## Relation between cobalt fractionation and its accumulation in metallophytes from South of Central Africa

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Metallophytes are plants that mostly occur on metal-rich soils. Some metallophytes grow particularly on soils contaminated by Co, especially in South of Central Africa. *Crepidorhopalon perennis* and *C. tenuis* show a variable ability to accumulate Co in shoots, which can be explained both by synergistic and antagonistic interactions among several trace metals [1]. In fact, Co accumulation in shoots is favoured by high Co concentrations and hampered by high concentrations of Fe and Mn in soils [2].

In this study, we focus on Co fractionation in soil in order to explain the large variation in Co accumulation in Crepidorhopalon perennis and C. tenuis species, and also the interactions among various trace metals. Organic matter, pH as well as total (using the mixture HF-HCl-HClO<sub>4</sub>) and extractable (acetate-EDTA 1 mol/L, pH=4.25) concentrations of Mn, Cu, Co, Fe, Ca, Mg and Zn, were measured. Cobalt fractionation was furthermore modelled using Windermere Humic Aqueous Model (WHAM 6) [3]. Positive correlation between sum of organic and free Co concentrations estimated by WHAM 6 and concentrations of extractable (acetate-EDTA) Co was found. Furthermore, fractionation modelling shows a strong affinity of Mn-oxides for Co, which can explain the lower Co levels in the plants grown on Mn-rich soils. The high Mn and Fe status of Cu-Co soil in South of Central Africa may actually exert a protective effect against the toxic effects of Co.

[1] Faucon *et al.* (2007) *Plant Soil* **301**, 29-36. [2] Faucon *et al.* (2009) *Plant Soil* **317**, 201–212. [3] Lofts & Tipping (1998) *GCA* **62**, 2609-2625.

## Bioavailability of tungsten in soils and tailings of mining areas with distinctive paragenesis (Northern Portugal)

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This paper compares five mining areas of Northern Portugal with distinctive paragenesis (Ervedosa Mine with cassiterite and diverse sulphides; Rio de Frades Mine and Regoufe Mine with wolframite, scheelite, cassiterite and sulphides; Adoria Mine with volframite, cassiterite and sulphides; and Tarouca Mine with scheelite, cassiterite and sulphides) for bioavailable levels of tungsten in soils and the resulting bioaccumulate levels in six species of plants (*Erica arborea* L., *Halimium umbellatum* (L.) Spach, *Pinus pinaster* Aiton, *Pteridium aquilinum* (L.) Kuhn, *Pterospartum tridentatum* (L.) Willk. e *Quercus faginea* Lam.).

The mechanisms relating to the mobility and bioavailability of this metal have been explored using sequential chemical extraction techniques. The procedure adopted in this study allows the separation of the water-soluble fraction, so the extracted chemical elements must be considered highly bioavailable because they are easily mobilised. The elements extracted from the so-called exchangeable fractions, which in this study were leached through the use of NH<sub>4</sub> OAc, are an important part of the potentially available elements and can be considered as an estimate of bioavailability.

Tungsten appears to be relatively immobile in most studied sites, but soils of Tarouca mine show significant increases in bioavailable fraction.

The soils of the Tarouca mine area stand out by their higher content of W in the bioavailable fraction. Probably as a result of easier fragmentation and dissolution of scheelite, compared to wolframite. This is reflected in the bioaccumulated concentrations in the tissues of the studied species at this site. It's in the samples of Tarouca mine that occur higher bioaccumulated levels of W than all five mines. This exemplifies the importance of soil mineralogy, controlling the biogeochemical distribution of elements.

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