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Rare earth elements (REEs): Effects on germination and growth of selected crop and native plant species

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HIGHLIGHTS

- Toxicity of three rare earth elements (REEs) were tested on native plants and crops.
- Dose–response studies were performed in artificial soil under greenhouse conditions.
- Chemical analyses were undertaken in all soils, but only in plants tested with Ce.
- Effects on growth parameters were detected at concentrations raising concerns.
- Increased REEs may become problematic under a number of environmental conditions.

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ABSTRACT

The phytotoxicity of rare earth elements (REEs) is still poorly understood. The exposure–response relationships of three native Canadian plant species (common milkweed, *Asclepias syriaca* L., showy ticktrefoil, *Desmodium canadense* (L.) DC. and switchgrass, *Panicum virgatum* L.) and two commonly used crop species (radish, *Raphanus sativus* L., and tomato, *Solanum lycopersicum* L.) to the REEs lanthanum (La), yttrium (Y) and cerium (Ce) were tested. In separate experiments, seven to eight doses of each element were added to the soil prior to sowing seeds. Effects of REE dose on germination were established through measures of total percent germination and speed of germination; effects on growth were established through determination of above ground biomass. Ce was also tested at two pH levels and plant tissue analysis was conducted on pooled samples. Effects on germination were mostly observed with Ce at low pH. However, effects on growth were more pronounced, with detectable inhibition concentrations causing 10% and 25% reductions in biomass for the two native forb species (*A. syriaca* and *D. canadense*) with all REEs and on all species tested with Ce in both soil pH treatments. Concentration of Ce in aboveground biomass was lower than root Ce content, and followed the dose–response trend. From values measured in natural soils around the world, our results continue to support the notion that REEs are of limited toxicity and not considered extremely hazardous to the environment. However, in areas where REE contamination is likely, the slow accumulation of these elements in the environment could become problematic.

1. Introduction

Since the Neolithic Revolution, humans have made systematic and organized use of natural raw materials. With the onset of industrialization and the use of fossil fuels that allowed for easier extraction and refinement of mineable ores, the amount of mined material has increased to a size comparable to what is being naturally cycled in the environment. Approximately 75% of the world's metal minerals are processed and consumed by a small number of highly industrialized nations which contain only 25% of the world's population. As a result of these high consumption and production rates in a relatively small proportion of industrialized nations, including Canada, the risk of contaminating soils, rivers and air with toxic elements is higher.

One group of metals that are becoming increasingly mined are the lanthanides, a group of 15 elements in the Periodic table that are vital in many industries and technologies involving metallurgy, ceramics, magnets, petroleum, electronics, medical imagery and more (Hurst, 2010). Lanthanides are composed of elements with atomic numbers 57 (lanthanum) through 71 (lutetium). In other classification schemes recognized by the International Union of

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Pure and Applied Chemistry (IUPAC), yttrium (#39) and scandium (#21) are combined with lanthanides to form the "rare earth elements" (REE) group due to their similar chemical and toxicological properties, and because these elements are often found in the same ore deposits (Connelly et al., 2005). The term "rare earth element" is however misleading as it does not reflect the elements' relative crustal abundances. For example, the average abundances of cerium (Ce; 60 mg kg^{-1}), yttrium (Y; 20 mg kg^{-1}) and lanthanum (La; 30 mg kg^{-1}) in the Earth's crust are comparable to common metals such as copper (Cu; 55 mg kg^{-1}), lead (Pb; 10 mg kg^{-1}), zinc (Zn; 70 mg kg^{-1}) and cobalt (Co; 30 mg kg^{-1}) (Tyler, 2004; Emsley, 2011). The term 'rare' instead refers to the fact that REEs do not concentrate in pure ore deposits such as gold, but are often mined from bastnasite (a fluorocarbonate mineral) and monazite (a phosphate mineral) deposits (Olmez et al., 1991).

In addition to conventional pollution sources, including the mining and refining of REE ore minerals, the firing of coal and oil/gas plants, and landfills leaching potentially toxic brews from discarded technology, phosphorous fertilizers can also be a considerable source of REE pollution (Volokh et al., 1990; Sloof et al., 1993; Todorovsky et al., 1997). Indeed, as mentioned earlier, a major source of REEs are phosphate minerals (monazites) from which specific phosphate-based fertilizers (PF) can be produced (Val'kov et al., 2010). REEs are not only found naturally in these mineral rocks, but are occasionally added to specific fertilizers used by the agricultural industry (Sabiha-Javied et al., 2010). PFs have been extensively used in agriculture for years and their popularity will only increase in the near future as technologies continue to develop. Similarly to reported USA trends, Canadian consumption and application of phosphate fertilizers has steadily increased since 1995, peaking at approximately 750 thousand tons per year in 2011/2012 (Statistics Canada, 2012). Initial low rates of REE accumulation in soils may lead to higher undesirable levels in areas where PFs are extensively used. Toxicological effects might become pronounced and undesirable in areas of intensive agriculture like the Canadian Prairies and the Great Lakes/St. Lawrence Corridor where 75% of the nation resides (Statistics Canada, 2001).

REEs are not known to be nutritionally essential in plants. However, many of these elements can compete with calcium in a number of calcium-mediated biological processes, which could account for some of the toxicity to plants. Due to their trivalent charges and thus higher charge density, REEs can likely displace the divalent Ca, which has a lower charge density, at Ca-binding sites in biological molecules. The effects of REEs on the various calcium-mediated biological processes in plants have been investigated by Brown et al. (1990). In their study, the authors coined the term "super-calcium", referring to lanthanum being analogous to Ca. The authors concluded that many enzymes and other functional proteins are inhibited by La. When this element displaces Ca from extra-cellular binding sites, the efflux of extra- and intra-cellular Ca can become inhibited, which in turn has negative consequences on the plant's health. While the toxicity of REEs is generally considered low, new applications and developing technologies in the agricultural, automotive and telecommunication sectors may increase the environmental levels of various REEs, and in turn, the concentrations exposed to native plants and other wildlife. As a result of their low toxicity, threshold limits and maximum permissible concentrations are poorly established (or not at all) in the literature.

Information on the influence and toxicity of REEs on plant development remain contradictory and obscure. A majority of dose–response studies have been performed under hydroponic conditions that are conducive to stronger effects and not necessarily representative of real world situations. Additionally, positive effects at lower doses (<0.5 REE mg kg^{-1} soil) are almost exclusively reported in Chinese literature. China was in fact the first country in the world to use commercial REE-fertilizers applied to crops in the form of foliar sprays, seed treatments or as additions to solid or liquid root fertilizer formulations (Hu et al., 2004). Yield increases ranging from 5% to 15% for numerous crop species under varying soil and nutrient conditions were reported by researchers such as Brown et al. (1990) and Hu et al. (2004). However, beneficial effects are difficult to state with certainty. REEs are often added as compounds containing nitrogen and other growth-promoting substances thus rendering element-specific conclusions difficult to deduce (Tyler, 2004).

Positive impacts of REEs on plant growth may be restricted to certain growth stages or specific soil conditions. He and Loh (2000) reported that in *Arabidopsis thaliana*, additions of Ce- or La nitrate to the growth medium significantly increased root development but had no effect on biomass, the number of rosette leaves produced or plant height during the vegetative growth stage. The authors also provide evidence that adding low concentrations (approximately 0.5 mg kg^{-1}) of either Ce- or La nitrate was most effective at promoting floral initiation. Other published work by Diatloff et al. (2008) reported that the addition of La and Ce did not increase the growth of corn (*Zea mays*) or mungbean (*Vigna radiata*) grown under hydroponic conditions and that growth was even inhibited at higher concentrations (>5 μM Ce). In another hydroponic experiment, Hu et al. (2002) reported inhibitory effects on primary root elongation of wheat (*Triticum aestivum* L.) and reductions in both dry root and shoot weights as well as a reduction in the mineral element content of plant tissues after the addition of La and Ce (and the combination of), at doses between 0.5 and 25 mg L^{-1}, to nutrient solution.

The bioavailability of compounds to plants is one of the most important issues for environmental studies. In fact, the influence of soil properties and plant absorption capabilities are two of the main drivers that govern the phyto-availability of an element. The most important soil variables that influence bioavailability include pH, redox potential, soil texture and organic matter content among many others (Cao et al., 2001). Interactions amongst elements and compounds even influence availability through antagonistic and/or synergistic mechanisms as chemically similar elements compete for the same binding sites (ex: Ca and REEs). Still, in general, the chemical composition of plants closely resembles that of their environment. Using plants as ecosystem health indicators or as contamination indicators (as part of biomonitoring programs) is increasingly studied and is a popular choice for modern monitoring programs.

The importance of primary producers as valued ecological components and their necessary inclusion as part of ecological risk assessment is widely recognized. However, there remains a paucity of information on the phytotoxic effects of many inorganic compounds. Due to the important questions surrounding the availability and toxicity of REEs to plants, this study will aim to investigate the toxicity of elevated soil levels of different REEs (La, Y and Ce) on three native Canadian plant species: common milkweed (*Asclepias syriaca* L.), showy ticktrefoil, (*Desmodium canadense* (L.) DC.) and switchgrass (*Panicum virgatum* L.), as well as on two crop species: radish (*Raphanus sativus* L.) and tomato (*Solanum lycopersicum* L.) that are commonly grown in North America and that are popular choices in toxicity studies. All species were grown in soil within growth chambers and were exposed to different concentrations of REEs in order to investigate their relative toxicity and availability to actively growing plants.

2. Materials and methods

The La, Y and Ce experiments were performed independently of one another. Table 1 summarizes and contrasts some of the materials and methods for each experiment. For the Ce experiment, it