As part of an extended project to understand the speciation of metal ions in contaminated lands, we conducted a series of chemical extraction experiments on soil and extracted the soil pore water to determine the speciation of Pb, Cd and Cu in a smelter impacted site. The chemical extractions show that soil organic matter and metal oxides (Fe and Mn) control the speciation of Pb, Cu and Cd in the soil. For Pb, these results are in agreement with previous EXAFS data on the same soils. The soil solution speciation is calculated with the help of the NICA–Donnan modelling approach. The modelling shows that Pb and Cu speciation is dominated by the dissolved organic matter while Cd is mainly in solution as a free aquo–ion. The speciation in the soil is also simulated by a model coupling both the binding to soil organic matter and metal oxides. The simulated partition coefficient (K_d) is in good agreement with the experimentally measured K_d.