

Heavy Metal Fractionation in Soils of Different Genesis

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Abstract. McLaren and Crawford's method for fractionating soil Cu was used to fractionate Cd, Cu, Ni, and Pb in soil samples from three soil profiles. Study sites are located in the most environmentally stressed areas of Slovakia (Rudňany and Banská Štiavnica surroundings) and the investigated three soil types: Dystric Cambisol, Eutric Planosol, and Fluvi-eutric Gleysol, are pedogenetically very different. At the Dystric Cambisol site, Pb was predominantly bound by soil organic matter and Cu was distributed mainly between organically bound and residual fractions in topsoils. Ni can be related to the behaviour of Fe: it is redistributed from the surface to deeper horizons. The portion of Cd, Cu, and Pb associated with iron hydrous oxides was prevailing within the Fluvi-eutric Gleysol where co-precipitation from groundwater occurs. Positive correlations were found between oxalate extractable Fe and heavy metal fractions. Inside the Eutric Planosol, Cd, Cu, and Pb were mainly Fe-bound, but negative correlations occur between oxalate extractable fractions of heavy metals and iron hydrous oxides content.

Keywords: soils, heavy metals, sequential extraction, geostatistics

Introduction

The heavy metal content in the soil at any location has been influenced by many factors such as the soil's parent material, the pedogenesis, the plant cover, land use, and many anthropogenic activities, including the transboundary air-pollution. The impact of contributing factors vary from place to place and consequently caused the spatial variation of the heavy metal content. The observed value embodies this variation plus the fluctuations arising from the sampling and analytical procedures (Oliver & Webster, 1991). The resulting heavy metal contents of soils are highly variable and an objective assessment of the pollution state is strongly limited. For these reasons, geostatistical methods were used for the investigation of spatial dependence and territorial distribution of heavy metal content in soils of Slovakia.

The observed distribution and accumulation of heavy metals in soils depend on a number of factors, including soil properties (pH, soil organic matter, clay minerals, Eh-conditions), soil pedogenesis, soil-plant relationships as well as amounts, forms and origins of the heavy metals (Alloway, 1990). The analytical methods and procedures are a useful tool to clear up these relationships.

The soil material varies greatly as size and chemical composition of the particles are concerned. Thus, the behaviour and fate of an element in the soil environment cannot often be reliably predicted, based on its total concentration. That is why a sequential extraction procedure was used to examine samples from several soil profiles. An overview of the use of extractants in

soil studies, including accompanied uncertainties, was made by Beckett (1989).

In our research the calcium chloride, pyrophosphate, and acid oxalate extractants were used. Despite the possible imperfections, it is generally supposed, that forms of heavy metals - exchangeable, organically bound and occluded by free oxides, respectively, are extracted. In a more or less different way these extractants were used for soil heavy metal analysis by McLaren & Crawford (1973), McLaren et al. (1986), Bogacz (1993), and Asami et al. (1995).

Materials and Methods

Soils were sampled from three soil profiles at different locations (mentioned below) by using the genesis (horizon) principal. The samples were air-dried and ground to pass a 2mm sieve before analysis.

The determinations of pH, total organic carbon, CEC, base saturation, and clay content were made by standard methods (Kobza et al. 1999). The sequential extraction of Fe, Pb, Cu, and Ni followed the flow diagram in figure 1.

The total content and the concentration of metals in different extractants were determined by atomic spectrometry methods (ETAAS, ICP-AES). The reliability of the used digested and fractionation procedures was tested by CRM soil materials (SO-2 and SO-4, CCRMP, CANMET, Canada).

Geostatistical analysis of existing data was performed with a software from U.S. Environmental Protection Agency (Englund & Sparks, 1991; Yates & Yates, 1990).

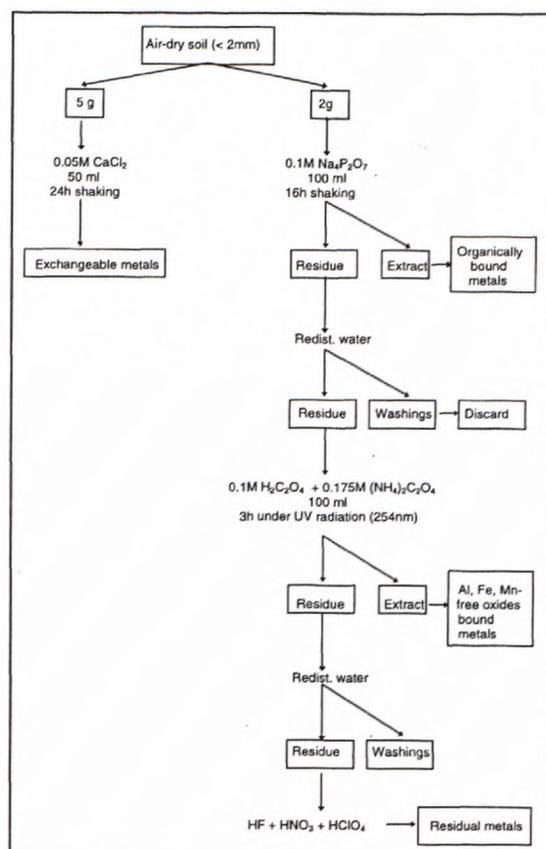


Figure 1: Sequential extraction scheme (modified version by McLaren and Crawford, 1973)

Geostatistical Investigation of Heavy Metals in the Soils of Slovakia

The data about heavy metal contents of topsoils were collected in the frame of the soil monitoring program (Linkeš et al., 1997) and supplemented by the data from a hygienical survey (collected by VUPOP Bratislava in 1990-1996). As a result, we have obtained irregularly placed sampling points, the topsoil of which has a known content of Cd (1148 sampling points), Pb (1301), and Hg (884). Their locations are shown in figure 2.

The distribution of all elements were strongly positively skewed. For subsequent geostatistical analysis the data were transformed by logarithmic or power transformations to stabilise variances. Isotropic variograms computed for the whole area could be described as the sums of nuggets plus exponential structures. Figure 3 shows the experimental values plotted as points and the model shown as the solid line.

Finally, we kriged the contents of Cd, Pb, and Hg over the 5 x 5 km blocks and mapped them (Fig.2). The nearest two sampling points within each octant around the estimated point were taken for calculation, making 16 in total. The metal contents show a regional pattern that seems to be linked with the spatial distribution of the soil associations, geology, mining and industrial activities, and emission effects as well.

The study sites were selected on the basis of these results (Fig.2). Experimental fields are located in the most

environmentally stressed areas in the Eastern (near Rudňany) and Central (near Banská Štiavnica) Slovakia. The studied soils belong to Dystric Cambisols, Eutric Planosols, and Fluvisols affected by gleyic processes (after FAO).

Properties of the Studied Soil Profiles

The study involved profiles of three soil types: Dystric Cambisol (DC), Eutric Planosol (EP), and Fluvi-eutric Gleysol (FG). The DC was much more acid (pH 2.9-4.1 in 1M KCl) than EP (pH 5.1-6.1) and FG (pH 5.0-6.6). The CEC of the DC, EP, and FG varied between 42-227, 126-184 and 198-476 mmol.kg^{-1} , respectively. The alkali plus alkaline earth cation saturation was <30% in the DC, but >70% in the two others. The total carbon content of the DC ranged between 4 and 15% in the A horizons and dropped to 0.3-2.9% in deeper horizons. In the EP and FG the carbon content varied between 0.4-2.9% and 0.2-1.0%. Free iron content (pyrophosphate plus oxalate extractable) ranged between 0.2-2.0 (DC), 0.9-1.7% (EP) and 0.9-1.3% (FG). The clay content varied between 9-19% (DC), 11-15% (EP) and 12-21% (FG). The mineral composition of the clay fraction was dominantly smectitic-illitic (DC and EP) and illitic-chloritic (FG).

The Study of Heavy Metal Behaviour in Soils through Sequential Extraction

Speciation of heavy metals in soils can be defined in many ways (Ure, 1990). First, it can be defined as the extraction and quantification of a soil phase, which is functionally designated in that its element content is, for example, the plant available content. Secondly, speciation can be defined operationally, i.e. by the extraction technique itself. The extraction will usually be designed to extract the element associated or bound to a particular soil phase. The use of selective extractants to quantify the element content in a particular phase is illuminated by the concept of "pools" of elements in soils, of different solubilities and mobilities, that can be selectively sampled by extractants of different strengths. By making use of a series of sequential extractions with reagents of increasing power, the individual phases can be isolated. Much work has been done on sequential extraction schemes for soils and sediments (Kersten & Forstner, 1989). The analysis of sequentially obtained fractions of heavy metals in studied soils leads to a better understanding of the influence of specific soil properties on the behaviour of heavy metals in soils.

Within the forest soil profile of Dystric Cambisol (DC) lead and copper were found to be concentrated in the surface horizons as a result of their adsorption by the soil organic matter (Fig.4) and due to the bioaccumulation and the emission origin as well. The topsoil contained lead mainly as organically bound (67-69%), Fe-bound and residual fractions contained 18-20 and 13%, respectively, of lead. Total copper was distributed mainly between organically bound (32-35%) and residual (56-59%) fractions, Fe-bound fraction contained 9% of Cu. In the

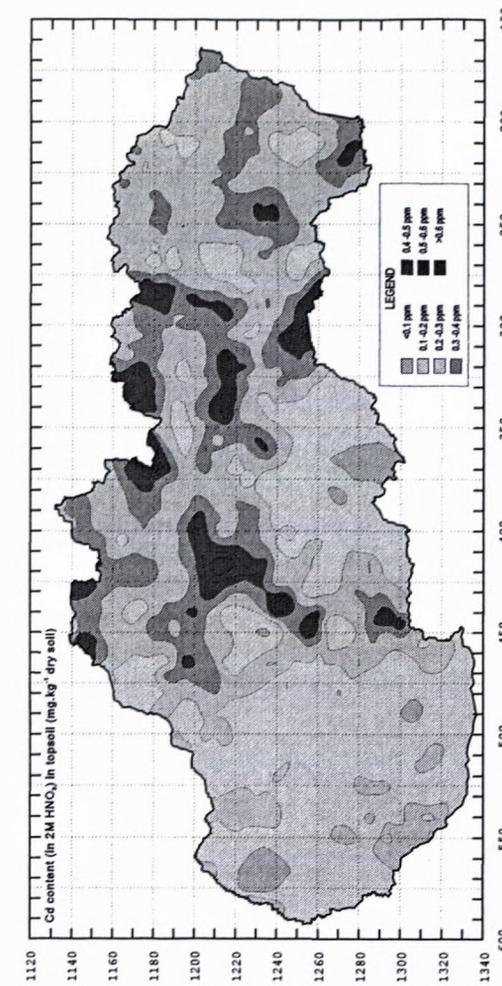
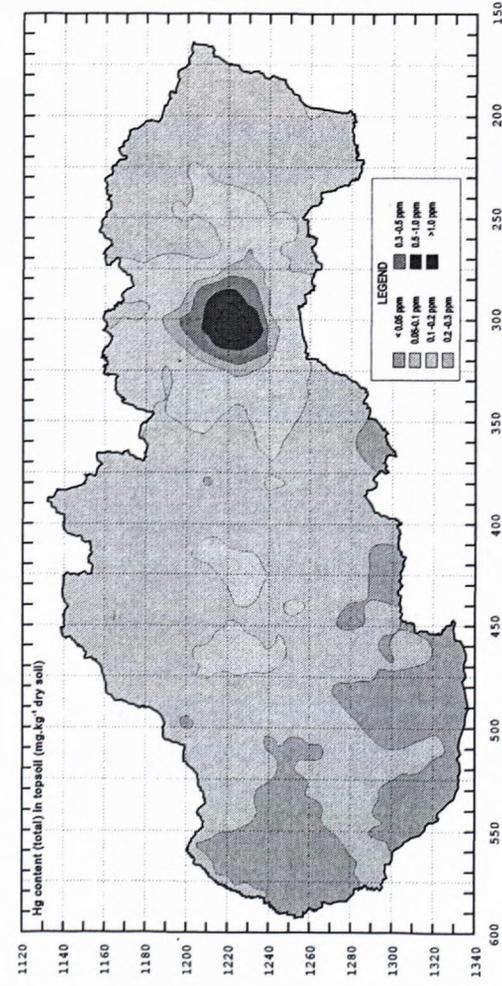
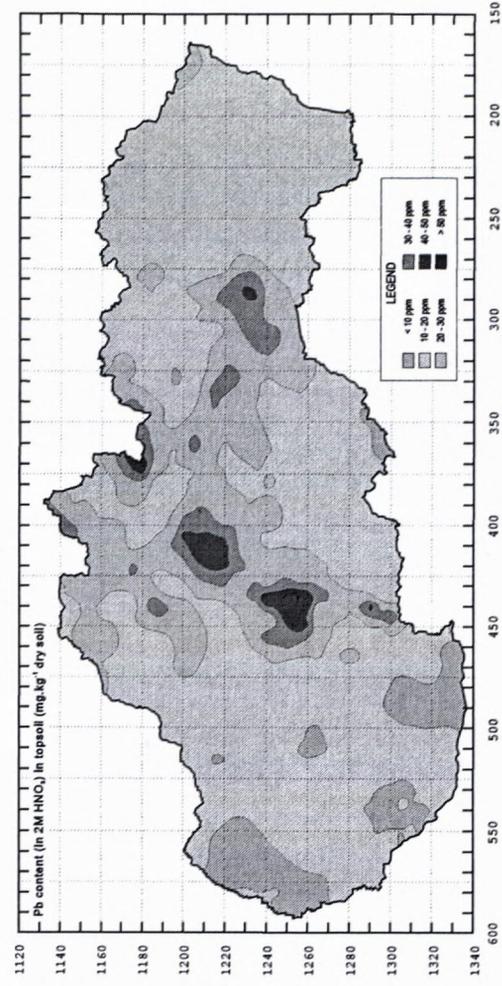
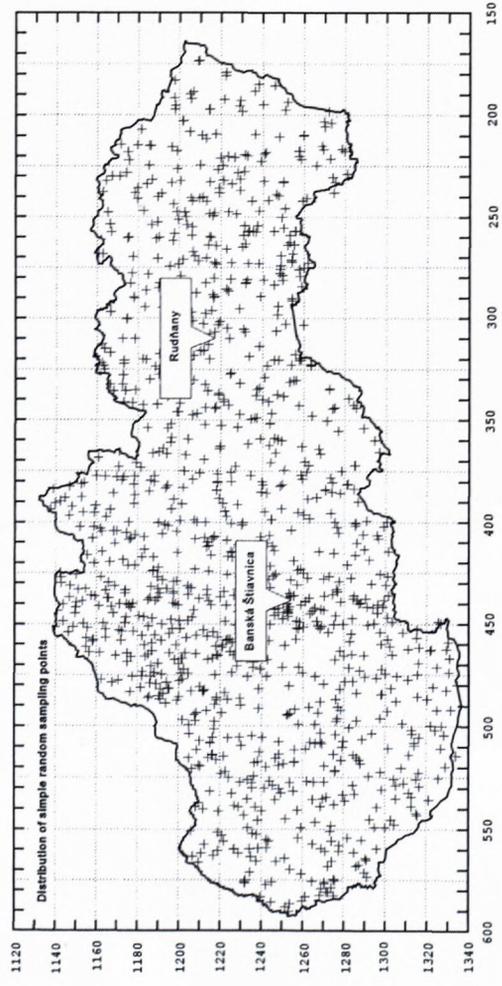


Figure 2: Study sites (Banská Štiavnica and Rudňany), locations of sampling points and isoline plots for selected heavy metals

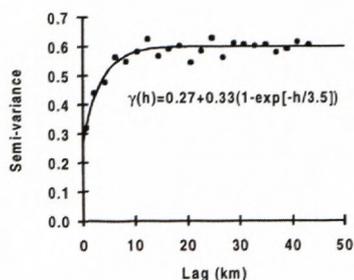


Figure 3: Example of experimental variogram for Cd [ln(ppm)]

subsoil horizons, a lower content of organically bound Pb (18-20%) and higher proportions of Fe-bound (38-49%) and residual (29-40%) lead were determined. Copper occurred predominantly in the residual fraction (78-91%) and much less as organically bound (4-18%) and Fe-bound (2-5%). A similar vertical distribution and relation to soil organic matter content has also been reported for heavy metals (i.e. Baker, 1990; Davies, 1990; Krosshavn et al., 1993).

The same conclusion for the forest soil profiles (DC) is obtained from diagrams in figure 5 where the determined content of pyrophosphate extractable Pb is directly proportional to organic carbon content. Atteia (1994) found a similar close relationship between the total Pb and the total organic matter content for Cambisol and Podzol in Switzerland. He explained the lower slope of the linear regression in Podzol as a result of a higher organic matter content in

Podzol for a similar Pb content. The similar dependence is valid for Cu, with the exception of the "Stara Voda" location influenced by mining activity in the past. In our case, the different slopes for Cu can reflect differences in the inputs into surveyed soil profiles.

Nickel shows a significantly different behaviour, even in the forest soil (DC) which is rich in organic matter content. Total nickel was distributed mainly in Fe-bound (21-48%) and residual (33-74%) fractions in the whole soil profile. The organically bound fraction contained only 2-18% of Ni. Correlation between the concentration of Ni bound to organic matter and the content of organic carbon in soil is insignificant (Fig.5). Nickel is concentrated in deeper horizons of the soil profiles and tends to be associated with accumulations of the Fe hydrous oxides, as follows from figure 5. The close dynamics of Ni and Fe in soils and the same vertical distribution pattern were found previously (i.e. McGrath & Smith, 1990; Atteia, 1994).

Since iron hydrous oxides are precipitated more extensively in soils affected by gleyic processes, they dominate the adsorption of the studied heavy metals inside both the Eutric Planosol (EP) and Fluvi-eutric Gleysol (FG) profiles (Fig.4). A tendency of the heavy metals to concentrate in this fraction is affected by the relative content of organic matter and iron hydrous oxides as well.

Within the Fluvi-eutric Gleysol (FG) profiles (with the exception of Gr horizon), total lead was distributed

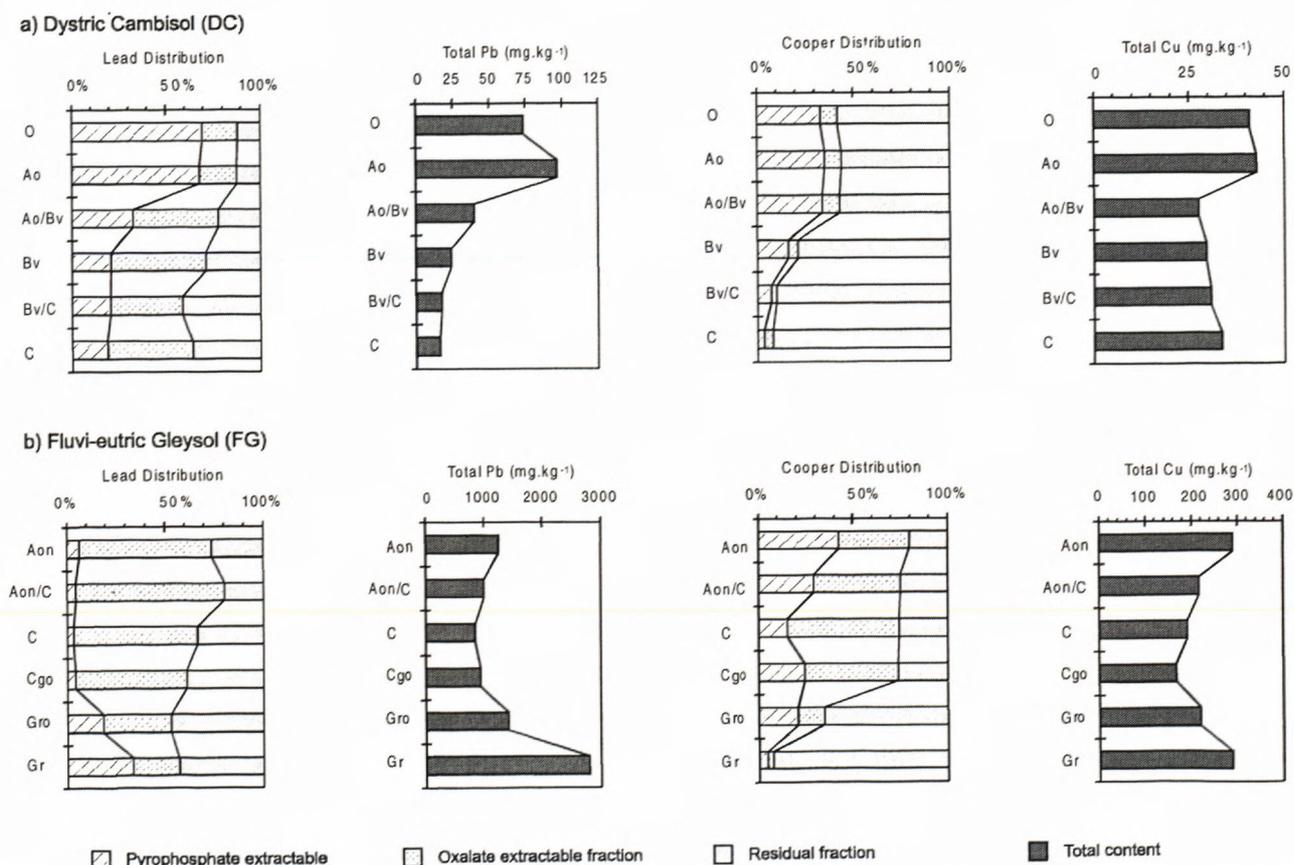


Figure 4: The distribution of organic (pyrophosphate), hydrous oxide (oxalate), and residual heavy metal fractions and their vertical distributions

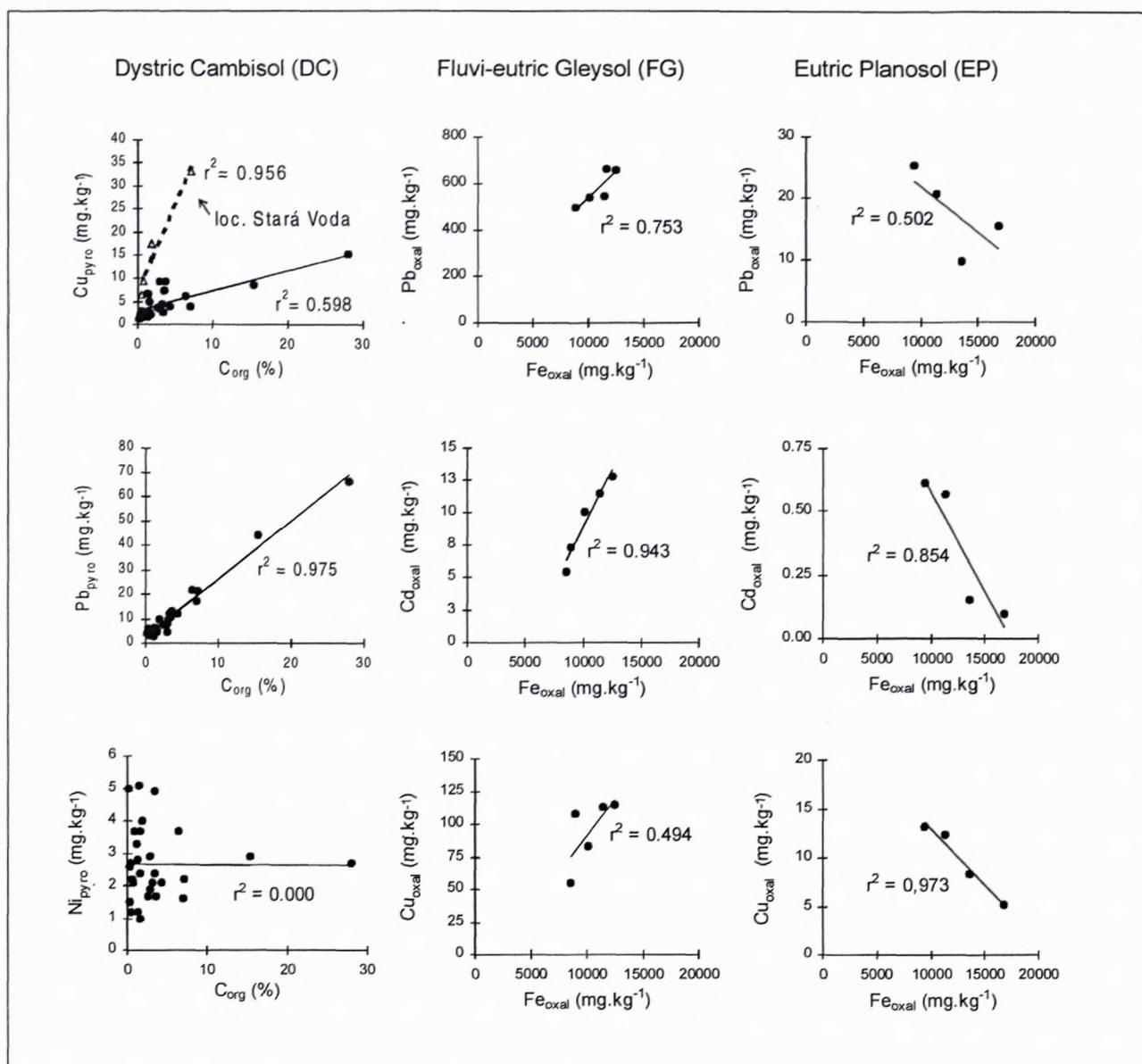


Figure 5: Relationships between heavy metal fractions and corresponding soil constituents

mainly as Fe-bound (57-75%) and residual (20-39%) fractions, only 2-7% of Pb was found as organically bound fraction (Fig. 4). Organically bound, Fe-bound, and residual fractions of copper contained 16-42, 38-60, and 20-26%, respectively, of copper. The oxalate extractable heavy metal contents are directly proportional to iron hydrous oxide contents (Fig. 5). This relationship results from the co-precipitation of heavy metals and iron hydrous oxides from the groundwater. That is why iron secondary oxides formation in the soil profile also leads to heavy metals accumulation in the same soil.

Inside the Eutric Planosol (EP) 55-78% of total Pb was found as Fe-bound, 19-44% in residual fraction and only 0.5-3% of organically bound Pb. These relationships among Pb, Cd, Cu, and iron hydrous oxide contents are indirect within the Eutric Planosol (Fig. 5). In Planosols, mobilization and precipitation of iron hydrous oxides

occur through oxidation and reduction following water-logging in the impermeable B horizon. Both iron concentration in deeper horizons and the emission origin of heavy metals cause the negative correlation in figure 5, at this location.

The calcium chloride extractable fraction accounted for only <1%, on average, of the total metal content and it was not subtracted from pyrophosphate extractable fraction either in the graphs or in the calculations.

Based on our results organic matter or iron hydrous oxides cannot be considered as selective sorbents for the individual element (Fig. 4). The amount of heavy metals adsorbed by organic matter or Fe hydrous oxides in soils depends greatly on the soil genesis and on the heavy metal origin. The different slopes in the above correlation graphs (Fig. 5) can reflect the differences in heavy metal loads or the different origins of heavy metal.

Conclusions

The obtained experimental results show the sequential extraction procedure as a source of valuable data on interactions between heavy metals and soil constituents, at selected locations. The above results suggest that pyrophosphate (organically bound) and oxalate extractable (Fe-bound) fractions represent the most important "pools" of heavy metals in the investigated soils. Within the forest soil profile of Dystric Cambisol (DC), lead and copper were found to be concentrated in the surface horizons. Pb was predominantly bound by soil organic matter and Cu was distributed mainly between organically bound and residual fractions. The total nickel was found mainly in Fe-bound and residual fractions in the whole soil profile. Iron hydrous oxides dominate the adsorption of studied heavy metals inside the both Eutric Planosol (EP) and Fluvi-eutric Gleysol (FG) profiles. Positive correlations were found between oxalate extractable Fe and heavy metal fractions within the Fluvi-eutric Gleysol where co-precipitation from groundwater occurs. Inside the Eutric Planosol, negative correlations occur between the oxalate extractable fraction of heavy metals and the iron hydrous oxides content. Based on our results, organic matter or iron hydrous oxides cannot be considered as selective sorbents for the individual element. The amount of heavy metals adsorbed by organic matter or Fe hydrous oxides in soils depends greatly on the soil genesis and on the heavy metal origin.

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