



## **Assessment of lead(II) fractionation in high altitude karst soils in Croatia**

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The mobility and distribution of Pb<sup>II</sup> and selected trace metals were studied in soils polluted by anthropogenic Pb in Croatian high altitude karst soils. The studies was performed on characteristic soil profiles which have been polluted by Pb from atmospheric deposition. The study was conducted by application and comparison of various methods for Pb<sup>II</sup> determination in various mineral fractions of soil, which included extractions with water, salt solutions including KCl and DCB, mixtures of, concentrated acids and the harmonized optimized BCR sequential extraction procedure. Lead isotopes were used to calculate anthropogenic sources of Pb and the depth of Pb migration in the soil profiles.

Calculated enrichment factors based on the metal/Sc ratios indicate that all analyzed soil profiles are polluted with lead to the depth of 25 cm. The lead isotope ratios <sup>206</sup>Pb/<sup>207</sup>Pb indicate that more than 50% of anthropogenic lead in top soil is derived from petrol combustion.

The labile percentage of Pb is the highest in the surface samples and varies from 83 to 95 %, while the deeper soil samples contain <70% labile Pb. The extraction with 0.11 mol dm<sup>-3</sup> CH<sub>3</sub>COOH (the first step of BCR) proved to be quite problematic for very acid soils (pH <4) and gave only 10% of exchangeable lead in comparison with 1 mol dm<sup>-3</sup> KCl. The concentration of Pb obtained by extraction with DCB which was used for the determination of crystallized iron oxyhydroxides showed good correlation with the Pb concentrations extracted in the reducible fraction of the BCR sequential extraction. The results which indicate that the first two steps of the BCR sequential

procedure are problematic for soils with both low and high pH due to the use of  $0.11 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH}$ , which has recently come to the attention to different authors as well as the authors of the BCR procedure.

It was possible to determine the following relative mobility of metals  $\text{Mn} > \text{Zn} > \text{Ni} > \text{Cu} > \text{Pb}$ , on the basis of the calculated partition coefficients ( $K_d$ ) for the simulated soil solution which is in accordance with the results of the first step of the sequential analysis. The distribution of Pb ionic species over the depth in the soil solution showed that the  $\text{PbHCO}_3^+$  dominates (80%) and it decreases slightly with the increase of pH to  $> 5$  in the deeper part of the profiles. Only 20% Pb is present as  $\text{Pb}^{II}$ .