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### Science of the Total Environment





# Silicon-based nanoparticles for mitigating the effect of potentially toxic elements and plant stress in agroecosystems: A sustainable pathway towards food security

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#### ABSTRACT

Due to their size, flexibility, biocompatibility, large surface area, and variable functionality nanoparticles have enormous industrial, agricultural, pharmaceutical and biotechnological applications. This has led to their widespread use in various fields. The advancement of knowledge in this field of research has altered our way of life from medicine to agriculture. One of the rungs of this revolution, which has somewhat reduced the harmful consequences, is nanotechnology. A helpful ingredient for plants, silicon (Si), is well-known for its preventive properties under adverse environmental conditions. Several studies have shown how biogenic silica helps plants recover from biotic and abiotic stressors. The majority of research have demonstrated the benefits of siliconbased nanoparticles (Si-NPs) for plant growth and development, particularly under stressful environments. In order to minimize the release of brine, heavy metals, and radioactive chemicals into water, remove metals, nonmetals, and radioactive components, and purify water, silica has also been used in environmental remediation. Potentially toxic elements (PTEs) have become a huge threat to food security through their negative impact on agroecosystem. Si-NPs have the potentials to remove PTEs from agroecosystem and promote food security via the promotion of plant growth and development. In this review, we have outlined the various sources and ecotoxicological consequences of PTEs in agroecosystems. The potentials of Si-NPs in mitigating PTEs were extensively discussed and other applications of Si-NPs in agriculture to foster food security were also highlighted.

#### 1. Introduction

Agriculture is the mainstay of growing economies; supplying food and consequently improving the overall quality of life. Different areas of agriculture is currently dealing with a wide range of challenges, such as irregular climate change, soil pollution from dangerous environmental pollutants like pesticides, heavy metals, and fertilizers, and significantly increased food demand due to a growing world population (Kumar and Sharma, 2022; Liu et al., 2023a; Liu et al., 2023b; Tsoraeva et al., 2020). According to a recent UN projection, the world's population will increase to 8.5 billion by 2030 and roughly 9 billion by 2050. Thus, there is a pressing need to raise food production by more than 50 % in order to meet the food needs of this continuously expanding population. Potentially toxic elements (PTEs) have gained global attention as one of the most harmful environmental pollutants in recent years. Environmental pollution from PTEs is a major concern on a global scale. A significant

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volume of wastewater from industrial processes that contains PTEs is released into the aquatic system, and this toxic discharge at high concentrations poses a substantial risk to the ecosystem (Dvorak et al., 2020). In addition to these, one of the main sources of PTEs is the chemical-based fertilizers used in soils during agricultural production (Malyugina et al., 2021). PTEs have bio-accumulation capabilities and are not biodegradable (Pandey and Tiwari, 2021). Its toxicity refers to the phenomena where the presence of metals in significant amounts may endanger human and animal life and cause metabolic changes (Inobeme, 2021). PTEs confer huge risk to soil microbial communities ranging from biochemical, structural to molecular alteration (Chen et al., 2022; SONOWAL et al., 2022; Zhao et al., 2022). These changes have a concomitant effect on soil fertility and agricultural productivity. Since PTEs have a detrimental effect on survival of microorganisms under adverse environmental conditions, several microbes have devised different mechanisms of survival. Surface water bodies that are exposed to wastewater discharge from manufacturing firms that utilize metals in large quantities serve as a fertile breeding ground for bacteria that are resistant to metals (Chaturvedi et al., 2021). Toxic chemical finds their way into the bacterial cell wall via various routes (Sharma et al., 2022), eliciting a range of responses in the cells due to high concentrations of these PTEs via activation of particular resistance mechanisms (Xavier et al., 2019). Therefore, there is an urgent need to employ nanotechnological means to remediate PTEs from the environment to avert impending ecotoxicological doom from this contaminant.

Applications for nanoparticles (NPs) in healthcare, industry, agriculture, and cosmetics have drastically increased recently (Adeel et al., 2019). Materials with at least one dimension less than 100 nm are typically referred to as NPs. According to the requirements, NPs with various particle sizes, geometries, and functionalities can be produced (Adeel et al., 2020). NPs have a number of benefits over regular materials, including high surface area, an increased number of surface reaction sites, strong catalytic efficiency, and special magnetic and optical and properties (Wang et al., 2019). NPs have been employed in environmental and agricultural applications. According to several research, NPs may enhance plant seed germination, oxidative stress resistance, photosynthesis, rhizome growth and development, crop quality and crop yield (Kah et al., 2019). On the one hand, NPs are used as nano pesticides (Hao et al., 2019), and nano fertilizers (Rui et al., 2018) which are easily absorbed by plants with low environmental release compared to conventional fertilizers (Lowry et al., 2019). However, further studies are still needed to determine the potential ecological risks (Lombi et al., 2019).

Silicon (Si) makes up around 70 % of the mass of soil and is one of the most prevalent elements in the Earth's crust (Siddiqui et al., 2020). Many positive effects of Si exposure are passed on to diverse plants, particularly gramineous and cyperaceous plants (Wang et al., 2017). Also, it could reduce the negative effects of abiotic and biotic stress that either directly or indirectly boost the plants' resistance to external challenges. Si-NPs have recently been identified as a unique source of Si that can be exploited to increase plant resilience to unfavorable environmental factors. The size, shape and other features of Si-NPs, however, are said to have a direct or indirect impact on how plants react when exposed to Si-NPs (Rastogi et al., 2017). In terms of Si-NP efficacy, it has been found that Si-NPs applied to the soil were more effective than Si-NPs applied to the leaves (Suriyaprabha et al., 2014). The oil content and growth of Cymbopogon citratus were significantly enhanced by Si-NP treatment (Mukarram et al., 2021). It promoted lignification in plant tissues and improved Avena sativa growth (Asgari et al., 2018). A nanosilica fertilizer enhanced G. max's leaf area index, net absorption rate, relative growth rate, and yield (Suciaty et al., 2018). The seed soaking and seed priming of Helianthus annuus in Si-NPs increased the root and shoot length, biomass, and the seedling's vigor index (Janmohammadi and Sabaghnia, 2015). Silicon dioxide nanoparticles (SiO<sub>2</sub>-NPs) have been demonstrated to enhance Agropyron elongatum seed germination and growth of its seedling (Azimi et al., 2014). Crops are found to benefit

from nano-SiO<sub>2</sub>-based fertilizers because they limit nitrogen and phosphorus loss through regulated release (Mejias et al., 2021). SiO<sub>2</sub>-NPs may be used to enhance photosynthetic pigments and speed up photosynthetic rate (Mejias et al., 2021). In addition to the numerous advantages of Si-NPs in agricultural production, Si-NPs have shown excellent result in environmental remediation. Several studies have demonstrated the successful application of Si-NPs in oil recovery (Khan et al., 2014; Rognmo et al., 2018; Yousefvand and Jafari, 2015). It has also been applied for the removal of lead metal via adsorption (Yang et al., 2013) and excess boron (Albertini et al., 2018). The numerous successful applications of SiO<sub>2</sub>-NPs highlight the enormous potentials for the remediation and mitigation of PTEs in agroecosystem. The aim of the review was to evaluate the potentials of silicon-based nanoparticles for mitigating the effect of potentially toxic elements and plant stress in the agroecosystems. Here, we have critically and exhaustively enumerated the sources and ecotoxicological impacts of PTEs in the agroecosystem. Further, we highlight the potentials of Si-NPs for mitigating/ removing of PTEs and plant stress to promote food security. Additionally, other applications of Si-NPs for sustainable agriculture towards food security including Si-NPs as pesticides, Si-NP application in delivery systems, in targeted delivery of nucleotides, proteins and other chemicals, and as nano sensors for pathogen and pesticide residue detection were elucidated. Despite the advantages of Si-NPs, there are concerns of ecological risk assessment. Based on this, we enumerated the potential risks and safety considerations associated with Si-NPs application in agroecosystem and suggested future perspectives to ensure the safe utilization and application of Si-NPs.

#### 2. Sources of PTEs in agroecosystem

The high incidence, accumulation and recalcitrance of PTEs in the agroecosystem is due to their adsorption to soil particles because of reactivity (Qian et al., 2020). Primary sources of PTEs including in the agroecosystem are anthropogenic and summarized under wastes from homes, industries, smelting plants, mining and agriculture (Singh et al., 2022; Zhang et al., 2023). Further, natural sources of PTEs include volcanic eruption, rainfall runoffs and weathering (Fig. 1) (Modabberi et al., 2018; Singh et al., 2022).

#### 2.1. Agriculture

The continued use of agrochemicals (pesticides, insecticides, herbicides and fertilizers), though with enormous benefits, is implicated for the deposition and accumulation of PTEs (Arsenic (As), Cadmium (Cd), Copper (Cu), Lead (Pb) and Zinc (Zn)) in soil and plants (Fig. 1) (Hou et al., 2020; Liu et al., 2020; Modabberi et al., 2018; Siddiqui et al., 2022; Weissengruber et al., 2018; Zhang et al., 2023). For example, the use of phosphate based fertilizers enhance crop production and disease prevention but contributes worrisome concentrations of Cd, Cr, Ni, Pb and Zn contamination to the agroecosystem (Singh et al., 2022; Weissengruber et al., 2018). Further, wastewater; a popular irrigation resource, introduce and accumulate PTEs (Cd, Ni, Pb) in the upper soil and plants (Hu et al., 2021; P. Liu et al., 2020; Singh et al., 2022). This presence is concerning, as accumulation in plants is sometimes higher than wastewater source (P. Liu et al., 2020) and Cd is the most toxic metal (Genchi et al., 2020).

#### 2.2. Mining

Mining introduces PTEs into the agroecosystem, threatening food security (Fig. 1). Zhang and others have reported the deposition of toxic metals; As and Hg into the agroecosystem from mining sites (Zhang et al., 2023). Their study combined Hg isotope and positive matrix factorization (PMF) techniques to confirm As, Hg, and Thallium (Tl) contamination due to historic mining from polymetallic mining. Further, agroecosystem degradation and public health consequences

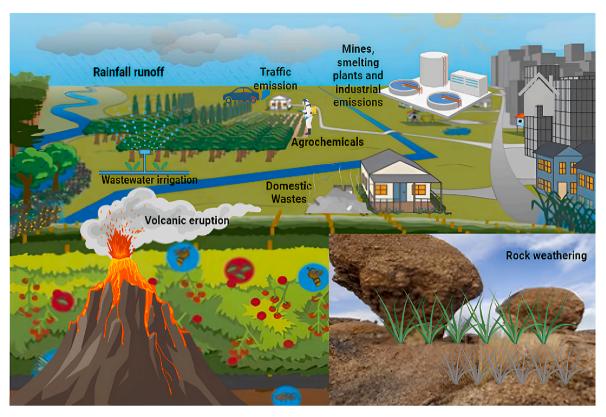


Fig. 1. Routes of PTEs entry into the agroecosystem; anthropogenic and natural routes. Volcanic eruptions, rock weathering and rainfall runoff represent natural sources of PTEs introduction to the agroecosystem while anthropogenic sources include agrochemicals, traffic emission, domestic wastes, emissions from industries, mines, smelting plants and waste dumps.

have been reported due to heavy metal deposition from coal mines, with up to 80 elements in coal (Siddiqui et al., 2022). Combining Monte Carlo simulation, PMF and finite mixture distribution model (FMDM) at Jharia coal mine, the authors scored mining second among other sources; contributing about 28 % of the total PTEs.

#### 2.3. Industrial and traffic sources

The emission of PTEs from industrial processes into the atmosphere, soil and water has been well documented (Fig. 1) (Hu et al., 2021; Siddiqui et al., 2022; Singh et al., 2022; Zhang et al., 2023). Incineration of industrial wastes, fossil fuel production/consumption and emissions resulting from industrial processes have placed the agroecosystem on the receiving end of PTEs (Hu et al., 2021; Singh et al., 2022; Wang et al., 2022). The discharge of untreated industrial wastes is also an important introduction route of PTEs (Liu et al., 2020). For example, Cr used in pharmaceutical and leather industries is introduced to the agroecosystems through industrial waste discharge. Studies posit that industries and traffic account for highest PTEs in the agroecosystem (Wang et al., 2022; Hu et al., 2021). The relationship between the concentration of Antimony (Sb), Cd, Cr, Cu, Pb and Zn and traffic movements due to abrasion, ageing and degradation is also reported (Cowan et al., 2021; Modabberi et al., 2018). In a 2021 study on the incidence and source of PTEs in Korea, transportation was highlighted for the highest concentration of PTEs in the agroecosystem (Jeong et al., 2021).

#### 2.4. Smelting plants

Smelting processes have been implicated as an important source of PTEs in the agroecosystem. The incidence of PTEs including As, Cd, Cu, Cr, Hg, Pb, Ni and Zn, at various levels of soil profile, has been reported at hazardous concentrations and successfully traced to smelting activities (Guillevic et al., 2023; Jeong et al., 2021; Vejvodová et al., 2022). The presence of Pb was reported and traced to a smelting plant that had shutdown operations for more than 200 years in France, highlighting the importance of smelting plants as an importance source of PTEs in the agroecosystem as well as the recalcitrance of PTEs (Guillevic et al., 2023). The incidence of PTEs in soil and vegetables (cucumber, pepper, zucchini) has also been traced to smelting plants in Czech republic (Vejvodová et al., 2022). Although, PTEs detected in this study were below the safe limit in soil, they surpassed permissible limits in food, presenting a significant cause for worry. Similarly, a smelting plant in Korea has been implicated for the incidence of Pb, Cu, As, Cr, Ni, Cd and Hg with actual sources linked to the transportation of raw materials to the smelting plant and further aggravated by the smelting activities (Jeong et al., 2021).

#### 2.5. Natural sources of PTEs

The incidence of PTEs in the agroecosystem threatening food security is linked to natural processes of weathering, erosion, volcanoes and roof run-off from rainfall (Fig. 1) (Modabberi et al., 2018; Siddiqui et al., 2022; Singh et al., 2022). Lithogenic activities; weathering, volcano and sedimentation, release PTEs from soluble metals that undergo biochemical processes into secondary minerals aiding the adsorption of PTEs (Palansooriya et al., 2020). Example weathering of carbonate rock is the source of limestone soil (Zhang et al., 2022) and volcanic ashes present abundant sources of PTEs in the agroecosystem (Palansooriya et al., 2020). Further, Al, As, Ba, Cu, Fe, Mn, Ni and Zn accumulate due to the weathering of amphibolite, feldspar, hematite and ilmenite (Kumar et al., 2022).

## 3. Ecotoxicological impact of PTEs on agroecosystem: a threat to food security

The life support system contains the agroecosystem and as in every other part of this robust system, self-serving processes ensure a balance and continuous flow of the needed materials including nutrients. In fact, the functionality and efficient running of the agroecosystem depends on the biogeochemical cycles such as the nitrogen cycle (Okeke et al., 2022b). These cycles depend on natural catabolic and anabolic reactions to continue, most of which depend on the successful energy transfer within and across trophic levels. PTEs inhibit the normal agroecosystem functions by limiting biodegradation and the successful nutrient cycling through pollution leading to consequent ecotoxicity on the fauna and flora; eventually threatening food security (Singh et al., 2022).

#### 3.1. Ecotoxicity of PTEs on agroecosystem flora

Potentially toxic elements include trace elements like Zn, essential for proper plant growth and development but toxic at elevated levels (Ghori et al., 2019) while others including Ag, As, Cd, Cr, Hg, etc., are toxic even at minute concentrations leading to plant diseases like chlorosis, putrefaction and leaf rolling (Chen et al., 2022; Xun et al., 2018). Primarily, the presence of PTEs at elevated levels hinder biodegradation and nutrient cycle (Singh et al., 2022). Eventual toxicity due to PTEs is linked to the accumulation of metals like Cu and Mn on the roots and shoots of plants (Angulo-Bejarano et al., 2021; Ghori et al., 2019; Liu et al., 2020), hampering physiological processes such as germination, growth, nutrient assimilation, enzyme activities and ultimately photosynthesis (Fig. 2) (Chen et al., 2022). The accumulation of metals in plants is implicated in the upset of pollination leading to reproductive unfitness in female plants (Xun et al., 2018).

Further, distortion in plant biodiversity and ecosystem functions, including nutrient/biogeochemical cycling, result to the accumulation

of PTEs (Lu et al., 2021). Interestingly, mechanisms to ameliorate ecotoxicity effects of PTEs on agroecosystem flora including uptake reduction, detoxification and protein synthesis could be inefficient against PTEs (Ghori et al., 2019). For instance, Hg absorption causes dehydration in plants as well as obstructing chloroplast and mitochondria functions (Ghori et al., 2019) and Ni causes oxidative stress, reduced growth and photosynthesis dysfunction (Singh et al., 2022). These challenges ultimately impact on plant production, posing an obvious threat to food security.

#### 3.2. Ecotoxicity of PTEs on agroecosystem fauna

Ecotoxicity reports of PTEs on the agroecosystem fauna, especially microorganisms important in system function, indicate an adverse effect due to accumulation of PTEs. As, Pb and Sb influence microbial diversity and richness (Dong et al., 2021; Huang et al., 2023). A study on the influence of As on the soil microbial ecology recorded a reduced Proteobacteria but increased Chloroflexi and Acidobacteria populations with distortions in other soil parameters including acid phosphatase, dehydrogenase, peroxidase, protease and urease worsened by low levels of nitrogen and phosphorus (Dong et al., 2021). This study also reported the increase in organic matter content, explained by the increased abundance of Acidobacteria and Chloroflexi, usually among the least abundant bacterial species in soil (Mhete et al., 2020) and associated with the removal of soil nitrogen and phosphorus (Speirs et al., 2019). Proteobacteria, usually the most abundant bacteria population (Mhete et al., 2020), is integral to the successful biogeochemical cycling of carbon, nitrogen, phosphorus and Sulphur (Cheng, 2023; Mhete et al., 2020).

Another study evaluated the combined effect of Sb and As contamination on soil microbial community and demonstrated a significant relationship even with low bioavailability index (Huang et al., 2023). Further, ecotoxicity studies of burrowing earthworm on exposure to

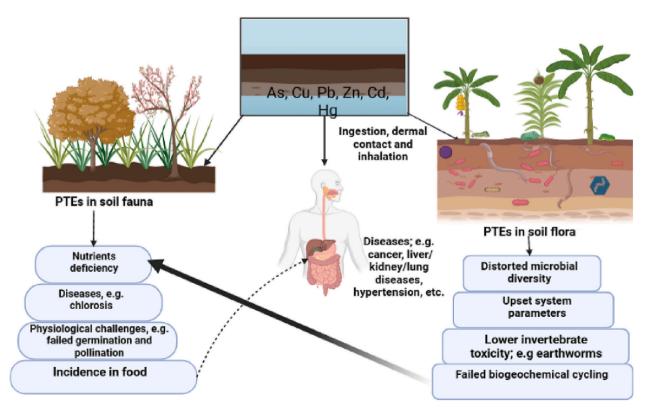


Fig. 2. Ecotoxicity of PTEs in the agroecosystem; fauna, flora and humans. The failed biogeochemical cycles is integral to the threat of PTEs to food security, worsened by challenges to plant physiological processes essential for food production, including germination and pollination. Plant diseases such as chlorosis linked to PTEs also impacts on food production, threatening food security.

PTEs such as Cd, reveal contaminant bioavailability, accumulation and toxicity (Kumar et al., 2008), thus affecting agroecosystem functions of earthworm (Van Groenigen et al., 2019). The richness of the agroecosystem is ascribed to earthworm casts richness as well as biogeochemical cycling in the earthworm gut, leading to the increase in soil nutrients and eventual productivity.

Overall, the upset in the normal fauna of the agroecosystem could lead to the eventual degradation of the soil environment, reduced soil production and severe threat to food security (Fig. 2).

#### 3.3. Ecotoxicity of PTEs on public health

In humans, trace elements including Cu, Mo, Ni and Zn are cofactors aiding enzyme-mediated metabolisms and physiological functions, though harmful at elevated concentrations (Banerjee et al., 2021a, 2021b). For example, Fe is key in proper mitochondrial functions but implicated at elevated concentrations for cell death due to DNA mutations and protein deterioration (Astuti et al., 2022). Dermal contact, inhalation and ingestion remain the principle routes of PTEs in humans with consequent diseases including cancer, kidney, liver and gastrointestinal diseases (Astuti et al., 2022; Li et al., 2018). For example, the carcinogenic tendencies of As is by the disruption of DNA synthesis as well as repair protocols while kidney and liver diseases are linked to exposure to Cd (Astuti et al., 2022; Taydé et al., 2023). Other studies have implicated PTEs in changed blood compositions, hypertension and reduced central nervous system activities (Qian et al., 2020). Bioavailability has been confirmed high in humans, influenced by gender and age, with concentrations of As, Cd, Cu and Pd in the blood (6.9 mg/kg), fingernails (90.5 mg/kg) and hairs (69.3 mg/kg) (Li et al., 2018).

# 4. Potentials of silicon-based nanoparticles (Si-NPs) for mitigating/removal of PTEs and plant stress to promote food security in agroecosystem

Silicon nanoparticles have found profound use in promoting sustainable agriculture. Being one of the most abundant elements on earth, numerous and diverse functionalities of silicon nanoparticles have been reported recently (Dhakate et al., 2022). Si-NPs mitigate the effects or counteract the bioaccumulation of potentially toxic elements such as heavy metals, excess salts, drought, flooding, microplastics, and nanoplastics. Silicon nanoparticles potentially mediate these plant stress factors that could hamper our agroecosystem's overall productivity and food security (Banerjee et al., 2021a, 2021b; Okeke et al., 2022b; Pu et al., 2023). Generally, major consequences of plants' exposure to the toxic environment or PTEs include oxidative stress, distorted physiological characteristics, reduced growth rate and yields, down-regulation of antioxidants and antioxidant enzymes, reduced photosynthetic pigment, and many more (Okeke et al., 2022c; Savchenko and Tikhonov, 2021).

Oxidative stress in plants is mainly caused by the drastic increase of reactive oxygen species (ROS) released due to either internally (metabolic) or externally stimulated unbalanced redox activities. Oxidative stress in plants most often leads to severe damage to several biomolecules such as protein, DNA, and RNA, as well as fostering the release of stress response mediators in plants (Enechi et al., 2022; Okagu et al., 2021). The application of silicon nanoparticles in remediating the destructive effects of oxidative stress in plants has been investigated in several recent studies, and generally, findings have reported impressive outcomes (Bansal et al., 2022). It is evident that plant exposure to PTEs promotes the release of ROS in the plant tissues, which could potentially overwhelm the de novo antioxidant system of the plants (Hasanuzzaman et al., 2020). Silicon nanoparticles (as summarized in Tables 1 and 2) have been shown to counteract this oxidative stress by activating or enhancing the activities of antioxidant enzymes such as catalase (CAT), ascorbate peroxidase (APx), superoxide dismutase (SOD), and others. Moreover, SiNPs foster the upregulation or overproduction of other nonenzymatic antioxidant metabolites such as anthocyanins, flavonoids, phenolics, glutathione, and others.

Other intricate activities of SiNPs include but are not limited to improving micro and macronutrient uptake systems and upregulating photosynthetic pigments, removing toxicants or pollutants, and many more (Rastogi et al., 2019). SiNPs are nontoxic to plants, as no toxicity has been reported so far. Studies have shown that plants exposed to SiNPs have upregulation in the expression of the silicon transporter (*Lsi1*) gene, possibly promoting salvaging activities on plants with induced stress from PTEs (Asgari et al., 2018). This section summarized exciting findings on the application of SiNPs to counteracting PTEs induced stress.

#### 4.1. Silicon nanoparticles and heavy metal-induced plant stress

Heavy metals are very common plant PTEs characterized by their high density and toxicity, even as low as ppb concentration. Plants exposed to heavy metals, majorly from soils or irrigation waters, have shown retarded growth and decreased productivity. Common heavy metals that affect plant includes chromium (Cr), cadmium (Cd), nickel (Ni), arsenic (As), and lead (Pb). Silicon nanoparticles, in recent studies, have been shown to alleviate the toxic effects of heavy metals in crops (Nweze et al., 2022; Okeke et al., 2021). Thind et al. (2021) reported the remediating effects of SiNPs (3 mM) on the Ujala wheat variety grown in soil contaminated with Cd (25 mg/ kg). The wheat plant treated with SiNPs showed increased growth rates and biomass, enhanced levels of photosynthetic pigments, and upregulated production of non-enzymatic antioxidant and antioxidant enzymes compared to their untreated counterpart (Thind et al., 2021).

Interestingly, the oxidative stress markers such as malondialdehyde (MDA), hydrogen peroxides ( $H_2O_2$ ), and superoxide radicals significantly decreased in the SiNP-treated plants. Finally, it was shown that the electrolyte leakage rate was drastically reduced in the treated plants (Thind et al., 2021). In a similar study, common beans (*Phaseolus vulgaris* L) grown in soil densely polluted with heavy metals (Cd, Ni, and Pb) recovered from the toxic effects after treatment with biostimulated SiNPs (5.0 mmol/L) and potassium silicate (10 mmol/L). In addition to restoring the redox balance of the plant, it was shown that the membrane stability, stomatal conductance, and net photosynthetic rate were significantly improved (El-Saadony et al., 2021). Some other similar and interesting findings are summarized in Table 1.

Heavy metals easily bioaccumulate in plants, and their toxicity also commonly causes macro and micronutrient uptake inhibition. However, SiNPs have been shown in many studies to mitigate these effects. Chen lab in (2018) reported that Rice plants (Oryza sativa L. cv. Xiangzaoxian 45), on exposure to Cd, bioaccumulate the heavy metal in the uppermost node of the plant, and this results in severe oxidative stress and poor productivity. However, on treatment with SiNP at an optimum concentration of 25 mM, a decrease in Cd accumulation in the mature of about 31.6-64.9 % was reported. More so, it was observed that SiNPs inhibited the translocation of Cd while enhancing the translocation of macro and micronutrients from the roots to the distal nodes. In more detail, the translocation factors for Cd were drastically reduced, while a corresponding enhancement of the expression of translocation factors for nutrients such as K, Mg, and Fe, Ca, Zn, and Mn (Chen et al., 2018b). Similar findings on improved nutrient uptake by plants treated with SiNPs have been presented in the following reports (El-Saadony et al., 2021; Thind et al., 2021) (Table 1).

#### 4.2. Silicon nanoparticles and plant stress induced by other PTEs

Several other abiotic and biotic stressors, including high salt concentration (salinity), non-metallic ions, drought, flooding, and UV radiation, are detrimental and toxic to plant viability and productivity (Table 2). Salinity or high salt concentration induces plant stress, suppressing plant growth, biomass, and yield (Zhao et al., 2021). In a recent

#### Table 1

Studies on the remediating activities of SiNPs on heavy metal-induced plant stress.

Stressor classification	Plants	Specific stressors or PTEs/ exposure level	Stress impacts	Conc. of SiNPs	Impact of stress tolerance, adaptation and mitigation (Possible mechanisms)	Reference
Heavy metal- induced oxidative stress and toxicity	Pea seedlings (Pisum sativum)	Chromium - Cr (VI) - 100 µM	<ul> <li>↓ plant growth</li> <li>↓ photosynthetic pigments and Chl fluorescence parameters like Fv/Fm, Fv/ F0, and qP</li> <li>↑ NPQ, MDA</li> <li>↑ SOD and APx</li> <li>↓ CAT, GRT, DhAR</li> <li>↓ micro &amp; macronutrients</li> </ul>	10 μM for 15 days	<ul> <li>↓ Cr accumulation</li> <li>↑ antioxidant defense system</li> <li>↑ nutrient uptake (Mg, Ca, K and P and B, Cu, Fe, Mn, Na, Zn)</li> <li>↑ Chl, Carotenoids, Total N content, and protein</li> </ul>	(Tripathi et al., 2015)
	Rice plants ( <i>Oryza sativa</i> L. cv. Xiangzaoxian 45)	Cadmium (Cd)	- Accumulation of Cd in the uppermost node of the plants	5–25 mM and 25 mM were the most effective	<ul> <li>Reduced the Cd concentrations in the mature grain by 31.6–64.9 %</li> <li>Plant nutrients such as K, Mg, Fe, Ca, Zn, and Mn and their translocation factors</li> <li>Decrease in the translocation factor for Cd.</li> <li>Summarily, SiNPs inhibit the translocation of Cd while enhancing the translocation of macro &amp; micronutrients</li> </ul>	(Chen et al., 2018b)
Heavy metal- induced oxidative stress and toxicity	Ujala wheat variety	Cadmium (Cd) 25 mg/ kg	<ul> <li>↓ biomass production,</li> <li>↓ photosynthetic pigments,</li> <li>↓ TSP, FAA, TSS, and phenolic contents,</li> <li>↑ APX, CAT, SOD, POD</li> <li>↑ reducing sugar</li> <li>↑ proline contents</li> <li>↑ MDA, H<sub>2</sub>O<sub>2</sub> content,</li> <li>↑ electrolyte leakage</li> </ul>	3 mM	<ul> <li>Improved growth</li> <li>↑ photosynthetic pigments,</li> <li>↑ levels of flavonoids,</li> <li>↑ TSP, phenolics, FAA, proline, TSS,</li> <li>↑ APX, CAT, POD, and SOD enzymes.</li> <li>↓ H<sub>2</sub>O<sub>2</sub> and</li> <li>↓ MDA</li> </ul>	(Thind et al., 2021)
	Phaseolus vulgaris L.	Cd, Ni, and Pb	-	Bio-Si-NPs (5.0 mmol/L) and potassium silicate (10 mmol/L)	<ul> <li>↑ Plant growth and production,</li> <li>↑ chlorophylls,</li> <li>↑ carotenoids,</li> <li>↑ transpiration rate,</li> <li>↑ net photosynthetic rate,</li> <li>↑ stomatal conductance,</li> <li>↑ membrane stability index,</li> <li>↑ relative water content,</li> <li>↑ free proline,</li> <li>↑ total soluble sugars,</li> <li>↑ N, P, K, Ca<sup>2+</sup>, K<sup>+</sup>/Na<sup>+</sup>,</li> <li>↑ activities of POD, CAT, APx, and SOD.</li> <li>↓ electrolyte leakage,</li> <li>↓ malondialdehyde,</li> <li>↓ H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub><sup>-</sup>,</li> <li>↓ Na<sup>+</sup>, Pb, Cd, and Ni</li> </ul>	(El-Saadony et al., 2021)
Heavy metal- induced stress	Zea mays L. cv. Nootan and Z. mays L. hyb. Shaktiman-4	Arsenate (As <sup>v</sup> ; 25 and 50 μM)	<ul> <li>Growth reduction</li> <li>↑ Oxidative stress</li> <li>↓ activities of APx, GRT, DhAR</li> <li>↑ SOD</li> <li>↓ Ascorbate and glutathione</li> </ul>	10 μΜ	<ul> <li>↑ Plant growth and yield</li> <li>↑ component of Ascorbate and glutathione cycle</li> <li>↑ activities of APx, GRT, DhAR</li> </ul>	(Tripathi et al., 2016)
	wheat ( <i>Triticum</i> aestivum L.)	Cd	<ul> <li>† Oxidative stress</li> <li>† H<sub>2</sub>O<sub>2</sub> and superoxide</li> <li>† Electrolyte leakages</li> </ul>	300–1200 mg/L	<ul> <li>Improved the dry biomass of the shoots, roots, spikes, and grains</li> <li>enhance leaf gas exchanges</li> <li>↑ chlorophyll <i>a</i> and b</li> <li>↓ electrolyte leakages</li> <li>↑ SOD, POD activities</li> <li>↓ Cd content of shoots, roots, and grains</li> </ul>	(Ali et al., 2019; Hussain et al., 2019)
	Tomato (Solanum lycopersicum L.)	arsenic (As) (3.2 mg/ L)	-↑ Arsenic bioaccumulation in roots, leaves, and stem - ↑ tomato yield at high conc	250 and 1000 mg/ L	<ul> <li>↓ Arsenic translocation</li> <li>↓ Tomato yield</li> <li>↓ Root biomass</li> <li>↑ Photosynthetic pigments</li> <li>↑ CAT and APx activities</li> </ul>	(González- Moscoso et al., 2022)
	Coriander (Coriandrum sativum L.)	Lead (Pb) 500–1500 mg/ kg of soil	<ul> <li>↓ plant biomass and vitamin C</li> <li>↑ flavonoid, MDA</li> <li>↑ antioxidant enzyme activities</li> <li>↑ tissue Pb bioaccumulation</li> </ul>	1.5 mM (Foliar application)	<ul> <li>↓ Pb bioaccumulation</li> <li>↓ plant defense system</li> <li>↓ MDA</li> <li>adjusted the POD, CAT, and SOD activities</li> </ul>	(Fatemi et al., 2021)

 $\uparrow$  - increase, stimulation, upregulation, accumulation, overexpression or activation;  $\downarrow$  - decrease, deactivation, down-regulation, inhibition, or inactivation; GRT - glutathione reductase; GST – Glutathione-S-transferase; and GPx – Glutathione peroxidase; SOD - superoxide dismutase; POD – peroxidase; CAT - catalase; APx - ascorbate peroxidase; GuPx- guaiacol peroxidase; DhAR - dehydroascorbate reductase MDA – malondialdehyde; MG – methylglyoxal; LPO – Lipid peroxidation; NPQ – non-photochemical quenching; Chl – Chlorophyll; GP – Germination Percentage; GR – Germination rate; MGT – Mean germination time; RWC – Relative Water Contents; TSP - total soluble protein, FAA - free amino acids, TSS t- total soluble sugar.

study, *Pisum sativum* grown in soil with high salt concentration (NaCl – 100 - 250 mM) was reported with significantly reduced plant growth and yield, decreased water retention capacity, distorted level of antioxidant and antioxidant enzymes as well as accumulation of Na<sup>+</sup> ion concentration in the shoot and leaves (Ismail et al., 2022). However, on treatment with SiNPs, these toxic effects were reversed. An improved vegetative growth estimated by increased plant height enhanced fresh and dry weight, and outstanding yield was achieved (Ismail et al., 2022).

In another study, high NaCl concentration (10 dS m<sup>-1</sup>) caused worrisome oxidative stress in soybeans (*Glycine* max L. *cv. M7*). The researchers reported a drastic increase in the expression of antioxidant enzymes such as CAT, POD, APx, and SOD in response to the increased  $H_2O_2$  and reactive oxygen radicals' concentration in the plant tissues (Farhangi-Abriz and Torabian, 2018). Moreover, lipid peroxidation, as well as MDA level, were significantly increased. Applying SiNPs to stressed plants alleviates the conditions by restoring redox balance, alleviating lipid peroxidation, and mopping out the high Na + ion concentration. Further, a better expression of antioxidant molecules and antioxidant enzymes was reported (Farhangi-Abriz and Torabian, 2018). Other reports with similar findings are summarized in Table 2 (Elsheery et al., 2020; Karimian et al., 2021).

Drought and water deficiency is another stressor of plants and often fosters high saline conditions for plant growth environments and hence the abovementioned chains of harmful consequences. In a recent study by Mahmoud et al. (2020), water-deficient growth condition for banana (*Musa acuminata* 'Grand Nain') was simulated by treating the soil with 3 % polyethylene glycol (PEG-8000). This experimental setup increased salinity (Na<sup>+</sup>), induced severe oxidative stress, and increased MDA levels. On treatment with SiNPs, the oxidative tension of the plant tissues was reduced, and a significant improvement in the vegetative growth and plant yield (Mahmoud et al., 2020). Alsaeedi et al. (2019) reported the accumulation of SiNPs in plants' leaves after treatment, regulating their gas transfer and water losses via transpiration, hence a better survival chance for plants growing in little water or drought conditions.

Flooding is another plant stressor of emerging interest, especially in areas of tropical climates. Flooding has been reported to induce hypoxia in plants, which fosters chain threads of oxidative and osmotic stress. Iqbal et al. (2021) recently reported that a simulated flooded planting condition for Muscadine Grape (*Muscadinia rotundifolia* Michx.) resulted in hypoxia and a corresponding increase in oxidative markers, lipid oxidation, and ROS. Moreover, the researchers reported a worrisome accumulation of osmolyte as well as an inhibition of micronutrient uptake. Treating this simulated setup with SiNPs restored the plants' nearbalance physiological and oxidative state. Interestingly, SiNPs boost the antioxidant defense system, upregulate the level of osmoprotectants such as proline and glycinebetaine, and fostered improved nutrient uptake (Iqbal et al., 2021).

Finally, other stressors such as UV radiation, reactive anions (fluoride ion), pesticides, microplastics/nanoplastics (Akan et al., 2021; Deme et al., 2022; Okeke et al., 2023; Okeke et al., 2022a; Okeke, Okoye et al., 2022; Okeke et al., 2022d; Okoye et al., 2022; Okeke et al., 2021), and others most often result in similar biochemical consequences as the above-discussed in plant tissues. Treating with SiNPs, as shown in a few studies (Table 2), alleviates these toxic effects (Banerjee et al., 2021a, 2021b; Pu et al., 2023; Tripathi et al., 2017).

## 5. Other applications of Si-NP for sustainable agriculture and food security

#### 5.1. Si-NPs as pesticides

In the field of agriculture, controlling pests and diseases is an essential task to ensure high crop yield and quality. However, traditional pesticides often have negative effects on the environment and human health. Therefore, there is a need for safer and more effective alternatives. One such alternative is the use of silicon nanoparticles as a pesticide. Silicon nanoparticles have shown promising results in controlling pests while being eco-friendly and non-toxic (Alimohamadian et al., 2022).

Research has shown that Si-NPs have broad-spectrum insecticidal activity against a range of pests. For example, Si-NPs have been shown to have an insecticidal effect on *Aphis craccivora, Liriomyza trifolii,* and *Spodoptera littoralis* (Thabet et al., 2021). Si-NPs can also inhibit the growth of fungi, viruses, bacteria, and nematodes making them effective against plant diseases (Rajput et al., 2021). Additionally, Si-NPs can enhance plant growth and increase crop yield (Roychoudhury, 2020). The mechanism of action of Si-NPs as a pesticide is not fully understood. However, it is thought that Si-NPs can penetrate the cuticle of pests and disrupt their cellular membrane, leading to cell death. Si-NPs can also damage the gut of the pests feeding on Si-NPs treated plants or causes external morphology malformation (Thabet et al., 2021).

Studies have shown that silicon nanoparticles can be effective in controlling a range of pests. For example, a study conducted by Kang et al. (2021) found that silicon nanoparticles significantly suppressed the growth of Fusarium wilt of watermelon (*Citrullus lanatus*) resulting in increased plant biomass and fruit yield up to 82 % when compared with untreated plants. Another study by Debnath et al. (2011) demonstrated the insecticidal activity of silicon nanoparticles against *Sitophilus oryzae*, a rice weevil that infests stored grains. The nanoparticles were shown to be effective in reducing the population of the weevils (up to 90 % mortality) and improving the quality of the stored rice.

In addition to their insecticidal properties, silicon nanoparticles have been shown to have antifungal activity against plant pathogens such as Fusarium and Phytophthora. The silicon-based nanomaterials can protect plants from diseases by enhancing their resistance to fungal pathogens. The nanoparticles act by stimulating the plant's immune system and reinforcing the plant cell walls, making them more resistant to fungal attack (El-Shetehy et al., 2021; Sun et al., 2010).

One major advantage of Si-NPs is their low toxicity compared to traditional pesticides. Traditional pesticides can be highly toxic to humans and the environment, causing numerous health and environmental issues. However, Si-NPs have been shown to be safe for human and environmental exposure when used in appropriate doses (Thabet et al., 2021). In addition, Si-NPs are also easy to manufacture and apply, making them a cost-effective alternative to traditional pesticides. Si-NPs can be synthesized using simple and inexpensive methods and can be easily applied using common agricultural techniques such as spraying or irrigation (Bhat et al., 2021b).

Despite the numerous advantages of Si-NPs, there are still some concerns regarding their safety and efficacy. Further research is needed to fully understand the long-term effects of Si-NPs on human health and the environment, as well as their potential impact on non-target organisms.

#### Table 2

Studies on the roles of SiNPs in mitigating other PTE-induced stressors.

Stressor classification	Plants	Specific stressors or PTEs/ exposure level	Stress impacts	Conc. of SiNPs	Impact of stress tolerance, adaptation, and mitigation (Possible mechanisms)	Reference.
Non-metallic ion- induced oxidative stress	rice cultivar, IR-64	Fluoride toxicity (25 mg/L of NaF for 20 days)	<ul> <li>↑Cobalt accumulation</li> <li>↑electrolyte leakage</li> <li>↑MDA, MG, and H<sub>2</sub>O<sub>2</sub></li> <li>↑NADPH oxidase</li> <li>activity</li> <li>↓photosynthesis due to</li> <li>chlorosis &amp; ↓ hill activity</li> </ul>	60 mg/L for 20 d	<ul> <li>↑ non-enzymatic antioxidant enzymes (anthocyanins, flavonoids, phenolics, and glutathione)</li> <li>↓ glutathione synthesis by activating GRT</li> <li>- activation of glyoxalases, GST and GPx</li> <li>↑ SOD, CAT, APx, and GuPx activities</li> <li>↑ nutrient uptake (Si, K, Zn, Cu, Fe, Ni, Mn, Se, and V)</li> </ul>	Banerjee et al. (2021a, 2021b)
Salt/Salinity-induced oxidative stress	faba bean ( <i>Vicia faba</i> L.)	NaCl (0, 50, 100, and 200 mM)	<ul> <li>↑ Germination</li> <li>parameters such as GR,</li> <li>GP, and MGT</li> <li>↓ plant growth and</li> <li>yield</li> <li>↓ N, P, Ca, and K in</li> <li>seeds</li> <li>↑ Na<sup>+</sup> Accumulation</li> </ul>	2 mM	<ul> <li>↑ GR, GP, and MGT</li> <li>↑ vegetative growth (plant height, fresh and dry weight) and RWC</li> <li>↑ Total yield</li> </ul>	Amira and Qados, 2014
	Pisum sativum	NaCl (100, 150, 200, and 250 mM)	<ul> <li>↓ Plant growth and yield ↓CAT         ↑ SOD, Peroxidases          </li> <li>↑ Na<sup>+</sup> Accumulation in roots and shoots         </li> <li>→ differential e</li> </ul>	3 mM	<ul> <li>twegetative growth (plant height, fresh and dry weight) and improved yield</li> <li>tRWC</li> <li>Antioxidant defense system</li> <li>Expression of antioxidant enzymes transcripts compare the salt-stressed plants</li> </ul>	Ismail et al., 2022
	Soybean ( <i>Glycine</i> max L. cv. M7)	NaCl (10 dS m <sup>-1</sup> )	<ul> <li>↓ root and shoot dry weight</li> <li>↓ K<sup>+</sup> in root and leaves</li> <li>↑ Na<sup>+</sup>, CAT, POD, APx, and SOD</li> <li>↑ Phenolic, Ascorbic, and α-tocopherol content</li> <li>↑ LPO, H<sub>2</sub>O<sub>2</sub>, oxygen radicals</li> </ul>	0.5 and 1 mM	<ul> <li>↑ K<sup>+</sup> concentration,</li> <li>↑ antioxidant activities, non- enzymatic compounds and</li> <li>↓ Na<sup>+</sup> concentration,</li> <li>↓ lipid peroxidation</li> <li>↓ ROS production</li> </ul>	Farhangi-Abriz and Torabian, 2018
Water-deficient and salinity-induced oxidative stress	banana ( <i>Musa</i> <i>acuminata</i> 'Grand Nain')	polyethylene glycol (PEG- 8000) induced the water- deficit conditions (3 %)	<ul> <li>Induced Abiotic and oxidative stress</li> <li>increase in MDA level</li> <li>accumulation of Na+</li> </ul>	150–600 mg/L	<ul> <li>Enhanced growth and chlorophyll contents</li> <li>↓ MDA</li> <li>induces K+ uptake</li> <li>↓ Modulate the Na + level</li> </ul>	Mahmoud et al., 2020
Hypoxia-induced oxidative and osmotic stress	Muscadine Grape (Muscadinia rotundifolia Michx.)	Flooding induced hypoxia	<ul> <li>↓Oxidative stress</li> <li>↑ Lipid peroxidation</li> <li>↑ ROS in leaves and roots</li> <li>- accumulation of osmolyte</li> <li>↓ micronutrient uptake</li> <li>- an overall reduction of plant growth</li> </ul>	250 ppm	<ul> <li>↑ SOD, CAT,</li> <li>↑ Ascorbic acid and glutathione content</li> <li>- accumulation of organic osmolytes such as proline and glycinebetaine.</li> <li>↑ Nutrient uptakes such as N, P, K, and Zn</li> <li>↓ Mn and Fe to a less toxic level</li> <li>- summarily, boost antioxidant activities, Osmo-protectant accumulation, and micronutrient</li> </ul>	Iqbal et al., 2021
Ultraviolet radiation- induced stress	wheat ( <i>Triticum</i> <i>aestivum</i> ) seedlings	UV-B radiation (ambient+2.8 kJ m <sup>-2</sup> ) at fluence rate of 0.4 W m <sup>-2</sup> for 8 h	<ul> <li>Declined photosynthetic performance,</li> <li>altered leave structures</li> <li>↑ H<sub>2</sub>O<sub>2</sub> and superoxide</li> <li>↑ Lipid peroxidation (LPO)</li> <li>↑ Electrolyte leakages</li> <li>↓ activities of SOD and APx</li> <li>↑ stimulated CAT, GuPx</li> </ul>	10 μΜ	regulation - Protection by possible NO- mediated triggering of the antioxidant defense system - ↓ counteract and reduce ROS - ↓ electrolyte leakages - ↓ Lipid peroxidation	Tripathi et al., 2017

 $\uparrow$  - increase, stimulation, upregulation, accumulation, overexpression or activation;  $\downarrow$  - decrease, deactivation, down-regulation, inhibition, or inactivation; GRT - glutathione reductase; GST – Glutathione-S-transferase; and GPx – Glutathione peroxidase; SOD - superoxide dismutase; POD – peroxidase; CAT - catalase; APx - ascorbate peroxidase; GuPx- guaiacol peroxidase; DhAR - dehydroascorbate reductase MDA – malondialdehyde; MG – methylglyoxal; LPO – Lipid peroxidation; NPQ – non-photochemical quenching; Chl – Chlorophyll; GP – Germination Percentage; GR – Germination rate; MGT – Mean germination time; RWC – Relative Water Contents; TSP - total soluble protein, FAA - free amino acids, TSS t- total soluble sugar.

#### 5.2. Si-NP delivery system (for fertilizers, herbicides, essential elements)

Silicon nanoparticles (Si-NPs) are one of the most promising nanocarriers for delivering various agrochemicals, such as fertilizers, herbicides, and essential elements. Si-NPs are biocompatible, biodegradable, and non-toxic, making them an ideal candidate for developing efficient and sustainable agricultural practices (Goswami et al., 2022).

#### 5.2.1. Si-NP delivery system for fertilizers

Fertilizers are essential for plant growth and development. However, the excessive use of fertilizers has adverse effects on the environment, including water pollution and soil degradation. Silicon (Si) is an essential nutrient for plant growth and development, and its deficiency can result in reduced crop yields and susceptibility to biotic and abiotic stresses (Zargar et al., 2019). Si nanoparticles (Si-NPs) have emerged as a promising delivery system for fertilizers due to their small size, high surface area, and ability to penetrate plant cells (Goswami et al., 2022). Si-NP delivery systems for fertilizers have been developed using various approaches, such as coating, encapsulation, and functionalization. For example, Wanyika et al. (2012) developed a mesoporous Si-NP-based fertilizer delivery system by coating urea with Si-NPs. According to the findings, urea that was coated with Si-NP had a release rate that was slower and lasted five times longer than urea that was not coated.

Several studies have investigated the potential of Si-NP delivery systems for improving the efficiency of fertilizers. Janmohammadi et al. (2016) showed that using organic fertilizers together with Si-NPs foliar spray had a notable positive impact on safflower production, and recommended it as a viable agricultural strategy. In general, Si-NPs have been shown to enhance the efficiency of fertilizer delivery to plants, resulting in improved crop yields and reduced environmental impacts.

#### 5.2.2. Si-NP delivery system for herbicides and other elements

Herbicides are widely used in agriculture to control weeds and improve crop yield, but their efficacy can be limited by their poor solubility, instability, and rapid degradation in the environment. Silicon nanoparticles offer a potential solution to these challenges by encapsulating herbicides and protecting them from degradation while improving their solubility and stability (Chaud et al., 2021). Silicon nanoparticles have been used to encapsulate a wide range of herbicides, including glyphosate, atrazine, and 2,4-D, among others. In addition to encapsulating herbicides, silicon nanoparticles can also be used to control the release of herbicides. This can be achieved by modifying the surface of the nanoparticles to create a controlled system. A study by Chen et al. (2018a, 2018b) showed that silica nanoparticles can encapsulate glyphosate with high efficiency, resulting in controlled release and utilization efficiency of the herbicide. In another study, Xu et al. (2021) demonstrated the effectiveness of mesoporous silicon nanoparticles as a nanocarrier to enhance the utilization of Pyraoxystrobin (Pyr) by cucumber plants by promoting the solubility and absorption of Pyraoxystrobin. The authors observed that the encapsulated pesticide exhibited greater activity than the free one.

Essential elements, such as iron, zinc, and copper, are critical for plant growth and development. However, these elements are often deficient in soils, resulting in reduced crop yields and nutritional value. Si-NPs have been proposed as a potential solution for delivering essential elements to plants. Si-NP delivery systems for essential elements have been developed using various approaches, such as surface modification and functionalization. For example, Tripathi et al. (2012) demonstrated that the exogenous introduction of Si resulted in the higher uptake of some mineral elements such as K, Fe, and Zn and promoted the growth of the rice seedlings. In another study by Aqaei et al. (2020) showed that potassium nano-silica (PNS) improved the absorption of nutrients such as N, K, Cu, Si and Mn and alleviated the negative effect of drought stress on maize plants.

## 5.3. Si-NPs for targeted delivery of nucleotide, proteins, and other chemicals

Silicon nanoparticles (Si-NPs) have gained significant attention as potential delivery vehicles for nucleotides, proteins, and other chemicals in plants due to their unique physicochemical properties, biocompatibility, and biodegradability. In recent years, various studies have been conducted to evaluate the potential of Si-NPs for the targeted delivery of these biomolecules in plants (Rastogi et al., 2019; Vats et al., 2022).

One such study by Hajiahmadi et al. (2019) demonstrated that mesoporous silicon nanoparticles (MSN) can effectively deliver DNA to plant cells, resulting in improved gene expression and enhancement of tomato resistance to *Tuta absoluta*. The study also revealed that Si-NPs have high stability and biocompatibility, making them suitable for use in plant biotechnology.

It is interesting to note that Chang et al. (2013) utilized MSN as a nanocarrier to transport foreign DNA into intact roots of *Arabidopsis thaliana*. This approach is significant as it eliminates the need for mechanical force, which can potentially damage the plant tissue. The study found that gene expression occurred not only in the epidermal layer but also in the inner cortical and endodermal tissues of the root. This is an important observation as it suggests that MSN-based delivery of DNA can effectively target multiple layers of plant tissue. Moreover, the study proposed MSN-based delivery as a novel alternative to conventional methods such as gene-gun or ultrasonic methods. Gene-gun and ultrasonic methods are well-established techniques but can be cumbersome, expensive, and require specialized equipment. MSN-based delivery offers a simpler, cost-effective, and potentially more efficient approach to genetic transformation in plants.

Martin-Ortigosa et al. (2012) developed a novel approach for delivering plasmid DNA and protein into plant tissues using mesoporous silica nanoparticles (MSNs) functionalized with gold (Au-MSNs). The researchers first examined the uptake and release of bovine serum albumin protein (BSA) by the Au-MSNs and observed that the nanoparticles were able to effectively deliver the protein into plant cells.

To carry out the delivery of plasmid DNA and protein, the researchers loaded the Au-MSNs with BSA and then coated the nanoparticles with plasmid DNA. They then delivered the coated nanoparticles into onion plant cells and observed the expression of marker genes one day after delivery, indicating successful delivery of the plasmid DNA and protein.

Overall, these studies suggest that Si-NPs hold promise as a versatile and effective tool for the targeted delivery of nucleotides, proteins, and other chemicals in plants. However, further research is needed to optimize delivery strategies and overcome the challenges associated with SiNP-mediated delivery in plants.

#### 5.4. Si-NPs as nanosensors for pathogen and pesticide residue detection

Nanotechnology has revolutionized the field of biosensors by providing a way to detect minute quantities of pathogens and pesticide residues with high sensitivity and selectivity. Silicon nanoparticles (Si-NPs) are among the promising materials that have been explored for this purpose. Si-NPs offer several advantages such as their small size, large surface area, and photoluminescence properties, which make them an ideal candidate for biosensing applications (Shivashakarappa et al., 2022; Su et al., 2012).

Several studies have reported the use of Si-NPs as nanosensors for pathogen detection. For instance, Mathelié-Guinlet et al. (2019) developed a Si-NP-based biosensor for the detection of *Escherichia coli*. The biosensor showed a limit of detection (LOD) of  $10^3$  CFU/mL in 10 min, which is comparable to the conventional methods. In another study, Wang et al. (2020) used SiO<sub>2</sub> and MnO<sub>2</sub> nanocomposites for the detection of *Salmonella typhimurium*. The biosensor was able to detect 21 CFU/mL of *Salmonella Typhimurium* in milk within 50 min selectivity towards *Salmonella typhimurium*.

Si-NPs have been explored for pesticide residue detection due to their high surface area, which provides a large surface for the adsorption of pesticide molecules. In a recent study, Jiang et al. (2023) developed a biosensor using Si-NPs (silicon nanoparticles) for the detection of chlorpyrifos, a pesticide commonly used in agriculture. The biosensor showed satisfactory recovery, which means it was able to accurately detect chlorpyrifos, and this makes it a promising candidate for future use in detecting this pesticide. The study's findings could have important implications for food safety and environmental monitoring, as chlorpyrifos can be harmful to humans and wildlife.

Si-NPs have shown great potential as nanosensors for pathogen and pesticide residue detection. Si-NP-based biosensors offer several advantages such as high sensitivity, selectivity, and low LODs, making them an ideal candidate for biosensing applications. Further research is needed to optimize the Si-NP-based biosensors for commercial applications.

#### 6. Risk assessment and safety considerations associated with SI-NPs application in agroecosystem

Risk assessment is a technique used to identify procedures that may cause habitats, to appraise the severity of the harm done and then stipulate methods to ameliorate the damage done by that procedure. This method involves 4 major steps which include hazard assessment, dose-response assessment, exposure assessment and risk characterization.

The findings of a scientific investigation on the characteristics of a chemical compound and its ability to contribute to adverse health effects on different ecological niche, microbes, plants, animals and humans is what is used to identify hazards. Hazardous compounds cause harm by incorporation and interact with cells, in order to elicit adverse responses that may lead to cellular damages (Hegde et al., 2015). In the agroecosystem, these cells may range from microbial cells to mega faunas, like plant root cells. These cellular damages may lead to the death of the whole organism. Additionally, these hazardous compounds cause an alteration in ecological niche of these organisms, causing hibernation, migration and or death of the inhabitants thereby leading to an adverse effect in the agroecosystem.

The major interest here are nanoparticles application and their possible toxicity in the agroecosystem while focusing on Silicon based nanoparticles. The general risks posed by most nanoparticles is their ability to adhere to plant roots and adversely impacting on mineral and water transport in the vascular tissues of plants. This adherence leads to clogging of root pores (Cañas et al., 2008). However, the key concern in silicon-based nanoparticles is usually the toxicity to plants and animals and by extension, man. This is due to their wide range of application in medicine, pharmaceutics, textile and agriculture (Bhat et al., 2021a, 2021b).

Silicon based NPs application to plants are considered safe because they are naturally and abundantly found in soil, plant parts such as the leaf epidermis and root endodermis. However, there are studies that have shown the adverse effect of silicon-based nanoparticles (Si-NPs) application in the agroecosystem. The adverse effects are greatly determined by its physicochemical properties such as the shape, charge, size, dispersity and particle size. Nano sized particles tend to exert more toxicity than its counterparts with the same chemical composition (Fadeel and Garcia-Bennett, 2010).

Some of the risks associated with application of silicon-based nanoparticles have been reported in different works. They have been implicated in the reduction of carbon and nitrogen content of microbial biomass in the soil, it has been shown to modify the preferential microbial (bacterial) organization in the soil (Simonin and Richaume, 2015). Silicon based nanoparticles have also been implicated in decreasing bacteria that can utilize organic forms of nitrogen, decreased amylolytic bacteria, oligotrophs, cellulolytic and microscopic fungi. (Lebedev et al., 2019).

Further, soil enzymes have been recorded to decrease on application of Si-NPs. Soil enzyme activities such as peroxidase, polyphenoloxidase and urease decreased in the findings of Lebedev et al. (2019). Studies on the effect of Si-NPs on a mega fauna (earthworm sp.) reported a negative impact on the protein metabolism of the earthworm. Furthermore, this has been seen as a major pathway by which other pollutants exacerbates their toxicity (Lebedev et al., 2019; Zhang et al., 2017). Di Marzio et al. (2018) also noted some cyto- and geno-toxicity in earthworms {Eisenia fetida (Oligochaeta, Annelida)}. These impacts could lead to the death of micro and mega fauna and by extension a decline in the population of the soil organisms. This implication can mean a reduced degradation rate of soil particulate organic matter, a deduction in nutrient turnover, availability and bioavailability to soil microbiota and plants, a possible deformation of the soil structure and aggregate formation, modification of soil hydraulics and temperature conductivity (Maggi and Tang, 2021).

Plethora of research have contributed to the belief that the adverse effects of NPs to plants is a factor of the physical interactions between the plant and the nanoparticles. Nanoparticles adhere to plant roots which go to moderate the transportation of water and minerals within the plant. This phenomenon can lead to some observed phytotoxicity in plants exposed to NP (Bhat et al., 2021a). (Le et al., 2014) has posited that Si-NP phytotoxicity experienced by plants may be associated with the changes in the soil pH induced by the addition of Si-NPs. The maximum phytotoxicity exceeding 20 % was observed at concentrations of 250 and 500 mg/kg in a study conducted by Lebedev et al. (2019). Silicon based nanoparticles ranging from 50 to 200 nm decreased the growth of a plant Arabidobsis. There were DNA damages observed within the root meristerm of Allium Cepa when Silicon based nanoparticles were applied at concentrations of 100 mg/mL. The plant growth and biomass of a Bt-cotton decreased after the application of Si-NPs (Bhat et al., 2021a; El-Sayed et al., 2021). Silicon based nanoparticles less than 20 nm inhibited the germination of rice seedlings. However, the particles above 20 nm seemed to have demonstrated positively towards other growth parameters (Asgari et al., 2018). The presence of Silicon based nanoparticles in the soil increases the stability of other more hazardous nanoparticle suspensions (TiO<sub>2</sub>, CuO and ZnO) in the soil (de Oliveira et al., 2017). These complications at different concentration shows the dependence of Si-NPs toxicity on its concentration. Therefore, to avoid such situations, it has become pertinent to determine the step-by-step role of silicon-based nanoparticles in plant growth. As stated earlier, the physicochemical properties (Size, shape, charge, stability, surface area, concentration) of the Si-NPs as well as plant age and specie are key factors to consider in order to achieve optimal benefits its application (Fig. 3).

#### 7. Conclusion and future perspectives

The scientific developments of the last decades have promoted industrialization, urbanization and improvement in human living standards despite a bludgeoning population. One potential danger of such advancement in scientific and industrial processing, however is the discharge of many types of pollutants into the environment. Among the different pollutants hitherto investigated, the predominance of potentially toxic elements (PTEs) is worrisome due to their grave impacts on human health and environmental conservation. The present report reviewed literature information on the sources of PTEs and their ecotoxicological impacts on the ecosystem. The potentials of Si-NPs in the removal of PTEs and other contaminants as well as their impacts on the soil agronomic properties, rhizospheric microbiome and roles in mitigating the impacts of stress during plant growth and development were adequately covered. Si-NPs play significant roles in promoting sustainable agriculture and combating food insecurity. The present review equally summarized data regarding Si-NP application as pesticides, nanosensors and vehicles for targeted delivery of agricultural products such as herbicides, fertilizers, genetic materials etc.

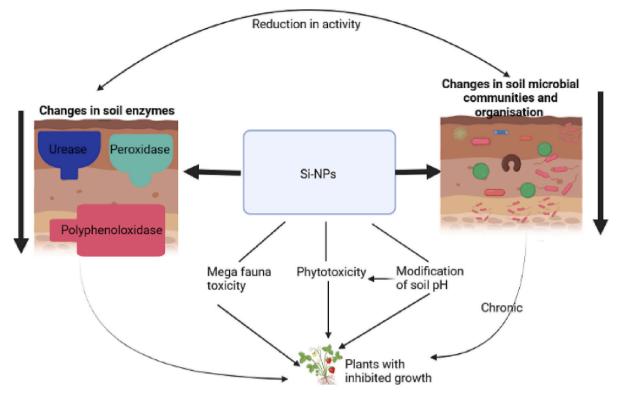


Fig. 3. Risks associated with Silicon Based nanoparticles in the agroecosystem. The arrow directions represent events and processes.

PTEs come from both natural and anthropogenic activities and include elements such as chromium, mercury, cadmium, copper, silver, vanadium, zinc etc. Being non-degradable, they potentially bioaccumulate by building along the food chain and eventually concentrating within humans. They are persistent, toxic and carcinogenic. Many PTEs have been implicated in numerous serious health conditions involving the lungs, kidney, brain, liver and the prostate. Several techniques have evolved over the years in effort to remediate compartments polluted with PTEs. The technologies which included some physical, chemical and biological treatment methods, were not successful. High energy and capital requirements, low rates of PTEs removal, finite recycling capacity and release of copious quantities of secondary wastes or sludge rendered them unfeasible and impractical to operate in the long run. Currently, the application of adsorbents such as metal-organic framework (MOF) has proven to be quite effective and sustainable in the remediation of water matrices polluted by PTEs.

Nanoparticles (NPs) contribute to plant growth and development through fostering plant tolerance, enhancing the rate of seed germination, improving translocation and soil fertility and resisting the impacts of pesticide residues. SI-NPs in particular, lower the rate of water permeability through the soil thereby promoting the performance of the plant through improving their physiological capacity,  $CO_2$  assimilation and plants biochemical responses.

The rhizosphere environment is home to a large community of microorganisms sustained by the secretions and exudates from the plant roots. The compounds in the released materials are crucial for plant growth and the development of a robust microbial community composed largely of nitrogen-fixing and phosphate-solubilizing microorganisms. The microbes stimulate plant growth through nutrient solubility, nitrogen fixation and organic acid production. These factors contribute to the moderation of the biochemical activities in the soils. The activities of Silicate-solubilizing bacteria (SSB) have been linked to the promotion of microbial biomass of soils and availability of Si to plants through the conversion of insoluble silicates into soluble Si in soils.

Environmental stresses negatively affect plant productivity and

constitute a formidable challenge to food security. Si-NPs application alter or significantly reverse the many non-beneficial responses of plants to abiotic perturbations by revamping the plants' cellular, antioxidative and photosynthetic machineries. During saline stress condition, for instance, the Si-NPs are beneficial to root development and plant biomass as well as the germination efficiency, leaf area and plant length expansion. However, increased plant productivity and carbon dioxide assimilation coupled with improvement in fruit quality were reported during Si-NPs intervention to cushion water stress. Heavy metal uptake and accumulation in plant tissues via the root transport system inevitably affect plant growth and development. Si-NPs reduces uptake of toxic ions in amended soils while a significant increment in agronomic properties were reported due to enhancement in the activities of antioxidative enzymes. The application of Si-NPs to soils effectively restored distortions in cellular structures commonly caused by heat stress. As a result, there was significant improvement in photosynthetic efficiency due to increase in the chlorophyll content in the leaves of crops.

The Si-NPs have promising applications in the field of agriculture. They enable crops to overcome stress conditions caused by climate change hence promoting food security. Some Si-NPs have been applied as protection to crops from the impacts of heavy metal toxicity and other soil mediated abiotic conditions. Currently, Si-NPs find novel applications as agricultural fertilizers, herbicides and even pesticides. The toxicity of Si-NPs against adult insects was thought to be due to impairment in the digestive functions of the alimentary tract or occlusion of the spiracles and tracheas. However, the mechanism by which Si-NPs control pests appear to be by interference with the protective hydrophobic-hydrophilic barrier leading practically to death.

Silicon nanocarriers fitted to specialized systems have been used to precisely deliver herbicides to the field environments in order to eradicate weeds and increase crop productivity. Modern agriculture makes use of technology such as nanoencapsulation to aid site-targeted delivery and the regulated release of agrochemicals such as proteins, nucleotides and fertilizers, for nutrient sufficiency, increased crop yields and improved plant resistance to disease and abiotic stresses. This ensures limited release and eco-protection of the environment. The application of metallic nanoparticles in sensing technologies have gained prominence in the field of agriculture. Si-NPs have been used as nanosensors for the detection of heavy metals in soil due to their sensitivity, sensor stability and resolution.

Looking forward, the application of Si-NPs has indeed revolutionized agriculture. In particular, the technology for the development of new crop cultivars resistant to various climate change and other ecological stresses have been developed. Si-NPs nanoparticles can be used to provide environmentally acceptable and sustainable alternatives to chemical fertilizers without interfering with nature's biological processes. When fully explored, the applications of Si-NPs may completely revamp and create effective solutions to the myriad of agricultural challenges facing mankind today.

#### CRediT authorship contribution statement

All authors contributed to the final manuscript submitted. ESO conceptualized and designed the work along with CON. All authors reviewed the outline and made contributions for improvement. ESO, EJN, TCE, CON, TPCE and CEIN wrote various sections of the manuscript and compiled into the first draft. All authors read the final manuscript and agreed prior to submission.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Please see bibliography.

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