Below-ground functional traits during nutrient-acquisition affect the availability of rare earth elements to plants

Oliver Wiche[1], Hermann Heilmeier[1], and Olivier Pourret[2]

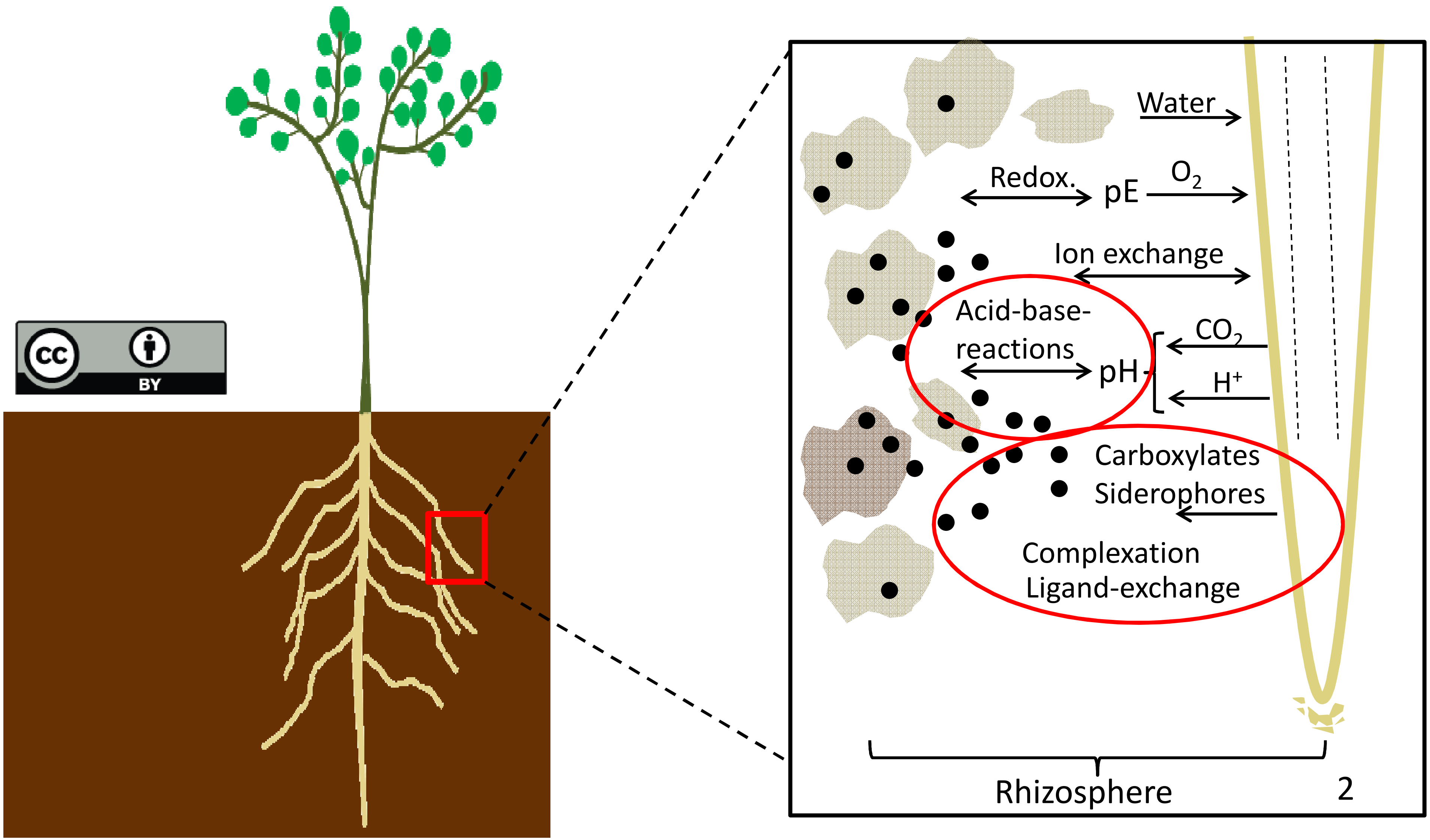
1 Institute for Biosciences, Biology/Ecology Unit

Oliver.Wiche@ioez.tu-freiberg.de

2 UniLaSalle, AGHYLE, Beauvais, France

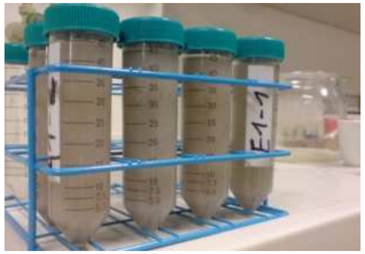
Rhizoshere effects on plant availability

Pflant availability = f (conc. in soil solution, chemical speciation, plant physiology)



Main research questions persued

1. What are the effects of root exudates (carboxylates, siderophores) and rhizosphere acidification on the mobility and speciation of REEs in soil?



2. How do changes in elemental speciation affect the uptake of Ge and REEs in plants?

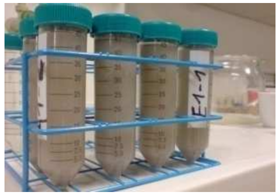
3. Do below-ground functional traits in nutrient acquisition influence the availability of Ge and REEs to soil-grown plants?

Methods I – Lab- and greenhouse-experiments

1. Mobilization and speciation of REEs – effects of artificial root exudates

Arable soil (pH 7,7) →

1, 10 mmol/l Citric acid (pH 5,8; 3,7)
100 µmol/l Desferrioxamine B (pH 7,5)
reference 1 (H_2O – pH 7,6)
reference 2 (HNO_3 – pH 3,7)



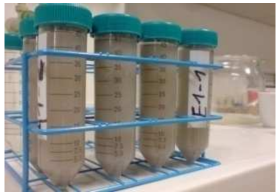
→ ICP-MS
LC-ICP-MS

2. Effects of artificial root exudates on the availability of REEs

Phalaris arundinacea (reed canary grass) → hydroponics →

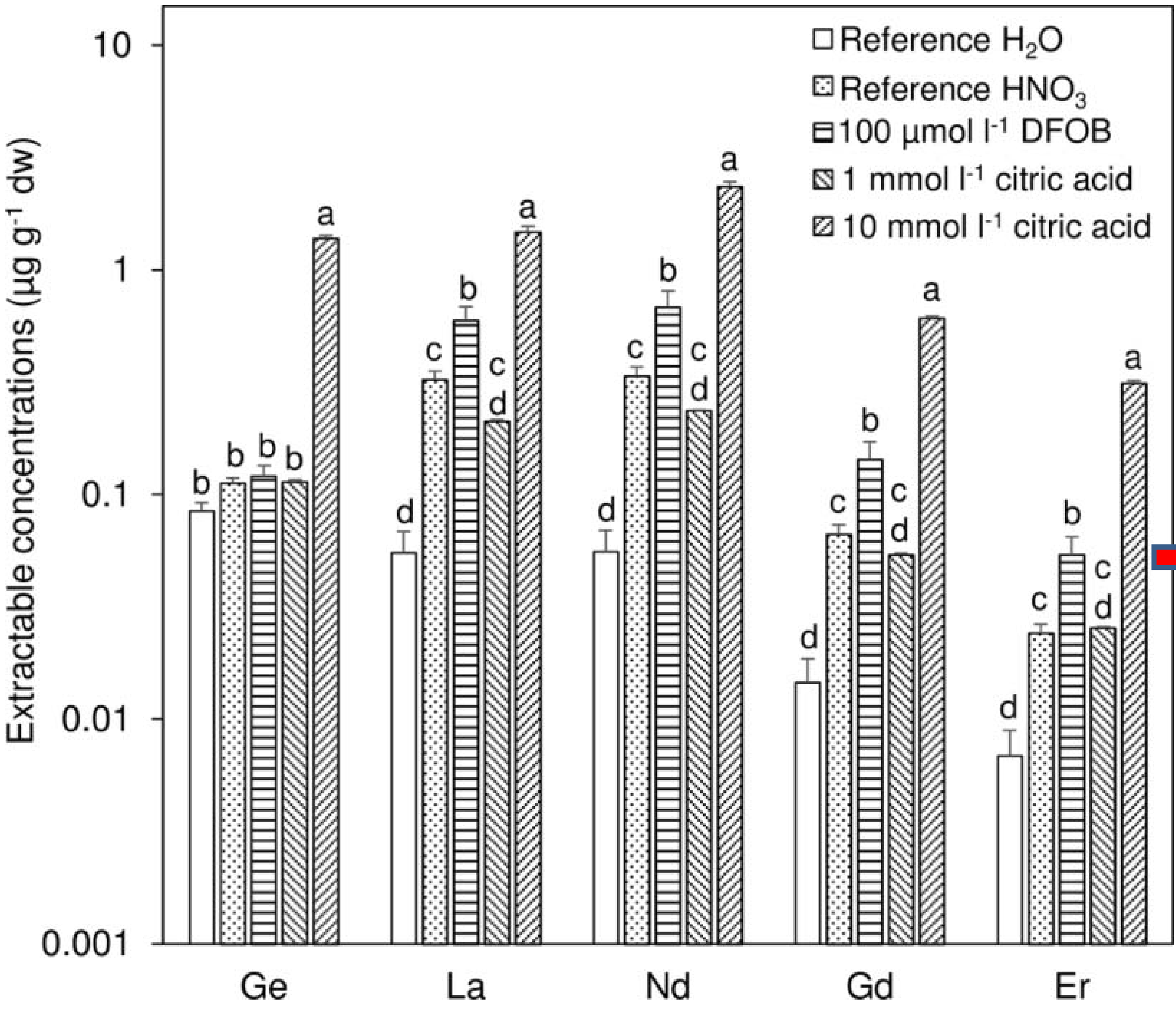
Single treatment with 0.5 l of
- 10 µmol/l Ge, La, Nd, Gd, Er
- 10 µmol/l Ge, La, Nd, Gd, Er
  + 100 µmol/l Citrate
  + 100 µmol/l Desferrioxamine B

96 h → ICP-MS
pH 6

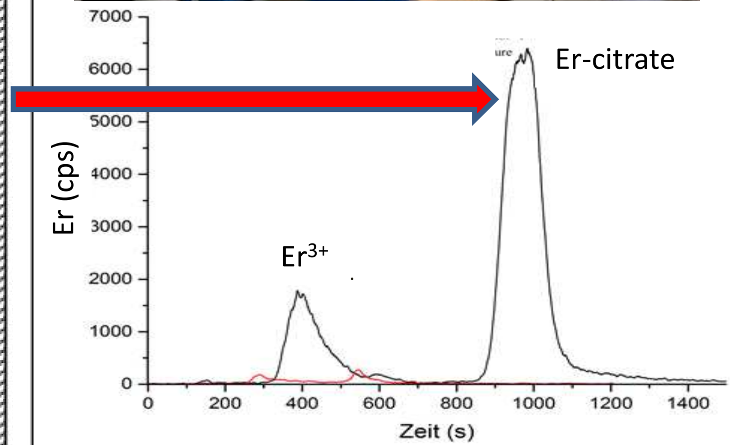


Results 1: Effect of artificial root exudates on the mobility and chemical speciation of Ge and REEs in soil

ICP-MS results of soil extracts

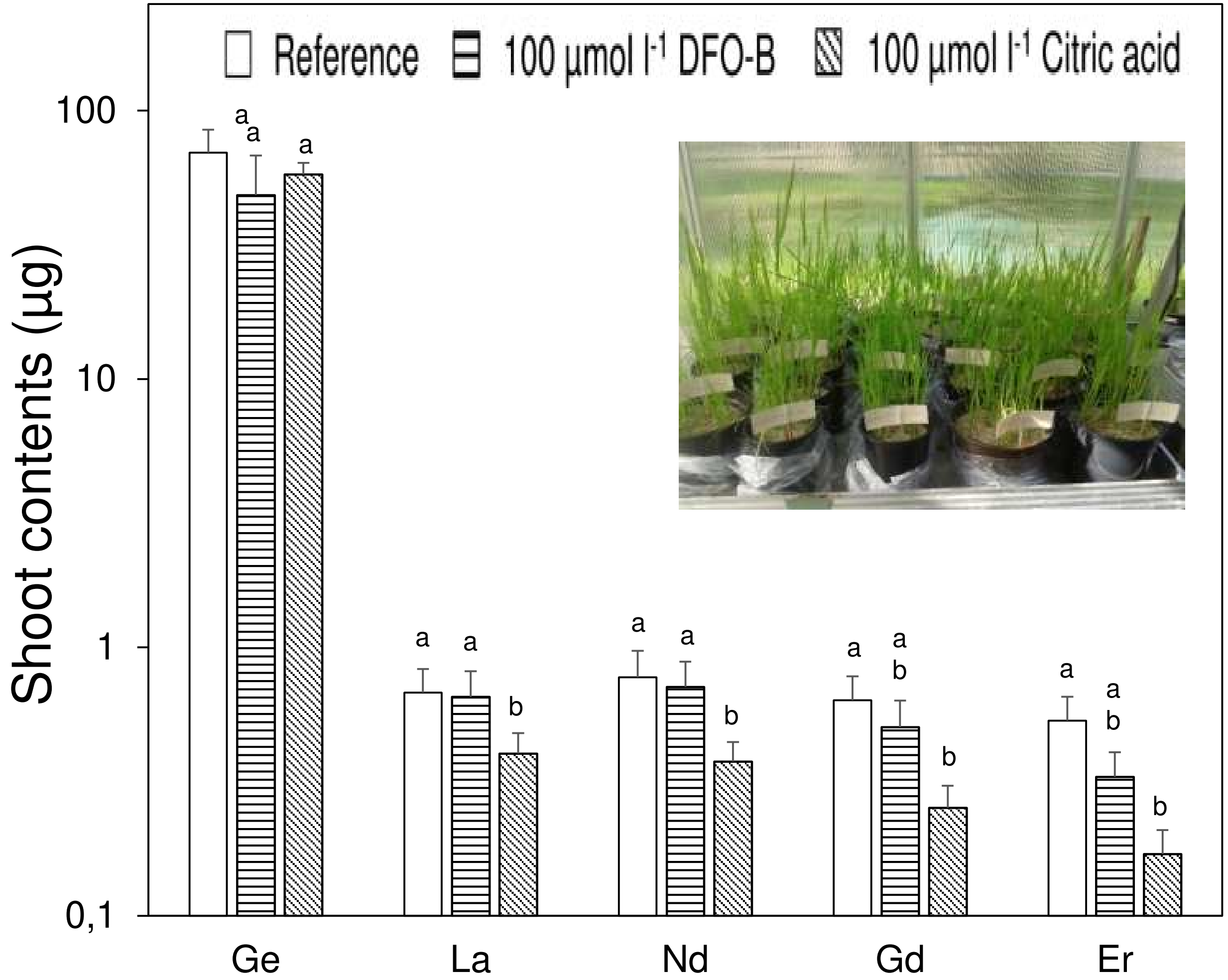


LC-ICP-MS of soil extracts



Wiche et al. (2017) International Journal of Phytoremediation 19, 746–754.

Results 2: Effect of elemental speciation on the uptake of Ge and REEs



→ Free REE-Ions as well as DFOB-REE complexes can be taken up by the plants while REE-carboxylate-complexes are discriminated relative to the ions during uptake.

Wiche et al. (2017) International Journal of Phytoremediation 19, 746–754.

Half-way mark summary

- Acidification and presence of citrate and DFOB increase mobility of REEs in the rhizosphere
- Carboxylate-complexes of REEs (and most probably also Ge) are not available due to a discrimination of the complexes during uptake

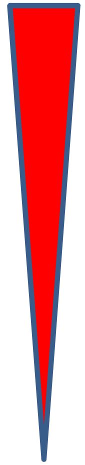
Methods II – field experiments

Soil texture	pH H_2O	SOM	Ge	La	Nd	Gd	Er
		%	mg/kg				
Ls	7,8	6,2	1,7	32	21	3,8	1,9

Forbs

- *Lupinus albus*
- *Lupinus angustifolius*
- *Brassica napus*
- *Fagopyrum esculentum*

P-efficiancy

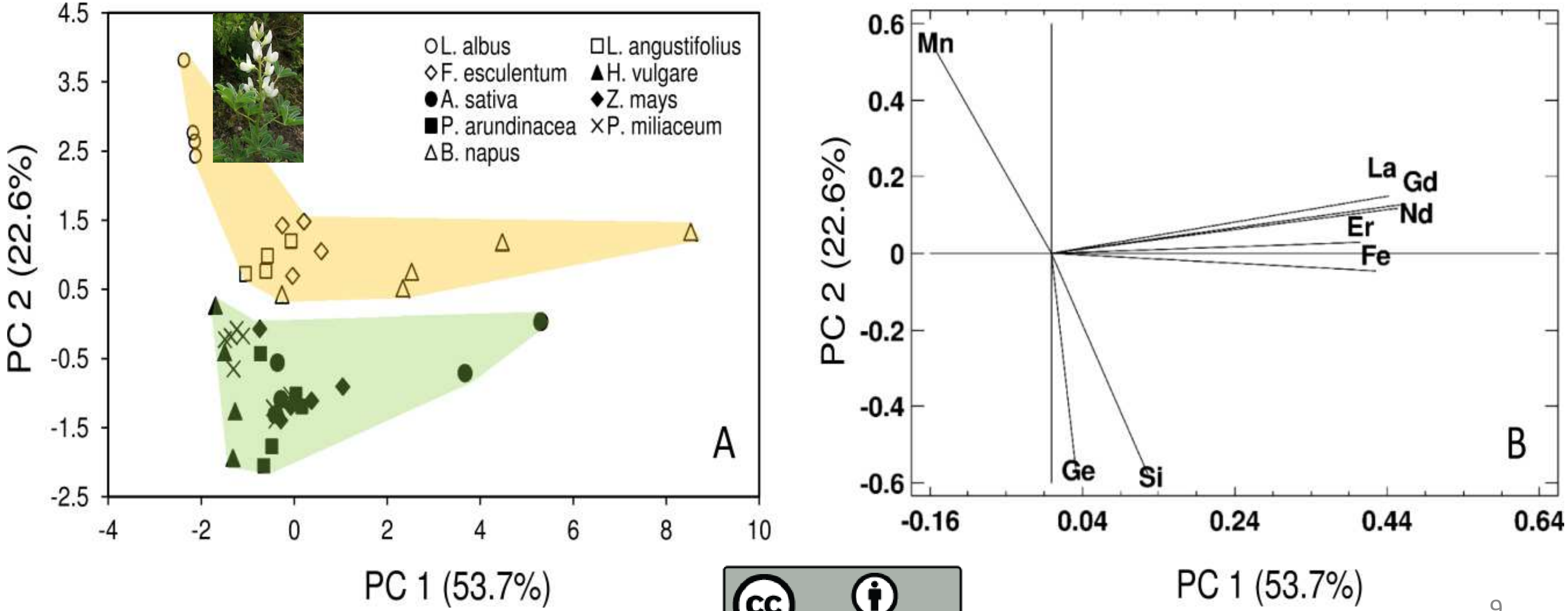


Grasses

- *Zea mays*
- *Avena sativa*
- *Hordeum vulgare*
- *Panicum miliaceum*
- *Miscanthus giganteus*
- *Phalaris arundinacea*
- *Miscanthus x giganteus*

Results 3: Effects of below-ground functional traits in nutrient acquisition on the accumulation of Ge and REEs in plants

Results of a PCA based on concentrations of Mn, Ge, Si, Fe and selected REEs in shoots of 9 plant species with different P-acquisition-strategies and –efficiencies



Wiche (2016)

Opinion

Leaf manganese accumulation and phosphorus-acquisition efficiency

Hans Lambers[1], Patrick E. Hayes[1], Etienne Laliberté[1], Rafael S. Oliveira[1,2], and Benjamin L. Turner[3,1]

[1]School of Plant Biology, The University of Western Australia, Stirling Highway, Crawley (Perth), WA 6009, Australia
[2]Departamento de Biologia Vegetal, Universidade Estadual de Campinas, Rua Monteiro Lobato 255, Campinas 13083-862, Brazil
[3]Smithsonian Tropical Research Institute, Apartado 0843-03092, Balboa, Ancon, Republic of Panama

Plants that deploy a phosphorus (P)-mobilising strategy based on the release of carboxylates tend to have high leaf manganese concentrations ([Mn]). This occurs because the carboxylates mobilise not only soil inorganic and organic P, but also a range of micronutrients, including Mn. Concentrations of most other micronutrients increase to a small extent, but Mn accumulates to significant levels, even when plants grow in soil with low concentrations of exchangeable Mn availability. Here, we propose that leaf [Mn] can be used to select for genotypes that are more efficient at acquiring P when soil P availability is low. Likewise, leaf [Mn] can be used to screen for belowground functional traits related to nutrient-acquisition strategies among species in low-P habitats.

Phosphorus-acquisition strategies

Here we explore the idea of using leaf [Mn] to indicate a carboxylate-releasing P-acquisition strategy. The rationale behind this contention is that the availability of both P and Mn are increased when roots release carboxylates into the rhizosphere [1] (Figure 1; see Glossary). The availability of some other micronutrients is also enhanced, but most of these do not lead to a signal as strong as that provided by Mn. The release of carboxylates into the rhizosphere is important for P acquisition, because they mobilise not only inorganic P, but also organic P, which can be a major fraction of soil P, especially when P availability is low [2].

Addressing this topic is timely, because there is a growing interest among plant ecologists in belowground functional traits, to complement the suite of 'easy-to-measure' aboveground traits [3]. Furthermore, because of the gradual decline in phosphate rock that is used to produce P fertilisers [4], there is an increasing need for more P-efficient cropping systems [5]. Therefore, a simple tool to screen for P-acquisition efficiency in crop species would be welcomed by agronomists and plant breeders.

Corresponding author: Lambers, H. (hans.lambers@uwa.edu.au).
Keywords: carboxylates; exudation; manganese; phosphorus; phosphorus-acquisition efficiency.

1360-1385/
 http://dx.doi.org/10.1016/j.tplants.2014.10.007

Manganese as a plant nutrient

The significance of Mn as an essential plant nutrient was firmly established in 1922 [6]. More recent work has revealed the role of Mn in redox processes, as an activator of a large range of enzymes, and as a cofactor of a small number of enzymes, including proteins required for light-induced water oxidation in photosystem II [7,8]. Crop plants that contain 50 μg Mn g^{-1} dry weight (DW) in their

Glossary

Arbuscular mycorrhiza: a type of mycorrhizal association that forms arbuscules or coiled hyphae (highly branched exchange structures) within cortical cells of the root.
Carboxylate: an organic anion, which is the organic acid minus the proton(s). For example, citrate is the carboxylate released from the deprotonation of the organic acid, citric acid.
Chelate: a compound that combines reversibly, usually with high affinity, with a metal ion (e.g., iron, copper, or manganese).
Cluster roots: bottle brush-like or Christmas tree-like structures in roots with a dense packing of root hairs, releasing carboxylates into the rhizosphere, thus solubilising poorly available nutrients (e.g., P) in the soil.
Ectomycorrhiza: mycorrhizal association, mostly in woody species, in which a fungal mantle covers fine roots.
Heavy metal: a metal with a mass density exceeding 5 g ml^{-1}.
Hyperaccumulating plant species: plants that typically accumulate 100 times more of a specific heavy metal than the concentrations that occur in nonaccumulator plants growing in the same substrates. For most elements, including Mn, the threshold concentration is 1000 μg g^{-1} DW, except for zinc (10 000 μg g^{-1}), gold (1 μg g^{-1}), and cadmium (100 μg g^{-1}).
Iron-regulated transporter (IRT): associated with the uptake of iron from the rhizosphere into root cells. It is not highly specific and transports other micronutrients.
Micronutrient: inorganic nutrients that a plant requires in relatively small quantities, such as copper, iron, Mn, molybdenum, and zinc.
Mycorrhiza: a structure arising from a symbiotic association between a mycorrhizal fungus and the root of a higher plant (from the Greek words for fungus and root, respectively; the Greek plural would be mycorrhizas, but the Latin plural (mycorrhizae) is also used).
Natural resistance associated macrophage protein (NRAMP): a divalent cation transporter associated with the uptake of transition metals, such as copper, iron, Mn, and zinc.
Nonmycorrhizal plant family: a plant family whose members predominantly are unable to establish a symbiotic association with a mycorrhizal fungus.
Rhizosphere: the zone of soil influenced by the presence of a root.
Scleromorphic: containing a relatively large amount of tough structures (sclerenchyma).
Sorption: the process referring to the binding of, for example, phosphate onto the surface of (i.e., adsorption) and inside (i.e., absorption) soil particles. The term was coined by McBain in 1909 [79]. In soil science, the noncommittal term 'sorption' is used to indicate all processes that result in the transfer of material from the soil solution to the solid phase.
Transition metal: any metal in the d-block of the periodic table, which includes groups 3–12 of the periodic table; the f-block lanthanide and actinide series are also considered transition metals and are referred to as 'inner transition metals'.

→ High shoot [Mn] indicates P-efficiency through exudation of large amounts of carboxylates

Rhizosphere properties of *L. albus*

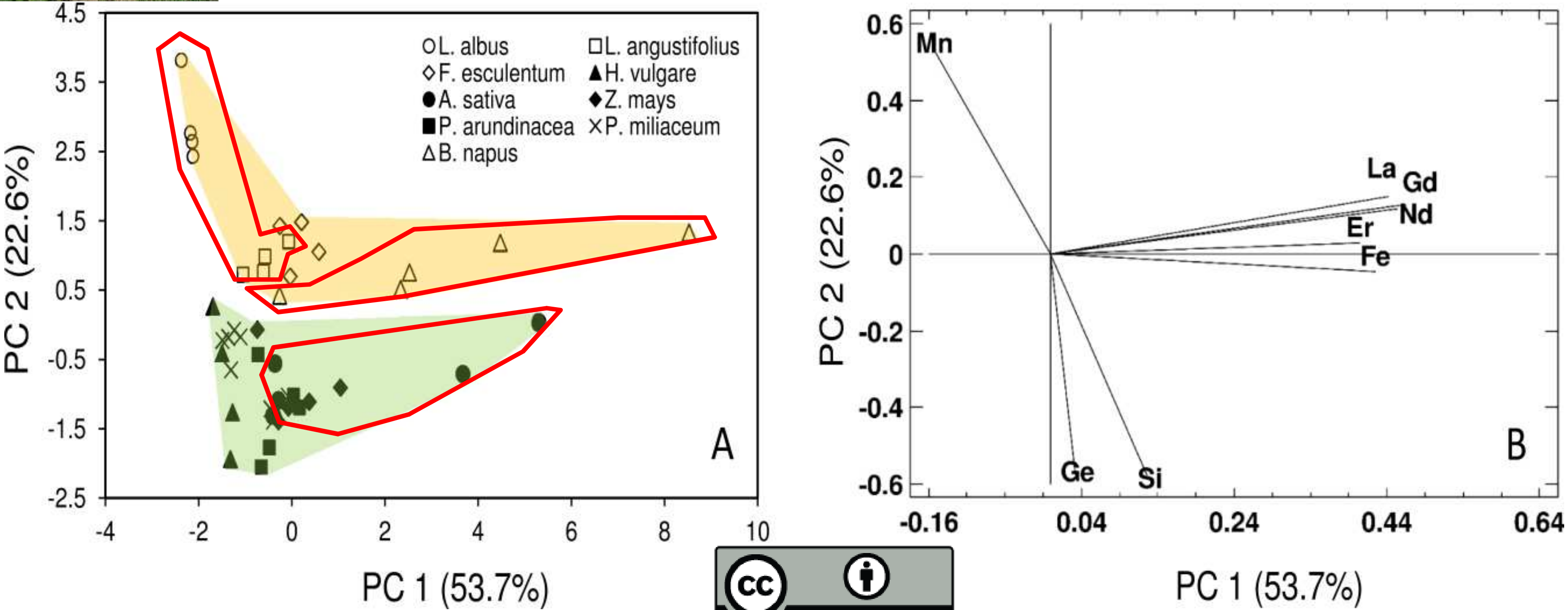
Water extractable element concentrations in bulk soil and rhizosphere soil of L. albus

	P	Fe	Mn	Ge	La	Nd
	μg l^{-1}					
Non-rhizosphere	1318	32249	192	1.5	15.3	12.4
Rhizosphere	506	7507	136	0.2	3.8	3.4

Carboxylate concentrations in bulk soil and rhizosphere soil of L. albus

	pH	Oxalate	Citrate	Malate	Laktate
		mg l^{-1}			
Non-rhizosphere	6.5 ± 0.1	1.2 ± 0.3	< 0.5	< 0.1	2.7 ± 0.5
Rhizosphäre	6.2 ± 0.1	3.3 ± 0.2	2.1 ± 1.4	0.2 ± 0.1	2.9 ± 1.8

Results 3: Variability of Ge and REE in plants – effect of rhizosphere properties?



- *L. albus* and *L. angustifolius* are P-efficient by releasing large amounts of carboxylates in the rhizosphere Hence, these plant species strongly mobilize REEs in the rhizosphere by the formation of soluble complexes. However, the complexes cannot be taken up by the plants resulting in very low REE concentrations.
- *B. napus* and *F. esculentum* do not deploy carboxylates to accesss P in soils. Instead these species acidify the rhizosphere followed by a strongly mobilization of REEs together with Fe and P. The mobilized REEs are not chelated by carboxylates and thus the free ions can be taken up by the plants resulting in high REE-concentrations in shoots.
- Grasses release siderophores to improve availability of micronutients (particularely Fe) in soils. This also increases mobility and uptake of REEs

Conclusions

- Availability of REEs (and Ge as well) is clearly controled by processes in the rhizosphere
- Ge accumulation in plants mostly follows a Si-acquisition strategy in grasses
- REE accumulation seems to depend on the chelation strength of root exudates and most probably depends on below-ground functional traits in Fe-acquisition
- In our current project we are exploring interactions between functional traits during nutirent acquisition (P, Fe) and REE-concentrations in plants along the Western Australian soil chronosequences. The outcome will improve our understanding in processes influencing REE-uptake and accumulation in plants. We hypothesize that concentrations and fractionation pattern of REEs could be potentially used as easy measureable indicators for nutrient accquisition strategies in the rhizosphere of plants.