Solid-phase speciation and surface binding of nickel in serpentine soils from the North-east of Portugal

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The aim of this work is to investigate and to compare solid-phase speciation and surface binding of Ni in serpentine (S) and nearby non-serpentine (NS) soils from the northeast of Portugal. The former commonly have high levels of trace metals like Ni, Cr and Co and low Ca/Mg ratios. In addition, serpentine soils have low concentrations of important nutrients like K and P. Low Ca concentrations combined with elevated soil concentrations of Mg and Ni are considered to be the main cause of serpentine soil toxicity (1).

Several soil samples were characterized in terms of selected physicochemical characteristics. Solid-phase speciation and surface binding of Ni were assessed through complementary wet chemical extractions. Surface bound Ni was divided into exchangeable (CaCl₂-extractable Ni) and both exchangeable and specifically adsorbed (EDTA-extractable Ni). Solid-phase speciation was evaluated by selective dissolutions of hydrous Mn oxides (hydroxylamine extraction - HH), amorphous Fe oxides (oxalic acid extraction – OX) and amorphous as well as crystalline Fe oxides (dithionite-citrate extraction - DC).

In non-serpentine soils surface bound Ni is mainly in an exchangeable form while in serpentine soils is mainly specifically adsorbed. The influence of soil physicochemical characteristics and of Ni bearing oxides (HH, OX, DC dissolutions) on Ni bioavailability (EDTA-extractable Ni) was examined. No relationship was found between EDTA-extractable Ni and clay content or amorphous iron oxides. A major association of Ni with hydrous Mn oxides was found. Pearson correlation analysis confirmed the influence of these oxides on Ni bioavailability (2).

Surface affinity for exogenous Ni was evaluated by adsorption studies on soils suspensions followed by voltammetric titrations at pH=7. Sorption data was fitted to a Langmuir isotherm assuming the formation of 1:1 Ni complexes with the soil surface binding sites. Although of the same order of magnitude, the concentration of surface groups of serpentine soils for Ni binding was higher than that of non-serpentine samples. Serpentine soils presented higher conditional surface formation constant, \( K_{\text{them}} \), which implies the existence of surface groups with higher nickel affinity. The manganese oxides seem to be the mainly responsible factor for Ni retention in the analysed serpentine soils (2).

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References