

Magnetic spherules in soils – an interdisciplinary investigation of heavy metal pollution

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Mapping of magnetic susceptibility as an indicator for heavy metal pollution was intensively used in recent years and polluted areas can be delimited quickly and at low cost. This study, funded by the Austrian Science Fund (FWF P 16314), focussed on the natural influences on the soil magnetic susceptibility to determine threshold values for non-polluted soils as well as on the links between heavy metals and magnetic pollution particles. Dried and sieved soil samples from the soil archives of east-austrian provinces were investigated by means of magnetic measurements as well as mineralogical and chemical analyses.

The natural magnetic susceptibility of soils is influenced by several factors; one of the most important is the water regime, independent of the parent material. Soil types that are formed by (partial) waterlogging have low susceptibilities (gleysol, stagnosol, stagnic phaeozem). A second group with generally low values are those with low pH-value and high amount of organic matter which may form complexing agents that release and relocate iron (podzol, half-bog soils). The analysis of the influence of the parent material showed that for example soils formed on rocks of the Bohemian Massif (granitoides, gneiss and granulite) display significantly distinct susceptibility distributions. The highest susceptibility values occur within Carinthia, where rocks of the Central Alps dominate, and in the Vienna basin on loess and other fine sediments where chernozem, parachernozem and colluvium are the main soil types. Soils formed on siliceous sandstone in the flysch zone have the lowest susceptibility values.

Polluted soils show medium to high values of saturation remanence, high susceptibility and low values of remaining saturation remanence after alternating field demagnetization (< 5 %). Three axis coercivity/ unblocking temperature spectra are dominated by a magnetically soft component (<70 mT) with corresponding unblocking temperatures of 570 °C. Unpolluted sites are indicated by low values for magnetic susceptibility and saturation remanence and medium (5–10 %) to high (>10 %) remaining saturation remanence. X-ray diffraction patterns were obtained from bulk samples. The main minerals were Quartz, Chlorite, Muscovite and Hornblende. In some samples calcite, dolomite or magnetite was present.

Magnetic extracts were used for scanning electron microscopy. Polluted soils were dominated by spherules with diameters ranging from 6 to >100µm, scale was detected in limited amount. Elemental analysis displayed spherules built of iron oxides or geometrically

formed iron oxides embedded into a silicate matrix in samples near steel works. Calcium-based matrix was only found in magnetic spherules in samples close to a cement plant. The heavy metals Cr, Mn, Ni, Ti, Cu, and Zn were found in elemental analysis, either in flakes attached to the surface of the spheres or within their internal structure. Extracts from unpolluted soils primarily consist of strongly weathered bed rock minerals. Samples from Carinthia contained some well preserved magnetite octahedrons.

In addition to the total elemental content determination a three-stage extraction procedure was performed on the bulk soil samples. This modified (BCR) three-stage extraction procedure allows to quantify metals in following bonds: 1. Exchangeable metals, water soluble and carbonates; 2. Metals bound to iron and manganese oxides (reducible); 3. Metals bound to organic matter and sulphides (oxidizable). The metals still bound after the 3rd extraction step are referred to as residuum. The determination of metals in the extracts was performed by ICP-MS. The major proportion of Cr, Co, Cu and Zn was found in the residuum, nevertheless samples near steel works contain significant amounts of Cr in the fraction bound to organic matter. Cadmium was mainly leached in the first and second extraction step.

The consistent results of the analyses indicate that heavy metals in the soils are present in mainly non-leachable form, although for certain heavy metals, such as Cr, significant amounts occur in chemical stages where they can be bioavailable.