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Copper and cobalt mobility in soil and accumulation in a metallophyte as influenced by experimental manipulation of soil chemical factors

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HIGHLIGHTS

- Organic matter supply decreased Cu mobility and accumulation in *Anisopappus chinensis* at 500 mg kg^{-1} Cu.
- Oxides of Fe and Mn supplies had little effect on Cu–Co mobility in soil and accumulation by plants.
- Anisopappus *chinensis* maintains high foliar Cu–Co without effect on growth while increasing Cu–Co mobility.
- *Anisopappus chinensis* is added to the short list of candidate cuprophytes for Cu–Co phytoremediation.

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ABSTRACT

The influence of Fe oxides, Mn oxides and organic matter (OM) on the Cu and Co mobility in soil and accumulation in the metallophyte *Anisopappus chinensis* (*Ac*), as compared with *Helianthus annuus* (*Ha*), was experimentally investigated. Growth and accumulation response when increasing the exchangeable Cu and Co concentrations in soil were also investigated. Plants were cultivated on soil where concentrations of Cu, Co, Fe oxides, Mn oxides and OM content were varied according to 36 treatments. The OM supply decreased the Cu mobility and increased the Co mobility, resulting in decreasing the foliar Cu of *Ac* and increasing the foliar Co of *Ha*. The Fe oxides supply could increase the Cu accumulation for *Ac*, but was not verified for *Ha*. Compared with *Ha*, *Ac* increasingly accumulated Cu and Co without negative effect on plant growth while increasing Cu and Co mobility to phytotoxic concentrations. The results revealed promising perspectives for the use of *Ac* in Cu-contaminated environment phytoremediation applications.

1. Introduction

Soil contamination by metals is critically increasing and has become a major environmental issue (Alloway, 1995; Smith and Huyck, 1999; Baize and Tercé, 2002). The Democratic Republic of Congo (DR Congo) is a region of intensive mining activities, especially in the province of Katanga, where a succession of natural Cu and Co outcrops occurs. These remarkable geological formations, where soil Cu and Co concentrations can reach tens of thousands of mg kg^{-1} (Duvigneaud, 1958), have become an epicentre of Cu and Co extraction. Katanga accounts for 5% and 47.5% of the world production of Cu and Co, respectively (USGS, 2014). Mining and ore-processing activities have contaminated the environment over huge areas, with negative impacts on human health (Banza et al., 2009).

In this context, new types of metalliferous habitats have appeared where the soil can be 1000 times more concentrated in Cu and Co than “normal” soils (Ernst, 1974; Baker et al., 2000;

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Reeves and Baker, 2000). These secondary metalliferous sites represent important sources of pollution, especially in sub-tropical regions. Indeed, the risk of metallic transfers through runoff and erosion is increased due to high rainfall (1200 mm) and the long dry season. It is therefore essential to find solutions to remediate these pollutions, and phytoremediation processes represent innovative solutions. Such techniques require the use of highly metal-tolerant plants. The vegetation of copper hills in Katanga hosts a large number of metal-tolerant species, referred to as cuprophytes (Duvigneaud and Denaeyer-De Smet, 1963; Ernst, 1974, 1990; Faucon et al., 2012a; Ilunga wa Ilunga et al., 2013; Séleck et al., 2013) and cobaltophytes (Duvigneaud, 1959). Among them, some are able to hyperaccumulate Cu and/or Co in their natural habitats (Brooks et al., 1986; Baker and Brooks, 1989; Reeves and Baker, 2000; Reeves, 2006; Faucon et al., 2007, 2009; Lange et al., 2014). Recently reviewed hyperaccumulation thresholds classified Cu and Co hyperaccumulators as species able to accumulate actively these metals in leaves at a level above 300 mg kg^{-1} (van der Ent et al., 2013).

Cuprophytes and cobaltophytes represent a fruitful pool of plant diversity for Cu and/or Co phytoremediation applications. However, in-depth knowledge of Cu and Co tolerance and accumulation are essential when envisaging phytoremediation of Cu- and Co-contaminated soils. Copper tolerance has been extensively studied, but little is known about Cu and Co tolerance among metallophytes from Cu- and Co-rich soils (Brooks and Malaisse, 1990; Harper et al., 1997, 1998; Faucon et al., 2012b). Moreover, Cu tolerance has been experimentally demonstrated only for cuprophytes from Katanga: *Haumaniastrum katangense*, *H. robertii*, *Aeolanthus biformifolius* (Lamiaceae) (Morrison et al., 1979; Chipeng et al., 2010; Peng et al., 2012); *Mimulus guttatus* (Scrophulariaceae) (Allen and Sheppard, 1971; Macnair, 1983); *Silene cobalticola* and *S. vulgaris* (Caryophyllaceae) (Baker et al., 1983; Song et al., 2004); and China: *Elsholtzia haichowensis* and *E. splendens* (Lamiaceae) (Jiang et al., 2004; Lou et al., 2004; Song et al., 2004), and has been demonstrated for Co only for *S. cobalticola* (Baker et al., 1983).

The ecology and evolution of Cu and Co accumulation and tolerance in these metallophytes remains poorly understood. In particular, many cuprophytes show extensive phenotypic variation of Cu and Co accumulation in their natural sites (Faucon et al., 2009; Lange et al., 2014) and some can be defined as 'facultative hyperaccumulators' (i.e. that hyperaccumulate metal when occurring on metalliferous soils, yet also grow on non-metalliferous soils) (Pollard et al., 2014). For example, Cu and Co levels in shoots of *Crepidorhopalon tenuis* (pseudometallophyte from Katanga) range from 80 to 1400 mg kg^{-1} and 61 to 1105 mg kg^{-1}, respectively (Faucon et al., 2009). Such variations for Cu can be genetic, especially due to genetic differentiations among populations (Faucon et al., 2012b; Peng et al., 2012). However, this also suggests an influence of soil factors on Cu and Co accumulation. The soil factors governing the accumulation patterns of Cu and Co in cuprophytes are poorly understood. Soil chemical parameters like pH, redox potential, OM quality and quantity, oxides, clays, sulfides and carbonates are known to influence metal mobility in soils (Kabata-Pendias and Pendias, 2001). In metalliferous soils, Cu may be adsorbed by OM and Fe oxides (FeOx) (Pourret et al., 2015a). The affinity of Cu for organic matter (OM) is well documented and it has been reported that insoluble OM with high molecular weight can reduce the Cu mobility in acidic conditions (Chirenje and Ma, 1999; Kumpiene et al., 2008). The stability of Cu in soils is also known to be more efficient in FeOx-amended soils (Kumpiene et al., 2008). In contrast to Cu, Co in metalliferous soils is mostly bound to Mn oxides (MnOx) (Lange et al., 2014; Pourret et al., 2015a); previous studies reported this strong affinity in acidic conditions (McKenzie, 1970; Childs, 1975; Li et al., 2004; Tongtavee et al., 2005; Luo et al., 2010).

Therefore, the availability of Cu and Co in soil can be indirectly driven by the complex interplay of many soil chemical parameters, including the mineralogical context, and ecological processes driving OM concentration in the soil. Variation in metal accumulation in plants may thus be strongly dependent on a broad range of factors, beyond the concentration of Cu and Co themselves. A previous study (Lange et al., 2014) explored the phenotypic variation of Cu and Co accumulation in *Anisopappus chinensis* (range: 4 to 2821 mg kg^{-1} and 3 to 1334 mg kg^{-1}, respectively), collected *in natura* among strongly pedogeochemically contrasted sites. It was found that metal accumulation in plants was influenced not only by the free Cu and Co concentration in the soil solution. Copper bound to MnOx and Co bound to OM represented a significant pool of available Cu and Co for plants. The concentrations of Cu and Co bound to FeOx also had a positive influence upon the Cu and Co accumulation variations, respectively.

This study aimed to test experimentally the influence of FeOx, MnOx and OM supply on (i) Cu and Co mobility in soil and (ii) Cu and Co foliar accumulation in *A. chinensis*. We also examined (iii) the plants' response, in terms of shoot biomass production and Cu and Co accumulation according to an increase of the Cu- or Co-exchangeable soil concentration. Our working hypotheses are as follows: (i) the OM and FeOx supply negatively affect the Cu mobility; (ii) the MnOx supply negatively affects the Co mobility; (iii) the MnOx and OM supply positively affects the Cu and Co accumulation in plants, respectively; (iv) variation in mobility of Cu and Co will translate into corresponding variation in accumulation in leaves; (v) increasing Cu or Co in soil increases Cu or Co in leaves, respectively, without plant growth inhibition.

2. Materials and methods

2.1. Plants and soil origin

Anisopappus chinensis L. Hook.f. & Arn. (Asteraceae, subfam. Asteroideae, tribe Anthemidae) is widely distributed in tropical Africa. It is a perennial pseudometallophyte (i.e. occurring both on metalliferous and non-metalliferous soils), widespread on the copper hills of Katanga and in the surrounding Miombo woodlands. The metallicolous populations exhibit broad variation in the Cu and Co concentrations in leaves *in natura*, as described in the introduction. The seeds of *A. chinensis* were collected from the Niamumenda copper hill population (GCSWGS84 DD: S 11.60492°; E 27.29400°) (Katanga, DR Congo). This region of South-Central Africa is characterized by a subtropical humid climate including a rainy (November to March) and a dry season (May to September). *Helianthus annuus* L. var. Sunspot (Asteraceae, subfam. Asteroideae, tribe Anthemidae), was chosen as a well-known non-tolerant control species (Chakravarty and Srivastava, 1992); seeds were commercially purchased (Sluis Garden).

The soil for the pot experiment was obtained from the upper 20 cm of a Luvisol from homogeneous old forest area (Beauvais, France, coordinates: N 49°28′13.88″, E 2°4′0.45″). The soil was sieved (5 mm) and mixed with river sand to obtain 20% sand. The soil was analysed by Acme Analytical Laboratories Ltd. (Vancouver Canada), accredited under ISO 9002. Briefly, 0.25 g soil was heated in HNO_3–$HClO_4$–HF to fuming and taken to dryness; the residue was further dissolved in HCl solution and diluted with ultra-pure water before Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) measurements. According to data quality result assessment, the measurement accuracy was estimated at ±5% for all the considered elements. The total concentrations of Cu, Co, Fe_2O_3 and MnO were respectively 5.5; 6.2; 24 400 and 850 mg kg^{-1}. The soil