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THE PCA OF PHYTOMINING: PRINCIPLES, CHALLENGES AND ACHIEVEMENTS

Hermann HEILMEIER & Oliver WICHE

Institute of Bioscience and Interdisciplinary Ecological Centre, TU Bergakademie Freiberg Leipziger Str. 29, D-09599 Freiberg (Germany), hermann.heilmeier@ioez.tu-freiberg.de; oliver.wiche@ioez.tu-freiberg.de

Abstract: Phytomining, a plant based technology which uses the capacity of plants and their associated microorganisms to accumulate commercially valuable elements in their biomass, is an alternative for winning commercially valuable elements when conventional mining is economically not viable e.g. due to low concentrations of metals in ore bodies. These elements will be accumulated in above-ground compartments of the plants according to the plant's capacity for uptake and distribution patterns. After harvesting the plants, the biomass can be utilized for energetic purposes, either by burning the phytomass or generating biogas via microbial fermentation. The classical elements used for phytomining usually occur at a few sites with high concentration, e.g. ultramafic soils, thus allowing high rates of accumulation in plants. An alternative approach is to use elements occurring ubiquitously in soils such as germanium (Ge) and rare earth elements (REEs), which are not essential for plant nutrition, but will be taken up by plants due to their chemical similarity with (essential) nutrients. Experiments in the greenhouse and in the field with several species of energy crops have shown high yields of Ge (up to 200 µg m^{-2}) in grass species (*Hordeum vulgare*, *Panicum miliaceum*, *Phalaris arundinacea*, *Avena sativa*, *Zea mays*), whereas REEs preferentially accumulated (up to 400 µg m^{-2}) in forbs (*Lupinus albus*, *L. angustifolius*, *Fagopyrum esculentum*, *Brassica napus*). However, a major limitation for the economic feasibility of phytomining in areas even with elevated soil concentrations of valuable elements is the low concentration of these elements which is usually found in the soil solution. Bioavailability of elements such as (heavy) metals and metalloids can be enhanced by processes in the rhizosphere, i.e. the root–soil interface with physicochemical properties of the soil being heavily modified by plant roots and their associated microorganisms. These processes include the exudation of metabolites from roots, causing many chemical reactions in the rhizosphere such as changes in pH and redox potential, sorption/desorption of cations and anions on/from soil colloids. Field experiments with mixed cultures of oat (*Avena sativa*) and white lupine (*Lupinus albus*) have shown elevated concentrations of, e.g., iron, lanthanium and neodyme both in the soil solution and in the above-ground biomass of oat. The elements accumulated in the plant biomass can be recovered e.g. by digesting the plant material via microbial fermentation, chemical agents or burning. Burning of biomass yields ashes, from which elements like Ge can be recovered via acidification and distillation with HCl. In the residues from the microbial fermentation concentrations of Ge and REEs were elevated by a factor of 100 compared to the original plant material. Furthermore, nutrients in the digestate can be used as fertilizer back in the field. In conclusion, the principal components of phytomining are (i) accumulation of target elements in plants, (ii) biomass yield for high rates of element and biogas harvesting, (iii) chelants and other root and microbial exudates to increase bioavailability of target elements, (iv) digestion of plant material, (v) extraction of target elements from digestates, (vi) fertilizer from fermentation residues or ashes used back in the field thereby closing material cycles.

Keywords: bioaccumulation, bioavailability, biogas, chelants, digestion, energy crops, germanium, phytoextraction, rare earth elements, rhizosphere,

1. INTRODUCTION

The development of novel processing techniques and products in the fields of transport, information, communication, energy, chemistry, environmental, medical and other technologies will create an increasing demand for "critical" or "strategic" resources in the near future (European Commission, 2010). Among the economically relevant elements we find transition metals such as indium (In), germanium (Ge) and rare earth elements (REEs). However, the increasing demand for these elements will not always be balanced by their ready supply. The risk of supply can be due to a number of factors, such as an agglomeration of certain countries or companies providing these elements. This is particularly true for Ge and REEs due to the dependence on the People's Republic of China for these elements (European Commission, 2010).

Therefore alternative methods for winning these critical elements are necessary. One of these alternatives is phytomining, a plant based technology which uses the capacity of plants and their associated microorganisms to accumulate commercially valuable elements in their biomass (Sheoran et al., 2009; Naila et al., 2019). Phytomining was established by Alan Baker and Robert Brooks who investigated world-wide distribution of metal-tolerant plants and their element composition on extreme sites (Baker & Brooks, 1989). Initially they focused on plant communities on serpentine soils in Tuscany which were enriched with nickel (Ni). Already in 1948, plant species which accumulate up to 7,900 µg g^{-1} in their leaves have been described there (Brooks, 1998). These plant species have been called "hyper-accumulators" since they can accumulate metals up to 100–1000 more than non-accumulating species in their shoots (Brooks, 1998). Until today, worldwide more than 700 hyper-accumulators have been described, with more than 80% of them accmumlating Ni (Jaffré et al., 2018). Thus, due to the high availability of Ni accumulating species, phytomining of nickel has been established as an economically viable process (Nkrumah et al., 2018).

2. PRINCIPLES OF PHYTOMINING

Phytomining is a plant-based phyto-extraction technology which has been proposed for "metal mining" by Baker & Brooks (1989), with a first demonstration of its economic feasibility by Nicks & Chambers (1995) for nickel (Ni), growing the Ni hyperaccumulator *Streptanthus polygaloides*. In the following, there have been a number of investigations on plants growing on soils containing high concentrations of metals (either naturally or due to environmental pollution) or mineral wastes. Apart from Ni hyperaccumulating plants, tobacco plants, e.g., have been used for mining gold (Krisnayanti et al., 2016) and *Miscanthus* or *Salix* species for mining palladium (Naila et al., 2019). According to the plant's capacity for uptake and distribution patterns these elements will be accumulated in above-ground compartments of the plants. After harvesting the plants, the biomass can be utilized for energetic purposes, either by burning the phytomass or generating biogas via microbial fermentation. Both of these technologies can be used as digesting procedures which prepare the plant material for extraction of the valuable elements (Fig. 1). The residues from biogas production can be used as fertilizer, thus closing material cycles.

The classical elements used for phytomining cited above usually occur at a few sites with high concentration, e.g. ultramafic soils, thus allowing high rates of accumulation in plants (Sheoran et al., 2009). An alternative approach is to use elements occurring ubiquitously in soils which are not essential for plant nutrition, but will be taken up by plants due to their chemical similarity with (essential) nutrients – usually without toxic effects. Among these elements are germanium (Ge) and rare earth elements (REEs). Due to its location in the periodic system of elements, Ge behaves very similar to silica (Si) which is the second most abundant element in the earth's crust. Because of its chemical similarity to Si, Ge is usually associated with Si, however, with a much lower abundance of 1:10,000. The average concentration of Ge in the earth's crust is 1.5 mg kg^{-1}, much less than e.g. lead (ca. 15 mg kg^{-1}) or zinc (ca. 40 mg kg^{-1}) (Rosenberg, 2007; Wiche et al., 2018). Rare earth elements have

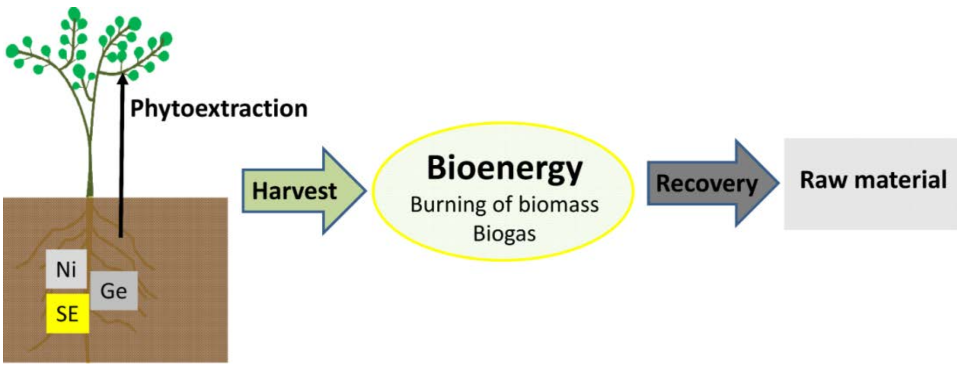

Figure 1. Principles of phytomining

a similar ion radius as calcium (ca. 1×10^{-10} m). Minerals with highest abundance of REEs are bastnasite (Ce,La,Nd,Y)[(F,OH)|CO_3], monazite (La,Ce,Nd)[PO_4] and xenotime (Y,Yb)[PO_4]. Average concentration of REEs in the earth's crust range from 66 (Ce), 30 (La) und 28 mg kg^{-1} (Nd) to 0.5 (Tm) and 0.3 mg kg^{-1} (Lu). With a total concentration of 150 mg kg^{-1} REEs are more abundant than copper and zinc (Kabata-Pendias, 2011).

Thus Ge and REEs offer an option for alternative phytomining strategies beyond classical elements concentrated at "hot spots" such as nickel or gold, either due to natural geochemical anomalies or due to anthropogenic pollution. Rather due to their ubiquitous occurrence, Ge and REEs are excellent candidates for phytomining e.g. on marginal land such as in post-mining landscapes, floodplains or brownfields. This spectrum of marginal sites has already been at the focus of growing second-generation energy crops such as miscanthus (Pidlisnyuk et al., 2014), other grass species (Ranjan et al., 2015) or oil crops (Gomes et al., 2019). Energy crops can be utilized via thermal or fermentative digestion which makes the valuable elements available for easy extraction from the plant material. Experiments in the greenhouse and in the field showed high yields of Ge in grass species, whereas REEs preferentially accumulated in forbs (Fig. 2). The high capacity of grass species for accumulation of Ge is due to their high uptake capacity for silica. Consequently we found a significant correlation between Ge concentration and Si concentration in above-ground biomass of greenhouse-grown plants ($r = 0.92$, $p < 0.001$). The concentration of REEs in shoots was significantly correlated with concentrations of iron (Fe) and phosphorus (P), for example lanthanium: $r_s = 0.65$ for Fe, $r_s = 0.58$ for P ($p < 0.001$; Wiche & Heilmeier, 2016). Thus grass species seem to be good candidates as accumulator plants for Ge, whereas forbs seem to be better accumulators for REEs.

3 CHALLENGE: THE BIO-AVAILABILITY OF VALUABLE ELEMENTS IN THE SOIL

Finding energy crops with a high accumulation capacity for valuable elements is only one task in phytomining, which can be based on existing knowledge from plant nutrition about accumulation of "indicator" elements such as Si, Fe or P as shown above. A major limitation for the economic feasibility of phytomining in areas even with elevated soil concentrations of valuable elements is the low concentration of these elements which is usually found in the soil solution. Even in an area like the Erzgebirge ("Ore Mountains") in the Freiberg region with high concentrations e.g. of Ge (2.6 mg kg^{-1}) or REEs (e.g. lanthanium: 40 mg kg^{-1}), only some 8% of total Ge soil content and 30% of REEs could be assessed as plant available via sequential extraction (Wiche et al., 2017a). Therefore concentrations of plant available valuable elements in the soil solution are too low for accumulation of these elements in the above-ground plant tissues as required for an economically attractive phytomining procedure.

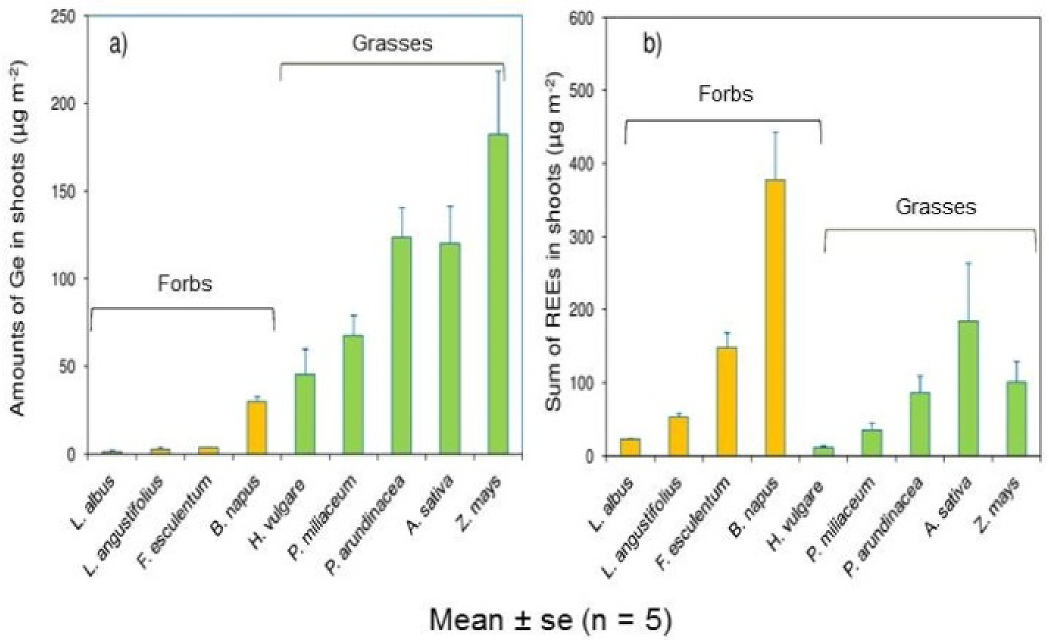

Figure 2. Accumulation of Germanium and Rare Earth Elements in various grass and forb species grown in the field (modified after Wiche & Heilmeier, 2016)

Traditionally there have been several agronomic approaches to enhance availability of metals for phytoextraction, such as addition of fertilizers and chelates or application of microorganisms (bacteria and mycorrhiza) to the soil (Sheoran et al., 2009, 2016; Naila et al., 2019). Whereas the artificial application of chelates such as ethylenediaminetetraacetic acid (EDTA) or (S, S′)-ethylenediamine-N, N′-disuccinic acid (EDDS) has been critisized for its potential environmental hazard already for several years (e.g. Hu et al., 2007; Ali et al., 2013), natural processes in the plant–soil system can be utilized for enhancing uptake of valuable elements by plants. Processes in the rhizosphere (the root–soil interface with physicochemical properties of the soil being heavily modified by plant roots and their associated microorganisms) are essential for enhancing bioavailability of elements such as (heavy) metals and metalloids (Seshadri et al., 2015; Ullah et al., 2015; Violante & Caporale, 2015; Sheoran et al., 2016; Abdu et al., 2017). These processes include the exudation of metabolites from roots, causing many chemical reactions in the rhizosphere such as changes in pH and redox potential, or sorption/desorption of cations and anions on/from soil colloids. Both plant roots and microbes can release siderophores, organic acids or enzymes that influence the solubility and bioavailability of heavy metals. Particularly legume species (e.g. lupine) can release organic acids such as citric and malic acid as chelating agents and acidify their root environment, thus enhancing bioavailability of limiting nutrients like phosphorus. This affects also the availability of Ge and REEs (Wiche et al., 2017b).

4. ACHIEVEMENTS

The problem of the low bioavailability of the target elements raises the question to what extent mixed cultures between metal(loid) accumulating plants and legumes such as lupine with their high root exudation activity can enhance the yield of phytomining activities by increasing accumulation of valuable elements in the target plants. In field experiments, mixed cultures of oat (*Avena sativa*) and white lupine (*Lupinus albus*) showed elevated concentrations of, e.g., iron, lanthanium and neodyme both in the soil solution and in the above-ground biomass of oat (Wiche et al., 2016a). The enhanced uptake of these elements by oat was accompanied by their depletion in the rhizosphere of white lupine (Wiche et al., 2016b). This shows the high relevance of biological processes in the rhizosphere for enhancing accumulation of valuable elements in target plants, which can be used by mixed cultures in agricultural practice.

However, accumulation of commercially valuable elements in (above-ground) plant biomass is the first step in phytomining only – elements have to be extracted again from the plant matrix. To that end, the plant matrix has to be digested, either by chemical agents, burning or microbial fermentation. Burning of biomass yields ashes, from which elements like Ge can be recovered via acidifying the ashes and distillation with HCl. After a further step – capturing $GeCl_4$ in an aqueous phase – changing the pH value of the medium yields the target product germanium dioxide (GeO_2) which can be sold on the market (Rentsch et al., 2016).

The second option – anaerobic microbial fermentation for producing biogas – was tested for reed canary grass (*Phalaris arundinacea*) which turned out to accumulate high amounts of Ge, but also REEs in some cultivars. Concentrations of Ge and REEs in the residues from the microbial fermentation were elevated by a factor of 100 compared to the original plant material. In addition to this positive effect on concentration of target elements, fermentation of reed canary grass biomass showed biogas yields which averaged 80% of maize silage. Thus there was a triple effect of microbial fermentation of this second generation energy crop accumulating trace elements: (i) high biogas yield, (ii) high yield of trace elements from the digested plant material, – and (iii) nutrients in the digestates to be used as fertilizer in closed material cycles.

5. CONCLUSION

After nearly 40 years of scientific experiments at different scales, phytomining is on the pathway to becoming an economically feasible alternative, particularly for elements whose concentration is too low for the huge investment of capital and environmental pollution associated with conventional mining. Rather valuable elements highly concentrated in soils or – probably applicable to a larger extent – ubiquitous elements which can be readily taken up by plants represent a promising target for plant-based extraction. However, for increasing the economic potential of phytomining, a number of essential steps is necessary to optimize and integrate individual processes (Fig. 3). First, valuable elements have to be accumulated in the target plants, which depends on several physiological processes such as root absorption, transport of elements to the shoot, distribution and sequestration in easily accessible shoot tissues. Second, the total amount of element heavily depends

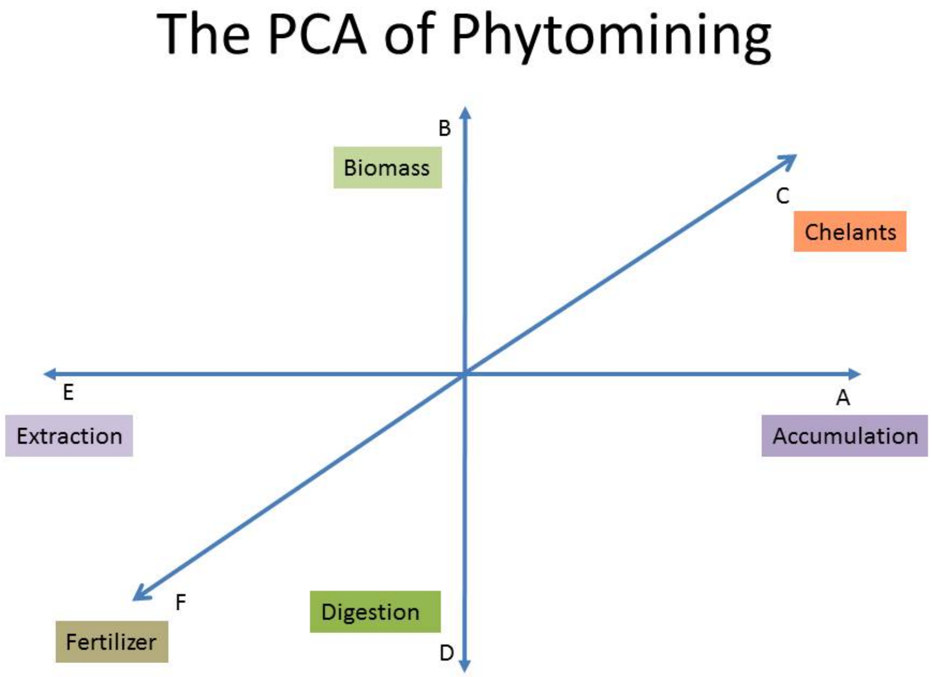

Figure 3. Principle Components of Phytomining

on plant biomass – therefore high-yielding (second-generation) energy crops are the best option. Third, availability of target elements in the soil has to be enhanced, e.g. by chelating or acidifying agents produced and exuded by plant roots and microorganisms in the rhizosphere. Fourth, the elements accumulated in the plant biomass have to be recovered, a process which can be supported e.g. by digesting the plant material via microbial fermentation. Fifth, various chemical procedures for extracting the valuable elements from the residues of the digestion process have to be applied in order to generate a product which can be sold on the market. Sixth, apart from the energy produced via biogas fermentation and the target elements extracted from the residues, nutrients can be recovered to be used as fertilizers back in the field, thus enhancing not only economic profit, but also closing material cycles and thereby improving the ecological balance of phytomining.

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REFERENCES

Abdu, N., Abdullahi, A.A. & Abdulkadir, A., 2017. *Heavy metals and soil microbes.* Environmental Chemistry Letters, 15, 65–84.

Ali, H., Khan, E. & Sajad, M.A., 2013. *Phytoremediation of heavy metals—concepts and applications.* Chemosphere, 91, 869–881.

Baker, A.J.M. & Brooks, R.R., 1989. *Terrestrial higher plants which hyperaccumulate metallic elements – a review of their distribution, ecology and phytochemistry*. Biorecovery, 1, 81–126.

Brooks, R.R., 1998. *Plants that Hyperaccumulate Heavy Metals.* CAB International, Wallingford (UK).

European Commission, 2010. *Critical Raw Materials for the EU.* Report of the Ad-Hoc Working Group on Defining Critical Raw Materials, Vol. 39. Brussels.

Gomes, L., Costa, J., Barbosa, B., Santos, F. & Fernando, A.L., 2019. *Is it feasible to produce energy crops in heavy metals contaminated soils?* European Biomass Conference and Exhibition Proceedings 2019, Pages 80–83.

Hu, N., Luo, Y., Wu, L. & Song, J., 2007. *A field lysimeter study of heavy metal movement down the profile of soils with multiple metal pollution during chelate-enhanced phytoremediation*. International Journal of Phytoremediation, 9, 257–268.

Jaffré, T., Reeves, R., Baker, A.J.M., Schat, H. & van der Ent, A., 2018. *The discovery of nickel hyperaccumulation in the New Caledonian tree Pycnandra acuminata 40 years on: an introduction to a Virtual Issue*. New Phytologist, 218, 397–400.

Kabata-Pendias, A., 2011. *Trace Elements in Soil and Plants*. 4th edition. Taylor & Francis, Boca Raton.

Krisnayanti, B., Anderson, C., Sukartono, S., Afandi, Y., Suheri, H. & Ekawanti, A., 2016. *Phytomining for artisanal gold mine tailings management*. Minerals, 6, 84.

Naila, A., Meerdink, G., Jayasena, V., Sulaiman, A.Z., Ajit, A.B. & Berta, G., 2019. *A review on global metal accumulators—mechanism, enhancement, commercial application, and research trend.* Environmental Science and Pollution Research, 1–23.

Nicks, L. & Chambers, M.F., 1995. *Farming for metals.* Mining Environmental Management, 3, 15–16.

Nkrumah, P., Tisserand, R., Chaney, R., Baker, A.J.M., Morel, J., Goudon, R., Erskine, P., Echevarria, G. & van der Ent, A., 2018. *The first tropical 'metal farm': Some perspectives from field and pot experiments*. Journal of Geochemical Exploration, 198, 114–122.

Pidlisnyuk, V., Stefanovska, T., Lewis, E. E., Erickson, L.E. & Davis, L.C., 2014. *Miscanthus as a productive biofuel crop for phytoremediation.* Critical Reviews in Plant Sciences, 33, 1–19.

Ranjan, V., Sen, P., Kumar, D. & Sarsawat, A., 2015. *A review on dump slope stabilization by revegetation with reference to indigenous plant.* Ecological Processes, 41, 14.

Rentsch, L., Aubel, I., Schreiter, N. & Bertau, M., 2016. *PhytoGerm: Extraction of germanium from biomass – An economic pre-feasibility study.* Journal of Business Chemistry, 13, 47–58.

Rosenberg, E., 2007. *Environmental speciation of Germanium*. Ecological Chemistry and Engineering, 14, 707–732.

Seshadri, B., Bolan, N.S. & Naidu, R., 2015. *Rhizosphere-induced heavy metal(loid) transformation in relation to bioavailability and remediation.* Journal of Soil Science and Plant Nutrition, 15, 524–548.

Sheoran, V., Sheoran, A.S. & Poonia, P., 2009. *Phytomining: a review.* Minerals Engineering, 22, 1007–1019.

Sheoran, V., Sheoran, A.S. & Poonia, P., 2016. *Factors affecting phytoextraction: a review.* Pedosphere, 26, 148–166.

Ullah, A., Heng, S., Munis, M.F.H., Fahad, S. & Yang, X., 2015. *Phytoremediation of heavy metals assisted by plant growth promoting (PGP) bacteria: a review.* Environmental and Experimental Botany, 117, 28–40.

Violante, A. & Caporale, A.G., 2015. *Biogeochemical processes at soil-root interface.* Journal of Soil Science and Plant Nutrition, 15, 422–448.

Wiche, O., 2016. *Plant Availability of Germanium and Rare Earth Elements in Soils*. PhD thesis, TU Bergakademie Freiberg.

Wiche, O. & Heilmeier, H., 2016. *Germanium (Ge) and rare earth element (REE) accumulation in selected energy crops cultivated on two different soils.* Minerals Engineering, 92, 208–215.

Wiche, O., Székely, B., Kummer, N.-A., Moschner, C. & Heilmeier, H., 2016a. *Effects of intercropping of oat (Avena sativa L.) with white lupin (Lupinus albus L.) on the mobility of target elements for phytoremediation and phytomining in soil solution.* International Journal of Phytoremediation, 18, 900–907.

Wiche, O., Kummer, N.-A. & Heilmeier, H., 2016b. *Interspecific root interactions between white lupin and barley enhance the uptake of rare earth elements (REEs) and nutrients in shoots of barley.* Plant and Soil, 402, 235–245.

Wiche, O., Zertani, V., Hentschel, W., Achtziger, R. & Midula, P., 2017a. *Germanium and rare earth elements in topsoil and soil-grown plants on different land use types in the mining area of Freiberg (Germany).* Journal of Geochemical Exploration, 175, 120–129.

Wiche, O., Tischler, D., Fauser, C., Lodemann, J. & Heilmeier, H., 2017b. *Effects of citric acid and the siderophore desferrioxamine B (DFO-B) on the mobility of germanium and rare earth elements in soil and uptake in Phalaris arundinacea.* International Journal of Phytoremediation, 19, 746–754.

Wiche, O., Székely, B., Moschner, C. & Heilmeier, H., 2018. *Germanium in the soil-plant system—a review.* Environmental Science and Pollution Research, 25, 31938–31956

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