaea</i> L.	Na <sub>2</sub> SeO <sub>4</sub>	150 ppm	Foliar fertilization	↑ fruit yield, photosynthesis and leaf water level	[120]
	<i>Cucumis sativus</i> L.	Na <sub>2</sub> SeO <sub>4</sub>	8 µM	Foliar fertilization	↓ membrane damage; ↑ plant biomass and fruit yield	[121]
	<i>Triticum aestivum</i> L.	Na <sub>2</sub> SeO <sub>3</sub>	1–2 ppm	Foliar fertilization	↑ biomass and root activity, ↑ proline content and peroxidase and catalase activity	[122]

\* Refers to cases where the “amount supplemented” corresponds in fact to the amount of Se that was already present; ↑ Increased; ↓ Decreased.

In order to benefit from Se in these interventions, it is important to consider if the plant species to employ belongs to the group of selenium-hyper accumulators or the non-accumulators, because this categorization will define the ability and resistance of the plant to carry out the expected mediation [104,107]. Se hyperaccumulator species act by sequestering Se available into their peripheral leaves, thus turning leaves into a defence mechanism against herbivory attacks [123].

Research has shown the potential of Se to act as an ecological fungicide, based on the results obtained when fighting sclerotinia stem rot disease in rapeseed (*Brassica napus*), which not only decreased as the level of Se in the plant increased, but also enhanced the growth of plant beneficial bacteria in the soil [19]. The growth of surrounding plants and reduced herbivory attacks have also been associated with the existence of ground depositions of Se or to Se hyperaccumulator plant species in the area [124]. Moreover, findings show that plants with high quantities of Se were less appealing to prairie dogs when presented with plant species that had low and high levels of Se, leading to the belief

that plants with as little as 38 ppm will gain a certain level of protection against these herbivores [125].

#### 4.1. Selenium as Green Fertilizer

In 1984, Finland began to supplement their compound fertilizers with sodium selenate in order to evaluate if this could improve the nutritional quality of their agricultural crops [126,127]. The amounts of Se have been revised and adjusted since then, bringing the supplementation levels as high as 10 ppm since 1998. This intervention allowed crops such as potato, carrot, cabbage (*B. oleracea* var. *capitata*), and spinach (*Spinacia oleracea*) to absorb selenate and convert it into organic Se compounds, specifically selenomethionine, which not only increased the Se content in food but also in the animal produce that was fed with supplemented crops [108].

The use of fertilizers in plants, such as pea, supplemented with Se enhanced plant photosynthetic capabilities while decreasing their lipid peroxidation rate [109]. Green tea, also proved to benefit from Se leaf spraying during producing season, which resulted in the colour of the leaves, aroma, and sweetness being more stable in the Se-enriched tea leaves than in the control samples over time [110]. Microgreens of basil (*Ocimum basilicum*) increased their antioxidant activity after being sprayed with sodium selenate [112], and species of chives (*Allium schoenoprasum*), garlic (*A. sativum*), and onion (*A. cepa*) demonstrated increased growth, yield, and antioxidant activity subsequent to the use of Se as a fertilizer [128].

The use of Se as a green fertilizer in sustainable agriculture, resulting in direct crop biofortification and strategies to evaluate Se-uptake capability by different types of agricultural crops have been implemented, although still to a reduced extent, around the world. Se is not an essential mineral for crop maintenance (because it does not lead to increased crop yield), which often discourages its application as a green fertilizer, so other minerals that result in a substantial economic benefit are employed instead [111]. Due to its positive effects at low concentrations, it is clear that, with sufficient research, Se could support sustainable agri-food production by promoting plant fitness and nutritional quality.

#### 4.2. Crop Biofortification

Biofortification continues to play a prominent role in the attainment of sustainable food systems around the world, as it is capable of delivering plant-based foods with an improved nutritional profile [129]. By manipulating the capability of agricultural crops to collect Se, it becomes possible to increase Se intake in humans and animals through the consumption of fruits, vegetables, cereals, and animal feed, thus providing beneficial effects for the health in a long term [130]. Several regions worldwide have very low quantities of Se and their population could suffer from a Se deficiency [103]. Countries such as Australia, China, Finland, and Congo experience this situation, and interventions destined to increase the dietary intake of Se to the recommended daily doses continue to be studied [131].

Legumes, such as peas and lentil (*Lens culinaris*), are an important source of plant protein shown to be able to keep up to 70% of Se in form of selenomethionine (SeMet), which is easier to absorb by the human body and less than 20% of inorganic Se after biofortification [113,114]. Leek (*A. porrum*) was also evaluated, showing that 60% of Se was bioaccessible in the stomach after consumption and up to 80% was available after reaching the small intestine [115]. Fruits, vegetables, and cereals have proven to be viable vehicles that can deliver Se through the diet [116,132], opening the possibility to develop novel sustainable biofortification tools through the use of Se.

#### 4.3. Phytoremediation for Sustainable Fertilization

It is important to consider the toxicity that Se can cause in plants or soils if administered in inadequate concentrations. Selenate has proven to be less toxic than selenite, this is because of the ability that selenite possess to be quickly absorbed by the plant [117], and

the unwanted effects of Se are mostly shown when Se incorporates organic compounds that act as Se analogues in the plant's sulphur metabolism [118].

Selenium contamination in soils, waste waters, and sediments are often seen in arid and semi-arid areas with seleniferous soils and heavy crop irrigation. Removal of these contamination traits represents a very laborious and, therefore, high-cost activity. Turning towards sustainable agriculture interventions to remediate this situation can foster a less costly solution. Certain Se-tolerant plant species that can collect volatile Se can be employed in the removal of Se from contaminated surroundings through phytoremediation. There are different reactions that can take place depending on the specific scenario, including phytoextraction, where Se is absorbed in plant roots and transported into the shoot in order to be removed or even harvested from the area, and phytovolatilization, which allows to remove Se forms such as hydrogen selenide, dimethyl selenide, dimethyl selenenyl sulphide, and dimethyl diselenide by releasing them back into the environment as volatile forms [133].

Terrestrial and aquatic species alike have shown to be competitive enough to grow at interesting speeds, while producing substantial biomass amounts after the Se removal from its settings [103]. It has been determined that the decrease in selenate in Se contaminated environments promotes the anaerobic respiration of a range of soil microorganisms, and that the reduction in soluble selenate and selenite to elemental Se reduces the toxicity of Se in plants. Drain water and its derivatives also benefit from Se phytoremediation by trapping the inorganic Se found in wastewater streams. Harvesting it as plant biomass can lead to the creation of a green fertilizer, which directly joins the cycle of sustainable agriculture, thus providing a natural fertilizer that can be used for crop biofortification, animal feed, or, even, biofuel creation [134,135].

#### 4.4. Interactions with Other Trace Elements

During plant growth, trace elements present in the soil are inevitably absorbed by roots and transported to aboveground plant tissues [136]. Nevertheless, Se can reduce the uptake of heavy metals through the formation of immobilised compounds by plants, especially in the rhizosphere, and, therefore, its application can alleviate metal toxicity in plants by regulating metal concentrations in plants [104]. Indeed, several studies suggest that Se can be used to reduce the uptake of potentially toxic elements, as it exhibits a strong antagonistic effect of a several heavy metals in plants such as Cd, lead (Pb), chromium (Cr), arsenic (As), and mercury (Hg) in plants [7,104,137]. For instance, Se has been shown to reduce the Cd toxicity, mainly by preventing oxidative stress in tomato (*S. lycopersicum*), regulating light utilization, repairing cell damages, and regulating gene expression, in crops such as grapevine, rapeseed, rice, tomato, wheat, and peach (*Prunus persica*) [137–141]. The mechanisms involved in this Se-mediated reduction in trace element toxicity in plants were recently reviewed [142], involving the inhibition of metal uptake and root-to-shoot translocation, the decrease in oxidative stress, the improvement of plant growth and photosynthesis, chelation, and compartmentalization of those compounds, as well as changes in metal species both in the soil and within the plant. Therefore, the use of Se might be crucial to help in the remediation of metal-contaminated soils, as far as the doses of Se used are well controlled, as the range of optimal Se rates for plant growth and human safety is quite narrow.

#### 4.5. Improving Water-Use Efficiency (WUE)

Water availability in farming is becoming harder to predict, as climate change effects continue to create warmer summers, droughts, and floods in areas of the world that only a few years ago had never experienced such conditions [143]. Over 90% of the crops grown in the European Union (EU) are rain fed, leading to uncertain water availability and subsequent water stress [119]. It appears that Se has a physiological and antioxidant effect in plant species exposed to abiotic stress by improving the dismutation of superoxide radicals that lead to the activation of peroxidase enzymes [144]. Olive trees (*Olea europaea*) under

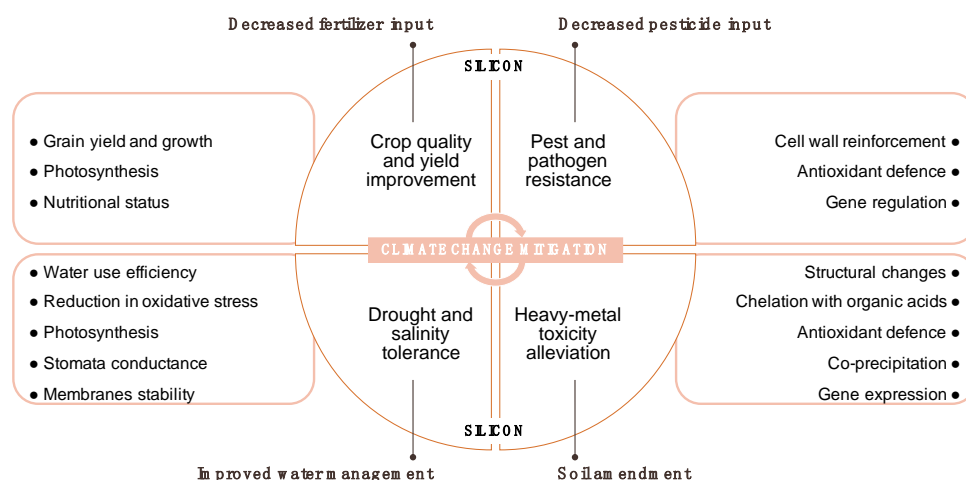
induced water stress and treated with a foliar spray solution containing sodium selenite showed increased photosynthetic ability and fruit yield, while keeping a considerable water level in leaves and showing improved WUE [120]. Selenium also proved to be of aid for species experiencing heat stress [121], promoting plant growth during periods with water shortage in rice and wheat [122,126].

All of the above-mentioned interventions point towards the adoption of natural and sustainable actions that have shown to be capable of ameliorating agricultural limitations resulting from climate change and/or soil exploitation. By following these actions, a circular model of sustainable farming can be set in place, while simultaneously assuring regular and controlled Se intake by humans and animals nationwide. The adoption of strategies that employ Se-rich plant species to phytoremediate the soil, while simultaneously developing a green fertilizer that leads to the harvest of fortified foods in seleniferous soils, becomes an interesting starting point for further research, bringing valuable information to policy makers, farmers, and consumers alike on how to harness all of the natural benefits that Se has to offer.

## 5. Silicon

Silicon, the second most common element in the Earth's crust, rarely occurs as a pure element, being majorly present in combination with other elements, forming oxides or silicates that are unavailable for plants' uptake [145]. Silicic acid is the Si available form for plants uptake, and its concentration ranges from 0.1 to 0.6 mM in the soil solution at a general agricultural pH level (between 5.5 and 7.5) [146]. This element is considered non-essential for plant growth; however, during the last two decades the interest in studying this element has grown impressively, and the effective role of Si in plant biology has been demonstrated [7]. In general, the crescent reports show that using Si as fertilizer is a major contributor to maintain plant productivity, especially, but not exclusively, under stress conditions [147–149], making this one of the most consensual elements in terms of the positive outcomes and contributions to sustainable agricultural practices. However, there is a gap of knowledge in regard to Si interaction with nutritional stresses and how this may impact Si utilization in agriculture [149,150].

As depicted in Figure 2, there are four main beneficial outcomes of using Si in agricultural crops: quality and yield improvement, pest and pathogen resistance, drought and salinity tolerance, and heavy metal toxicity alleviation. Therefore, the range of Si applications in agricultural context is very wide and helps in the reduction in pollutant fertilizers and pesticides [151]. Due to these positive effects, Si is in fact suitable for organic farming and can be an important tool in sustainable agricultural practices [152].



**Figure 2.** The role of silicon in climate change mitigation and the mechanisms that support sustainable agricultural practices, i.e., decreased fertilizer and pesticide input [151,153–168], improved water management [35,169–178], and soil amendment [130,157,161,179–190].

Additionally, Si seems to have an important role in climate change mitigation, as there are evidences that Si cycling helps to control atmospheric CO<sub>2</sub> concentrations [157]. Although Si concentration in plant tissues seems to decrease under these adverse climatic conditions [191], Si supplementation was reported to be an effective measure to maintain legume productivity under predicted climate change scenarios, i.e., elevated CO<sub>2</sub> and increased temperatures [192].

### 5.1. Quality and Yield Improvement

The effect of Si in agricultural crop quality and yield improvement is related to its impact on crops' ability to respond to diverse biotic and abiotic stresses. Hence, the mechanisms behind Si action in enhancing general plant fitness are important to prime plants' defence and the ability to acclimate to adverse conditions [193]. However, it is still a matter of controversy if Si by itself, without an underlying stress, can promote plant growth, function, or metabolic activity [194].

Scientific evidences suggest that fertilization of rice plants with 17.3 mg Si ha<sup>-1</sup> under field conditions [154], or with 1.67 mM or 2 mM Si solution under hydroponic conditions [153,155], significantly increases grain yield and plant growth. Silicon application also seems to impact photosynthetic mechanisms in different crops [195], but usually in association with an additional stress. For example, it was shown that: (i) the application of 150 kg ha<sup>-1</sup> Si led to a higher photosynthetic rate, together with increased stomatal conductance in maize grown in field conditions [158]; (ii) application of 2 mM Si increased net photosynthetic and transpiration rates, stomatal conductance, and chlorophyll fluorescence efficiency in rice and barley plants under hydroponic conditions [153]; and (iii) the addition of 1.5 mM Si induced the expression of photosynthesis-related genes in rice plants under hydroponic conditions [157].

Si also impacts crops growth and development by managing plants nutritional status. This role in metal distribution and protection against micronutrient deficiencies [153,156,163,164], together with the beneficial effects in crop growth and development, can lead to a decreased utilization of fertilizers in agriculture. Since synthetic fertilizers contribute to a large share of environmental pollution, replacing part of their utilization with this beneficial element could improve the sustainability of agricultural practices.

### 5.2. Pest and Pathogen Resistance

As recently reviewed [147,152], there are many evidence that show that the application of Si in agricultural crops has a protective role against several biotic stresses. This is of primary interest to achieve sustainable crop production, since the use of pesticides not only poses a risk to the ecosystems [196], but it might also be aggravated due to climate change. Plant supplementation with Si showed a suppressive effect of several plant diseases in important food and feed crops, including, e.g., *R. solani* and *Magnaporthe oryzae* in rice [197], *Podosphaera aphanis* and *Tetranychus urticae* in strawberry [198], and *F. graminearum*, *Pyricularia oryzae*, and *Pyrenophora tritici-repentis* in wheat [199,200].

The most important mechanisms associated with Si action in biotic stress (Figure 2) are cell wall reinforcement, through which plants become more rigid and resistant, creating a physical barrier to pathogen penetration and decreasing plant palatability and/or digestibility to herbivores [164]; activation of antioxidant defence, such as an ROS scavenging system and increase in phenolic compounds concentration [166]; and gene regulation, specifically in increasing the activation of pathogenesis related proteins and the expression of the jasmonic acid/ethylene marker genes that induce resistance against biotic stresses [168].

### 5.3. Tolerance to Drought and Salinity

The addition of Si-based formulations to agricultural crops may have a role in balancing nutritional status, which in turn, can help mitigating the effects of drought, salinity, or other abiotic stresses. Benefits of Si have been reported in plant water balance, particularly under salt-induced osmotic stress conditions [171,173,177,201–203], by: (i) increasing WUE,



for example, through the up-regulation of aquaporin gene expression to increase water uptake; (ii) reducing oxidative stress, by triggering the activity of antioxidant enzymes (e.g., APX and CAT) and decreasing hydrogen peroxide; (iii) modulating photosynthesis and stomata conductance, improving photosynthetic rates, transpiration rates, and chlorophyll concentration; and (iv) increasing membranes' stability, by decreasing membranes' lipid peroxidation and helping to maintain cell membrane integrity (Figure 2). By modulating these key mechanisms, Si can promote plant resilience in arid or semi-arid conditions, contributing to sustainable crop growth and productivity under the predicted scenarios of water shortage.

#### 5.4. Alleviation of Heavy-Metal Toxicity

Currently, a large percentage of soils have high concentrations of toxic metals or metalloids, being unsuitable for agriculture [204]. Although these lands have been overlooked in the past years, their restoration or remediation is now an important strategy to increase the ratio of usable land in the world. An increasing amount of evidence has shown that Si has the ability to counteract the negative effects of certain elements such as Al, Cd, Pb, Cu, Zn, Cr, or As that, when in high dosages, represent a serious threat for living organisms and jeopardise the agricultural system [205].

The main mechanisms proposed for Si action against toxic metals are summarised in Figure 2. Similarly to the mechanisms to cope with pathogen attack, to alleviate heavy metal toxicity Si induces structural changes to strengthen the plants, such as, root elongation, suberin development, and increased cell-wall extensibility and thickening of the endodermis [181,182]; and Si improves the photosynthetic apparatus [206], increasing membrane and tissue stability, especially in the leaves. Another well-described mechanism induced by Si to detoxify heavy metals is the stimulation of organic acids' exudation from plants to chelate metal ions. When Si was supplied to crops, such as tomato, wheat, and cucumber (*Cucumis sativus*), it formed complexes with organic acids as well as Cu and Cd, including aconitate, malate, and citrate, [181–183]. As also demonstrated for water and salinity stress as well as pest and pathogen resistance, the stimulation of antioxidant enzyme activity is a key process in Si's protective role against toxic metals. When challenged with heavy metal toxicity, plants often display increased levels of oxidative stress as well as membrane permeability and degradation due to lipid peroxidation [121]. Under heavy metal stress, the application of Si was shown to benefit numerous crops, including soybean, barley, rice, cotton, banana, and peanut [207], by increasing the ascorbate-glutathione [184] and glyoxalase [208] systems and enhancing the activity of scavenging enzymes, such as SOD, POD, and CAT [186,206].

Silicon can co-precipitate with different heavy metals, for example, Cd [187], Cu [188] and Mn [161], hence decreasing their mobility from roots to shoots and, consequently, decreasing their accumulation in the shoots. Additionally, increased compartmentation of heavy metals in plant tissues after Si application has been reported, leading to an increased metal concentration in plant roots compared to shoots [209]. For instance, Si application was shown to reduce Al, Cr, Cd, Mn, and Zn transport from roots to shoots, by cell wall retention and vacuole compartmentalization, which decreases their concentration in the shoots, thus preventing adverse effects on photosynthetic machinery and on grain production of several crops [161,189]. All these above-mentioned mechanisms are linked to alterations in gene expression, as Si supplementation alters the genetic response of heavy-metal-challenged plants. For example, Si modulated photosynthesis-related gene expression in Zn-stressed plants [157]; suppressed the expression of heavy metal transporter genes [161,189]; and induced the expression of encoding genes for important stress-tolerance enzymes and organic compounds, such as polyamines, in Cd-stressed plants [190]. Despite the promising pieces of evidence on the role of Si in promoting plant fitness under potentially limiting levels of toxic metals, the lack of empirical data still constrains the possibility to take advantage of this element in promoting the sustainability of metal-contaminated agroecosystems.

## 6. Sodium

Sodium nutrition remains a controversial topic. Although  $\text{Na}^+$  is mainly known by its toxicity due to the salt stress caused at high concentrations, there is some evidence that at low concentrations  $\text{Na}^+$  might have a beneficial role in plants [27]. While  $\text{Na}^+$  is not essential by all plants for basic metabolism, it can promote plant growth and be essential for some species [210,211]. It has been shown that when used in small quantities, similar to micronutrients,  $\text{Na}^+$  can improve plant metabolism and synthesis of chlorophyll, plus it can aid in stomata control, which might be helpful to regulate the internal water balance [212]. In fact, at low levels,  $\text{Na}^+$  is not only inoffensive but can be greatly beneficial, particularly when potassium ( $\text{K}^+$ ) is at low concentrations, as it can be partially replaced by this element due to their chemical similarity via non-selective cation transporters. Accordingly, as far as the plants have the capacity to do  $\text{Na}^+$  uptake, as well as to translocate it to the shoot and to compartmentalise it in their vacuoles, many of the functions played by  $\text{K}^+$  can be fulfilled by  $\text{Na}^+$ , including osmotic adjustment of the large central vacuole and cell turgor regulation, which allows for cell enlargement or long-distance transport of anions [211,213].

### 6.1. Promotion of Plant Growth and Sensorial Quality

Sodium application has been shown to be beneficial for several crops, including barley, wheat, pea, tomato, rapeseed, carrot, cotton, cabbage, radish, vetch, asparagus (*Asparagus officinalis*), broccoli (*B. oleracea* var. *italica*), brussels sprout (*B. oleracea*), caraway (*Carum carvi*), celery (*Apium graveolens*), chicory (*Cichorium intybus*), flax (*Linum usitatissimum*), horseradish (*Armoracia rusticana*), millet (*Setaria italica*), oat (*Avena sativa*), beets (*Beta vulgaris* spp.), rutabaga (*B. napobrassica*), and turnip (*B. rapa* subsp. *rapa*), by stimulating their growth [211,214–218]. Additionally, the taste of several crops including asparagus, barley, broccoli, and beet has been shown to be improved by the addition of small amounts of Na [219]. However, the molecular and metabolic regulatory networks underpinning beneficial plant responses to Na supplementation remain unclear. In fact, the effect of Na research in plants physiology and productivity has been focused on its toxicity, but considering  $\text{Na}^+$  only as a toxic ion might be a simplistic approach, limiting the possibility to take advantage of this element to support sustainable plant production. As such, the effects of beneficial elements such as Na should deserve more attention in order to improve crop production under potential limiting conditions [219,220].

### 6.2. Potassium Nutrition

The role of Na was already demonstrated to be beneficial for some agronomical crops, namely in rice plants where  $\text{K}^+$  was limited and  $\text{Na}^+$  uptake was proven to be key for biomass production [221]. Furthermore, even when  $\text{K}^+$  supply was adequate, the partial replacement of  $\text{K}^+$  by  $\text{Na}^+$  was demonstrated to have positive effects in some crops. In sugar beet, when 2.5 mM  $\text{K}^+$  + 2.5 mM  $\text{Na}^+$  was replaced by 5 mM  $\text{K}^+$ , an increase in the dry weight and sucrose concentration in the storage root of the plant occurred [213]. Moreover, in beets, it was observed that for vascular function  $\text{Na}^+$  can replace  $\text{K}^+$ , thus compensating nearly 95% of the plant's K requirement [211]. Similarly, for olive trees under  $\text{K}^+$  deficit conditions, the addition of  $\text{Na}^+$  produced higher growth, stomatal conductivity, assimilation capacity, and leaf starch concentration, thus reducing deficiency symptoms [222]. Further research regarding  $\text{Na}^+$  use is, thus, of high interest, as partial substitution of  $\text{K}^+$  by this element might be important, especially in soils where  $\text{K}^+$  availability is limited. This substitution could lower agriculture's dependence on expensive potash fertilizer, thus contributing for a more sustainable agriculture [219]. Nevertheless, although several researchers have explored the possibility of  $\text{K}^+$  substitution, at least in part by  $\text{Na}^+$ , the available information is not enough and more insights regarding this topic are needed [215–218].

### 6.3. Promoting Water Use Efficiency (WUE)

Wakeel et al. [218] reported that the positive effects of Na extend beyond its known osmotic role to positively influence plant metabolic function. Regarding its osmotic role, it is expected that Na enhances drought resistance by improving stomatal regulation, thus increasing cell turgor and expansion. In fact, Hampe and Marschner [223] demonstrated that Na supplementation reduced the stomatal conductance under drought stress, thus enhancing the relative water content of the sugar beet. Unfortunately, the benefits of Na<sup>+</sup> in drought tolerance of agronomical crops has yet been poorly explored, and more studies regarding this subject could be useful to potentiate the use of Na<sup>+</sup> to counteract water stress and/or economise water usage. Due to the urgent need to increase agricultural production through a balanced use of resources and inputs (e.g., fertilizers and water), understanding the role and the benefits of Na use for drought tolerance enhancement of agronomical crops should be dully pursued [224].

## 7. Future Perspectives

Increased demand for water and food production is forcing our natural resources to scarcity, therefore, a sustainable approach to water resources and nutrient management in agriculture is vital. As demonstrated, the available literature revealed that the addition of these beneficial elements improved biotic and abiotic stress tolerance in several plants, along with many other discussed benefits, leading to the belief that the adoption of more sustainable practices in agriculture could be successfully implemented by farmers and agricultural systems around the world. Therefore, the utilization of these elements may be one approach to improve the growth of crops and to increase the production in arid or semi-arid areas and under adverse conditions, but it could also serve as a preventive intervention in lands that have not yet been depleted. The mechanisms behind these beneficial effects are still largely unknown, increasing the need for further exploration and commitment of higher authorities that promote these studies. The pathways by which Al, Co, Se, Si, and Na moderate plants' responses in face of different stimuli still need further investigation, especially regarding the molecular and biochemical mechanisms behind their beneficial actions. Moreover, the development of agronomically safe formulations of these elements is still under development, and further research efforts could facilitate novel practices that improve plant performance while imposing little pressure to already-challenged ecosystems.

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