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Soil organic matter influences cerium translocation and physiological processes in kidney bean plants exposed to cerium oxide nanoparticles

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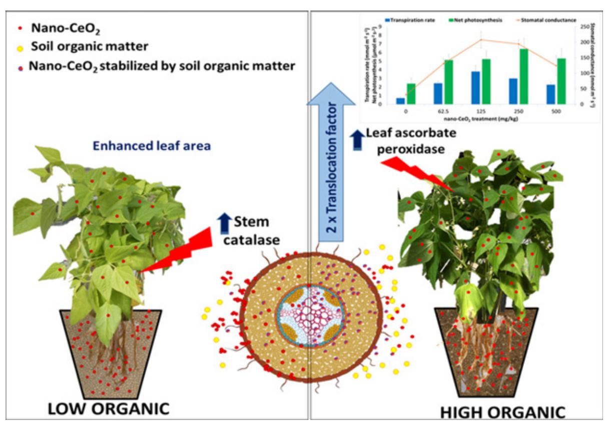
HIGHLIGHTS

- Ce translocation to leaves was facilitated by higher organic matter (OM) in soil.
- Lower soil OM increased leaf cover area in nano-CeO_2 exposed plants.
- Nano-CeO_2 effects on metabolic processes were more notorious in OM enriched soil.
- Nano-CeO_2 increased antioxidant enzyme activities in the aerial tissues.

GRAPHICAL ABSTRACT



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ABSTRACT

Soil organic matter plays a major role in determining the fate of the engineered nanomaterials (ENMs) in the soil matrix and effects on the residing plants. In this study, kidney bean plants were grown in soils varying in organic matter content and amended with 0–500 mg/kg cerium oxide nanoparticles (nano-CeO_2) under greenhouse condition. After 52 days of exposure, cerium accumulation in tissues, plant growth and physiological parameters including photosynthetic pigments (chlorophylls and carotenoids), net photosynthesis rate, transpiration rate, and stomatal conductance were recorded. Additionally, catalase and ascorbate peroxidase activities were measured to evaluate oxidative stress in the tissues. The translocation factor of cerium in the nano-CeO_2 exposed plants grown in organic matter enriched soil (OMES) was twice as the plants grown in low organic matter soil (LOMS). Although the leaf cover area increased by 65–111% with increasing nano-CeO_2 concentration in LOMS, the effect on the physiological processes were inconsequential. In OMES leaves, exposure to 62.5–250 mg/kg nano-CeO_2 led to an enhancement in the transpiration rate and stomatal conductance, but to a simultaneous decrease in carotenoid contents by 25–28%. Chlorophyll *a* in the OMES leaves also decreased by 27 and 18% on exposure to 125 and 250 mg/kg nano-CeO_2. In addition, catalase activity increased in LOMS stems, and ascorbate

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Photosynthetic pigments
Phytotoxicity

peroxidase increased in OMES leaves of nano-CeO_2 exposed plants, with respect to control. Thus, this study provides clear evidence that the properties of the complex soil matrix play decisive roles in determining the fate, bioavailability, and biological transport of ENMs in the environment.

1. Introduction

Along with the vast array of applications that the various classes of engineered nanomaterials (ENMs) offer, they are associated with unknown risks throughout their life cycle in different environmental conditions. The fate of ENMs in the environment depends on their physicochemical properties (like composition, particle size, surface charge, and dissolution) as well as the nature of the target environmental matrices (Cornelis et al., 2014; Peijnenburg et al., 2015). In addition, modulating the ENM properties for various biological applications such as medicine (Nguyen and Zhao, 2015) and agriculture (Kah et al., 2013), also makes them bioavailable to other non-targeted species, as they likely transport and distribute across different media (Liu and Cohen, 2014). This poses serious challenges towards a precise hazard and risk assessment of ENMs to aid regulatory measures and decision-making.

Recent computational modelling and simulation studies on the environmental fate of ENMs involving mass flow and multimedia apportionment have estimated that the major fraction of the released ENMs during production, usage, and disposal, finally accumulate in soils or sediments (Collin et al., 2014; Liu and Cohen, 2014; Keller and Lazareva, 2014). This raises concerns due to the possibility of transport of the ENMs from the soils to agricultural crops and, eventually, bioaccumulation in the food chain (Judy et al., 2011; Gardea-Torresdey et al., 2014; Hawthorne et al., 2014; Majumdar et al., 2015b), or leaching to the groundwater (Quik et al., 2010). Soil properties including texture, porosity, pH, ionic strength, organic matter, and mineral composition play a pivotal role in determining the aggregation, dissolution, chemical transformation, bioavailability, and migration of ENMs in the porous media, as well as in their interactions at the nano-bio interface (Schwabe et al., 2013; Cornelis et al., 2014; Garner and Keller, 2014; Read et al., 2015; Conway and Keller, 2016). Soil organic matter (SOM) is primarily (60–80%) composed of humic acids, fulvic acids, and humin, which are direct products of plant residue decomposition (Brady and Weil, 2008). Evidences show that organic acids like humic and fulvic acids stabilize several metal oxide nanoparticles (NPs) in aqueous solutions, including nano-CeO_2 (Yang et al., 2009; Schwabe et al., 2013), zinc oxide (nano-ZnO) (Zhang et al., 2009), and titanium oxide (nano-TiO_2) (Zhang et al., 2009; Domingos et al., 2009), owing to enhanced charge and/or steric stabilization (Quik et al., 2010). This prevents aggregation of ENMs, possibly leading to their stability and prolonged suspension in the soil pore water or increased mobility through plant roots. Johnson et al. (2009) demonstrated enhanced mobility of nano-zero valent iron (nZVI) in granular media in the presence of natural organic matter.

Due to increasing potential applications of nano-CeO_2 in electronics, catalysis, fuel additives, agriculture, and medicine (Collin et al., 2014), recent phytotoxicity studies are more focused on realistic exposure conditions (Holden et al., 2016). Consolidation of several soil-based studies with nano-CeO_2 may reach to a consensus that although, it is actively transported within plants, it is less detrimental in terms of effects on growth and metabolic processes compared to other metal oxide NPs (Wang et al., 2012; Priester et al., 2012; Zhao et al., 2013, 2015). However, negative effects have been also reported on nitrogen fixation in soybeans (Priester et al., 2012), crop yield in corn, cucumber and soybeans (Zhao et al., 2013, 2015; Priester et al., 2012), and also on the nutritional quality of the edible seeds in different plants like rice (Rico et al., 2013) and kidney beans (Majumdar et al., 2015a). Surprisingly, filial generations of *Brassica rapa* plants were shown to experience higher oxidative stress compared to parent plants (Ma et al., 2016b). Although the literature on the fate and toxicity of nano-CeO_2 keeps on growing exponentially, there have been very few investigations directly addressing the role of SOM in the nano-plant interactions under natural conditions. Schwabe et al. (2013) reported that supplemented organic matter enhanced root adsorption of Ce in pumpkin and wheat plants exposed to 100 mg/L nano-CeO_2 suspended in Hoagland culture medium. In corn plants, lower Ce translocation to aerial tissues was observed in organic matter rich soil, compared to natural unenriched soil amended with bare as well as alginate-coated nano-CeO_2 (Zhao et al., 2012b). According to Zhang et al. (2016), silty loam soil with lower SOM content (~2%) had more exchangeable/bioavailable fraction of Ce, leading to higher translocation to radish shoots, compared to loamy sand soil (~12%). This suggests that soil components have a high potential to modulate the surface properties of ENMs. This modulation can change the transport within plants and the effects of ENMs in plant health and metabolic processes. Extensive research is needed in order to fully understand these phenomena.

To the best of the authors' knowledge, there are no existing reports investigating SOM dependent toxicological response in plants exposed to nano-CeO_2. In this study, we examined the effect of nano-CeO_2 at varying concentrations on physicochemical properties of the soils and the effects on kidney bean plants grown for 52 days from germination. The Ce uptake by roots and further translocation to aerial parts were analyzed using inductively coupled plasma-optical emission spectroscopy. We examined varying SOM content as a factor of the changes in various physiological markers like net photosynthesis, stomatal conductance, transpiration, and leaf area. Additionally, photosynthetic pigments and the activities of antioxidant enzymes in different tissues were assessed to investigate stress response in the plants.

2. Materials and methods

2.1. Cerium oxide nanomaterials

The nano-CeO_2 particles (~8 nm, Meliorum Technologies, Rochester, NY) were procured from The University of California Center for Environmental Implications of Nanotechnology (UC-CEIN). Keller et al. (2010) characterized these NPs as 100% cubic ceria nanorods (95.14% pure), measuring (67 ± 8) nm × (8 ± 1) nm, (≤10% polyhedral; 8 ± 1 nm) with a surface area of 93.8 $m^2\ g^{-1}$. Suspensions of nano-CeO_2 in Millipore water (MPW) were prepared using 30 min bath sonication and characterized for size and zeta potential using Zetasizer Nano ZS90 (Malvern Instruments, Worcestershire, U.K.). The measurements were done in triplicates, each with three consecutive readings for technical replication.

2.2. Soil collection and preparation

Natural soil was collected from an agricultural field in Fabens, TX (N 31° 29′ 02.1″, W 106° 08′ 27.2″, elevation 1102 m, mineral horizon, depth 55 cm). The soil was classified as sandy loam soil (64% sand, 31% silt, 5% clay) according to USDA soil texture classification. Half portion of the collected soil was amended with Miracle-Gro potting mix at 2:1 (v/v) ratio to enhance the SOM content. Based on comparative SOM content (Majumdar et al., 2015a), the collected natural soil (4.2%) was called low organic matter soil (LOMS) and the potting mix added soil (10.1%) was called organic matter enriched soil (OMES). According to