Heavy metal distribution in minesoils and accumulation in plants growing in a Pb/Zn-mining area in NW Spain

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The aim of this study was to detect metal-tolerant plants with potential for phytotechnologies. For this we evaluate the distribution and chemical fractionation of heavy metals in soil and their accumulation by plants growing in an old Pb/Zn mine in NW Spain. Minesoils (I=0-20 cm, II=20-40 cm) and shoots of the dominant plants (*Cytisus scoparius, Cytisus multiflorus, Betula celtibérica y Salix atrocinerea*) were obtained from 39 sampling points on a (100m x 100m) regular grid. Soils (<2 mm fraction) and plant tissues were digested with a mixture of concentrated HNO3:HCl in a microwave oven, and total concentrations of metals (Zn, Pb, Cd, Cu, Cr, and Co) were analysed by AAS. A metal fractionation scheme was carried out following a modified BCR protocol which targets the following metal fractions: exchangeable (1M NH_4Cl, 16h); carbonate-bound (0.11M CH_3COOH, 16 h); iron and manganese oxide-bound (reducible; 0.10M NH_2OH. HCl adjusted to pH 2.0, 16 h); organically bound and sulphide metals (oxidisable; 1M NH_4OAc adjusted to pH 2.0, 16 h) and residual (silicate-bound; acid digestion as above). Metals were analysed in each extraction by AAS. Total metal contents in minesoils presented a high level of heterogeneity and an overall pollution with Zn, Pb and Cd was shown. We found values ranging from 340-52000 mg kg^{-1} for Zn, 46-6100 mg kg^{-1} for Pb, 2-95 mg kg^{-1} for Cd, 21-160 mg kg^{-1} for Cu, 5-41 mg kg^{-1} for Ni, 2-21 mg kg^{-1} for Cr, and 5-27 mg kg^{-1} for Co. Although there was a great variability, the residual fraction was dominant, representing generally more than 50% of total Cd, Zn, and Pb. Of the non-residual fractions, Cd was detected in both exchangeable and oxidisable pools, while carbonate-bound and reducible fractions represented a minor percentage of the total concentration. The maximum concentrations of metals were detected in Salix atrocinerea (800 mg kg^{-1} for Zn, 4.2 mg kg^{-1} for Cd and 29 mg kg^{-1} for Cu) and Citisus scoparius (19 mg kg^{-1} for Pb). Betula celtiberica and Salix atrocinerea were Zn- and Cd-accumulator species (Bioaccumulation Factors (BF) of up to 44 and 30 for Zn and Cd, respectively), so that could be useful species in phytoextraction processes. On the other hand, Citisus scoparius and Citisus multiflorus were metal-excluder species, and could be interesting in the process of phytostabilization and revegetation of contaminated soils.

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