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Bioavailability and geochemical forms of Pb and Zn in Kosovo contaminated soils

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Mitrovica area (northern Kosovo) presents contamination by PTE in agricultural soils caused by smelter emissions and their transfer and accumulation in cultivated plants. Soil A and B, sampled from two sites in Mitrovica municipality, showed a total content of Pb and Zn of 2153 and 3087 mg kg^{-1}, and 3214 and 4619 mg kg^{-1}. A pot experiment was performed to understand the phytoremediation potential of two non-food crops (Sorghum bicolor L. Moench and Brassica napus Westar), chosen for their economic importance and heavy metal accumulation capacities. Bioconcentration factor, translocation factor and tolerance Indexes clearly indicated a better performance of canola in tolerating Pb and Zn, especially in soil B, even if contained higher amounts of both metals. To evaluate different chemical and physical forms of Pb and Zn in the two soils, a modified BCR extraction scheme was employed to determine amounts bound to different soil components: exchangeable fraction (acid-soluble, carbonate and exchangeable bound), reducing fraction (metal bound to Fe- or Mn-oxides), oxidizable fraction (organic and sulphide bound), and residual fraction (strongest binding with crystalline structure). A comparison of the sum of Pb and Zn concentrations obtained from BCR relative to total digestion values (pseudo-total concentrations) showed recoveries close to 100%. Very small amounts of Pb were released during step 1 (exchangeable fraction) (6,86% - soil A and 2,12% - soil B). The highest concentration of Pb, 62,62% in soil A and 56,68% in soil B, decreased in the reducing fraction (step 2), probably occurring mainly as forms bound to Fe/Mn oxides. Step 3 (oxidizable-organic matter “OM” and sulphides) released amounts of 23,15% and 20,32% of total Pb in soil A and B. Residual fraction presented very different amounts of Pb (7,87% in soil A and 20,88% in soil B). Unlike Pb, no important differences were found in the distribution of Zn among the various fraction of the two soils, with the greater amounts contained in the exchangeable fraction of both soils, 31.11% in soil A and 21.92% in soil B. Very small amounts of Zn were released during step 2 (19,3% in soil A and 22,27% in soil B) whereas step 3 released the highest amounts of Zn in both soils (36,56% in A and 40,17% in B). Residual fraction presents similar amounts of total Zn, 13,03% in A e 15,64% in B, showing an opposite trend with respect to Pb. So, a major portion of total Pb was associated to the reducing fraction, while Zn was found mostly in oxidable one, indipendent on the origin of samples. Pb strongly interacts with Fe-/Mn oxides, and, in soil B, a greater amount is immobilized in the residual fraction. These results suggest lower mobility and bioavailability of Pb in soil B with respect to soil A, partially explaining the pot experiment.