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Germanium (Ge) and rare earth element (REE) accumulation in selected energy crops cultivated on two different soils

Oliver Wiche *, Hermann Heilmeier

Institute for Biosciences, Biology/Ecology Group, TU Bergakademie Freiberg, Germany
Interdisciplinary Environmental Centre, TU Bergakademie Freiberg, Germany

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ABSTRACT

Accumulation of germanium (Ge) and rare earth elements (REEs) in shoots among the functional groups of nine selected energy crops were investigated in a semi-controlled lysimeter experiment. Five species belonging to the functional group of grasses (*Hordeum vulgare*, *Zea mays*, *Avena sativa*, *Panicum miliaceum* and *Phalaris arundinacea*) and four species from the group of herbs (*Lupinus albus*, *Lupinus angustifolius*, *Fagopyrum esculentum* and *Brassica napus*) were cultivated in parallel on two soils with slightly alkaline (pH = 7.8) and slightly acidic (pH = 6.6) conditions. After harvest, concentrations of Ge, La, Nd, Gd, Er, P, Fe, Mn and Si in shoot tissues were determined with ICP-MS. Concentrations of Ge were significantly higher in grasses than in herbs. Conversely, concentrations of La and Nd were significantly higher in herbs than in grasses. Highest concentrations were measured in *B. napus* (REEs) and *Z. mays* (Ge). Concentrations of Ge significantly positively correlated with that of Si in the shoots showing low concentrations in herbs and high concentrations in grasses, indicating a common mechanism during the uptake in grasses. Concentrations of REEs correlated significantly positively with that of Fe and P. Cultivation of species on the slightly acidic soil significantly increased the uptake Ge in *L. albus* and *P. arundinacea* and the uptake of La and Nd in all species except of *P. arundinacea*. Our results clearly show that species from the group of grasses are most suitable for a phytomining of Ge. Species with efficient mechanisms for the mobilization of P and Fe in the rhizosphere seem to be most suitable for a phytomining of REEs.

1. Introduction

Germanium (Ge) and rare earth elements (REEs) are raw materials with a growing demand for the production of high-tech devices and engineered systems such as electric automobiles, infrared optics, fiber-optic technology, displays and semiconductors. The global demand for Ge was estimated at 28 tons (Ge) in 2006 and is expected to increase eight-fold within the next decade (Gunn, 2014). For the REEs the global demand is estimated to grow by 3.9% from 120,000 tons in 2014 to 150,766 tons in 2020 (Kumari et al., 2015). Unlike most commercially used elements, REEs and Ge are rarely concentrated into mineable ore deposits (Rosenberg, 2007; Kumari et al., 2015). Since Ge and REEs occur widely dispersed in soils, a promising chance to improve supply of these elements could be phytomining. The average concentration of Ge in the earth crust is estimated at 1.6 $\mu g\ g^{-1}$ (Rosenberg, 2007). The REEs comprise a group of 16 elements including lanthanum (La), the group of lanthanides and yttrium (Y) that are prevalent in the earth crust with concentrations varying from 35 $\mu g\ g^{-1}$ lanthanum (La) and 40 $\mu g\ g^{-1}$ neodymium (Nd) to 6 $\mu g\ g^{-1}$ gadolinium (Gd) and 3.5 $\mu g\ g^{-1}$ erbium (Er) (Tyler, 2004). Unfortunately, under most soil conditions bioavailability of Ge and REEs in soils is expected to be low (Tyler and Olsson, 2001). In the soil–plant system Ge behaves chemically similar to Silicium (Si). In absence of organic ligands Ge is mainly present as monogermanic acid ($Ge(OH)_4$) in soil solution similar to Si ($Si(OH)_4$) (Nikolic et al., 2007). However, due to its high affinity to form stable complexes with organic ligands (Pokrovski and Schott, 1998), surface complexation and co-precipitation with Fe-/Mn-oxy-hydroxides (Pokrovsky et al., 2006), the mobility of Ge in soil solution and availability to plants often appear to be limited (Kurtz et al., 2002). In contrast, under most geochemical conditions REEs form 3+ cations, only Ce might also form 4+ cations (Wyttenbach et al., 1998). For the REEs a variety of processes affect their mobility in soils like sorption onto soil particles and colloids (Wu et al., 2001; Davranche et al., 2015), precipitation with phosphates (Johannesson et al., 1995) and complexation with organic and

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* Corresponding author at: Institute for Biosciences, Biology/Ecology Group, TU Bergakademie Freiberg, Germany.

E-mail address: oliver.wiche@ioez.tu-freiberg.de (O. Wiche).

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inorganic ligands like organic acids, carbonates and sulfates (Gu et al., 2000; Pourret et al., 2007), as well as interactions with Fe- and Mn-oxides (Cao et al., 2001; Davranche et al., 2015).

Typical steps of phytomining involve the accumulation in a plant species, harvesting the biomass and burning it to produce a bio-ore (Anderson et al., 1999). Two basic strategies can increase the efficiency of phytomining: (i) using hyper-accumulator plants characterized by high capacities to accumulate certain elements in above-ground biomass and (ii) using metal-tolerant species with a high formation of biomass together with (iii) enhancement of plant available fractions of metals in soil (Brooks and Robinson, 1998; Karimzadeh et al., 2012). Until today no hyper-accumulators for Ge and REEs are known, except of some ferns which accumulate REEs in concentrations up to 1 mg g^{-1} in La (Wyttenbach et al., 1998). Since the use of ferns for phytomining on arable soils is not possible for practical reasons, optimization of the phytoextraction process is dependent on the knowledge of suitable plant species for bioaccumulation as well as a sound understanding about processes controlling bioavailability of the target elements in the soil–plant system. In the present study we report the results of a field experiment were we tested selected bioenergy crops for their potential for a phytomining of Ge and REEs, since energy crops are typically characterized by high yields per unit ground area. Additionally the effects of soil pH and distribution of elements among soil fractions on the uptake in shoots were studied. In total nine different species were tested including five species belonging to the functional group of grasses (*Hordeum vulgare*, *Zea mays*, *Avena sativa*, *Panicum miliaceum* and *Phalaris arundinacea*) and four species from the group of herbs (*Lupinus albus*, *Lupinus angustifolius*, *Fagopyrum esculentum* and *Brassica napus*). Due to the chemical similarities between Ge and Si and a higher ability of grasses to accumulate Si (Ma and Yamaji, 2006) we hypothesize that differences in physiology among the functional groups should also lead to differences in the accumulation of Ge and REEs in the investigated plant species. Indeed, such a comprehensive knowledge allows one to optimize phytomining of the mentioned elements. In this study Ge was selected together with La and Nd as representatives of the light REEs (LREEs) and Gd and Er as representatives for the group of heavy REEs (HREEs).

2. Material and methods

2.1. Field experiment

The experiment was carried out in a semi-field lysimeter at the off-site soil recycling and remediation center of Bauer Umwelt Company in Hirschfeld (Saxony, Germany). The lysimeter consists of a concrete basin with an area of 400 m^2 and a depth of 1.8 m. The basin was sealed with a layer of a PVC tarp on the ground to test a phytoextraction approach without the risk of groundwater contamination. The lysimeter was filled separately with two different homogenized top soils (300 m^3 each). For the investigation of soil effects on the accumulation of Ge and REEs in plants two soils with similar concentrations of total Ge and REEs but differing pH and fractions of elements in soils were selected. The first soil was a top soil from a road construction site near Freital (Dresden, Saxony) (hereafter referred to soil A) and the second soil was a topsoil from a mining affected area in the vicinity of Freiberg (Saxony, Germany) (hereafter referred to soil B) classified as luvisols. Soil A was a silty loam with a pH (H_2O) 7.8. Soil B was a silty loam with a pH (H_2O) 6.6 (Table 1). Initial plant available nutrient concentrations of the soils (before fertilizer application) are shown in Table 1.

2.2. Geochemical soil properties

In both soils, total concentrations of Ge and REEs were similar (Table 2); however, there were differences in the distribution of elements among different soil fractions that were operationally defined according to Kurtz et al. (2002) (Table 2). For the measurement of total concentrations a melting digestion with Na_2CO_3 and K_2CO_3 according to Alfassi and Wai (1992) was performed. REE-containing soil fractions were identified by a sequential dissolution analysis according to Kurtz et al. (2002). Six operationally defined soil fractions were extracted in sequence: Mobile/exchangeable elements by shaking with 1 M ammonium acetate (pH 7) for 24 h (Fraction 1), acid soluble elements by shaking with ammonium acetate buffered to pH 5 for 5 h (Fraction 2), elements bound to oxidizable matter by gently heating with 10 ml H_2O_2 for 5 h in a ammonium acetate buffer solution (Fraction 3). Non-crystalline components, predominantly Fe, Mn and Al-oxides were isolated by selective dissolution with acid 0.2 M ammonium oxalate (pH 3.2) in the dark (Fraction 4). Crystalline Fe and Al-sesquioxides were treated with a mixture of 0.2 M ammonium oxalate and 0.1 M ascorbic acid. After each step the solid and supernatant was separated by centrifugation and concentrations of elements in the supernatant were measured by inductively coupled plasma-mass spectrometry (ICP-MS). Residual fraction (fraction 6) was calculated as the difference between total concentrations and concentrations in fractions 1–6.

In both soils, the slightly alkaline soil A and the slightly acidic soil B only 0.2% of total Ge and about 0.5% of bulk concentrations of La, Nd, Gd and Er were easily accessible by leaching with NH_4-acetate (pH 7) (Table 2). In both soils, concentrations in fractions 4–6 represented more than 98% and fraction 6 (refractory silicates) more than 80% of total Ge. However, there were significant differences between the soils with regard to elements bound to oxidizable material (fraction 3) as well as those bound to amorphous and crystalline oxides (fractions 4 and fraction 5). The slightly acidic soil B contained significantly higher concentrations of Ge and REEs in fraction 3 and significantly lower concentrations in fractions 4 and 5 ($p < 0.05$).

2.3. Plant growth

In this experiment five species belonging to the functional group of grasses (*H. vulgare*, *Z. mays*, *A. sativa*, *P. miliaceum* and *P. arundinacea*) and four species from the group of herbs (*L. albus*, *L. angustifolius*, *F. esculentum* and *B. napus*) were tested. Each species was cultivated on five plots (five replicates) per soil substrate with an area of 4 m^2 each (size of each plot 2 m × 2 m). To compare the concentrations of metals in different species and the functional groups, the grasses and herbs, respectively, all species were cultivated in total on 45 plots on the slightly alkaline soil A (Table 3). This design allows to compare the mean concentrations in different species under soil conditions typically found in agriculturally used, limed soils of the Erzgebirge (Saxony, East Germany). Furthermore, for the comparison of the accumulation in different species growing on different soils, six selected species (Table 3) were cultivated in parallel in 30 plots on the slightly acidic soil B. The spatial arrangement of plots was randomized within each soil. Surrounding each plot a 0.5 m buffer zone was kept without vegetation to prevent interactions between neighboring plots. On each plot plants were seeded in rows with seed densities corresponding to agricultural practice (Table 3). After 21 days of germination and plant growth all plots received an NPK fertilizer with respect to the individual needs of species. Application of fertilizer was repeated every second week to maintain a constant nutrient supply over the whole experiment and prevent N deficiency e.g.