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Lead pollution and podzolisation in NW Spain

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Lead atmospheric pollution in southern Europe dates back to some 3,000 years ago. Since then Pb has been added to soils through atmospheric deposition enriching the superficial horizons in this metal. Up to now it is not clear for how long pollution Pb will be recycling and its long-term effects in the soil environment. In podzols a self-cleaning of the superficial horizons has been proposed under decreasing atmospheric deposition. Cheluviation and burial into the spodic horizon may sequester significant amounts of Pb and other metals. At the same time, the downward transport of pollution Pb to deeper horizons may provide a unique opportunity to get insights on the intensity of podzolisation. Studies carried out in forest soils in Sweden demonstrated that pollution Pb has penetrated at least down to 35 cm in the soil column.

In line with these studies we have analyzed two podzols (an umbric and an haplic podzol) from NW Spain, developed on the same quartzitic colluvium under present humid and temperate climatic conditions. We made a continuous sampling each 5 cm to provide a high vertical resolution. Total Pb, as well as Al, Si, Fe, Ga, Ti and Zr were determined by XRF and C and N using a LECO TruSpec CHN analyser. Fractionation of Al, Fe, Mn, and Si was evaluated using selective dissolution techniques: KCl, $LaCl_3$ and $CuCl_2$ extracts for Al (Al_K, Al_{La}, Al_{Cu}); Na-pyrophosphate, acid NH4-oxalate and NaOH for Al, Fe, Mn and Si (Al_{PY}, Mn_{PY}, Fe_{PY}, Al_{OX}, Mn_{OX}, Fe_{OX}, Al_N, Si_N). The concentrations of these elements in the extracts were measured by AAS.

Average Pb concentrations decrease from the litter layer to the E horizon (O 8.1 $\pm$1.0, A 7.2 $\pm$3.7, E 3.7 $\pm$0.7 μg g^{-1}), then they increase from the EB transition to reach a maximum in the upper part of the spodic horizon to decrease again to the base of

the soil (EB 11.0 $\pm$2.2, Bhs 17.2 $\pm$3.2, Bs 11.7 $\pm$1.6, BwC 12.0 $\pm$4.4 μg g^{-1}). Pb accumulation in the soil horizons follows the same trend (O 16 $\pm$2 A 74 $\pm$33, E 47 $\pm$9, EB 123 $\pm$8, Bhs 203 $\pm$35, Bs 169 $\pm$23, BwC 174 $\pm$64 mg m^{-2} cm^{-1} of soil). The large heterogeneity in the bottom-most horizon is due to higher Pb concentrations and accumulation in the haplic than in the umbric podzol. Lead concentrations were positively correlated to total Fe, Ti and Ga (r 0.80-0.75) but negatively to Si (r -0.77) supporting a significant Pb mobility during podzolisation. Although correlations to total Al and high stability Al-OM complexes (Al_{PY}- Al_{Cu}) were lower (r 0.66-0.63), higher correlations were found with exchangeable (Al_K, r 0.78 for A and E horizons, 0.75 for B horizons) and low to moderate stability Al-OM complexes (Al_{La}, Al_{Cu}) (r 0.86-0.73 for all horizons and 0.80 for the spodic horizons). This suggests that mobile Pb may essentially be linked to exchangeable sites and low to moderate stability metal-humus complexes.

Enrichment factors calculated using Si as immobile element and normalized to the Pb/Si ratio of the parent material averaged to 0.6 $\pm$0.4 in the A horizon, 0.2 $\pm$0.04 in the E, 0.8 $\pm$0.3 in the EB, 2.0 $\pm$0.9 in the Bhs, 1.1 $\pm$0.2 in the Bs and 1.0 $\pm$0.4 in the BwC. Despite this general trend differences were found for both soils. The umbric podzol showed a larger maximum Pb enrichment in the A horizon (1.4) than the haplic podzol (0.9), but the later showed Pb enrichment at the base of the B horizons (1.6). While the superficial enrichment in the umbric podzol may be the result of atmospheric Pb pollution, the basal enrichment in the haplic is coincident with an increase in low stability Al-OM complexes.

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