Environmental Pollution 204 (2015) 32–38

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

The influence of gadolinium and yttrium on biomass production and nutrient balance of maize plants

Jessica Saatz [a], Doris Vetterlein [b], Jürgen Mattusch [a], Matthias Otto [c], Birgit Daus [a, *]

[a] UFZ – Helmholtz-Centre for Environmental Research, Department of Analytical Chemistry, Permoserstrasse 15, 04318 Leipzig, Germany
[b] UFZ – Helmholtz-Centre for Environmental Research, Department of Soil Physics, Theodor-Lieser-Strasse 4, 06120 Halle, Germany
[c] TU Bergakademie Freiberg, Institute of Analytical Chemistry, Leipziger Strasse 29, 09599 Freiberg, Germany

ARTICLE INFO

Article history:
Received 17 December 2014
Received in revised form
6 March 2015
Accepted 30 March 2015
Available online

Keywords:
Corn
Rare-earth elements
Bioavailability
Critical raw materials
Root-shoot transfer

ABSTRACT

Rare earth elements (REE) are expected to become pollutants by enriching in the environment due to their wide applications nowadays. The uptake and distribution of gadolinium and yttrium and its influence on biomass production and nutrient balance was investigated in hydroponic solution experiments with maize plants using increasing application doses of 0.1, 1 and 10 mg L^{-1}. It could be shown that concentrations of up to 1 mg L^{-1} of Gd and Y did not reduce or enhance the plant growth or alter the nutrient balance. 10 mg L^{-1} Gd or Y resulted in REE concentrations of up to 1.2 weight-% in the roots and severe phosphate deficiency symptoms. Transfer rates showed that there was only little transport of Gd and Y from roots to shoots. Significant correlations were found between the concentration of Gd and Y in the nutrient solution and the root tissue concentration of Ca, Mg and P.

1. Introduction

The group of rare earth elements (REE) consists of 17 elements; the lanthanides and lanthanum (La) together with scandium (Sc) and yttrium (Y). Due to their atomic weight, ionic radii and therefore similarities in behavior, they are classified as light REE from La to neodymium (Nd), medium REE (MREE) from samarium (Sm) to holmium (Ho), and heavy REE (HREE) with the elements erbium (Er) to lutetium (Lu), as well as Y and Sc (Liu et al., 2012; Tyler, 2004).

The name rare earth is misleading, as the elements are not scarce when taking into account their relative abundance in the earth crust. Only economically attractive deposits are not very common and in recent years China built up a monopoly for mining and processing (Massari and Ruberti, 2013).

Soil total contents of REE reported from China are in the range of 76 and 629 mg kg^{-1} (Ye et al., 2008). To assess bioavailability of REE several methods have been suggested. For example leaching with ethylendiaminetetraacetic acid (EDTA), showing that on average 16% of the total content is extractable, and with a tendency for LREE being more easily available than HREE, though the most bioavailable element was Yttrium (25%) (Loell et al., 2011a, 2011b; Rao et al., 2010).

Due to their worldwide use in a broad range of technologies, and the lack of profitable recycling methods, REE are expected to be emerging pollutants. Gadolinium (Gd), for instance, is used as contrast agent in magnetic resonance imaging and as a result, released into surface water by hospital effluents. A positive Gd-anomaly in the distribution patterns of REE could be found in rivers and lakes downstream of cities in Europe, indicating an anthropogenic accumulation (Brioschi et al., 2013).

Furthermore, REE phosphates, nitrates, chlorides and oxides have been applied since the 1970s on large scale as fertilizers or growth promoters in China's agriculture and animal husbandry. About 1100 tons REE per year were consumed for agricultural purposes, for instance, in concentrations ranging between 50 and 700 mg L^{-1} as foliar application (Pang et al., 2002; Ruiz-Herrera et al., 2012). REE are reported to promote growth, flowering and quality and coloring of fruits, improve the resistance to drought, acid and metal stress (Pang et al., 2002).

Inconsistent results are reported in the literature, probably as a result of differences in application form and level as well as plant species or the element in question (Tyler, 2004). While Xiong et al. and Zhang et al. report growth stimulation by fertilization with up to 40 mg L^{-1} for wheat, rice and rape, Hu et al. (2002) report growth inhibition of rice roots with 5 mg L^{-1} fertilization in hydroponic solutions. Diatloff et al. (2008) tested the influence of La on the growth of maize plants and found that concentrations up to

* Corresponding author.
E-mail address: birgit.daus@ufz.de (B. Daus).

http://dx.doi.org/10.1016/j.envpol.2015.03.052
0269-7491/

0.09 mg L^{-1} can enhance the root growth but not the overall biomass production, while concentrations of 0.5–25 mg L^{-1} La inhibited the primary root growth along with a reduction in the dry weight of root and shoot in a hydroponic study.

The validity and possible mechanism behind this effect are still unknown, but as the REE are considered non-essential elements to plants and other organisms, these phenomena are often assigned to a shift in the nutrient balance of the plants (Tyler, 2004).

The environmental behavior of these metals determines whether they pose a threat by accumulation and possibly enter the food chain. Up to now most studies deal with LREE La and Ce, only few studies investigated MREE and HREE. Influence of Gd and Y, two elements which pose a possible anthropogenic contamination in the future are not well studied.

Hydroponic solutions were used as a simplified system compared to pot experiments as the adsorption and desorption processes onto mineral phases, which normally take place in soil, can be avoided. Maize was chosen as an important agricultural crop and major source of food, sugars, cooking oil and animal feed which produces high amounts of biomass (Hussain et al., 2012). The uptake of REE, their root-shoot transfer and their impact on nutrient uptake and distribution was investigated by analyzing root and shoot tissue for nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca), boron (B), manganese (Mn), copper (Cu), zinc (Zn), molybdenum (Mo), iron (Fe), Gd and Y respectively. The influence of the REE on the plants will be discussed in comparison to a control treatment without application of REEs.

2. Materials and methods

2.1. Plant growth and harvest

The maize seeds (*Zea mays* cv. Ronaldinho, KWS SAAT AG, Einbeck, Germany) were sterilized for 10 min in a 10% H_2O_2 solution (Merck, Germany), rinsed and soaked for further 10 min in deionized water. They were germinated between folded layers of filter paper moistened with a saturated $CaSO_4$ solution for 7 days at 25 °C. Equally strong seedlings were chosen and transferred to a plastic pot containing 2 L of the nutrient solution (modified from Römheld and Marschner (1990)). The nutrient solution was made up of analytical grade chemicals: 0.7 mM K_2SO_4, 0.1 mM KCl, 0.5 mM $MgSO_4$, 2 mM $Ca(NO_3)_2$, 0.02 mM Na[Fe(EDTA)], 0.1 mM KH_2PO_4, 10 μM HBO_3, 0.5 μM $MnSO_4$, 0.5 μM $ZnSO_4$, 0.2 μM $CuSO_4$ and 0.01 μM $(NH_4)_6Mo_7O_{24}$ in deionized water.

The $Gd(NO_3)_3$ or $Y(NO_3)_3$ (Strem Chemicals, Germany) were chosen as representatives of MREE and HREE, and a standard solution (2 g L^{-1}) was given to the nutrient solution, adjusting the concentration to 0.1, 1 and 10 mg L^{-1}, (0.63, 6.3 and 63 μmol Gd L^{-1} and 1.12, 11.2 and 112 μmol Y L^{-1}) respectively. Each treatment was replicated three times. The pH value of the solution was set between 5.5 and 6.5, using HNO_3, 5%, and NaOH, 10%, using a pH-meter (ISFET electrode, IQ240-06 with PH16SS, IQ Scientific). Solutions were renewed every 2–3 days. The solutions were constantly aired using a pump (Tetra, APS) for each pot. The plants were grown in a growth chamber under controlled conditions (350 μmol m^{-2} s^{-1} PAR, 14/10 h day/night-rhythm, 23/18 °C and 60% air humidity).

After 21 days the plants were harvested, sampling stem, roots and old leaves and the three youngest leaves separately. The roots were washed thoroughly and rinsed with de-ionized water and carefully dried using a soft paper towel. All plant samples were dried in an oven (Heraeus T6120) at 65 °C for 24–48 h until the weight was constant and then homogenized using a rotor mill (Retsch, L-Ultra Centrifugal Mill ZM 1).

2.2. Sample digestion and analysis

About 0.1 g of the dried and homogenized plant sample was weighed into micro-Teflon vessels. The sample was wetted with 0.5 mL HNO_3 (65%, SUPRAPUR, Merck, Germany) and stayed under the fume hood overnight. On the next day further 0.5 mL HNO_3 and 0.2 mL H_2O_2 (30%) (Merck, Germany) were added to the sample and it was digested using a microwave (MLS, Ethos Nova 1000) with the following temperature program; 10 min: 20 °C–150 °C, 20 min: 150 °C–220 °C, 20 min: 220 °C, and 2 h cooling.

The aqueous extracts were transferred to centrifugation tubes and filled up to 5 mL with de-ionized water (18.2 MΩ cm, Direct-QTM 5 system; Millipore). Samples were centrifuged for 10 min at 3500 rpm. Total concentrations of the elements B, Mn, Cu, Zn, Y, Mo and Gd were determined using inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7700) by measuring the intensities m/z 11 (B), 55 (Mn), 63 (Cu), 66 (Zn), 89 (Y), 95 (Mo), 157 (Gd). Calibrations were carried out using diluted ICP Certipur multi-element standard solution VI (Merck, Germany) and REE standard solution I (CLMS-1, SpexCSP; United Kingdom). The elements Ca, Mg, P, S and Fe were measured from the same digested solutions using inductively coupled plasma-atomic emission spectrometry (ICP-AES, Spectro Arcos, Spectro Analytical Instruments GmbH).

N in plant tissue was determined by a VARIO EL elemental analyzer (Elementar GmbH). Phosphate in fresh and used nutrient solutions was monitored via photometric method (Thermo Scientific, Gallery Plus) (DIN ISO 15923-1, 2012).

2.3. Statistical analysis

Statistical analysis were performed using STATISTICA 64 (StatSoft) and Statist 2.0 (Institut für Rechtsmedizin und Verkehrsmedizin der Universität Heidelberg, 2005). Means of replicates and evaluation of significance were determined by t-test ($n = 3$, $f = 2$, $Q = 95\%$) and the Dixon outlier test was used to identify outliers ($Q = 95\%$, $n = 3$).

3. Results

3.1. Influence on biomass production

Shoot biomass, expressed relative to the control treatment without application of REEs, only decreased at concentrations of 1 mg L^{-1} (Gd) and 10 mg L^{-1} (Gd, Y) (Fig. 1).

The control plants produced 15.4 g biomass shoot tissue and 2.77 g roots, when taking into account the dry weight. When adding Gd to the nutrient solution; the plants grown in the lowest concentration of 0.1 mg L^{-1} showed no significant difference compared to the control, but the concentration of 1 mg L^{-1} reduced the biomass production by 37% for the shoot and 27% for the roots. The highest concentration, 10 mg L^{-1} Gd, reduced shoot growth by 67% and root biomass by 35% compared to control.

For Y, there is no trend with increasing concentrations, only the highest concentration (10 mg L^{-1}) was detremental to plant growth, reducing biomass production by 93% for shoots and 88% for roots compared to control treatment. These plants were small with dark red stripes along the leaves. Pictures of roots and shoots can be found in the supplementary material.

Root/shoot ratios (Fig. 2) increased for both, Gd and Y, with increasing concentrations, with exception of the treatment Gd 1 mg L^{-1}. This indicates that root growth is impeded less than shoot growth.