Silicon
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REVIEW PAPER

Silicon Potential to Mitigate Plant Heavy Metals Stress for Sustainable Agriculture: a Review

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Abstract

In recent decades, environmental pollution due to presence of toxic metal elements come across globally with severe threats to plants, soil, humans, and animals. The major causes behind this are rapid and injudicious industrialization, intensive farming, faulty mining activities, and wastes which get accumulated in the soil at higher toxic concentration after long term exposure. Even a slight upsurge in the heavy metal concentration beyond permissible limit causes harmful effects to all the living entities. The acquaintance of plants to metal contaminated growing media diminishes crop performance by altering vegetative and reproductive development that eventually affect sustainability of agricultural production. Silicon (Si) exhibits a significant key role in minimizing heavy metal poisonousness in plants. Amending soil with silicates reduces toxic effect of heavy metals by involving various mechanisms and stimulates crop development by lessening various stresses due to biotic and abiotic factors. Here, we reviewed the most recent research development using silicon as amendment for mitigation of adverse impacts of heavy metals in plants. The paper will be describing about the advanced technologies related to usage of silicon in crop cultivation to enhance sustainable crop production by altering and (or) improving metal contaminated soils.

Keywords Heavy metals · Silicic acid · Si nutrition · Stress · Phytotoxicity · Yield

1 Introduction

Heavy metal contamination is the main cause of health peril that causes numerous serious illnesses worldwide and even may lead to death in case of long time exposure [1–3]. Recuperation of heavy metal contaminated soil ecosystems, affected by rapid and injudicious industrialization, intensive agricultural practices, faulty mining activities, and waste disposal has become a great challenge for mankind [4]. The continuous pile up of metals in terrestrial systems also affects health of plants, animals, and humans, or even a slight increase in their concentration beyond permissible limits can hostilely affect the soil [5–7]. The massive area of agricultural land is radically adulterated due to toxic metal(oid)s like copper, lead, nickel, chromium, mercury, zinc, arsenic, and cadmium particularly nearby urban or peri-urban cities [8]. In such areas, cultivation of crops without deteriorating produce quality is an incredibly challenging concern. The problem becomes more serious when cultivated land is shrinking every day due to developmental activities and huge pressure to generate more repasts to feed the populace growing exponentially. Utilization of sewage and sludge from cities or effluents generated from industries is a potential source for heavy metal contamination of agricultural land. Long-term applications of industrial effluent or municipal sewage water as irrigation is accruing substantial load of toxic metals in the soils that ultimately distresses human health on consumption of such contaminated food items like food grains, fruits and vegetables [9]. Additionally, the yield sustainability of crops is dropped because of prolonged acquaintance of cultivated crops to metal contaminated growing media. Apart from that, soil fertility

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loss and disproportion of nutrients because of higher concentration of toxic metals, result's in dwindling of crop yield [9, 10]. The presence of excesses concentrations of metal ions modified the beneficial nutrients extraction pattern, accumulation, and movement to different plant parts [11]. Worldwide in several regions, majority of the cultivated area used for farming has been drastically polluted with huge concentration of heavy metals, particularly cadmium, lead, and zinc [12]. Accumulation of these metals in the environment at a toxic level causes severe health hazards to all living organisms. The mercury (Hg) released from various industrial processes is residual in the environment, which is highly toxic when ingested or breathed and showing biological accumulation in all aquatic organisms, especially in fish and shellfish [13]. The persistent acquaintance to aerial Hg may results in serious jeopardize to central nervous system (CNS) [14].

Usage of silicon can allay harms of multifarious heavy metal contamination and long-term risk in agriculture [15, 16]. Silicon considered as a critical element for plant resistance against biotic (pest and diseases) as well as abiotic (drought, salinity, metalloids) stress [17]. The plants prefer to absorb available soil Si through roots as monosilicic acid [18, 19]. Silicon presents abundantly (28%) almost in all types of soil [20] but most of it exists in the form of silicon dioxide that is non-soluble and unattainable to plants. Also, some of the soils are deficient in monosilicic acid to fulfill plant's requirement [21]. Subsequently, declining of Si in the soil can harmfully reduce the plant development and exhibiting abnormal characters [22]. Several studies reported that silicon diminished the abiotic stresses including higher heavy metal concentration and enhanced plant tolerance [23–26]. Therefore, innovative approaches and technologies are requisite for long-term safe monitoring and sustainable food production from such metal contaminated soils for cultivating variety of crops. This review will discuss probable significance related to silicon in alleviating metal(oid)s exertion in various plant species by involving various promising mechanisms and recent developments in silicon-based mitigation of heavy metal stresses.

2 Heavy Metals and their Harmful Effects

Usually, toxic elements (Cd, Cu, Pb, As, Hg, Cr) are not required by the plant for their normal growth and development and hence called as non-essential elements [10, 27] and even their small proportion can be poisonous to the living individuals. Build-up of heavy metals within topsoil occurred due to various man made events caused by innumerable infra-structure developmental activities and urbanization results into a serious concern for humanoid, agro-ecosystem and all living entities [28]. In cultivated land, mainly uses of agrochemicals (pesticides, phosphate fertilizers) are caused to deposit bulk of heavy metals. Accrual of heavy metals above certain limits can restrict various physiological and metabolic activities by influencing the water uptake by plants [29], mineral element uptake and their mobilization [30], chlorophyll formation and photosynthesis [31], respiratory system [32], gene expression [33], increase of reactive oxygen species (ROS) [34], enzymatic actions and hormones equilibrium [35]. The disintegration of active surface of soil due to contamination of toxic heavy metals cause a major threat to food chain of plants, animals, and humans. Presence of trace elements in salt solutions, which are wastes of various branches of industry, municipal cities, and agriculture, are highly toxic [36]. The acquaintance of metal toxicities disturb the plant metabolism and further morphology that results in intimidating of food security.

Initially, heavy metals did not exhibit any visible sign in soil after their exposure or take time to appear symptoms. Soil vicissitudes become apparent only when the destruction of vegetation appears and transforming entire surface of the soil in the wasteland [37]. Excess of heavy metal beyond critical limit restrict various cellular and molecular functions of protein, lipid, and thylakoid membrane. Disturbances within thylakoid membranes, organelles are requisite for photosynthetic activity, which correlated with senescence processes [38–40]. Moreover, contamination of food chain is pathway for entry of these toxic elements to the hominids and animals through consumption of contaminated eatables, and causes significant harms to individual's health [1, 9].

The heavy metals like cadmium are commonly used in paints, cosmetics, batteries, lasers and TVs at larger scales. Cadmium gets accrued in plant tissue at their non-toxic level but it is harmful to the animals when they feed upon. Cadmium deposition in vital organ of humans above 200 mg/kg is hazardous which exhibit toxic effects to the human body [41]. The indications of toxicity appear as lungs cancer, bone demineralization, affecting proper functioning of the kidney, liver and blood at higher concentration [42]. Higher concentration of arsenic in wheat seedlings impaired physiological parameters like reduction in hill activity by 30% and decrease of chlorophyll content by 28% and further reduction in starch content by 26% due to increased level of phosphorylase which results in enhancement of sugar content by 61% in plant tissues [43]. The accumulation of arsenate in plants also decreases level of essential macro and micro nutrients.

3 Silicon Content in Soil

Silicon in its all forms is the 2nd most plenteous element (28%) inside soil next to oxygen, varied from 0.52 to 47%. On an average one kilograms of soil contains about 50–400 g of silicon. The basalt and orthoquartzite restrain more concentration of silicon ranging from 23 to 47% as compared to carbonaceous rocks (carbonites, limestones) that contain only traces of the Si element [20, 44]. Silicon is categorized into three different segments namely liquid, adsorbed, and solid-phase. Due to weathering of silicate-containing minerals, Si released to soil solution by the process of precipitation and neoformation of authigenic Si constituents [45]. Based on soil chemical nature (pH), Si may found as SiO_2 (silica), $Si(OH_4)$ (silicic acid), or xH_2OSiO_2 (silicate) [46]. The most available form of silicon in soil is amorphous silica (Asi) which is considered foremost silica pool to plant preference. Silica in the form of dioxide (SiO_2) is most usable by plants [47] whereas, sulfuric acid (H_4SO_4) is frequently absorbed [48]. Silicon in plant system is absorbed with the help of three pathways: passive, active, and rejective [49]. The level of Si in soil (deficient or sufficient or optimum) depends on plant uptake and rate of its replenishment [50].

The most common water solubilized Si within soil are polysilicic acid and monosilicic acid [51]. Monosilicic acid mainly presents in adsorbed condition [52] and hence has low potential to move within soil [53]. The availability of higher amount of monosilicic acid in soil helps to plants in absorption of nutrients like phosphorus [54]. Silicon as H_4SiO_4 is plant-accessible fraction while polysilicic acid is unavailable to plant; however, it is in close contact with soil particles with the help of silica bridge making, that enhanances soil aggregation and soil moisture bearing capability [55]. The polysilicic acids play crucial role in soil physical traits by impeding soil structure development and moisture level.

3.1 Silicon Absorption and Translocation Mechanisms in Plants and their Function

Monosilicic acid is the most absorbable Si form taken up by plants in soil solution. After absorption, Si moves through different plant parts via various influx and efflux transporters and gets deposited in leaf epidermal cells. The concentration of H_4SiO_4 in soil suspension lies between 0.1 to 0.6 mM [56] and varied from 1 to 100 g kg^{-1} depending on the plant types, indicating biggest array of the beneficial soil elements [57]. Plants absorb silicic acid with the help of lateral roots through various mechanisms (active, passive, and rejective) [58]. Based upon Si uptake rate and their content, plants showing more uptake of Si over the water are categorized into active mostly cereals e.g. *Oryza sativa*, *Triticum aestivum*, and *Hordeum vulgare*, while, plants with equal level are categorized into passive (e.g., *Avena sativa*) and last one as rejective, plants with lesser absorption level [58]. The deposition of silica (H_4SiO_4) in leaf tissues get transformed into hard polymerized silica gel ($SiO_2.nH_2O$) after loss of water that termed as phytoliths. The amount of silica accrued in leaf epidermal cells is non-mobile and hence it could not be translocated to new developing leaves. Monosilicic acid or orthosilicic acid (H_4SiO_4) is known to be the most preferable form or fraction of silicon absorbed by plant species through their roots [59, 60]. The 90% of absorbed silica is transformed into amorphous silica in plant cellulose structure [61].

Based on the Si uptake or their accumulation ability, plants are broadly classified in three different classes: high accumulators (10 to 100 g kg^{-1}) monocots (wheat, sugarcane, rice, barley) falls under this category [62, 63] whereas, intermediate accumulate less Si (5–10 g kg^{-1}) and most of the monocots comes under this class. Among all, dicotyledons which contain <5 g kg^{-1} Si are known as low Si accumulators (Table 1). Silicon removal rate of crops is varied based on crop type and it ranges from 210 to 224 mt annually throughout the globe [64–66]. Among the plants, sugarcane, rice, and wheat accumulated highest quantity for Si (300–700, 150–300 & 50–150 kg ha^{-1}) [67] with mean intake of 50–200 kg of Si ha^{-1} among different plants (Table 2) [69]. Mostly, graminaceous plants uptake higher concentration of Si as compare to any other plants category and absorption ability of plant species play significant role in terms of their beneficial effects.

3.2 Silicon Mechanisms in Mitigation of Heavy Metal Stress

Silicon mediated alleviation of heavy metals are broadly classified in the two categorize i.e. internal and external [68, 70]. The exterior method of silicon includes amelioration of metalloids by absorption or increases inactivity of metals or modifies the existing form through mixing of silicates materials. Whereas, interior methods comprise a set of other various mechanisms namely: stimulating antioxidant enzyme action, formation of complex, and compartmentalization, etc. that helps in reducing adverse effects of heavy metal toxicity [68]. The broadly accepted methods are immobilization of metals from topsoil on soil basis apart from activation of enzymatic and non-enzymatic antioxidants, chelation, co-precipitation, gene expression, modified structure, compartmentalization, and complex formation etc. on plant basis (Fig. 1).

Table 1 Plant categorization based on their Si uptake capability (% dry weight basis)

High accumulator (>1.5% Si)	Intermediate accumulator (1.5%–0.5% Si)	Non accumulator (< 0.5% Si)
Rice	Soybean	Sunflower
Sugarcane	Pumpkins	Tomato
Wheat	Cucumber	Grapes
Lentils	Rose	Snapdragon
Spinach	Squash	Gerbera
Ferns	Chrysanthemums	Petunia
Horsetail	Marigold	Geranium
Mosses	New Guinea Impatiens	Begonia
Conifers	Zinnia	Pansy

Table 2 Silicon removal rates of different major crops [68]

Crop	Harvest area (M ha)	Si removal rate (kg ha^{-1})	Estimated annual removal rate (tons)
Barley	1.278	50–200	159,766
Maize	32.555	50–200	4,069,371
Oat	0.556	50–200	69,475
Rice	1.203	500	601,287
Sorghum	2.307	50–200	288,347
Soybean	29.841	50–200	3,730,068
Sugar beat	0.485	50–200	60,604
Sugarcane	0.362	300	108,569
Wheat	19.865	50–150	1,986,480
Total	168.810	50–200	11,073,967

The translocation and further dispersal of heavy metals among plant parts are influenced by silicon to enhance survival of the plants in higher metal stress condition. The defensive role of silicon in plants may lead to accumulation of polysialic acid inside plant cells. Thus, increasing concentration of polysialic acid inside plant cell wall, upsurges plant hardiness or toleration ability which eventually impedes the stress factors [71].

Addition of silicon compounds to the soil remediates heavy metal(oids) by involving different process and pathways through scavenging reactive oxygen species [72]. The presence of higher level of reactive oxygen species are responsible for enhancement of malondialdehyde along with lipid peroxides that inhibits functioning of enzymes and amines in plant cell wall followed by oxidation of proteins [73]. These results occurred due to increased level of reactive oxygen species because of oxidative stress. In growing media like tissue culture, Si addition declines ions movement due to that uptake and translocation of metals from roots to shoots gets inhibited. Studies reported numerous mechanisms which take place within plant cell for alleviating metal stress such as iteration of gene expression, metal-chelation, co-precipitation, alteration of the plant structure, and antioxidant enzymes' activation [24, 62, 74]. Silicon detoxifies heavy metals by means of chemical or physical mechanisms or their combination. For instances, co-precipitation of heavy metals with silicon is the chemical process whereas decline of upward movement of heavy metals to above-ground plant parts (shoot, leaves, grains) is physical mechanism by changing plant structure like apoplastic barrier [75]. The overwhelming of heavy metal toxicity using silicon widely observed in higher plants. Silicon improves soil health by reducing excess concentration of metal(oid)s and other toxic elements.

Silicates enhance P availability to plants by forming silicified tissues in plant and thereby reducing adverse impact of metal toxicity (Fe, Al, Mn). The co-deposition of silicon along with metals in soil solution as well as in plant roots shrinks the content of toxic metal(oid)s. Hence, it is difficult to Si precipitated metal(oid)s to move various plant parts thereby tumbling possible toxic harms to the plant [76, 77]. Silica deposition in shoots and leaf epidermis act as a mechanical barrier and hence provide mechanical strength to the plant [78–80]. Si in the plants reduces toxicity by constraining absorption and further movement of metal(oid)s [81], metal precipitation

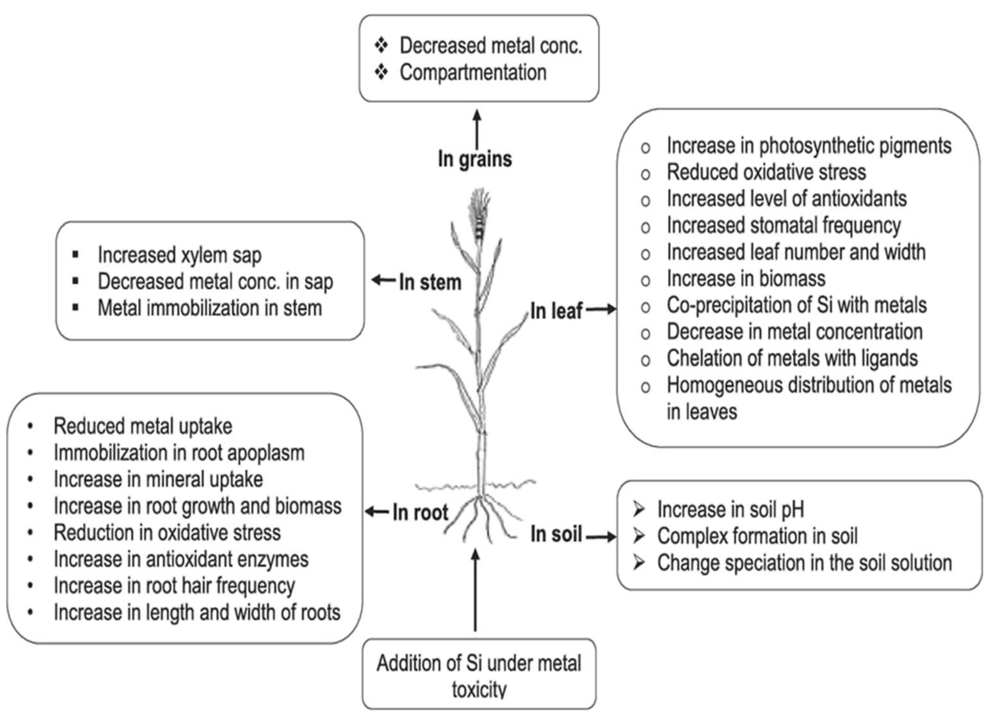

Fig. 1 Diagrammatic representation of Si mediated heavy metal stress mitigation mechanisms (Adopted from Adrees et al. [24])

[24], triggering of antioxidant enzyme activities [23], complex formation & compartmentation [82], enhancing photosynthetic efficiency [83], and by modifying gene appearance [84]. The detailed text of different mechanisms explained below:

3.2.1 Coprecipitation and Adsorption

Addition of silicon to soils having higher concentration of Al^{+3}, detoxify excess content by forming alumino-silicates or hydroxyl-aluminosilicates inside the root apex of plant apoplast [85]. Similarly, co-precipitation of silicates takes place under cadmium stress in *Oryza sativa* shoots [75], with Zn as zinc silicate in *Minuartia verna*. In rice shoot, silicon accrual with Cd has been also reported in center as well as border of phytolith [86].

3.2.2 Activation of the Antioxidant Defense System

Stockpile of metal(oid)s in soil profile beyond permissible limits produces ROS in higher concentration that results in disturbances of various metabolic process in the plants [24, 87]. Supplementation of silicon leads to stimulate the antioxidant enzymatic or non-enzymatic activities in plants in response to heavy metal contamination [19] to minimize oxidative stress by decreasing reactive oxygen species production. Antioxidants provide protection against injuries occurred from oxidative stress to cell walls besides maintaining plant integrity through exclusion of ROS [88] in plant cell organelles like cytosol, apoplast, peroxisomes, plastids etc. [89, 90]. These activities takes place in PGP (peroxisomal glutathione peroxidase), water cycle, and ascorbate glutathione routed through various cycles and processes. Here, superoxide anions transformed to peroxides with the help of enzymes superoxidase dismutase and hydrogen peroxide broken down to H_2O and O_2 through catalase enzyme [91, 92]. Silicon treatment stimulated antioxidants enzymatic and non-enzymatic activities whereas declining content of H_2O_2 along with malondialdehyde [93]. On Cd toxicity, silicates addition dwindled H_2O_2, EL, MDA in *Solanum nigrum* [94] and other stressed plants like Cd [95], Zn [96], and Pb stress [97]. Moreover, the similar effects of Si application on antioxidants were also reported in maize [98], wheat [95], rice [99] and peanut [100]. [72] reported that SOD and CAT activity was upsurge on Si application.

3.2.3 Metal Compartmentalization

It is an another important mechanism through which Si detoxify metal(oid)s by their dissemination to various plant parts or tissues that minimizes metal toxicity effects. Silicon application to plant enhanced the mechanism of compartmentation. Silicon treatment reduced Zn translocation from below ground portion to above ground portion i.e. vegetative plant parts, thereby reduced Zn concentration of rice shoots due to binding up of Zn to the cell wall [101]. Similarly, in wheat, use of Si reduces Cd transport to vegetative and economic parts from roots [102] and 33% decrease in rice Cd accrual [103]. Soil amendments containing Si inhibited the uptake of As (III) by crop plants [104]. Shedeed et al. [105] confirmed that amendment of soil with Si had a reduction effect on Cu, Ni, Pb, Cd and V in the shoot by (66.5, 86.6, 23.5, 28.7 and 66.3) percent and (81.5, 89.6, 66.7, 18.9 and 65.9) percent, respectively in roots of *Vigna unguiculata* L. in comparison to control. Silicon application stimulates root exudates by which it limit uptake and transportation of heavy metals from soil to various vegetative plant parts (shoots, foliage, grain etc) [88, 100] or decreasing the free metals in plant organs which reduces the translocation activity in apoplasm [24]. Shi et al. [103] concluded that exogenous application of Si reduced concentration of Cd in symplast and apoplast without altering their distribution ratio. The compartmentalization of Cd in cell wall is an important mechanism of Si mediated tolerance to Cd toxicity [86] and Cu and Cd stress in Arabidopsis [106]. Addition of Si in rice reduces transport of Zn from below ground to above ground plant parts through increasing cell wall bound fractions of Zn in *Oryza sativa* L. shoots [93, 107].

3.2.4 Metal Complexation or Chelation

This mechanism comprises chelation of metal(oid)s with flavonoid or phenolics or organic acid compounds. In case of Al toxicity, Si treated maize plant increased phenol exudation by 15 times higher as compared to untreated plants. The phenolic compounds (catechin, quercetin) exhibit higher Al-chelating activity for alleviating higher concentration (poisonousness) inside apoplast root tip [108]. Under Al toxicity, Si application in maize increased content of malic acid and hence reduced Al injuries to the plants through chelation by malic acid. Similarly, adding of Si in *Triticum aestivum* has declined movement of Cu from soil or roots to stem which may be attributed to enhanced concentration of citric acid, malic acid, and aconitate in wheat roots [109]. In recent days, a new methodology has been developed for mitigation of Al in *Triticum aestivum* using Si enriched biochar [110]. It is a cost-effective approach to alleviate phytotoxicity by chelating Al with Si-biochar. It not only decline volume of soil exchangeable Al but also inhibit lethal Al immigration to various plant parts. In sorghum plants, Al-Si complex in mucigel and external cellular tissues inhibited cell wall ligation of toxic aluminium [111].

3.2.5 Structural Alterations

Soil amendment with Si diminishes deleterious influences of heavy metal stress by altering morphological and anatomical characters of the plants. Silicon treatment enhances plant growth and developmental phases from germination to vegetative and reproductive stage that encounters metal stresses. Substantial reduction in Ni accrual in leaf, stem, and root was reported after silicon application which resulted in increased plant growth attributes and biomass [112]. Si treatment also augmented dry matter produce accumulation of different plant parts of rice crop while minimizing Cd and Zn content of root, shoot, foliage, and seed [113]. In case of Cd toxicity, enhanced growth of suberin lamellae in endodermis with Si application reported in rapeseed and mustard [114]. Moreover, silicon application moderated inner and outer cell wall, epidermis and other plant organelles in Cd and Zn toxicity [74], developing casparian bands, suberin lamellae, and vascular tissues in roots of *Zea mays* on application of Si under Cd stress [96, 115].

3.2.6 Altering Gene Expression

Silicon modifies expressions of genes for alleviating metals toxicities in plants. In *Arabidopsis* cultivated under Cu stress, Si addition triggered the genes associated with formation of a chelating agent i.e. metallothioneins (MTs), a well-known chelating agent [116]. In rice, upregulation of heavy metal transporter (OsLSi1 and OsLSi2) and downregulation of gene transporter (OsHMA2 & OsHMA3) has been reported [40]. Similarly, under Cu stress enhancing manifestation for phytochelatin synthase 1 (PCS1), while declining appearance for metallothionein gene (MT1a), which attributed to silica application [117]. The upregulation of expression of gene OsLsi1 and downregulation of expression of Nramp5 in rice has been reported due to Si application under Cu stress [118]. Silicate downregulated expression of gene (*LCT1*) associated with Cd absorption through plasma membrane and then outflow inside apoplasm or vacuole as of cytosol (*HMA2*) and upregulated expression of phytochelatin synthase 1(*PCS1*). In wheat, the gene *IRT1* involved in Fe transport was upregulated through Si treatment in below and above ground plants parts (i.e. roots & leaves) in excess of Cd [119].

4 Influence of Si over Physiological Parameters

Exogenous silicon application to the crop plants improved different physiological activities that lead to improved growth. Application of silicon fertilizers in cotton minimized metal's harmful effects under Cu stress by enhancing gas exchange, photosynthetic pigments and decreased oxidative stress, outflow of electrolytes, H_2O_2 concentration, and TBARS in vegetative parts of *Gossypium hirsutum* plant [120]. Similar findings have also been documented after adding Si nano particles in *Triticum aestivum* plantlets [121]. Application with Si-NPs increases enzymatic action of peroxidase, super-oxide dismutase, catalase etc. while reducing the EL and oxidative stress. [122] recorded that Cd @ 2.5 mg/L had not affected significantly the physiological activities (chlorophyll a, RWC, leaf area). The use of Si in *Lallemantia royleana* augmented antioxidant enzyme bustle by 23%, 55% and 30%, respectively, as compared to control at Cd concentration below 10 mg/L [122]. Similar results have also been recorded for excess of Cd in chilies (*Capsicum annum*). The supplementation of Si enhances the content of proline, nitrous oxide (NO), hydrogen sulfide, increased silicon content of leaf, photosynthetic characteristics that provide plant resistance to Cd stress [123].

Amending soil with silicates mitigates detrimental effects of heavy metals within plants by improving growth as well as development and enhancing various physiological parameters and PS-II quantum efficiency [124]. For instances, applying Na_2SiO_3 has reduced the concentration of H_2O_2 and MDA in *Glycine max* L. plants, which has been increased by 25% and 79% when K is deficient in the growing media [125]. Similar findings with respect to improved physiological characteristics were also described by [126] in rice seedlings. In addition, the silicon fertilization mitigated injurious effects of acid rain to rice plants. Adding Si to soil as a fertilizer improved entire plant biomass by enhancing morphological and physiological characteristics besides fiber value. The increased Si content in plant tissues makes plant more tolerant to various metal stresses [69].

5 Effect of Si on HMs in Soil and Plants

Using Si as nano-Si fertilizer exhibits crucial prelude in minimizing heavy metal(oid)s toxicity in plants in addition to soil. The earlier literatures concluded that foliar spray of nano-Si particles to wheat reduced content of Cd by 16 to 58%, 19 to 64%, and 20 to 82%, respectively in shoots, roots and grain as compared to their soil applied application (11–53%, 10–59%, and 22–83%) over the control [121]. Findings indicated that foliar application of Si nano-particle is more significant in drop down of metal content in wheat than their soil application. Similarly, in another study, application of Si NPs significantly reduced Pb content (by 14.3–31.4%) in rice shoots than application as common Si (27.6–54.0%) due to reduced translocation of Pb to vegetative parts and further decreased rice grain Pb deposition. The Pb translocation factor (TF) decreased by 15.0–29.3% and 25.6–50.8% from roots to shoots and by 8.3–13.7% and 15.3–21.1%, respectively from shoots to grains after addition of common Si and Si NPs [127]. Additionally, the application of "organic and inorganic nano-Si" as foliar spray diminished grain Cd concentration by 23.8 and 27.1% [128].

Application of silicon in cotton seedlings significantly reduced concentrations of Cu in below and above ground plant parts (foliage, trunk, roots) relative to Si untreated plants [120]. [129] revealed that Si reduced Cd content of *Oryza sativa* by 11.45–51.85% under acidic purple soil while reduction was higher for purple calcareous soil (26.93–43.77%) with the same level of cadmium. The content of Cd in rice root, shoot, foliage, and seed lessened by about 47, 16, 11 and 89% with silicon application (Cd plus Si versus Cd), whereas, 11, 18, 39 & 23% decrease when silicon and zinc were added with cadmium, with a sharp reduction in seed content (1.2 ± 0.8 to 0.1 ± 0.01 mg/kg) [105]. Besides, the available concentration of Cd in soil augmented by 48% although diminished significantly in the shoots after Si supplementation and retarded Cd accrual in the shoots via internal mechanisms through restricting Cd^{2+} root uptake [130].

The use of steel slag or basic slag is now growing rapidly as soil ameliorant and silicon fertilizer to remediate soil by reducing metal(oid)s mobility and bio-availability. Basic slag has ability to remove contaminants from polluted soils and add nutrients to soil as well. It contains approximately 173 g/kg as total Si and 17 g/kg as soluble Si [6]. The amount of calcium and phosphorus in basic slag makes it a potential liming agent to upsurge the precipitation and sorption of metals such as Cu and a prospective fertilizer encouraging plant growth and increasing soil physicochemical properties. The introduction of basic slag augmented soil pH, plant-available Si, while reducing metal concentration. Using pulverous slag at the rate of 1.0% and 3.0% significantly reduced cadmium, copper, and zinc content of *Oryza sativa* by 82.6–92.9%, 88.4–95.6%, and 67.4–81.4%, respectively than control [131]. The Cd concentration of early and delay sown *Oryza sativa* seed was 48% and 63.5% lesser when steel slag was added @ 2000 mg/kg SiO_2 with respect to control (no steel slag added), while, Pb content of rice grain was not significantly affected [132]. This may be due to decreased mobility of Cd in soil through application of steel slag. Under acidic soil, the soil pH has greater influence on solubility of Cd which decreases with increasing levels of soil pH thorough mixing of alkaline materials [106, 133]. In addition, the greater stratum area and penetrability of basic slag assisted to Cd removal by absorption [134] and reduced Cd absorption into rice grain [132]. Alternatively, Si decreases Cd accumulation and translocation at tissue level in plants [119].

The application of Si and Se in sprinkling form or small droplets was found more effectual in tumbling accumulation of Cd in *Oryza sativa* by decreasing Cd translocation and accrual to stem [126]. The vegetative parts of *Lallemantia royleana* was accumulated higher concentration of cadmium (84.1 mg/kg) when there was no Si treatment added under Cd application @ 10 mg/L. The values of shoot-root quotient (0.195) was higher with 2.5 mg Cd/L when silicon was not applied, due to that Cd concentration in plant growing medium has been increased and hence translocation factor decreased significantly [122]. Bio-availability of Si mitigated toxic effects of Cu in *Triticum durum* @ 30 μM Cu, whereas, on other side Cu caused to enhance silica content in roots appreciably and restricted absorption and translocation of Cu to shoots [109]. Silicon addition boosted the activity of peroxidase, catalase and superoxide dismutase whereas declining values of malondialdehide, H_2O_2, & EC in plants, however, the concentration of Ni and its accumulation in cotton plants in leaf, stem, and roots were reduced [112]. Similarly, root to shoot Ni translocation was dwindled with silicon addition applied through external sources and improved endogenous Si content maintained optimal accumulation of osmolytes with other secondary metabolites [135]. Under Cr stress, Si supplementation did not caused significant changes in root Cr concentration [136]. However, shoot Cr content declined in comparison to plants not treated with silicon, elucidating mitigation of excess Cr concentration due to root Cr impounding. Zeolite is likewise a 'hydrated alumino-silicate' substances having ability to absorb metal(oid)s [36]. Applying zeolite to the *Brassica napus* moderated Pb dynamics within soil hence, lessened seed Pb content of crop [137].

Split application of silicon in rice at transplantation, tillering and panicle initiation minimized Cd accumulation in the grain within acceptable limit (0.2 mg kg^{-1}) which reduces probability of Cd health risk index [138]. Alike, the higher dose of Na_2SiO_3 (12.5 g kg^{-1}) reduced Pb level in brown rice by augmenting soil pH and restricted Pb translocation transfer from soil to economic part i.e. grains, in particular the transfer of Pb from root to stem due to increased soil available silicon. Further, results showed that $PbSiO_3$ is precipitated in soil and root after applying a high dose of Na_2SiO_3 due to increased concentration of Pb-ferrihydrite and reduced soil Pb-humic acids (Pb-HAs) and roots Pb-pectin. Restriction of root to shoot transfer was moderately caused by $PbSiO_3$ precipitation over surface or inside the roots [139]. The incessant utilization of crop stubbles is taken into account as low cost bio-sorbents and a realistic approach to metals immobilization in polluted soil. Soil available Cd was considerably lesser in rice straw treatment attained significantly lower soil available Cd than their control, while Pb levels decreased in wheat straw treatment. Applying organic amendments like biochar, rice or wheat straw decreased the concentration of Cd by 50.9%, 69.5%, and 66.9%, respectively in maize shoot. Also, shoot Cd accumulation was decreased by 47.3%, 67.1%, and 66.4%, respectively [140]. Likewise, rice husk ash (RHA) is a waste material produced in large amounts in many regions around the world, and its disposal can be problematic. The integration of rice husk into soil (1% *w*/w) reduced arsenic content by 25–50% in grain deprived deleterious impact on grain Cd concentration, produce, or dissolved methane levels [141]. Also, arsenic (As) content in roots increased (99.78 mg kg^{-1}), and thereby reduction in leaves (1.20 mg/kg) and stem (2.13 mg/kg) of maize plant significantly reduced @ 1 mmol L^{-1} Si [142].

6 Influence on Crop Development and Productivity

Earlier studies well documented that silicon is neither corrosive nor polluting element, and also not hazards even applied excessively and thus provides plants with both economic and ecological benefits. Addition of silicon not only enhances crop yield but also improves quality of crop and further its deficiency cause loss of plant's genetic potential to endure aversive environmental surroundings [143]. The significance of silicon in growing crop and improving yields has been elaborated in various literatures. Application of silicon increases root system, stem, number of tillers, chlorophyll content, absorption of nutrients, and therefore, increased yield and quality almost in every crop. Principally in the circumstances of extreme stressful growing situations (e.g. water scarcity, excess metal(oid)s, salinity, pathogen, insects), there will be greater possibility of achieving positive results from Si application [69, 79]. The yield improvement mechanism is positively correlated with plant tolerance capability to withstand biotic and abiotic stresses. In addition, bioactive silicon helps to take up more nutrients and make better use of water and minerals, thereby sinking their necessities in crop production for water, fertilizers, and plant protection chemicals. Moreover, exogenous Si supplementation expands plant development through moderating mineral nutrients like sodium, magnesium, silicon, and phytohormones adsorption and alleviates extent of stress [144].

Deposition of the superfluous content of metal(oid)s in cultivated lands (or) soils diminished plant expansion as well as quality of produce cultivated on such contaminated land [10]. Exogenous application of Si amendment under arsenate stress has stimulated growth of wheat seedlings by altering the metabolic cycle in nitrogen metabolism [145]. Silicon addition detoxify Cr in *Oryza sativa* under excess concentration, thereby reducing Cr content in vegetative plant parts and reversed negative impacts on protein content and substantiality [136]. The foliar application of silicon improved *Oryza sativa* harvest by 17.2 to 25.5% under calcareous soil [129]. The silicon and selenium containing fertilizer enhanced nutritious value of *Oryza sativa* grain through rising concentration of protein, selenium, and silicon with substantial decrease in Cd values [129]. Likewise, Si nano-particles also significantly improved dry matter of stem (24–69%), roots (14–59%), spikes (34–87%), and seeds (31–96%) in foliar spray whereas, 10–51, 11–49, 25–69, and 27–74% increment was observed under soil-applied Si NPs over control [121].

Slag application significantly increased rice grain yield by 14.3% and 16.7% higher in the Si @ 1600 and 2000 mg SiO_2/kg soil treatments respectively, compared to treatment with no slag application and Si concentration in rice straw were 78.7% and 89.3% higher than control [131]. Alike, application of pulverous slag @ 1.0% significantly stimulated rice growth, and restricted when treated at 3.0% [131]. Silicon addition drop down deleterious impacts of cadmium on crop development and yield because of antioxidants stimulation and declining of Cd movement towards shoots [122]. In cotton, nickel stress inhibited considerably morphological and physiological parameters like plant development, dry matter accumulation, photosynthesis etc. but these negative effects reversed after Si addition [112]. The spiking of nickel at 150 μM shortened root and shoot elongation by about 35 and 53%, Chl by 58%, gas exchange parameters P_N by 36.84, *A* 55.61% while increasing content of H_2O_2, MDA, and methyl glyoxal by 3.23, 2.07, and 3.32 folds. Correspondingly, silicon application in mustard @ 10^{-5} M alleviated nickel toxicity through stimulation antioxidant enzymes, glyoxalaseas well asascorbate glutathione (AsA-GSH) [135].

Silicon application in 3 split doses improved plant development, yield, and photosynthetic efficiency in rice under Cd stressed high pH soil and reduced grain metal concentration [138]. Foliar application of silicon along with salicylic acid or solitary application of salicylic acid does not rectify shortage of nitrogen in *Oryza sativa*, but its supplementation improved grain yield about 18.6% more [146]. The silicic acid intake in plants increases cytokinin biosynthesis. The leaves which exposed to silicic acid or having high silica content, reach senescence at slower rate [147]. Similarly, unutilized Si-rich waste of rice production i.e. husk, have less labile carbon and arsenic than rice straw and hence may be used as an environmentally safe and economically feasible Si resource to decrease As content [141]. Incorporation of rice straw in heavy metal contaminates soil is advantageous in mitigating their toxic effects through immobilization besides enhancing soil organic carbon (SOC), which is beneficial for soil microorganisms [140]. Studies indicated that application of nano form silica had significant impact on overall plant development and yield improvement under multifarious metal polluted land apart from their alleviation [128].

Under sandy soil of Brazil, addition of Si as fertilizer augmented quantity, size, and meterage of melon yields with improved Si content and other mineral element absorption [148]. [149] also supported these findings with conclusion that topdressing of silicon in rice at reproductive phase amplified growth characteristic and yield attributes more efficiently because of more retention time as well as its residual influences. While in contradiction, the foliar applied Si was not so influential due to delivery of less quantity with short term influence [150]. The increases in rice cultivar were 31%, 57%, and 16% for dry roots biomass, and 28%, 27%, and 11% for dry shoot biomass under Si applications (Cd + Si, Zn + Si, Cd + Zn + Si) in comparison to treatments without silicon addition (Cd, Zn, Cd + Zn) [130]. Addition of silicon with Cr improved plant growth attributes like height, tillers/plant, root elongation, and foliage expansion in *Hordeum vulgare* comparison to Si untreated plants [23, 151]. The percent increment in stubbles dry weight (19.9 & 22.0), root dry weight (17.2 & 19.4), and grain yield (15.2 & 13.6), respectively have been reported in Japonica and Indica rice cultivar, after slag amendment application [152] and by 10.3–15.2% increased rice grain yield [153].

7 Influence on Soil Nutrients

The stockpile of metal(oid)s inside soil modifies nutrient mineralization, their uptake and transport from root to shoot besides alteration of enzymatic functioning [154]. Despite of the positive effects of Si addition, it also helps in alleviating toxic effects of mineral nutrients. With increasing tolerability of plants against nutrient poisonousness, Si correspondingly mitigates signs associated with scarcity of indispensable mineral elements. Under arsenate stress, Si nutrition revamped the arsenate-induced effects by increasing nitrate (NO_3^-) absorption and subsequently elevated nitrite (NO_2^-) plus amino acid concentration. Supply of silicon augmented nitrogen metabolism through stimulating related enzymes while decreases content of NH_3^+ accrual that results in amplified total and soluble N values [43]. Similarly, the application of Si mitigates the detrimental impact of boron deficiency or toxicities in case of excess soil B concentration [124]. Foliar application of Si mitigates the B deficiency whereas, Si application through nutrient solution proved superior for correcting higher concentration of B i.e. under toxicity.

The findings illustrated proper regulation of K^+ accrual through Si in xylem, and play important role in maintaining plant-water status in situations where K is lacking. The application of silicon increased K^+ concentration significantly in xylem sap, whereas xylem sap osmotic potential was decreased [155]. Applying silicon as sodium silicate enhanced plant P content to optimum value in many plant species. Moreover, Si helps in stimulation of root Pi acquisition through enhancing exudation rate of malate and citrate acid. Silicon promoted root secretion of organic acids, leads to Pi mobilization in rhizosphere that up-regulated Pi transporters in *Triticum aestivum* roots [156]. Under K-deficient medium, usage of Si to *Glycine max* plantlets markedly increased potassium use efficiency. Application of sodium silicate (Na_2SiO_3) increased K content by 105.4, 83.4, and 58.8%, respectively in foliage, shoot, and roots of K deficient saplings [125]. Correspondingly, addition of Si @ 0.5 mM enhanced plant development, Zn, and Si levels in foliage, raised Zn deposition in roots and further translocation towards shoots in mitigating Zn deficiency symptoms [157]. Because of improved plant growth and development, turns into more dry matter yield attributed to upgraded nutrient use efficiency (NUE) in the plants due to Si enrichment [158].

Sandy soils of Brazil with silicon increased mining of macro and micro beneficial nutrients by *Cucumismelo* var. *cantalupensis* [148]. Increasing soil respiration in soils where P is deficient, stands another advantage of Si supplementation. Another benefit of silicon application is maintaining of P mobilization and hence, playing crucial role in P management in most of the soils [159]. The percent increment in soil organic carbon (11.6 & 14.6) and readily mineralizable carbon (37.3 & 42.7) was observed after amending soil with slag under two rice cultivars i.e. Japonica and Indica [160]. Moreover, due to enhanced dry biomass produce after Si addition, the percent increase in content of available P (33.2 & 33.0), exchangeable Ca^{2+} and Mg^{2+} (47.3 & 46.9 and 60.2 & 65.0), aqueous iron and silicon (160 & 183 and 898 & 718), respectively was obtained in Japonica and Indica cultivar, although 15.4 and 16.8% decline in content of ninhydrin reactive nitrogen. Besides it, upgrading photosynthetic efficiency rate (21.1 & 18.0%), dry biomass N, P, Si content about 20.1 and 22.2%, 17.0 and 18.4%, and 29.9 and 30.5% higher, respectively [160].

8 Effect of Si on Soil Microbial Community

For most terrestrial ecosystems, soil microbes are indispensable constituents and perform a significant role in cycling mineral of compounds and disintegration of organic material [161]. Only confined studies are attempted on the efficacy of silica fertilization on microbial composition of soil, their population, structure, activities, and factors that affect it. Exposure to environmental stress triggereddue to heavy metals, however, typically declines diversity and functional bustle of microbial soil communities and letdowns ecological steadiness group interactions. The lethal consequence due to heavy metals mainly occurs when metal or metal(oid)s intermingle with proteins or enzymes and interrupt different metabolic activities [162]. Several studies made earlier considered soil microbial activity to be critical sign of soil decadence arising from metal(oid)s [163, 164]. [165] confirmed long term soil exposure to heavy metal(oid)s diminished population of bacteria and fungi sharply. Supplementation of slag ameliorants efficient in silicon steepened SMB (soil microbial biomass) and enzyme activity like α- and β-glucosidase,α- and β-galactosidase, α-mannosidase, and α-fucosidase and augmenting few bacterial taxas characterizing copiotrophic habitat with some special function for ecosystem services beneficial to plant. Application of slag as amendment substantially enhanced microbial biomass carbon (MBC) of Japonica and Indica subspecies of *Oryza sativa* by 26.2 and 30.3% [160]. In addition to that, enzymmatic activity associated with N and P cycling (leucine-aminopeptidase, trypsin and alkaline phosphomonoesterase, phosphohydrolase) has increased noticeably with slag amendment. Increase in proportionate profusion of proteobacteria and actinobacteria (28.9 & 25.2 and 52.2 & 50.7%), while the values decreased significantly for acidobacteria (31.4 & 36.1), bacteroidetes (25.3 & 29.2), nitrospirae (40.6 & 45.4), and chloroflexi (74.7 & 61.9) percent, respectively under Japonica and Indica subspecies of *Oryza sativa* [160].

9 Environmental Impact of Si Fertilization

9.1 Carbon Sequestration

Many studies have well recorded restoration of the atmospheric carbon dioxide (CO_2) into soils in the past as a way to combat impact of changing climate. It was well reported that mineral carbonation of CO_2 has greater sequestration potential [166]. Alike, influences of Si fertilization on microbial community, here also only few literatures are available pertaining to efficacy of silicon on carbon sequestration in cropping systems. Application of basic slag with biochar in rice cultivated lands decreases active soil organic carbon pools which were due to enhancing early crop soil C sequestration [149]. The carbonic anhydrase (CA) enzyme helps in formation of silicate weathering and carbonates and henceforth acts as a key enzyme in biomimetic CO_2 sequestration [167]. Application of different types of biochar directly involves in soil carbon sequestration. The rice husk charcoal (RC) @ 20 and 40 g/pot produced significantly higher contents of soil C than control and increased ratios of soil C-N. The soil C content upsurge from its initial value to that after rice harvest reflects soil C sequestration level. Soil C sequestration amounts for RC20 and RC40 were 550%, and 851% respectively, over control [168]. Studies have indicated that farming with rocks could be another better choice for improving carbon sequestration in soils [169]. The terrestrial bio-geochemical Si cycle greatly influences SOC stabilization and thus controls universal carbon balance and environmental changes. This cycle protects SOC through amorphous silica besides forming complex of silicon with iron (Si-Fe) and aluminum (Si-Al). Likewise, incorporation of silica enriched biomass constituents into soil also, may be better option for enhancing carbon sequestration by controlling terrestrial Si cycle [170]. Silicon deposits as phytoliths have major effects of occluding organic carbon on the bio-geochemical impounding of environmental CO_2. Application of silica fertilizer in rice has ability to raise PhytOC levels from 0.94 to $1.16–2.17 \times 10^6$ tons CO_2 annually [171].

9.2 GHGs Emission

One of the important source contributing methane (CH_4) plus nitrous oxide (N_2O) gas emission is agricultural activities, liable to global warming [172] and hence must be appropriately managed for maintaining the ecological balance. The Linz-Donawitz (LD) slag amendment (2.0 Mg/ha) markedly decreased production rate of CH_4 in submerged paddy soil by 17.8–24.0% and increased microbial activity compared with unamended control [153]. The application of silicate amendments (4 Mg/ha) reduced total seasonal CH_4 flux by 20 and 36% (from 38.1 and 27.9 g/m^2) in tillage and no-tillage control units. Addition of Si @ 4 Mg per hectare using no-tillage method reduced aggregate periodic CH_4 flux by 54% over the control tillage treatment [173]. These results may be attributed to increased availability of Fe in soil modified with slag, thereby Fe served as substitute for electron acceptor and helps in suppression of CH_4 expulsion. Likewise, steel slag might also be valuable resource for greenhouse gas expulsions reduction. Steel slag application @ 8 Mg/ha reduced CH_4 and N_2O emissions by 56% (from 2.34 to 1.03 mg/m^2/h) and 98% (from 32.43 to 0.41 μg mg/m^2/h), respectively and augmented crop yield about 4.2 and 9.1% higher under early and delay sown *Oryza sativa* [174]. Similarly, addition of fly ash, phosphogypsum, and blast slag as silicon amendments @ 10 Mg/ha declined aggregate periodic CH_4 expulsion by 20, 27, and 25%, besides increasing grain produce about 17, 15 and 23% more, respectively with respect to control treatment in rice [175]. [176] revealed that steel slag applications @ 1.0 and 2.0 Mg/ha diminished methane expulsion (12.6 to 18.7%), and nitrous oxide expulsion (34 and 38%), respectively. Moreover, the application of silicate modifies soil microbial community and their composition, and enhanced functional genes or activities associated with labile carbon decadence, C plus N conversion, P usage, detoxifying metal(oid)s, oxidizing methane, while diminishing those associated with methane producing processes and denitrification. Their application substantially declined gene (mcrA) profusion related to methanogen while intensified gene (pmoA) copiousness to methanotroph [160].

10 Future Perspectives

- Most of the work has been done at a molecular and physiological level but at the field level not much information available. The environmental situations for laboratory and field experiments are extremely diverse whereas field conditions are governed by various environmental factors that enormously affected crop cultivation and sometimes also beyond control. Hence, now more emphasis should be focused on alleviating heavy metal stress by cultivating crops in the field.
- The use of organic and natural soil ameliorants should be encouraged for alleviating metal stress. Using such materials may not only reduces metal stress but also come out as eco-friendly and environmentally safe. It will also

- improve the soil health by supplementing many micro and macronutrients and benefiting the microbial biomass.
- The chemical dynamics of silicon in soil and its interference with soil components, their influences on release of plant-available Si needs to be addressed clearly.
- Research efforts are needed to develop management practices for silicon fertilization for a number of agronomic and horticultural crops.

11 Conclusions

The Si fertilization is a viable, environmentally safe and profitable practice for sustaining future crop cultivation. Using silicon to the crop or soil not only improving plant growth characteristics and expansion with their productivity but also renovate the degraded lands by increasing their soil health through mitigation of many biotic plus abiotic exertions including heavy metals by involving various avoidance or tolerance mechanisms. Moreover, the appropriate usage of Si in agriculture is eco-friendly substitute to agrochemicals in farming that help in minimizing the adverse effects arising due to multiple stresses. Addition of silicon to the heavy metal contaminated soils will help in reducing concentration of multiple metals in the crops that leads to low risk of health hazards to human and animals transported via food chain contamination. Further, Si fertilization reduces crop yield losses resulted from pest and disease infestation.

Abbreviations B, Boron; CAT, Catalase; CO_2, Carbon dioxide; EL, Electrolyte leakage; GHGs, Green house gases; H_2O_2, Hydrogen peroxide; MDA, Malondialdehyde; NUE, Nutrient use efficiency; OC, Organic carbon; PhytOC, Phytolith occluded carbon; POD, Peroxidase; ROS, Reactive oxygen species; SOC, Soil organic carbon; SOD, Superoxide dismutase; TBARS, Thiobarbituric acid reactive substances

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Authors' Contributions This is a review article. The author VM collected and compiled recent literatures on silicon roles and their mechanisms with respect to plant physiological and metabolic responses. MLD collected and summarized the latest research findings related to heavy metal contamination and their impact on plant growth and soil health. JKS briefly explained about the significance of silicon fertilization to combat climate change. AKP reviewed and edited whole content of the manuscript critically and thrown some light on future perspectives of silicon fertilizer usage in agriculture. All authors read and approved the final manuscript.

Declarations

Conflict of Interest The authors declare that there is no conflict of interest.

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