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Research article

Cerium dioxide and zinc oxide nanoparticles alter the nutritional value of soil cultivated soybean plants

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ABSTRACT

The aim of this study was to determine nutrient elements in soybean (*Glycine max*) plants cultivated in farm soil amended with nCeO$_2$ at 0–1000 mg kg^{-1} and nZnO at 0–500 mg kg^{-1}. Digested samples were analyzed by ICP-OES/MS. Compared to control, pods from nCeO$_2$ at 1000 mg kg^{-1} had significantly less Ca but more P and Cu, while pods from 100 mg kg^{-1} nZnO had more Zn, Mn, and Cu. Plants treated with nZnO showed significant correlations among Zn, P, and S in pods with Zn in roots. Correlations among pod Zn/root Zn was $r = 0.808$ ($p \leq 0.01$) and pod P/root P was $r = 0.541$ ($p \leq 0.05$). The correlation among pod S/root S was $r = -0.65$ ($p \leq 0.01$). While nCeO$_2$ treatments exhibited significant correlations between pod Ca/root Ca ($r = 0.645$, $p \leq 0.05$). The data suggest that nCeO$_2$ and nZnO alter the nutritional value of soybean, which could affect the health of plants, humans, and animals.

1. Introduction

Roots of soil cultivated plants indiscriminately absorb essential and non-essential elements from the soil solution (Epstein, 1994; Peralta-Videa et al., 2009). This enhances the law of natural gradient, which is obeyed by soil chemical elements (Brady and Weil, 1999). The uptake of nutrient elements by plants is governed by the availability of elements, the ability of the plant to accumulate the elements, and the competition among elements (Kabata-Pendias and Pendias, 2001). Absorption by roots is affected by the interaction of elements that can be antagonistic, synergistic or multiplicative (Peralta-Videa et al., 2003). Under no water deficit, ion absorption by roots is also affected by several factors including plant species, soil type, soil pH, and organic matter (Brady and Weil, 1999; Lavado et al., 2001; Maathuis, 2009). In natural environments, a combination of these factors can determine the uptake and accumulation of elements in plant tissues. It has been reported that, during the late period of growth, soybean plants cultivated in acid soil accumulated more cationic elements in stems and leaves than plants cultivated in neutral soil (Wang et al., 2000). Murakami and Ae (2009) reported that soybean shoots (Suzuyutaka cultivar), accumulated less Zn in an andosol (pH 6.1) than in a fluvisol (pH 5.3).

A few reports have described the effects of some lanthanide elements in plants. Most of these reports indicate that lanthanum (La) negatively affects several growth parameters in plants. For instance, in wheat, the addition of La (0.5–25 mg L^{-1}) to the hydroponic medium inhibited primary root elongation, reduced roots and shoots dry weight, and the content of Ca, Mg, K, Cu, Zn (Hu et al., 2002). In *Juglands nigra*, La reduced fine root growth, photosynthesis, the content of chlorophyll *a*, and the concentration of Mg, Ca, Ni, and P in roots and shoots (Nicodemus et al., 2009). Lanthanum also decreased the main root length, plant height, leaf area, and the dry weight of roots, stems and leaves of hydroponically grown soybean seedlings (Wen et al., 2011). Conversely, reports indicate that cerium (Ce), another member of the lanthanide series, stimulates root growth and other plant functions. For

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example, Yuan et al. (2001) reported that "Changle", a fertilizer with 50.2% of Ce, increased root growth in rice (*Oryza sativa*) seedlings. In cowpea plants (*Vigna unguiculata*), low levels of Ce (0.713–17.841 μM) were positively associated with foliar chlorophyll content, dry matter production, and nitrate reductase activity (Shyam and Aery, 2012). Conversely, Diatloff et al. (2008) reported that 5·0 μm Ce decreased corn shoots dry weight by 32%. However, to the authors' knowledge, there are no reports on the effects of rare earth element oxide nanoparticles (NPs) on the uptake and accumulation of macro and micro elements in crop plants.

The effects of NPs on plants will depend, among others, on the type of soil and the ability of plants to adjust to the toxicity effects. Zhao et al. (2012a,b) also reported that the mobility and bioavailability of NPs in soil is strongly affected by soil organic matter, which also increased the concentration of Ce in corn (*Zea mays*) roots. This suggests that the type of NP and soil conditions will affect the accumulation of nutritional elements in plants grown in NP impacted soils. Recently, Priester et al. (2012) reported the uptake and distribution of Ce and Zn in soybean tissues grown in farm soil impacted with low, medium and high concentrations of either *n*CeO_2 or *n*ZnO. The data showed that both the *n*CeO_2 and *n*ZnO affected soybean growth parameters; however, the effects of both nanomaterials in nutrient accumulation have yet to be reported. In the present manuscript we report a study aimed to determine the effects of both the *n*CeO_2 and *n*ZnO on macro and micro nutrient accumulation in different organs of soybean plants, particularly in pods. While there are increasingly insights into when and how nanomaterials affect plant growth and yield, this research addresses a gap toward understanding the implications of nanomaterials in soil on plant nutrient uptake, and thus, food crop nutritional quality.

2. Materials and methods

2.1. Soil source and characteristics

As described in Priester et al. (2012), the soil for this research was obtained from an organic farm in Carpinteria, CA (N 34° 23′ 40″, W 119° 28′ 40″). Prior to use, sieved soil samples (2 mm) were air-dried at room temperature, and stored at 4 °C. Before treatment, the samples were analyzed for texture, pH, saturation, cation exchange capacity, soluble salts, organic matter, total nutrients (C, Cu, Fe, Mn, N, Zn), extractable nutrients (B, Ca, Cl, Cu, Fe, Mg, Mn, Na, P, Zn, HCO_3, CO_3, NH_4, NO_3) and exchangeable nutrients (Ca, K, Mg, Na) by the UC Davis Analytical Laboratory (Davis, CA; http://anlab.ucdavis.edu/). This data was included in the supporting information of Priester et al. (2012). In the present manuscript, we included the ICP data for macro and micro elements after treatment application.

2.2. Nanoparticles and addition to soil

Ten nm *n*ZnO and eight nm *n*CeO_2, both from Meliorum Technologies, Rochester, NY, were added to the soil approximately 24 h before planting. The NPs were added as a powder to soil to obtain final concentrations of 50, 100 and 500 mg *n*ZnO kg^{-1} and 100, 500 and 1000 mg *n*CeO_2 kg^{-1}. The procedure was previously described in Priester et al. (2012).

2.3. Planting

The planting protocol was described in Priester et al. (2012). Briefly, control and NP treated soil samples of 2.4 kg each, were deposited in polyethylene bags and placed within 4-L polyethylene/polypropylene blend garden pots previously lined at the base (inner) with polyethylene mesh (Easy Gardener, Waco, TX.) and bottom-filled with 400 g of washed gravel (1.25–2.5 cm). All bags had 20 holes of 5 mm for drainage. The entire root system was within the bags and allowed for easier removal from the pots at harvest time. Dwarf soybean seeds (Early Hakucho, variety product #5555) purchased from Park Seed Company (Greenwood, SC) were germinated in peat pellets and transplanted to the pot soil when the true leaves emerged (18 days after planting). At the center of each pot, a hole of 3.8 cm diameter and 5 cm deep was drilled and a seedling was then transplanted. Each treatment had four replicates. The experiment was conducted in a climate-controlled greenhouse under full sunlight and a temperature range of 31 °C max and 12 °C min. For ten pots, sensors (model 5TE, Decagon) were installed into the soil for periodic direct measurement of water content, temperature, and conductivity.

2.4. Watering

During the whole growth period, the pots were watered every 72 h to reach a total of 150 L of water per m^3 soil. During the first week, the pots received 100 mL at each watering time. In the subsequent irrigation events, the amount of water/pot increased as follows: to 200 mL from days 9–21, 250 mL from days 21–27, and 300 mL from day 27 until the completion of the experiment. At each watering, a sub-sample of H_2O was measured for Zn and Ce concentrations by ICP-AES (atomic emission spectroscopy). Cerium was not detected; Zn was present in concentrations ranging from 0 to 0.17 mg L^{-1}, and accounted for a cumulative addition of <0.1 mg per pot. Water content, conductivity, and temperature were measured immediately before and after each watering using a Decagon ProCheck data recorder connected to the buried sensors (Pullman, WA).

2.5. Harvesting description

The plants were harvested after ~48 d of growth in the NP treated soil (Priester et al., 2012). Roots and shoots were severed at the crown of the plant with a razor blade and weighed. The shoots were separated by stem, leaves, and pods and weighed separately. The separate tissues were oven dried (70 °C/72 h) in paper bags prior to digestion for ICP analysis. The root system of each plant was removed by first carefully breaking apart the soil with a metal scoopula, followed by rinsing (1 min, 3 times) in deionized water (DI) H_2O. The root system was allowed to air dry (~15 min) before weighing. Nodules for ICP analysis were massed, oven dried (70 °C/72 h), and massed a second time to determine water content. Root tissues for ICP analysis were dried and massed as described above. After harvesting, soil samples were stored (4 °C, and −80 °C) for future analysis.

2.6. ICP analysis

For the ICP analysis, the oven dried samples were acid digested assisted by a microwave oven (CEM acceleration reaction system; Mathews, NC). Plant samples from the *n*ZnO treatments were digested following the EPA 3051 method. Soil samples were digested with a mixture of concentrated plasma-pure HNO_3 and HCl (1:3) (*Aqua regia*). Plant samples from the *n*CeO_2 treatments were digested with concentrated plasma-pure HNO_3 and H_2O_2 (30%) (1:4) as described by Packer et al. (2007) with slight modifications.

To validate the digestion and analytical method, standard reference materials from NIST 1547, 1570a and 2709a were digested and read as samples, obtaining recoveries between 90 and 99%. To validate the ICP readings, every ten samples, the blank and samples spiked with Ce and Zn at 10 mg L^{-1} were read. The average readings