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Heavy metal fractionation and pedogenesis in subalpine and alpine soils on ophiolitic materials, western Alps

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Soils on ultramafic materials are usually rich in Mg, Fe and heavy metals (particularly Ni, Cr, Mn, Co). These chemical properties could cause toxicity effects on biological communities.
Metal fractionation shows the soil phases to which metals are associated (exchangeable, associated with organic matter, with amorphous or crystalline Fe or Mn oxides, in the crystal structure of primary minerals), and thus it is strictly related with metal mobilization and bioavailability.
Ni, Cr, Mn, Co and Fe fractionations (6 fractions, analysed by a selective sequential extraction technique) were analysed in 6 subalpine and in 17 alpine soils (i.e., respectively under coniferous forest or above the present-day treeline) in the ophiolitic area of Mont Avic Natural Park (Valle d'Aosta, Italian Alps), on soils formed from metal-rich serpentinite or from metal-poor mafic rocks and calcschists.
The results show a tight relationship between vegetation, soil forming processes, metal fractionation and bioavailability: below and above the present-day treeline soil forming processes and metal speciation change dramatically. Serpentinite soils are always extremely rich in metals, but metal speciation in analogous habitats is similar on every substrate.
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Under subalpine forest, the main pedogenic process is podzolization. In the extremely acidic and leached podzolic soils, all metals are mobilized and their lowest concentration is in the bleached E horizon, while there is a higher content in organic matter-rich surface horizon and in the spodic (illuvial) B. Not considering the amount associated with primary minerals (residual fraction), all the fractions of Ni, Co and Mn are strictly correlated with each other: in A and Bs horizons, the greatest amount is associated with organic matter and with crystalline Fe-oxides. The content in easily mobilizable forms associated with Mn and amorphous Fe oxides is only slightly lower. The greatest amount is in the residual fraction, as pedogenic forms are easily removed from the soil profiles by leaching; this is particularly evident in E horizons. Cr is less released by weathering, and the greatest fraction is associated with organic matter and amorphous Fe-oxides. No Cr could be detected associated with Mn oxides. The high mobility of metals in these soils increases their bioavailability.
Above the treeline, the situation changes dramatically. Leaching is important only on stable, flat surfaces. Total and pedogenic fractions of Ni, Cr, Co and Fe increase from the bottom to the top of the soil profile, while all forms of Mn are strongly depleted in the upper horizons because of chemical reduction due to waterlogging at snowmelt. In fact, Mn is particularly sensitive to reduction processes.
The most important factors involved in metal geochemistry are erosion and cryoturbation, which bring "fresh", metal-rich materials on the top of the profiles; weathering later releases the metals associated with pedogenic materials. The weak leaching due to limited acidification increases the concentration of potentially bioavailable metals (Fe, Co, Cr, and Ni) in the biologically active soil horizons. All metals are mobilized by waterlogging at snowmelt: extremely high contents of "labile" pedogenic forms of metals also in deep horizons of soils developed on metal-poor materials. However, the concentration due to the processes described above is stronger than leaching for Ni, Co, Fe and Cr.