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Influence of ionic cerium and cerium oxide nanoparticles on *Zea mays* seedlings grown with and without cadmium☆

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ABSTRACT

Cerium (Ce^{4+}) and cerium oxide nanoparticles (CeO_2-NPs) have diversified reported effects on plants. Once dispersed in the environment their fate is not well understood, especially in co-existence with other pollutants like cadmium (Cd). The effect of co-application of Ce and Cd are reported in various studies, but the role of Ce source (ionic or bulk) and nanoparticle size is still unknown in cereal plants like maize (*Zea mays*). To better understand the synergistic effects of Ce and Cd, 500 mg kg^{-1} Ce coming from ionic (Ce^{4+} as $CeSO_4$) and CeO_2 nano sources (10 nm, 50 nm, and 100 nm) alone and in combination with 0.5 mg Cd kg^{-1} sand were applied to maize seedlings. Growth, physiology, root structure, anatomy, and ionic homeostasis in maize were measured. The results revealed that Ce^{4+} resulted in overall decrease in seedling growth, biomass and resulted in higher heavy metal (in control sets) and Cd (in Cd spiked sets) uptake in maize seedlings' root and shoot. The effects of CeO_2-NPs were found to be dependent on particle size; in fact, under Cd-0 (non-Cd spiked sets) CeO_2-100 nm showed beneficial effects compared to the control. While under co-application with Cd, CeO_2-50 nm showed net beneficial effects on maize seedling growth parameters. The Ce alone, and in combination with Cd, altered the root suberin barrier formation. Both ionic and nano Ce sources alone and in co-existence with Cd behaved differently for tissue elemental concentrations (Ce, Cd, micronutrients like B, Mn, Ni, Cu, Zn, Mo, Fe and elements Co, Si) suggesting a strong influence of Cd–Ce coexistence on the element's uptake and translocation in maize.

1. Introduction

In the modern era of industrialization, anthropogenic activities are increasing soil and water pollution, in which heavy metal pollution is prominent (IPCS, 1992b; WHO, 2007; 2019). Among heavy metals, Cd is a persistent pollutant with well reported adverse effects on plants and animals. The main toxic effect on mammals includes nephrotoxicity, teratogenicity, reproductive toxicity, carcinogenicity, and endocrine toxicity (Goering et al., 1995; Waalkes, 2000). Because of these effects, it has been categorized as a human carcinogen by the World Health Organization's International Program On Chemical Safety (IPCS, 1992a, 1992b; IPCS, 2005–07). The main sources of this pollutant in the environment are mining, electroplating, and paint and ceramic industries (Hayat et al., 2019) releasing Cd from their effluents or into the air (Rani et al., 2020; Hill et al., 2021; Villen-Guzman et al., 2021). The uncontrolled and excessive use of phosphatic fertilizer is also found to be linked with Cd incursion in soil (Bramley, 1990; Grant, 2018). The influx of Cd into the human food chain not only occurs directly via

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environmental deposits (*e.g.,* air, jewelry, ceramics, etc.) but also using Cd contaminated food (derived from cereal crops grown on contaminated soils) (Naeem et al., 2019; El Rasafi et al., 2020). Cadmium pollution also affects crop growth and produce quality (El Rasafi et al., 2020) in addition to endangering animal (eating contaminated fodder) and human health (Hayat et al., 2019). The second major environmental issue is the fate of engineered nanoparticles that are being used in diverse fields of industry and agriculture (Simonet and Valcárcel, 2009; Maurer-Jones et al., 2013; Marghoob et al., 2022), and their fate in the ecosystem has become a concern as the use of nanotechnology is increasing (Stern and McNeil, 2007; Sohail et al., 2019, 2021). The widespread application of nanotechnology in integrated pest and nutrition management of agriculture is also contributing in NPs intrusion into the biosphere (Pramanik et al., 2020; Neme et al., 2021).

The rare earth metals are important class of metallic elements with diverse application in field of electronics, technology development and national defence (Drobniak and Mastalerz, 2022) thus are of the most economical importance now a days (Ilankoon et al., 2022). The global mining of rare earth elements has doubled between 2010 and 2021 (from 133,000 metric tons to 280,000 metric tons) as reported by Garside (2022). Cerium is an important rare earth metal with widespread uses in industry, biomedical science, and agriculture while its nanomaterials are also being used in diverse fields (Binnemans, 2006; Ahmad et al., 2018; Ayub et al., 2019). The effects of cerium on plants are diverse and dependent upon the type and sources of cerium as a divergent effect of bulk, ionic and nano cerium have been reported for radish (*Raphanus sativus*) (Zhang et al., 2015), *Brassica rapa* (Ma et al., 2015) and tomato (*Solanum lycopersicum*) (Barrios et al., 2016). Besides the source of Ce, the particle size of its compounds also affects its bioavailability and effects on plants, as observed for the two wild plant species *Holcus lanatus* and *Diplotaxis tenuifolia* exposed to Ce-NPs of two particles sizes (25 nm and 50 nm) (Lizzi et al., 2021). The main reason behind this variable effect is the prominent change in surface chemistry of Ce-NPs (Cresi et al., 2017; Dinesha et al., 2021), which can also affect its solubility, translocation, and bioavailability to plants.

The metallic nanoparticles have different chemistry than their counter bulk metal owing to their diverse surface chemistry, particle size, oxidation states of metals and nature of chemical bonding. Worldwide nanoparticles are being produced in bulk for various commercial purposes and there are many non-point sources of their including in environment (Bundschuh et al., 2018). The rare earth nanoparticles are an important class of nanoparticles as their use in agriculture and industry is increasing tremendously (Haque et al., 2014; Rim, 2016; Tommasi et al., 2021). Among all rare earth NPs, Cerium NPs are the most important as they are being used in energy storage, polishing, catalyst, personal care and cosmetics products and biomedical industries and its market is projected to touch $2.1156 billion by 2030 (Allied Market Research Report A01390, 2021).

The variable effects of cerium-cadmium coexistence system (Ce–Cd interaction) in crops are highly dependent upon source and particle size of Ce, making the Ce–Cd system overly complex to understand (Gschneidner and Calderwood, 1988; Cresi et al., 2017; Rossi et al., 2016, 2017a; Dinesha et al., 2021). The alone and coexisting application of Cd and Ce compounds is an interesting subject of investigation and studies have shown that Ce application can help in alleviation of Cd stress via the modulation of carbon assimilation and decreasing oxidative stress (Wu et al., 2014). The CeO_2-NPs (0 and 500 mg kg^{-1}) and Cd (0, 0.25 and 1 mg kg^{-1}) co-application in dry soil showed a net higher accumulation of Ce in plants while Cd uptake remained statistically unaffected in *Glycine max* (Rossi et al., 2017b, 2017c). It was reported that *Glycine max* grown hydroponically under CeO_2-NPs and Cd had significantly reduced shoot accumulation of Cd (Rossi et al., 2018). These divergent findings and lack of work on cereal crops make Ce–Cd interaction in maize a prominent topic to work on. In fact, maize (*Zea mays*) is an important food crop and a heavy metal hyperaccumulator, resulting in very high accumulation of Cd in its tissues if grown on contaminated soil (Popa et al., 2010), which can become a health hazard due to higher Cd accumulation in grains (El-Hassanin et al., 2019; Liu et al., 2020). The same behavior can be anticipated for rare earth metals like Ce and can be of concern, as proper permissible limits for rare earth metals in agroecosystems is yet to be defined.

The application of Ce-NPs and cadmium in maize have shown interesting effects in our previous findings (Fox et al., 2020). The reported work suggested that CeO_2-NPs (as a dispersion of polyvinylpyrrolidone (PVP) coated CeO_2-NPs) can significantly affect root apoplastic barriers, biomass, and maize seedling physiology; but no effect on Cd translocation was observed. The present investigation was planned to study the effect of Cd and CeO_2-NPs on shoot growth, gas exchange parameters, root anatomy, physiology and anatomy, and elemental distribution in maize seedlings. A concentration of 0.5 mg kg^{-1} Cd and 500 mg kg^{-1} Ce obtained from variable sources, ionic Ce and CeO_2-NPs (10 nm, 50 nm, and 100 nm), were applied.

2. Material and methods

2.1. Material collection, characterization, and preparation

The cerium oxide nanoparticles (CeO_2-10 nm-NPs, CeO_2-50 nm-NPs and CeO_2-100 nm-NPs) were purchased from U.S. Research Nanomaterials, Inc. (Houston, TX, USA). The Ce salt (Cerium Sulfate – Ce (IV) Sulfate), Reagenz, powder (Nitrogen flushed); Cd salt (Cd sulfate-$CdSO_4$); Nitric acid (TraceMetal Grade, 67–70% HNO_3, Fisher Chemical); H_2O_2 (JT Baker Hydrogen Peroxide, 30% ULTREX II Ultrapure Reagent) were purchased from Fisher Scientific Int. (Pittsburgh, PA, USA). For growing media, Sakrete™ play sand (Atlanta, GA, USA) was used, while Hoagland salt mixture (Hoagland Complete Medium - plantmedia.com) was used as a nutrition media.

The sand (50 g) and nanoparticles (5 g each) were sent to the University of Florida Nanoscale Research Facility (Gainesville, FL, USA) for characterization (via scanning electron microscopy and energy dispersive X-ray) of soil and nanoparticles. The scanning electron microscopy (FEI NOVA 430 Nano SEM) was regulated at a voltage of 5 kV, spot size of 3.0 and a working distance of 4.6 mm. Magnification was set from 200 kX to 400 kX. The chemical characterization was done using energy dispersive X-ray (EDX) analysis at a voltage of 10 kEV. Data was collected for 50 s for each sample at 5 mm working distance and a spot size of 4.5.

Plastic pots of 500 mL volume were filled with 600 g sand and were added with 4 sources of 500 mg kg^{-1} Ce (Ce-ionic, CeO_2-10 nm-NPs, CeO_2-50nm-NPs, and CeO_2-100 nm-NPs) and two levels of Cd (0, 0.5 mg kg^{-1}) including 2 controls [Uncontaminated Control (UCC) and Contaminated with Cd Control (CC)]. The 2-way factorial statistical arrangement was followed making a total of 10 treatments replicated 7 times each on July 8th, 2021. The detailed treatment plan is given in

Table 1
Treatment plan: experimental design of maize (Zea mays) seedlings under different concentrations of cadmium and cerium of different sources in greenhouse conditions.

Cd-0	Uncontaminated Control (UCC)
	Ionic Ce (IV) @ 500 mg Ce kg^{-1} dry sand as $CeSO_4$
	Ce 500 mg kg^{-1} dry sand from CeO_2-10 nm NPs
	Ce 500 mg kg^{-1} dry sand from CeO_2-50 nm NPs
	Ce 500 mg kg^{-1} dry sand from CeO_2-100 nm NPs
Cd-0.5	Contaminated Control (CC; Cd 0.5 mg kg^{-1} dry sand as $CdSO_4$)
	Ionic Ce (IV) @ 500 mg Ce kg^{-1} dry sand as $CeSO_4$ + Cd 0.5 mg kg^{-1} dry sand as $CdSO_4$
	Ce 500 mg kg^{-1} dry sand from CeO_2-10 nm NPs + Cd 0.5 mg kg^{-1} dry sand as $CdSO_4$
	Ce 500 mg kg^{-1} dry sand from CeO_2-50 nm NPs + Cd 0.5 mg kg^{-1} dry sand as $CdSO_4$
	Ce 500 mg kg^{-1} dry sand from CeO_2-100 nm NPs + Cd 0.5 mg kg^{-1} dry sand as $CdSO_4$

Table 1.

2.2. Plant growth

Maize (*Zea mays*) seeds (Hybrid Bicolor Synergistic Corn) were purchased from Johnny's Selected Seeds (Winslow, ME, USA). Seeds were treated with 10% bleach solution in distilled water for 5 min followed by a set of three rinses with distilled water to eliminate any bleach residues. Seeds were then left on the laboratory bench to dry. From sterilized seeds, five healthy seeds were sown in pots on July 17th and, after germination on the 19th, were thinned to two healthy seedlings and subsequently thinned to one on July 21st, 2021. On the same day as sowing, the first irrigation with 30 mL of 5% Hoagland solution in distilled water was done. The subsequent irrigations were made with 25 mL of 25% Hoagland solution in distilled water. Additionally, the final irrigation was done with 10 mL of 100% Hoagland solution. A total of 6 irrigations were made (from July 17th, 2021 to August 3rd, 2021). The greenhouse in which the experiment was conducted (located at University of Florida Institute of Food and Agricultural Sciences (UF/IFAS) Indian River Research and Education Center (IRREC), Fort Pierce, FL, USA) was not completely controlled, as there is a layer of permeable mesh and two fans to control the temperature of the system.

2.3. Growth and physiological data recording

2.3.1. Shoot growth and gas exchange measurements

Once seedlings had acquired height of around 20–25 cm (V3), their physiological parameters were recorded (on August 2nd, 2021) with a Li-6800 (Li-Cor, Lincoln, NE, USA). The recorded parameters were as follows: transpiration rate (TR), net assimilation rate (AR) and ambient to leaf CO_2 flux (ACO). On 3rd of August (16th day since germination) plants were harvested which were mostly on V3 stage (plant with three visible collared leaves). For harvesting, UCC pots were selected and separated, plants were taken out carefully and sand was washed off from the roots with distilled water twice in the greenhouse before being brought to the lab for data recording. The CC pots were the second set of harvesting, followed by each treatment separately (to avoid cross contamination). First, shoots were separated and washed with distilled water twice. Plant height (cm), diameter (cm) and fresh weight (g) were recorded using a ruler, a digital caliper (Neiko 6" Stainless Steel Digital Caliper, Neiko Tools USA, China) and a digital balance (Sartorius, Göttingen, Germany), respectively.

2.3.2. Root growth measurements

The roots of plants were carefully separated and scanned with EPSON Perfection V800 photo scanner and images were analyzed with WinRHIZO (Regent Instruments Inc, Quebec City, Quebec, Canada) software for root growth [number of tips, number of forks, number of crosses, root length per unit volume of sand (cm cm^{-3}), average root diameter (mm), total root length (cm), total root surface area (cm^2), total root projected area (cm^2) and total root volume (cm^3)] parameters. Root fresh weights were also recorded. After fresh weights were recorded, the three best growing tips from each root were cut and stored in 15 mL methanol and kept at 4 °C. The difference in weight, after the tips were removed, was recorded, and used for correction of root dry weight later. After these recordings, plant samples were dried at room temperature and then placed in paper bags and kept in an oven at 65 °C for five days until a constant weight was achieved.

2.4. Apoplastic barriers' visualization

The root tips (stored in methanol at 4 °C) were taken out and washed with distilled water twice. The protocol developed by Lux et al. (2005) was used to stain root tips in order to visualize apoplastic barriers. The tips were incubated in a fresh 0.01% w/v Fluorol yellow solution (prepared in lactic acid) at 70 °C for 30 min in the dark (covered with aluminum foil) followed by 3 consecutive 5 min baths with distilled water. For counter staining, 0.5% w/v solution of aniline blue was prepared in distilled water and roots were incubated in this solution for 30 min (dark-covered with aluminum foil) followed by 3 consecutive 10 min baths to remove any residues from the root surface. Sample tips were mounted on microscope glass slides and visualized under Leica DM 1000 LED (Wetzlar, Germany) fluorescence microscope equipped with UV filter. The images obtained were than analyzed through ImageJ (NIH, Bethesda MD) software. Digital caliper (Neiko 6" Stainless Steel Digital Caliper, Neiko Tools USA, China) and ImageJ software were used to quantify total length of suberin barrier formation from root tip.

2.5. Elemental analysis

A known masses (in grams) of plant tissues were placed into digestion tubes, mixed with 10 mL nitric acid (TraceMetal Grade, 67–70% HNO_3, Fisher Chemical), covered with small glass funnels (to assist in backflow of fumes) and kept overnight in a fume hood. On the following day, digestion tubes were set up on manual temperature-controlled Digestion System 40 (model Tecator Digestion System), and temperature was increased gradually to 75 °C for 1 h, followed by 95 °C for 3 h. The solution was then cooled down to room temperature and 2 mL 30% H_2O_2 solution was added, and temperature was increased gradually to 75 °C and retained until complete digestion of organic material and discoloration was achieved. The digestates were diluted to 50 mL, filtered with Whatman's 42 filter paper, and further diluted 10 times to obtain 2% acid concentration for elemental analysis. The elemental analysis was performed at the Chemistry and Biochemistry Department, Missouri State University using ICP-MS (Inductively coupled plasma-mass spectrometry) Agilent 7900 equipped with SP4 autosampler. The acquired concentration of all elements (ppm and ppb) was converted to mg kg^{-1} dry shoot mass by using following formula:

$$\text{Element Concentration in Tissue}\left(\text{mg kg}^{-1}\right) = \frac{(\text{ICP given concentration in ppb})}{\text{mass of tissue used for digestion (g)}} \times \frac{50\ (\text{final volume})}{1000\ (\text{conversion factor ppb to ppm})} \times 10\ (\text{Dilution to achieve 2\% acid level})$$

2.6. Statistical analysis

The experiment was conducted under 2-way factorial design (Ce source and Cd levels being the two factors). An ANOVA under 2-way factorial was used for statistical significance determination. Seven replicates were used for growth, physiology, and root barrier data while four were used for elemental analysis data sets. The Statistix software, version 10 (Tallahassee, FL, USA) was used for ANOVA and pairwise comparison using least significant differences (LSD) with level of significance of 5% ($p < 0.05$). The correlations heat map was made with R (https://www.r-project.org/).

3. Results

3.1. Sand and nanoparticles characterization

Twenty mL of distilled water was added to the growth media (*i.e.*, 1 g of sand) and the concentrations of the various elements indicated that the sand had the potential for releasing elements and nutrients in varying concentrations. The analyzed elements (reported here as means μg kg^{-1} dry sand or ppb ± SD) were found to be as follows: B (30.80 ± 4.38), Mn (18.14 ± 5.68), Ni (14.31 ± 7.45), Cu (70.05 ± 15.74), Zn (345.35 ± 77.01), Mo (3.07 ± 0.21), Fe (944.95 ± 436.23), Si (6929.87 ± 2228.68), Co (58.81 ± 49.33), Cd (1.03 ± 0.80) and Ce (6.54 ± 2.43). The electric conductivity (EC) and pH (mean ± SD) of the sand suspension (1:5 sand to distilled water) was 7.90 ± 0.80 μS cm^{-1} and 7.70 ± 0.26, respectively. The scanning electron microscope (SEM) images showed surface properties of sand crystals while EDX analysis showed elemental composition of sand samples (Fig. S1). For the CeO_2-10 nm NPs, SEM showed that the nanoparticles do exist in this range (although not exactly 10 nm because it is an average particle diameter) (Fig. S2). The EDX analysis of these NPs confirmed the presence of Ce, O, and Cl in the NPs. The SEM images of CeO_2-50 nm NPs confirmed the particles size to be in the range and the EDX analysis showed presence of Ce, O and Cl in NPs (Fig. S3). Similar results were obtained from CeO_2-100 nm NPs and this particle size was confirmed (Fig. S4).

3.2. Maize seedlings growth

Cadmium (0.5 mg kg^{-1}) had a nonsignificant impact on shoot fresh weight (SFW) although a net decrease of 18% (nonsignificant compared to UCC, $p > 0.05$) was seen. Application of Ce^{4+} (500 mg kg^{-1}) showed potential toxicity to maize seedlings resulting in a significant decrease of 62% in SFW in Cd-0 sets compared to control. In the same set, Ce sources CeO_2-10 nm NPs and CeO_2-50 nm NPs showed a nonsignificant decrease in shoot fresh weight of 24% and 9% compared to UCC, respectively. The Ce source CeO_2-100 nm NPs caused a net increase (significant) of 27% in SFW compared to control (UCC). For Cd-0.5 sets, again Ce^{4+} ($CeSO_4$) showed significant toxicity (with 51% decrease compared to UCC while 40% reduction compared with CC) which was not significantly different from effects observed in Cd-0 sets, while Ce application from sources CeO_2-50 nm NPs resulted in a significant increase of 45% (compared to Cd control or CC) while a non-significant increase of 19% compared to uncontaminated control (UCC). The CeO_2-100 nm NPs also showed net significant increase of 17% in SFW compared to CC.

The root fresh weight (RFW) was significantly affected by Cd with a 27% decrease compared to UCC. In Cd-0 sets, Ce^{4+} has again shown toxicity to roots resulting in a significant decrease of 53% in root fresh weight compared to UCC and Ce coming from $CeO_2$100 nm NPs showed a significant increase of 37%. For Cd-0.5 sets, again, ionic Ce resulted in significant 42% reduction in RFW compared to CC while 58% reduction

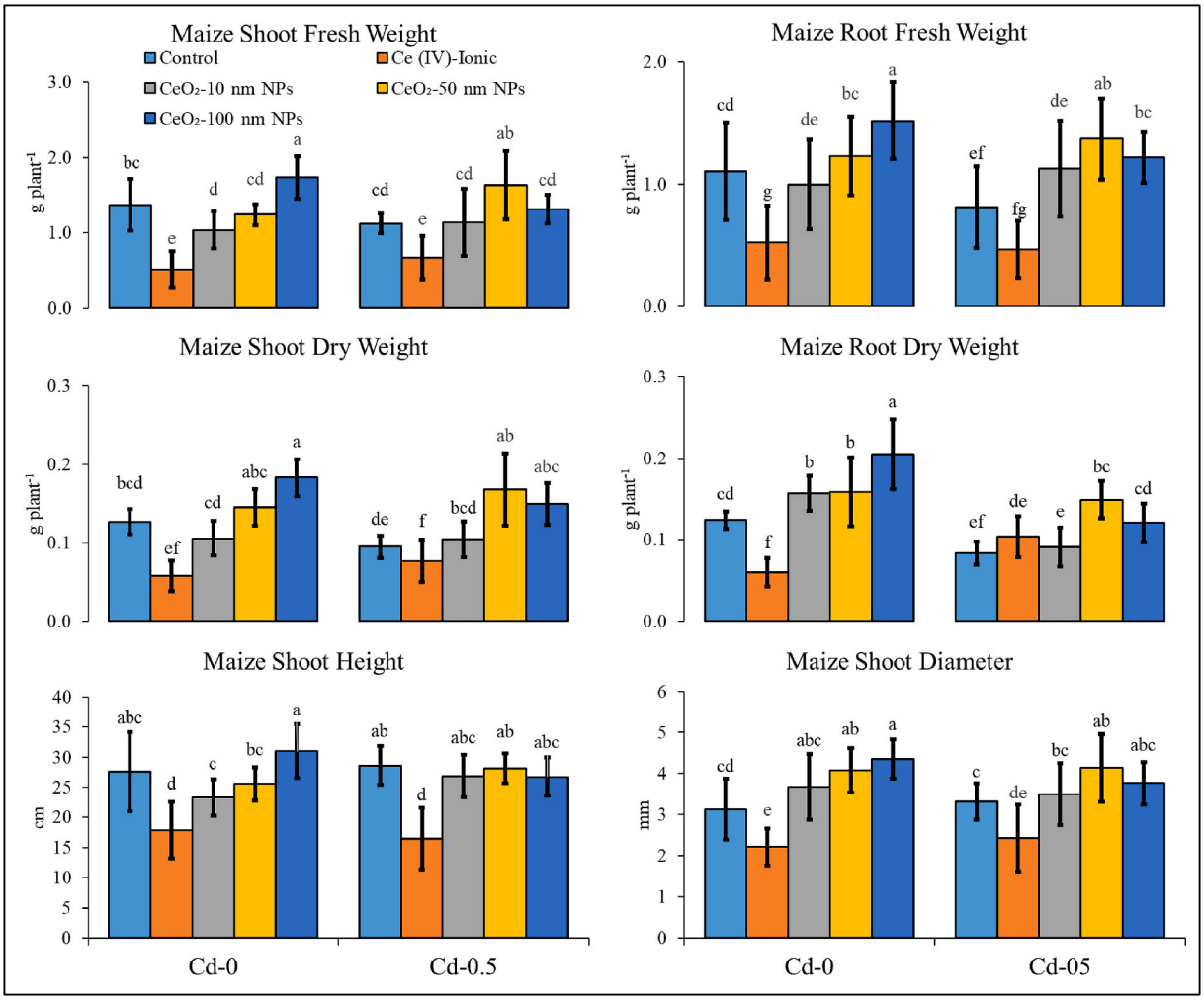

Fig. 1. Growth response of maize (*Zea mays*) under Cd 0 and Cd 0.5 mg kg^{-1} sand affected by cerium sources (ionic, nano-10 nm, 50 nm, and 100 nm) applied at 500 mg Ce kg^{-1} sand. A: Maize Shoot Fresh Weight (g $plant^{-1}$); B: Maize Root Fresh Weight (g $plant^{-1}$); C: Maize Shoot Dry Weight; D: Maize Root Dry Weight (g $plant^{-1}$); E: Maize Shoot Height (cm); F, Maize Shoot Diameter (mm). Mean labeled with different letters are significantly different by ANOVA following Least Significant Difference (LSD) pair wise comparison at 5% ($p < 0.05$) level of significance and error bars are of standard deviation−SD ($n = 7$).

was seen compared to UCC.

In Cd-0 sets, the shoot dry weight (SDW) was found to be highest for CeO_2-100 nm NPs with significant 45% increase compared to UCC while ionic Ce resulted in significant 54% decrease compared to UCC. For Cd-0.5 sets, CeO_2-50 nm NPs showed a significant increase of 77% compared to CC and a non-significant 33% increase compared to UCC, while ionic Ce resulted in a significant 19% decrease compared to CC while a significant 39% decrease compared to UCC.

The root dry weight (RDW) also decreased with Cd stress (a significant of 33% observed in CC compared to UCC). In Cd-0 sets, the ionic Ce again was significantly toxic for plant root where a net decrease of 52% was recorded. The CeO_2-10, 50 and 100 nm NPs sources showed a significant increase of 26%, 28% and 65%, respectively in RDW compared to UCC. For Cd-0.5 sets Ce^{4+} showed a significant decrease of 16% compared to UCC but a non-significant increase of 24% was seen compared to CC. The co-application of Cd with CeO_2-10, 50 and 100 nm has resulted in net increase of 9% (non-significant), 78% (significant) and 45% (significant), respectively (Fig. 1).

The plant height (PH) was affected by Ce sources in both Cd-0 and Cd-0.5 sets with ionic Ce significantly decreasing plant height 35% in Cd-0 sets compared to UCC while significant 42% and 40% decreases was observed in Cd-0.5 sets compared to CC and UCC, respectively. The plant diameter (PD) was lowest in ionic Ce sources both in Cd-0 as well as Cd-0.5 sets with a significant 29% decrease in Cd-0 sets compared to UCC while significant 27% and 22% decrease compared to CC and UCC, respectively.

3.3. Maize seedling gas exchange measurements

Ionic Ce decreased transpiration rate (TR) and assimilation rate (AR) of maize seedlings significantly in Cd-0 sets as well as in co-existence with Cd-0.5. Highest TR was seen in both controls (CC and UCC) and no significant effect of 0.5 ppm Cd was observed. For TR, NPs application showed no significant effect both in Cd-0 or 0.5 sets. Ionic Ce showed a significant decrease of 40% compared to UCC in Cd-0 sets, while in Cd-0.5 sets a net significant decrease of 55 and 65% was observed compared to UCC and CC, respectively. For AR, Ce^{4+} showed toxic effect with a significant decrease of 54% in Cd-0 sets, while for Cd-0.5 sets a significant decrease of 73% and 79% was observed compared to UCC and CC, respectively. No significant differences were observed for ACO results (Fig. 2).

3.4. Root length, diameter and volume

Total root length (TRL) was highest for CeO_2-100 nm NPs applied sets compared to UCC (control in Cd-0 sets) and a significant decrease of 83% was observed in Ce^{4+} applied pots indicating the toxicity of ionic Ce applied at 500 ppm. For Cd-0.5 CeO_2-100 nm NPs sets showed a non-significant increase of 38%, and for CeO_2-50 nm NPs a significant 56% increase was observed compared to CC. For average root diameter (ARD), plant treated with Ce^{4+} showed more primary roots both in Cd-0 and Cd-0.5 sets. For total root surface (TSA) and projected areas (TPA), Ce^{4+} showed toxicity with a significant decrease of 75% and 53% compared to UCC. In Ce^{4+}-Cd sets, a significant decrease of 71% and 63% was observed compared to UCC while a significant 64% and 56% decrease was observed compared to CC in TSA and TPA respectively (Fig. 3). For root length per unit volume (RLPUV) ionic Ce showed a significant decrease of 83 and 79% in Cd-0 and Cd-0.5 sets compared to UCC, and a significant decrease of 70% compared to CC. The number of root tips were significantly lowest with Ce^{4+} in both Cd-0 and Cd-0.5 sets with a 73% decrease in Cd-0 set (compared to UCC) and 76% and 69% decrease for Cd-0.5 sets compared to UCC and CC, respectively. The CeO_2-NPs (10, 50 and 100 nm) helped significantly increase the number of maize root tips with 47, 58 and 68% increase in Cd-0 sets compared to UCC, respectively. Number of forks also showed Ce toxicity with a significant 79% decrease in Cd-0 sets compared to UCC, and for Cd-0.5 sets,

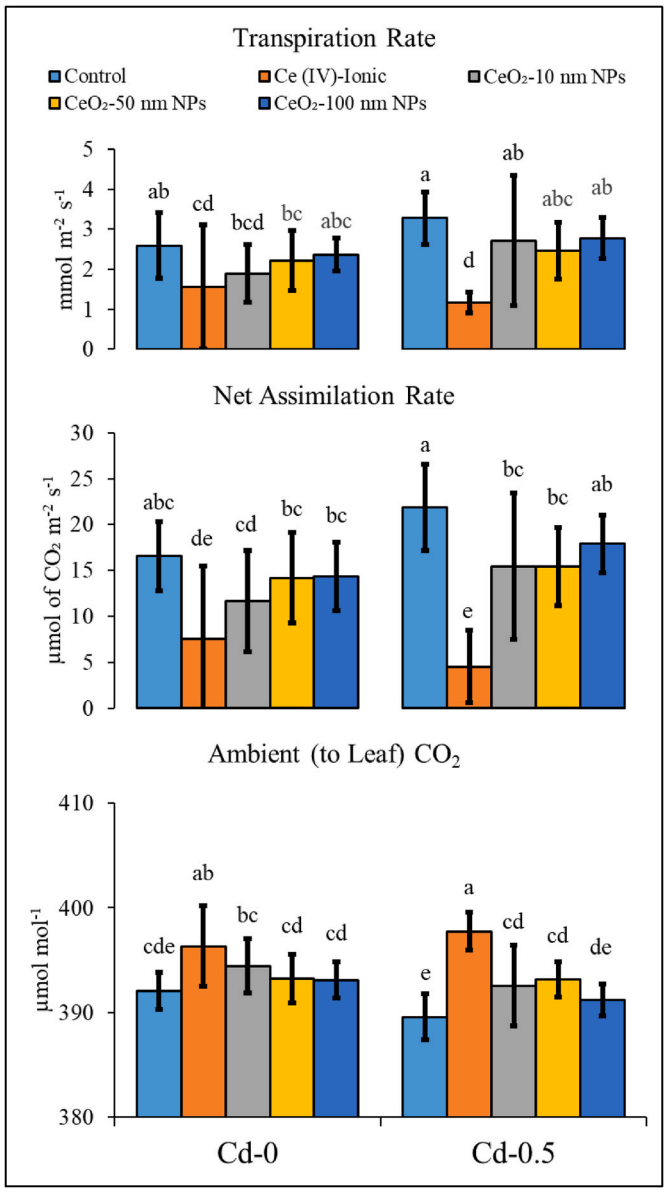

Fig. 2. Physiological response of Maize (*Zea mays*) under Cd 0 and Cd 0.5 mg kg-1 sand affected by cerium sources (ionic, nano-10 nm, 50 nm, and 100 nm) applied at 500 mg Ce kg-1 sand. A: Transpiration Rate (mmol m^{-2} s^{-1}); B: Net Assimilation Rate (µmol m^{-2} s^{-1}); and C: Ambient (to leaf) CO^2 (µmol mol^{-1}). Mean labeled with different letters are significantly different by ANOVA following Least Significant Difference (LSD) pair wise comparison at 5% ($p < 0.05$) level of significance and error bars are of standard deviation−SD ($n = 7$).

a significant decrease of 68% and 74% compared to CC and UCC, respectively was observed. The CeO_2-50 nm and 100 nm NPs have shown an increase of 25% and 46% in Cd-0 sets compared to UCC, respectively. For root crosses, a significant decrease of 86% was observed in ionic Ce and Cd-0 set compared to UCC, while for Cd-0.5 sets, a significant decrease of 79% and 73% was observed compared to UCC and CC, respectively.

3.5. Apoplastic barriers visualization

Fig. 4A represents a cross-section of root visualizing a complete development of suberin barriers, while Fig. 4B represent forming suberin barriers. The root barrier (RB) length measured from the root tip was highest for UCC, and Cd introduction resulted in a decrease of RB length. In Cd-0 sets where ionic Ce was applied, the root barriers started

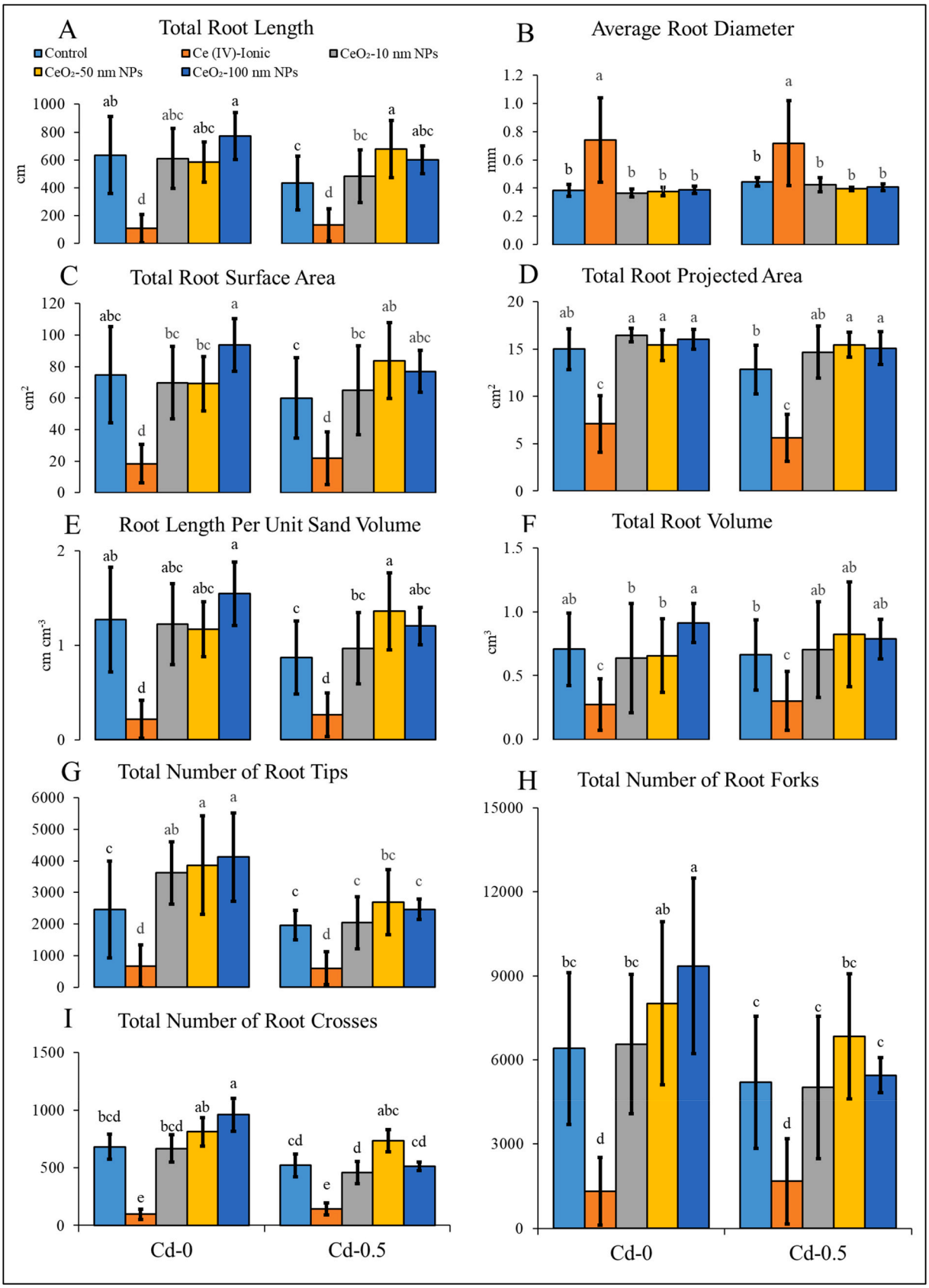

Fig. 3. Root Growth parameters of Maize (*Zea mays*) under Cd 0 and Cd 0.5 mg kg^{-1} sand affected by cerium sources (ionic, nano-10 nm, 50 nm, and 100 nm) applied at 500 mg Ce kg^{-1} sand. A: Total Root Length (cm); B: Average Root Diameter (mm); C: Total Root Surface Area (cm^2); D: Total Root Projected Area (cm^2); E: Root Length Per Unit Volume (m cm^{-3}); F: Total Root Volume (cm^3); G: Total Number of Root Tips; H: Total Number of Root Forks; I: Total Number of Root Crosses. Mean labeled with different letters are significantly different by ANOVA following Least Significant Difference (LSD) pair wise comparison at 5% ($p < 0.05$) level of significance and error bars are of standard deviation−SD ($n = 7$).

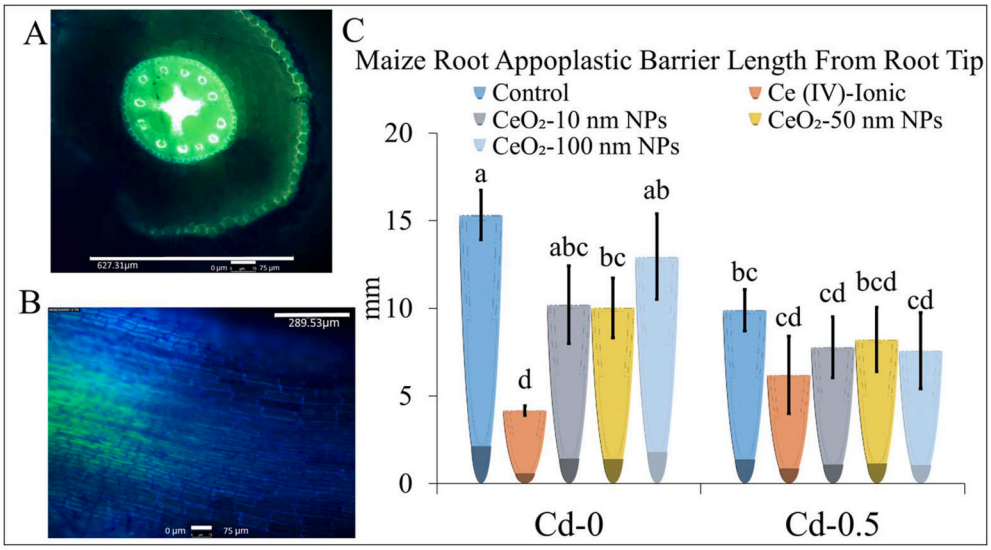

Fig. 4. Root Suberin Lamellae length under Cd 0 and Cd 0.5 mg kg^{-1} sand affected by cerium sources (ionic, nano-10 nm, 50 nm, and 100 nm) applied at 500 mg Ce kg^{-1} sand. A: Cross section of root with full barrier formation; B: Full Root Tip Lateral view (green color representing stained suberin barriers); C: root barrier distance from tip as the Mean labeled with different letters are significantly different by ANOVA following Least Significant Difference (LSD) pair wise comparison at 5% ($p < 0.05$) level of significance and error bars are of standard deviation−SD ($n = 7$). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

to form earlier confirming the toxicity of Ce. The CeO_2 (10 nm, 50 nm, and 100 nm) NPs application in Cd-0 sets resulted in variable effects with only CeO_2-50 nm NPs causing a significant decrease compared to UCC. For Cd-0.5 sets, all sources of Ce were not significantly differing in their effect on RB length from tip (Fig. 4C).

4. Elemental analysis

4.1. Cadmium and cerium contents

The Ce contents were significantly ($p < 0.05$) affected by Ce sources. In Cd-0 sets highest shoot Ce contents of 37.47 ± 15.74 mg kg^{-1} dry mass (mean ± SD) were observed, where ionic Ce was applied. This trend was different for Cd-0.5 sets where highest Ce contents of 32.18 ± 17.64 mg kg^{-1} dry shoot mass were observed for CeO_2-100 nm NPs. For root Ce, in Cd-0 sets highest contents (significantly higher from other doses) were found where Ce^{4+} was applied while for nanoparticles the root Ce contents were not found to be varying significantly.

In Cd spiked sets, Ce^{4+} application resulted in an increase (compared to CC) in Cd accumulation and the highest Cd accumulation of 25.13 ± 2.87 mg Cd kg^{-1} dry mass was observed. The CeO_2-10 nm NPs, 50 nm NPs, and CeO_2-100 nm NPs resulted in decrease of Cd shoot accumulation with total contents of 3.71 ± 3.05, 5.22 ± 3.97, and 3.79 ± 1.86 mg Cd kg^{-1} dry mass, respectively. For maize roots, combined application of ionic Ce and Cd resulted in higher Cd accumulation than CC with a total 107.76 ± 37.50 mg Cd kg^{-1} dry root mass while the nanoparticles application showed no significant effect on root Cd contents with respect to CC (Fig. 5).

4.2. Micronutrients and beneficial elements

The micronutrients B, Mn, Ni, Cu, Zn, Mo, Fe, and beneficial element (Si and Co) content was measured in plant tissue and relative effects of cerium source alone and in combination of Cd were observed ($p < 0.05$). The ionic Ce resulted in highest shoot Si uptake in Cd-0 set along with CeO_2-10 nm NPs in Cd-0 and lowest amounts were observed for CeO_2-50 and 100 nm NPs sets (both in Cd-0 and Cd-0.5). The root Si was highest for CeO_2-10 nm NPs with Cd-0.5, while lowest contents were observed in CeO_2-50 nm NPs applied in Cd-0 sets. For Co, lowest shoot contents were observed in CeO_2-100 nm NPs in Cd-0 sets, and in roots, NPs resulted in higher root Co contents for Cd-0.5 sets while in Cd-0 net decrease was evident (Fig. 5).

Ionic Ce application without Cd resulted in highest shoot and root B contents while in co-existence with Ce (all sources) and Cd showed no significant difference among Ce. For Mn, highest shoot and root contents were observed in ionic Ce sets while for Ce and Cd sets, the shoot Mn contents were highest in CC and in ionic Ce applied sets, while no significant difference was observed for root Mn concentrations. In Cd-0 sets ionic Ce resulted in higher Ni accumulation in maize shoot and root. The shoot and root Cu contents were higher for Cd-0.5 sets compared to Cd-0 sets. In Cd-0 sets, ionic Ce, CeO_2-10 and 50 nm NPs resulted in higher shoot Cu concentration than UCC, while for CeO_2-100 nm NPs supplemented sets no significant difference was observed. For maize roots, ionic Ce resulted in highest root Cu concentration in Cd-0 sets. Like Cu, Zn contents were also found to be increasing (in CC compared to UCC) with Cd application. The ionic Ce resulted in highest uptake of Zn in Cd-0 sets while CeO_2-100 nm NPs supplemented sets resulted in the lowest uptake. The highest Mo shoot contents were found in Cd-0.5 CC while the lowest was found in Cd-0.5 pots spiked with ionic cerium. Similarly, root Mo contents were highest in controls (CC and UCC) and CeO_2-100 nm NPs spiked Cd-0 sets, while low contents were found in ionic cerium with Cd-0.5 sets. The highest shoot Fe contents were observed in ionic Ce with Cd-0 and Cd-0.5 CC set while low content was observed in CeO_2-100 nm NPs spiked control set (Cd-0). For root Fe, highest contents were observed in plants grown in controls and in CeO_2-10nm NPs and Cd pots while lowest Fe contents were observed in CeO_2-50nm NPs control (Cd-0) pots (Table 2).

5. Discussion

Maize seedling growth, biomass and physiology was found to be affected by Cd. Cadmium toxicity in maize is reported to interrupt basic growth, physiology, and cellular biochemical attributes due to initiation of oxidative stress (Pál et al., 2006; Rizwan et al., 2017). The role of Ce under Cd stress in plants is divergent depending upon source of Ce, application methods, and doses. In this study, Ce^{4+} was applied and reported to be toxic for maize seedling growth and biomass at 500 mg kg^{-1} (Fig. 1) which could be due to its role in increasing uptake of micronutrients (Table 2) and Cd (Fig. 5). In control (Cd-0) sets, the ionic Ce was showing toxicity to maize seedling growth parameters which could be due to toxic excessive uptake of micronutrients. For maize shoot the permissible limits of all micronutrients are given in Table 3. The ionic Ce supplemented Cd-0 sets has shown accumulation of excessive concentrations of Cu, Zn and Fe in maize shoot depicting possible toxicity and probable cause of stunted growth. While for Cd-0.5 sets, Cu, Zn, and Cd toxic accumulation (above 0.02 mg kg^{-1}) was prevalent which further enhanced the toxicity of Ce. The prevalent high metal accumulations in maize seedling root also affected root growth,

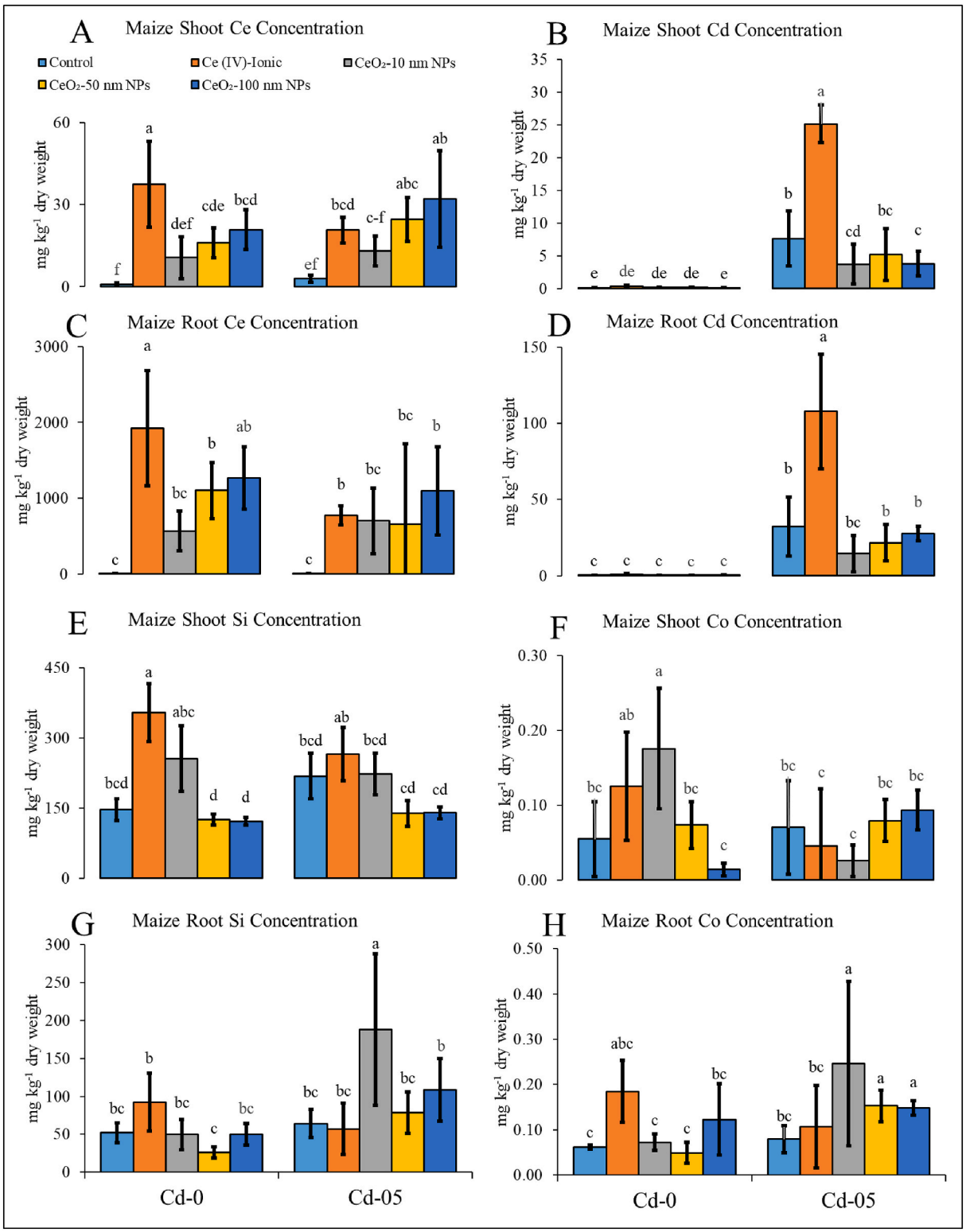

Fig. 5. Cadmium (Cd), Cerium (Ce), Silicon (Si) and Cobalt (Co) contents of maize under Cd 0 and Cd 0.5 mg kg^{-1} sand affected by cerium sources (ionic, nano-10 nm, 50 nm, and 100 nm) applied at 500 mg Ce kg^{-1} sand. A: Maize Shoot Ce Concentration (mg kg^{-1}); B: Maize Shoot Cd Concentration (mg kg^{-1}); C: Maize Root Ce Concentration (mg kg^{-1}); D) Maize Root Cd Concentration (mg kg^{-1}); E: Maize Shoot Si Concentration (mg kg^{-1}); F: Maize Shoot Co Concentration (mg kg^{-1}); G: Maize Root Si Concentration (mg kg^{-1}); H Maize Root Co Concentration (mg kg^{-1} Mean labeled with different letters are significantly different by ANOVA following Least Significant Difference (LSD) pair wise comparison at 5% ($p < 0.05$) level of significance and error bars are of standard deviation−SD ($n = 4$).

Table 2
Effect of various cerium sources on elemental contents of maize (*Zea mays*) under Cd 0 and Cd 0.5 mg kg^{-1} sand affected by cerium sources (ionic, nano-10 nm, 50 nm, and 100 nm) applied at 500 mg Ce kg^{-1} sand. A 2-way ANOVA was used with letters representing significantly different sets by LSD value ($p < 0.05$) with $n = 4$.

Cerium (500 mg kg^{-1} dry sand)	Cadmium (mg kg^{-1})		Mean	Cadmium (mg kg^{-1})		Mean	Cadmium (mg kg^{-1})		Mean	Cadmium (mg kg^{-1})		Mean	Cadmium (mg kg^{-1})		Mean
	0	0.5		0	0.5		0	0.5		0	0.5		0	0.5	
	Shoot B (mg kg^{-1})			Shoot Mn (mg kg^{-1})			Shoot Ni (mg kg^{-1})			Shoot Cu (mg kg^{-1})			Shoot Zn (mg kg^{-1})		
Control	13.07 ab	12.12 ab	12.59AB	5.23c	6.17bc	5.70B	0.52c	0.71bc	0.62 B	14.30c	27.45 ab	20.87AB	61.84d	125.88bc	93.86B
Ce-Ionic	15.80a	9.87b	12.84A	14.21a	10.16 ab	12.18A	1.55a	1.25 ab	1.40A	28.25 ab	29.21a	28.73A	181.04a	149.57 ab	165.31A
CeO_2-10nm-NPs	9.06b	9.41b	9.23BC	3.64c	5.74c	4.69B	0.54c	1.06abc	0.80 B	18.45abc	21.85abc	20.15AB	109.64bcd	154.14 ab	131.89A
CeO_2-50nm-NPs	8.24b	10.81b	9.52ABC	3.39c	5.73c	4.56B	0.45c	0.64bc	0.54 B	15.95bc	14.91c	15.43B	82.75cd	99.58cd	91.17B
CeO_2-100nm-NPs	9.14b	9.03b	9.08C	4.78c	4.27c	4.53B	0.82bc	0.50c	0.66B	9.83c	16.62bc	13.23B	67.45d	88.37cd	77.91B
Mean	11.06A	10.25A		6.25A	6.41A		0.78A	0.83 A		17.36A	22.01A		100.54A	123.51B	
	ANOVA (p) Cd (0.4484); Ce (0.0603); Cd × Ce (0.1643)			***ANOVA (p)*** Cd (0.8593); Ce (0); Cd × Ce (0.1948)			***ANOVA (p)*** Cd (0.7105); Ce (0.0041); Cd × Ce (0.2866)			***ANOVA (p)*** Cd (0.0969); Ce (0.0152); Cd × Ce (0.4998)			***ANOVA (p)*** Cd (0.03793); Ce (0.0001); Cd × Ce (0.0812)		
	Root B (mg kg^{-1})		Mean	**Root Mn** (mg kg^{-1})		Mean	**Root Ni** (mg kg^{-1})		Mean	**Root Cu** (mg kg^{-1})		Mean	**Root Zn** (mg kg^{-1})		Mean
Control	8.50bcd	9.10abc	8.80A	3.24b	2.66b	2.95B	1.18bc	1.32bc	1.25AB	20.49bc	27.44 ab	23.96A	39.96d	141.13abc	90.55B
Ce-Ionic	13.58a	4.32d	8.95A	7.19a	2.34b	4.77A	2.28a	0.89bc	1.59A	35.87a	15.15bc	25.51A	230.37a	98.33bcd	164.35A
CeO_2-10nm-NPs	9.90abc	12.85 ab	11.38A	2.66b	2.96b	2.81B	1.57 ab	1.35bc	1.46AB	13.23c	24.88abc	19.06AB	80.37bcd	172.45 ab	126.41AB
CeO_2-50nm-NPs	7.37cd	11.39abc	9.38A	1.89b	3.33b	2.61B	0.74c	1.17bc	0.95B	12.00c	15.11bc	13.56B	63.24cd	92.40bcd	77.82B
CeO_2-100nm-NPs	9.60abc	13.35a	11.48A	2.36b	2.89b	2.63B	0.91bc	1.12bc	1.02AB	17.03bc	17.67bc	17.35AB	133.20bc	123.84bcd	128.52AB
Mean	9.79 A	10.20A		3.47A	2.84A		1.34 A	1.17A		19.72 A	20.05 A		109.43A	125.63A	
	ANOVA (p) Cd (0.6888); Ce (0.2832); Cd × Ce (0.0011)			***ANOVA (p)*** Cd (0.1139); Ce (0.0055); Cd × Ce (0.0001)			***ANOVA (p)*** Cd (0.3541); Ce (0.1291); Cd × Ce (0.0198)			***ANOVA (p)*** Cd (0.916); Ce (0.1097); Cd × Ce (0.0208)			***ANOVA (p)*** Cd (0.4321); Ce (0.085); Cd × Ce (0.007)		
	Shoot Mo (mg kg^{-1})		Mean	**Root Mo** (mg kg^{-1})		Mean	**Shoot Fe** (mg kg^{-1})		Mean	**Root Fe** (mg kg^{-1})		Mean			
Control	1.48 ab	1.82a	1.65A	0.97a	0.90 ab	0.93A	146.76bc	245.69a	196.23A	137.25a-d	134.44a-d	135.84A			
Ce-Ionic	0.86cd	0.51d	0.68B	0.42de	0.18e	0.30B	253.98a	148.07bc	201.03A	165.03 ab	141.15a-d	153.09A			
CeO_2-10nm-NPs	0.75cd	1.05bcd	0.90B	0.56bcd	0.81abc	0.68A	179.12b	154.94bc	167.03AB	99.46cd	186.40a	142.93A			
CeO_2-50nm-NPs	0.91bcd	1.26abc	1.08B	0.45cde	1.02a	0.74A	140.99bc	129.07bc	135.03BC	92.33d	140.03a-d	116.18A			
CeO_2-100nm-NPs	0.74cd	1.16bc	0.95B	0.64abcd	0.87 ab	0.75A	121.89c	138.99bc	130.44C	117.08bcd	156.89abc	136.99A			
Mean	0.95A	1.16A		0.61A	0.76A		168.55A	163.35A		122.23B	151.78A				
LSD critical value of comparison	***ANOVA (p)*** Cd (0.111); Ce (0.0009); Cd × Ce (0.3291)			***ANOVA (p)*** Cd (0.0899); Ce (0.0008); Cd × Ce (0.0366)			***ANOVA (p)*** Cd (0.6444); Ce (0.0004); Cd × Ce (0.0001)			***ANOVA (p)*** Cd (0.0329); Ce (0.4961); Cd × Ce (0.0867)					

Table 3
Plant micronutrient analysis permissible levels in maize shoot: elemental concentrations per unit mass of maize shoot (mg kg^{-1}).

Micronutrient Name	Low	Sufficient	High	Maximum Permissible Limit
B[a]	<5	5–25	>25	
Mn[a]	<20	20–300	>300	
Ni[b]				67.9[b]
Cu[a]	<5	5–20	>20	73.3[b]
Zn[a]	<20	20–60	>60	99.4[b]
Mo[a]	<0.1	0.1–10	>10	
Fe[a]	<50	50–250	>250	425.5[b]

[a] Shoot concentration limits as described in Rashid, A. and Memon, K.S., 1996. Soil science. National Book Foundation.

[b] Ni permissible limit as per World Health Organization (WHO), 1989. Report of 33rd meeting, Joint FAO/WHO Joint Expert Committee on Food Additives, Toxicological evaluation of certain food additives and contaminants No. 24, International Program on Chemical Safety, WHO, Geneva.

with lowest growth, biomass, length, area, and volume (Fig. 3). The ionic Ce also resulted in lower TR and AR showing a stress physiological response. The work of Zhang et al. (2015) showed that application of ionic cerium (Ce^{3+}) sourced from $CeCl_3$ at 10 mg $CeCl_3$ L^{-1} showed a negative effect on radish (*Raphanus sativus*) while bulk CeO_2 enhanced radish growth and CeO_2-NPs showed no significant effects on radish growth parameters. In our investigation, the toxicity of ionic Ce (Ce^{4+} at 500 mg Ce per kg sand) was observed while nanoparticles affected maize differently. Related results were reported by Skiba and Wolf (2019) in which ionic Ce (Ce III from cerium nitrate at 200 mg L^{-1}) showed toxicity compared to control set of pea (*Pisum sativum*).

The other sources of Ce used in our investigation were CeO_2-10 nm, CeO_2-50 nm, and CeO_2-100 nm NPs. CeO_2-100 nm NPs were beneficial for plant growth and biomass in Cd-0 sets, while in combination with Cd, CeO_2-50 nm NPs had more prominent beneficial effects. This divergent effect of NPs can be attributed to variable surface chemistry as the lattice chemistry of cerium NPs controls presence of free oxygen radical (ROS) on its surface (Deshpande et al., 2005) and with a decrease in particles size the oxygen density increases, affecting oxidation of Ce (conversion of Ce^{3+} to Ce^{4+}). This result primarily occurs via oxidation of Ce^{3+} to Ce^{4+} and due to higher Ce^{3+} size compared to Ce^{4+}, this conversion causes strain on NPs surface and enhances their reactivity, therefore particle size of NPs must be considered while studying their environmental toxicities. The shoot and root biomass parameters (fresh and dry weights) of maize seedlings were affected by NPs in Cd-0 as well as Cd-0.5 sets. The growth promotional response of CeO_2-NPs is reported in studies with different effects observed depending upon application dose and crop under investigation. Gui et al. (2015) concluded that 100 mg kg^{-1} CeO_2 NPs applied to lettuce (*Lactuca sativa*) resulted in higher growth compared to the control, while higher concentrations of CeO_2 resulted in toxicity to plants. The toxicity of higher concentrations of NPs were found to be associated with disruption in antioxidant metabolism of plants. At lower concentrations, the growth promotional activity can be correlated with the potential role of CeO_2-NPs in physiological attribute enhancement. The work done by Mohammadi et al. (2021) showed that lower concentrations of CeO_2-NPs (50 mg L^{-1}) showed enhanced growth, physiological and biochemical parameters (antioxidants), thus reverting the adverse effects of salinity on Moldovan balm (*Dracocephalum moldavica*). In another investigation by Cao et al., 2017), the CeO_2-NPs (coated and uncoated) applied at 100 mg kg^{-1} resulted in net enhancement of soybean (*Glycine max*) growth via increase in photosynthesis rate and Rubisco activity for both types of NPs, but higher concentrations (500 mg kg^{-1}) of NPs resulted in decreases in plant growth parameters and inhibited Rubisco activity. Similar findings were observed in our previous work on C_4 plant maize (Fox et al., 2020) where NPs application resulted in higher biomass.

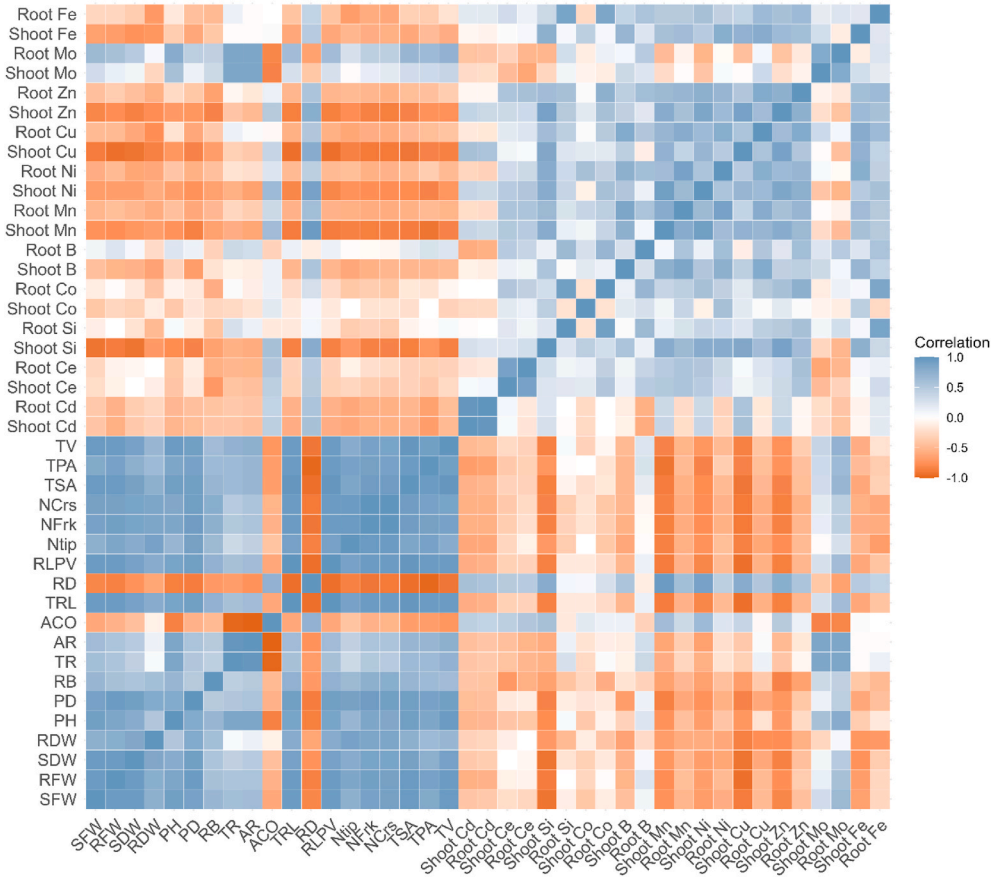

Fig. 6. Correlation tree map among acquired parameters of maize seedling (n = 10): shoot fresh weight (SFW), root fresh weight (RFW), shoot dry weight (SDW), root dry weight (RDW), plant height (PH), plant diameter (PD), root barrier length (RB), transpiration rate (TR), assimilation rate (AR), ambient to leaf CO2 (ACO), total root length (TRL), average root diameter (RD), root length per unit volume (RLPV), number of root tips (Ntip), number of root forks (Nfrk), number of root crosses (Ncrs), total root surface area (TSA), total root projected area (TPA), total root volume (TV), shoot and root elemental contents (Cd, Ce, Si, Co, B, Mn, Ni, Cu, Zn, Mo, and Fe).

The effect of CeO_2-NPs on plant biomass also depends upon exposure conditions and plant species explaining why contrasting effects of various doses of CeO_2-NPs can be seen in literature (Drzewiecka-Matuszek et al., 2005; Wang et al., 2012; Zhao et al., 2014; Skiba et al., 2021). The observed variability in effects of 10 nm, 50 nm and 100 nm particle sized CeO_2-NPs in this study is an extension to the existing knowledge of NPs being overall beneficial under Cd-0 sets. The effect of Cd toxicity on plant growth, development and nutritional attributes is also a well-studied phenomenon and in our previous work (Fox et al., 2020), where PVP coated CeO_2-NPs applied in combination with Cd (0.5 ppm) resulted in lower plant biomass. This can be due to enhanced antioxidant activity by Cd (Anjum et al., 2015) and higher concentration mediated toxicity of CeO_2-NPs (Mohammadi et al., 2021) which is amplified with co-existence. The variable effects of Ce NPs size on plant growth under Cd stress is not very well understood and our investigation showed that 50 nm CeO_2-NPs were more beneficial compared to 100 nm under Cd-0.5 sets. The variability in effects of NPs on maize growth parameters can be attributed to their variable Ce^{3+}:Ce^{4+} surface presence, Cd adsorption capacity and mobility in plant making only the 50 nm NPs beneficial. For ionic Ce, the combined Ce–Cd treatment was significantly detrimental for plant growth and only plant diameter increased compared to ionic Ce and Cd-0 set. The applied Ce^{4+} as $CeSO_4$ showed toxicity to maize growth and biomass parameters. The effect of Ce sources and Cd alone and in combination was also observed in our investigation and Cd applied at 0.5 mg kg^{-1} increased seedling TR and AR which can be justified by the plant response to Cd stress, and it is reported that Cd is toxic for maize (Ling et al., 2017). The ionic Ce toxicity was also visible in TR and AR.

The Cd toxicity resulted in early formation of root barriers (resulting in lower average length from root tip) compared to control. For Cd-0 sets, the ionic Ce resulted in early formation of root barriers followed by 10, 50 and 100 nm NPs. For Cd-0.5 sets, nonsignificant effect of application of Ce (from any source, ionic or nano) was observed. In our previous work (Fox et al., 2020) PVP coated CeO_2-NPs applied at 500 mg kg^{-1} applied under 0.5 ppm Cd stress resulted in lowering of root barrier length which can be explained due to the variable nature of NPs. The correlation analysis among all parameters shows that heavy metal elements negatively correlate with root barrier formation (Fig. 6).

The Ce sources significantly affected the accumulation and distribution of Ce, Cd, and other elements in maize tissue. For maize root Ce, the ionic Ce resulted in highest content in Cd-0 sets, and CeO_2-10 nm NPs resulted in the lowest accumulation. The variability in Ce contents of maize in exposure to various Ce sources might be due to their variable translocation in plant as ionic Ce is more mobile compared to nano Ce (Zhang et al., 2015; Barrios et al., 2016; Skiba and Wolf, 2019). For Cd, the ionic Ce resulted in a net increase of shoot and root Cd contents due to interference of Ce with heavy metal uptake by plant roots and shoots (Skiba and Wolf, 2019) as reported in maize via development of root barriers (Fox et al., 2020; Liu et al., 2021a, 2021b). The elemental distribution in plants was varied with application of Ce and micronutrients (B, Mn, Ni, Cu, Zn, Mo, Fe, Si and Co) that might be due to the role of Ce NPs in root barrier formation under abiotic stress (Rossi et al., 2017; Fox et al., 2020; Liu et al., 2021a) or via affecting plant growth and nutritional chemistry as observed in wheat (Rico et al., 2014). Once plant roots encounter any pollutant, they tend to limit uptake through the formation of root apoplastic barriers, which can counteract heavy metal accumulation. Under Cd-0 sets, ionic Ce was acting as a pollutant at the applied concentration which resulted in early formation of root barriers.

6. Conclusion

The Ce–Cd interaction in maize seedling is still an ongoing topic of investigation. In the present study, Ce applied at 500 mg kg^{-1} dry sand has shown variable effects alone and in combination with Cd. The effect of Ce on maize seedling growth, physiology, root anatomy and plant elemental composition were different, suggesting an active role of Ce source as well as particles size of CeO_2-NPs in plant responses. At the applied concentration (500 ppm Ce) the ionic Ce was overall toxic for maize seedling, while CeO_2-100 nm NPs in Cd-0 sets and CeO_2-50 nm NPs in Cd-0.5 sets showed positive effects on maize seedling growth attributes. The contrasting obtained results suggested that further research is needed to better understand this topic.

Author contributions

Muhammad Ashar Ayub: Conceptualization, Methodology, Formal data, Formal analysis, Investigation, Funding acquisition, Writing original draft, Data Visualization. Muhammad Zia ur Rehman: Conceptualization and project administration. Hamaad Raza Ahmad: Conceptualization and project administration. John-Paul Fox: Methodology, Writing – review & editing. Preston Clubb: Methodology Alan L. Wright: Methodology, Investigation, Resources, Writing – review & editing. Muhammad Anwar ul Haq: Conceptualization, Supervision, Project administration, Writing – review & editing. Muhammad Nadeem: Writing – original draft. Cyren M. Rico: Methodology, Investigation, Resources, Writing – review & editing. Lorenzo Rossi: Conceptualization, Supervision, Methodology, Resources, Writing – review & editing, Project administration.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Lorenzo Rossi reports financial support was provided by National Institute of Food and Agriculture. Muhammad Ashar Ayub reports financial support was provided by Higher Education Commission Pakistan. Cyren Rico reports financial support was provided by National Science Foundation.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2023.121137.

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