Chapter 12.2

Element case studies: Copper & Cobalt

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Abstract Cobalt is economically considered as a critical metal. The main known Co ore deposits are found in the Katanga Copperbelt (Democratic Republic of Congo) where a high richness of Cu-Co tolerant and accumulator plants have developed. Cobalt mining has disseminated and disseminates large quantities of wastes in the environment and becomes a major environmental issue. Reduction of environmental risks and Co dispersion can be performed by phytoremediation and/or agromining, using trace element tolerant and putative hyperaccumulator plants originated from the biodiversity of natural Co/Cu-enriched habitats. Accumulation of foliar Co to $>300 \mu\text{g g}^{-1}$ is exceptionally rare globally, and known principally from the Copperbelt of Central Africa. This chapter highlights advances on Co accumulation in plants, examines the potential of a Co accumulator in agromining, and defines perspectives for Co agromining by designing multi-functions and services of agroecosystems by a functional plant traits approach.

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12.2.1 Introduction

Cobalt is one of the elements defined as a critical metal over the next 5–15 years (Pourret and Faucon 2016). Demand for Co increased considerably after the Second World War, driven by the use of high-purity Co in jet engines and gas turbines. Cobalt demand and corresponding production have further accelerated in the past thirty years. Indeed, it reflects the increased use of Co as an essential constituent of materials used in high-technology industries including rechargeable Li batteries, superalloys and catalysts (Crundwell et al. 2011). The main known ore deposits are found in the Katangan Copperbelt (Democratic Republic of Congo) where 48% of the known world reserves are identified. The Katangan Copperbelt acts as the major producer of cobalt (Fig.1) accounting 50.8% of the world production in 2015 (USGS 2016). Minor resources of Co originate from lateritic nickel mines worldwide (Decrée et al. 2015). The average cobalt price ranges from 25 000 to 30 000 US\$/t in the last couple of years (London Metal Exchange values).

Moreover, over a century, mining has disseminated large quantities of wastes in the environment and become a major environmental issue (Pourret et al. 2016). As a consequence, these activities have created secondary metalliferous substrates with elevated concentrations of trace elements including Co (more than 1000 times greater than the concentration in normal soil) (Faucon et al. 2011, 2012). Such exploitation results in huge occupation of soil (over 30 000 km²) and implies soil degradation (Dupin et al. 2013). In southeastern Central Africa, trace elements contamination constitutes a major environmental issue related to low pH of Ferralsol increasing trace elements mobility, intense erosion by rainfall in the rainy season, and aerial dispersal of metal particles by wind in the dry season (Pourret et al. 2016). Besides, Co is highly toxic and directly impacts human health, given as there is an elevated cobalt (Co) exposure in the general population of southern D.R. Congo (Banza et al. 2009, Cheyns et al. 2014, Squadrone et al. 2016).

Reduction of environmental risks and Co dispersion can be performed by phytoremediation and agromining, using trace elements tolerant and putative hyperaccumulator plants from the plant biodiversity of natural habitats enriched in Cu and Co (Ilunga et al. 2015; Boisson et al. 2015; Faucon et al. 2016). Agromining is an alternative treatment for contaminated soils, and an application of phytotechnologies to exploit secondary resources. Agromining was studied at field scale (Chaney et al. 2007; van der Ent et al. 2015; Bani et al. 2015), but is limited to Ni. Cobalt agromining may, therefore, be considered for Co-contaminated lands because 30 putative Co hyperaccumulator plants were highlighted in southeastern of DR Congo (Brooks et al. 1980; Reeves and Baker 2000; Faucon et al. 2007) and of the possible attainable yields and the high metal product value.

Cobalt accumulators present a high variation of foliar Co concentration that can be explained by genetic variation and chemical soil factors involved in Co availability (Lange et al. in press). Besides, Co accumulators present high functional diversity (i.e. in life cycles, lateral spreading capacity, type and depth of underground system, growth phenology, N symbiotic fixation, etc.)

(Ilunga et al. 2015) that has an influence on ecosystem processes such as biomass productivity, Co mobility and transfer, etc. (Faucon 2015). Cobalt agromining should consider intra and interspecific variation of leaf Co accumulation and functional plant diversity to design multi-functional and services of these new cropping systems.

In this chapter, we focus on putative Co hyperaccumulator plants and their implication in Co agromining. We review recent advances on Co accumulation, examine the potential of a Co accumulator in agromining and define perspectives for Co agromining by designing multi-functions and services of agroecosystem using a functional plant traits approach.

12.2.2 Variation in cobalt accumulation

Cobalt tolerant populations have been reported in the literature in several dozen species collected from nature (i.e. from Cu and Co steppic savanna), but the capacity to grow under elevated Co concentrations without toxicity symptoms or growth inhibition has less been demonstrated experimentally (Lange et al. in press). Cobalt accumulation variation has been demonstrated between three closely related *Silene* taxa (Baker et al. 1983). Cobalt accumulation exists in *Anisopappus chinensis* (Asteraceae) as foliar Co concentration increases in relation to Co soil concentration without a decrease of biomass or toxicity symptoms (Lange, 2016).

High inter and intraspecific variation of Co accumulation exists (Faucon et al. 2007, 2009, Lange et al. 2014). This high phenotypic variation of Co accumulation can be explained by variation Co total concentration in soil and chemical soil factors influencing Co mobility and availability (Faucon et al. 2009). The Cu-Co outcrops have high total soil Co concentrations (up to 3451 $\mu\text{g g}^{-1}$) from which a fraction is mobile (39–2146 $\mu\text{g g}^{-1}$) (Pourret et al. 2016). This permits high Co accumulation by *A. chinensis* (up to 2822 $\mu\text{g g}^{-1}$ foliar Co). Overall, the strong affinity of Mn oxides for Co may explain the lower Co mobility in Mn-rich soils (Collins and Kinsela 2011, Lange et al. 2014). Cobalt accumulation (in *Crepidiorhopalon perennis* (Linderniaceae) and *A. chinensis*) was strongly influenced by free Co and by Co adsorbed onto the OM and Fe oxide fractions (Lange et al. 2014).

The most tolerant taxon of *Silene* was the less accumulating for a given soil Co concentration. The intra-specific variation of Co accumulation by metallophytes from natural Co-enriched soils has not yet been tested. For the facultative metallophyte *Anisopappus chinensis*, the strong variation in the degree of Co tolerance between populations suggests intra-specific variation of accumulation (Lange 2016).

12.2 Potential of cobalt agromining

Cobalt agromining was proposed in last decade as a possibility using Ni-hyperaccumulator species on ultramafic soils (Homer et al. 1991). However, Ni limits the uptake of Co in most Ni-hyperaccumulator plants (Malik et al. 2000) and so negatively influences the performance

of Co agromining. Best candidate species for Co agromining are plants with elevated extracting yields (i.e. biomass x Co shoot concentration) and plants that are both tolerant to Cu and Co given as most Co tolerant plants grow in Cu-Co rich soils in southeastern of D. R. Congo.

Lange (2016) evaluated Co agromining potential using metallicolous populations of *A. chinensis* from Co-enriched soils presenting elevated leaf Co concentrations in nature (30–2822 $\mu\text{g g}^{-1}$). Mean of shoot biomass of individuals of *A. chinensis* ($n = 20$) was 0.8 g (range: 0.14–3.79 g). Biomass productivity (Y_{bio}) was estimated to 16 $\text{g/m}^2/\text{year}$ whether 160 kg/ha/year (range: 20–320 kg/ha/year). Total Co phytoextracted ($Y_{\text{Co}} = F_{\text{Co}} \cdot Y_{\text{bio}}$) /ha/year from a contaminated soil using plants of *A. chinensis* from “Fungurume V” was 176 g/ha/year (max: 864 g ha^{-1}) (Lange 2016). Due to the great variability of its ability to extract Co from the soil, agromining using *A. chinensis* should be improved by plant selection and genotyping (Chaney et al. 2007). Potentially, Co agromining could be improved by performing a multispecies system introducing other Co tolerant and accumulator species. Legume species such as *Crotalaria cornetii* (Fabaceae) which grows in natural and secondary metalliferous habitats (Leteinturier et al. 2002) can improve facilitation process and increase biomass productivity and potentially Y_{Co} . Such an innovative system on Co contaminated soils could lead to an increased phytoextraction yield as some species are known to accumulate Co in their shoots more effectively than *A. chinensis*, such as *Haumaniastrum robertii* (Lamiaceae, Co leaf concentration : 4000 mg kg^{-1}) (Morrison et al. 1981). This first evaluation on phytoextraction of soils contaminated by Co in Tropical Africa has shown limited achievable yields of Co phytoextracted. Perspectives would be to test it at field scale with a multi-species system, introducing functional diversity of Co-accumulator plants (species and populations) (Figure 2).

12.2.3 Functional plant diversity of cobalt agromining systems

In the last decade, considerable progress in ecology has been achieved due to the elaboration of the concept of functional traits. Functional traits are defined as “morpho-physio-phenological traits which impact fitness indirectly via their effects on growth, reproduction and survival” (Violle et al. 2007). Relationships between traits associated with the response of organisms to environmental factors such as resources and disturbances (response traits), and traits that determine effects of organisms on ecosystem functions (effect traits), are recently studied in few processes and ecosystem services (Garnier et al. 2016).

Phytoremediation and agromining generally attempt to study effects of species or species mixtures on ecological processes to restore and design ecosystems independently of a functional trait approach (Faucon 2015). Agromining based on taxonomical description does not allow quantifying effect of plant species on ecosystem processes and services. Challenge is to link recent literature on below and aboveground functional traits of plant and ecosystem processes such as trace element mobility, water transfer and sediment transport, to improve ecological engineering and associated services, especially agromining yield, landscape

restoration, reduction of trace element transfer and water contamination, carbon sequestration, etc.

From 30 putative Co accumulators that present high variability of morphology, life cycle and physiology (Ilunga et al. 2015; Malaisse et al. 2016), several traits could be selected to develop multifunctional Co agromining system.

12.2 Plant functional diversity to improve Co agromining

In Co accumulators, functional divergence of root traits should be considered to improve biomass productivity and yield of Co agromining. Effectively, the intercropping with functional diversity of crop species corresponds to temporal and spatial niche differentiation in resource acquisition for these species, associated with an increase in productivity compared to a monoculture (Li et al. 2014; Faucon et al. 2015). Spatial niche differentiation associated with root morphology and the capability to exploit nutrient in soils can also explain the way in which species colonize the soil profile and the total soil volume occupied by the crop (Lynch 2011). Physiological root traits should also be considered to improve Co agromining yield, especially root-induced processes such as proton and/or carboxylate releasing which would directly affect Co availability in rhizosphere (Lange et al. in press). In contrary to functional diversity (FD) of root traits, FD of leaf traits and plant height can present a negative effect on biomass productivity explaining by an increased light competition.

12.2 Plant functional traits involved in landscape restoration, and Co transfer

Traits of perennial cycle, high lateral spreading capacity and growth phenology at the dry season, will be prioritized to develop a dense cover to restore landscape, reduce runoff and soil erosion and thus, Co transfer (Egoh et al. 2011). Functional diversity (FD) should be considered to improve these ecosystem services, such as FD of deep underground system, to improve root density and thus soil cohesion and stability (Gyssels et al. 2005), of growth phenology (both dry and rainy seasons) (Ilunga et al. 2015).

12.3 Conclusions

The application of Co accumulator plants in agromining is limited because their accumulation characteristics mean that only in soils with high concentration of available Co plants may yield sufficient accumulation in the shoots to develop this technology. Cobalt agromining may be considered for strongly Co-contaminated soils and tailings, because Co is economically considered a critical metal (Gunn 2014). Perspectives are to understand relationships between plant functional traits and ecosystem processes/services, to design multi-functional and multi-services agromining systems.

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FIGURE CAPTIONS

Figure 1. Production of cobalt (data collected from mineral commodity summaries yearly published by USGS).

Figure 2. A few putative Co accumulator plants. A: *Anisopappus chinensis* Hook.f. & Arn. (Asteraceae) © Lange B, B: *Haumaniastrum robertii* (Robyns) P.A. Duvign. & Plancke (Lamiaceae) © Faucon M-P, C: *Crepidorhopalon perennis* (P.A. Duvign.) Eb. Fisch. (Linderniaceae) © Faucon M-P, D: *Buchnera henriquesii* Engl. (Orobanchaceae) © Séleck M, E: *Acalypha cupricola* Robyns (Euphorbiaceae) © Lebrun J., F: *Triumfetta welwitschii* Mast. (Malvaceae) © Séleck M.

FIGURE 1

FIGURE 2