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Influence of cerium oxide nanoparticles on the soil enzyme activities in a soil-grass microcosm system

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ABSTRACT

Engineered nanoparticles (NPs) released in the soil, water, and air can return to the environment through the agronomic land application of biosolids, and their potential effect on agricultural ecosystems is most concerning. Soil enzyme activity, often treated as an indicator of soil quality and soil biota, is also useful in determining the sustainability of agricultural ecosystems, particularly soil physico-chemical and microbiological processes. The objective of this research was primarily to determine whether CeO_2 NPs would affect soil quality and fertility by changing soil enzyme activities. The concentration and exposure time-dependent potential toxicity of CeO_2 NPs on soil microorganisms was examined by testing the activity of three enzymes—urease, phosphatase, and β-glucosidase—in a soil-grass microcosm system, and estimated through specific enzyme assays. NPs were applied at different concentrations at 0, 100, 500, and 1000 mg/kg soil mixtures in separated pots in which organic hard red wheat (*Triticum aestivum*) was grown. The effect of exposure time of NPs on soil enzyme activity was also examined through different harvest time events, by mowing the wheatgrass at weeks two, thirteen, and twenty-two and analyzing the soil enzyme activities for three cut groups, which were then compared with those in non-cut groups. Higher NP concentration above and equal to 100 mg/kg was found to inhibit urease and β-glucosidase activities, and to stimulate the phosphatase activity. Specifically, the inhibition effect from CeO_2 NPs on urease activity for the non-cut 1 and cut 1 groups increased from −5.07% at a 100 mg/kg concentration to −13.2% at a 500 mg/kg concentration to −19.91% at a 1000 mg/kg concentration, compared to the treatment without CeO_2 NPs. The inhibition effect from CeO_2 NPs on beta glucosidase activity for the cut 2 group increased from −0.32% to −70.84% at the 100 mg/kg and 1000 mg/kg concentrations, while an inhibition percentage for the non-cut 2 group was between −16.89% to −50.22% at the 100 mg/kg and 1000 mg/kg concentrations. The non-cut and cut 1 groups exhibited the greatest effect on promotion of the phosphatase activity, with an increase from 97.46% to 131.37% to 181.45% at 100, 500, and 1000 mg/kg concentrations, respectively, compared to the 0 mg/kg concentration. The aging effect of CeO_2 NPs indicated that a longer contact time between NPs and the soil alleviated the impact from CeO_2 NPs on soil enzymes, and potentially reduced the ecotoxicity of NPs in the soil environment.

1. Introduction

Engineered nanoparticles have been developed in large quantities for use in a wide range of industrial applications (Casals et al., 2008; Keller et al., 2013; Roco, 2011). This significant and widespread use of engineered nanoparticles following accidental releases or from end of life cycle disposal has made their introduction into the environment inevitable (Gottschalk and Nowack, 2011). Nanoparticles in sizes ranging from 1 to 100 nm and with unique physico-chemical properties are not only be valuable materials to science and industry, but also hazardous materials to the environment and organisms (Klaine et al., 2008). Therefore, exploring the potential impacts of engineered nanoparticles in the environment is critical to assess the toxicity risk to human health and ecosystems. The potential effect of engineered nanoparticles on agricultural ecosystems, particularly on their soil physico-chemical and biological processes is most concerning. Nanoparticles come in contact with soil and plants through deposition from the atmosphere, transportation through bodies of water bodies, and through the application of nanofertilizers and biosolids in wastewater sludge (Gardea-Torresdey

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et al., 2014; Gogos et al., 2012; Keller et al., 2013; Suppan, 2013). As a cheaper nutrient and organic matter alternative to fertilizers, biosolids are widely used in agriculture (Antolín et al., 2010). However, those biosolids may contain high concentrations of engineered nanoparticles based on types (Gottschalk et al., 2013; Keller and Lazareva, 2014).

Of the many engineered nanoparticles available, cerium oxide nanoparticles (CeO_2 NPs) are of particular concern in that the level of production and use of CeO_2 NPs are immense (Piccinno et al., 2012). CeO_2 NPs, are normally used as additives to catalyze diesel fuel engine systems to reduce emissions, as agents to polish materials such as glass, and as materials for UV light adsorption (Cassee et al., 2011; Dahle and Arai, 2015; EPA, 2009; HEI, 2001). There are several pathways by which CeO_2 NPs may find their way into the environment. For example, cerium oxides from abandoned engines and polished materials drift into the environment and are transported into water bodies and soil systems. CeO_2 NPs are also present in both the effluents and biosolids of wastewater treatment plants (Barton et al., 2015; Blaser et al., 2008; Limbach et al., 2008). The potential amounts of CeO_2 NPs ending up in the soil, water, air, and landfill have been assessed at 1400, 300, 100, and 8200 metric tons/year, respectively (Keller et al., 2013).

Therefore, it is critical to undertake research to elucidate the effect of engineered nanoparticles in the soil-water environment, particularly in terms of the possible ecotoxicological effects (Handy et al., 2008a, 2008b; Unrine et al., 2008), as they may be released for the first time in the soil, water and air, or as they may return to the environment for a second time through the agronomic land application of biosolids. Many studies undertaken to investigate the toxicological effects of nanoparticles have focused on aquatic and terrestrial microorganisms (Blaise et al., 2008; Jemec et al., 2008; Lovern et al., 2007; Lovern and Klaper, 2006; Roh et al., 2010; Velzeboer et al., 2008; Wang et al., 2009), and microbes (Antisari et al., 2013; Bae et al., 2010; Bandyopadhyay et al., 2012; Fang et al., 2010; Frenk et al., 2013; Gajjar et al., 2009; Lee et al., 2009; Pelletier et al., 2010). However, few studies have investigated the potential influence of engineering nanoparticles on soil enzyme activities (e.g. Joško et al., 2014; Tong et al., 2007). Indeed, the alterations of soil enzymes activities may affect soil biological systems which may have important ecological and economical outcomes.

The evaluation of microbial activity as an indicator of soil quality to assess environmental changes is more rapid and sensitive than monitoring soil physico-chemical properties. The elements and phenomena that affect soil microbial activity also govern soil enzyme activities that are integral to soil biology, and nutrient cycling within plants (Sinsabaugh et al., 1993). As a consequence, soil enzyme activity is one indicator of soil quality and soil biota, and therefore larger indicator of the sustainability of agricultural ecosystems, particularly the soil physico-chemical and microbiological processes (Aon and Colaneri, 2001). Soil enzyme activity is a sensitive indicator of changes on soil quality and fertility, particularly for nutrient availability, as well as soil biota that are induced by and through the environment (Chen et al., 2003). Water is not only a limiting factor in agricultural ecosystems. Indeed, the availability of essential nutrients of nitrogen and phosphorus are important for the sustainable growth and development of agricultural ecosystems.

Very limited data is available on the effect of nanoparticles on soil enzyme activities, and the data that is available indicates conflicting activity responses when different enzymes were exposed to nanoparticles. Specifically, ZnO, Cr_2O_3, CuO and Ni NPs (10, 100 and 1000 μg g^{-1} soil) exhibited inhibiting and promoting effects on the activities of acid and alkaline phosphatases, dehydrogenase, and urease, as a function of soil type, contact time, and NP size (Joško et al., 2014). Also Ag NPs (1–100 μg g^{-1} soil) inhibited the activities of phosphomonoesterase, arylsulfatase, β-D-glucosidase, and leucine-aminopeptidase (Peyrot et al., 2014). Ag NPs (1–1000 μg g^{-1} soil) may inhibit the activities of urease, acid phosphatase, arylsulfatase, β-glucosidase (Shin et al., 2012). Although Ag NPs (0.32 μg g^{-1} soil) did not affect the activities of β-glucosidase, β-cellobiohydrolase, acid phosphatase, chitinase, and xylosidase, a limited inhibition was observed on the activity of the leucine-aminopeptidase (Hänsch and Emmerling, 2010). Zero valent iron nanoparticles (10,000 μg g^{-1} soil) promoted the activity of dehydrogenase, while the activity of fluorescein diacetate hydrolase was not hindered (Cullen et al., 2011). In addition, Zn and ZnO NPs (2000 μg g^{-1} soil) was observed to inhibit the activities of acid phosphatase, β-glucosidase, and dehydrogenase (Kim et al., 2011). Multiwall carbon nanotubes (5000 μg g^{-1} soil) exhibited a negative effect on the activities of β-glucosidase, β-*N*-acetylglucosaminidase, acid phosphatase, cellobiohydrolase, and xylosidase (Chung et al., 2011). However, the single walled carbon nanotubes (1–1000 μg g^{-1} soil) decreased the activities of b-1,4-glucosidase, b-1,4-xylosidase, b-1,4-*N*-acetylglucosaminidase, cellobiohydrolase, while the activities of the L-leucine aminopeptidase was increased (Jin et al., 2013). Although fullerene nanoparticles were observed to limit the inhibition of the activities of urease, acid phosphatase, β-glucosidase, and dehydrogenase (Tong et al., 2007). TiO_2 and ZnO NPs significantly enhanced the activities of catalase, protease and peroxidase, while no effects of the activity of urease were increased (Du et al., 2011).

Unfortunately, little is known about ecotoxicological effects of CeO_2 on the critical biogeochemical cycles, particularly on soil enzyme activities linked to the C, N and P cycles. Urease, phosphatase and β-glucosidase are plant- and/or microbe-produced enzymes of primary importance for their role in the C, N and P cycles in various soil ecosystems. Urease, which is an indicator of soil quality for nitrogen cycling, acts on organic matter containing nitrogen, mostly urea, and produces inorganic nitrogen ammonia (NH_3), which then is transformed to ammonium (NH_4) and available for the uptake in plants (Bandick and Dick, 1999; Zimmer, 2000). This microbial-secreted urease is very resistant to environmental breakdown in the soil (Zantua and Bremner, 1977). Phosphatase, which indicates phosphorous cycling in the soil-plant system, hydrolyzes organically-formed phosphorus into plant-available phosphate (Henneberry et al., 1979). β-Glucosidase, which is an excellent indicator of decomposition of organic matter in the soil, produces simple sugars and smaller organic structures to provide energy for soil microbes and enable further microbial enzyme activity (Bandick and Dick, 1999).

Introduction of CeO_2 NPs to soil ecosystems may occur repeatedly as waste water, biosolids, and/or fertilizers are applied to land surfaces. Significant environmental doses of CeO_2 NPs may accumulate in soils as a result of these repeated applications because of agricultural practices. Consequently, these environmental conditions create a realistic exposition of soil microorganisms to CeO_2 NPs. Our research focuses on how CeO_2 NPs impact soil quality and the aging effects of nanoparticles. We work with CeO_2 NPs that may be introduced to agricultural soils through the land application of biosolids, waste water, in phosphate fertilizers, or dispersed in diesel engine exhaust. The main objective of this research was to investigate the effect of CeO_2 NPs on biochemical soil quality indicators—soil enzyme activities—in order to evaluate their toxicity to soil ecosystems. To test the potential toxicological effects of CeO_2 NPs on the soil biochemical dynamics, we performed a study that involved microcosms that were prepared using agricultural soil from Illinois and organic soil and planted with wheatgrass. An accelerated cropping management and harvesting system was employed under a sodium grow light to simulate normal growth over time and regrowth of plants following harvest—wheatgrass cutting—events, under different CeO_2 concentrations (0, 100, 500 and 1000 mg/kg soil). Three harvests over 22 weeks were performed for the normal growth (also known as non-cut group). Similarly, over the same period, three cuts and three harvests of the plants were also performed to simulate plants regrowth. At the time of each harvest, soil enzymes activities were examined as a function of various dose treatments of CeO_2 NPs, enzyme types, contact time and cut type. Urease, phosphatase and β-glucosidase were the three enzymes selected to examine in this study because of the critical role these soil enzymes play in biogeochemical