

SPECIATION OF SELECTED HEAVY METALS IN SOILS AND PLANT AVAILABILITY

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ABSTRACT

Twenty four soil samples from three different locations and twenty seven samples of 5 wild plants were analyzed for the content of Cd, Pb, Co, Ni, Cu, Zn, Cr, Mn, Fe, Na, K, Mg and Ca. The form of the metal constituent in the soil has been also determined.

INTRODUCTION

Considerable amount of research activity in recent years have been devoted to evaluate the effects of heavy metal pollution on soils. Amended soil-plant systems have also been reported in different works [1] but not much studies have been made about the relationship between soil metal speciation in natural soils and plant availability.

A large number of methods have been described for the selective extraction of metals in soils [2]. However, the most used one is the method proposed by Tessier et al. [3] where five types of compounds can be determined: namely exchangeable, as carbonates, related to Fe-Mn oxides, linked with organic matter + sulphides and residual fraction.

Apart from metal speciation, there are other determinations to be taken into account in natural soil-plant systems; for instance the percentage of metal uptake by wild herbage which is quite high via leaves in industrialised areas [4] and the fact

that heavy metals artificially added to soils are more loosely bound than those originally present [5].

The objectives of this introductory work have been restricted to study the distribution of metals (micro and macroconstituents) in the selected soils and plant content of those elements.

EXPERIMENTAL

For this study, 24 soil samples were taken in three different locations and wild plants were collected, when possible, in the selected locations. The wild species chosen were *Poa*, *Pteridium aquilinum*, *Diplotaxis*, *Plantago lanceolata* and *Trifolium repens* and the number of plant samples was 27.

Firstly, soil general properties were determined by conventional methods (Table 1).

Secondly, in order to evaluate total amounts of Cd, Pb, Co, Ni, Cu, Zn, Cr, Mn, Fe, Na, K, Mg and Ca in soils and plants, an acid digestion method was used [6]. The samples were digested with a mix of HF:HNO₃:HClO₄.

Finally, the method of speciation based on sequential extractions [3] was adapted for this study. This method includes the following consecutive steps:

1. Extraction with 1 M ammonium acetate at pH 7 so that the exchangeable fraction was determined.
2. Extraction with 1 M acetic acid added to the residue from the previous step. This is the fraction associated with carbonates.
3. Extraction with a 0.04 M solution of NH₂OH.HCl in 25 % acetic acid at 100°C for 3 h in order to determine metals associated with Fe-Mn oxides.
4. Extraction with a 30 % solution of H₂O₂ (pH 2 with HNO₃) at 85°C for 2 h. This extraction step was repeated and finally a 3.2 M solution of NH₄OAc in 20 % HNO₃ was added. Metals associated with organic matter and sulphides were so determined.
5. The residual fraction was determined by difference.

Table 1. Mean values and standard deviations of soil parameters
(24 samples)

Soil parameter	Mean value	Standard deviation
% Clay + Silt	13.73	15.23
% Sand	84.33	14.59
Carbonates (%CO ₂)	3.60	4.40
C _{Org} (%)	2.44	1.06
Conductivity at 25°C (mho/cm)	128.84	74.49
CEC (meq/100g)	17.51	4.38
% Loss, 900 °C	10.95	5.54
% Loss, 400 °C	6.79	3.09
% Loss, 100 °C	1.95	1.84
pH	6.78	1.25

Table 2. Mean values and standard deviations of metallic micro and macroconstituents
in the selected soils

Element	Mean value	Standard deviation
Cd (µg/g)	1.36	0.91
Pb(µg/g)	130.5	172.0
Co(µg/g)	13.47	9.18
Ni(µg/g)	60.42	137.48
Cu(µg/g)	66.30	83.74
Zn(µg/g)	161.8	175.8
Cr(µg/g)	35.00	14.63
Mn(µg/g)	513.0	508.8
Fe(µg/g)	1730	905
Na(µg/g)	4160	2550
K(µg/g)	13730	8780
Mg(µg/g)	2255	1420
Ca(µg/g)	40530	30590

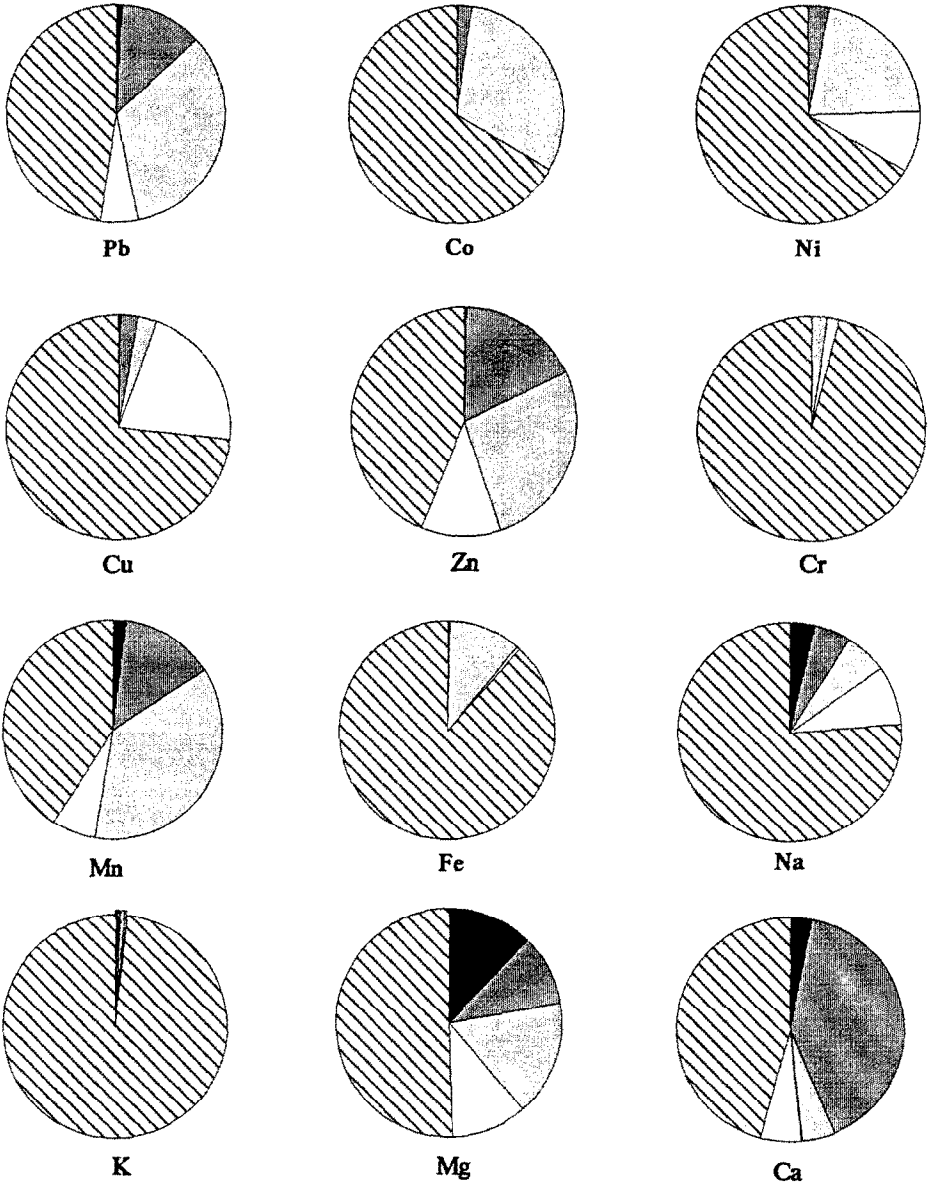


Figure 1. Average distribution of metallic species in the studied soils

- Exchangeable
- Carbonates
- Oxides
- Organic matter+sulphides
- ▨ Rest

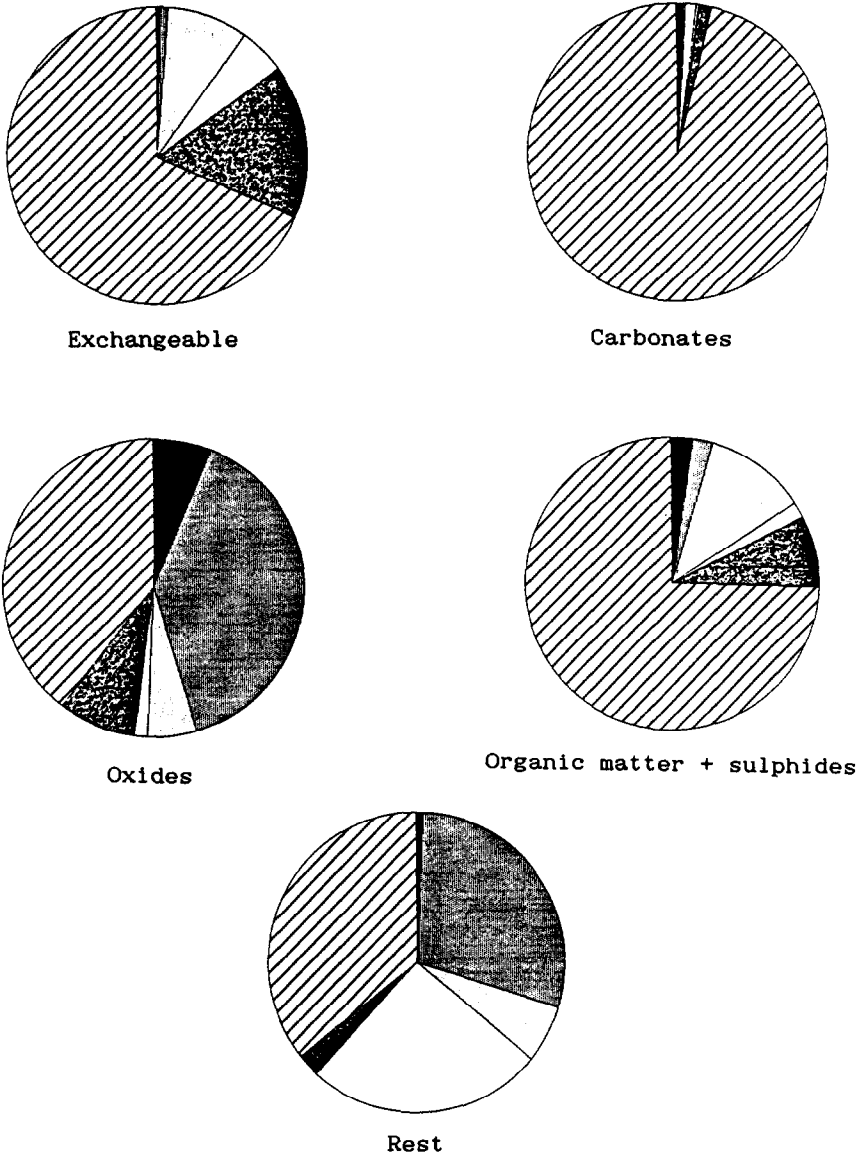


Figure 2. Average distribution of metallic microconstituents (Cd, Pb, Co, Ni, Cu, Zn, Cr and Mn*) and Fe, Na, K, Mg and Ca in the soil speciation fractions

Microconstituents, Fe Na K Mg Ca

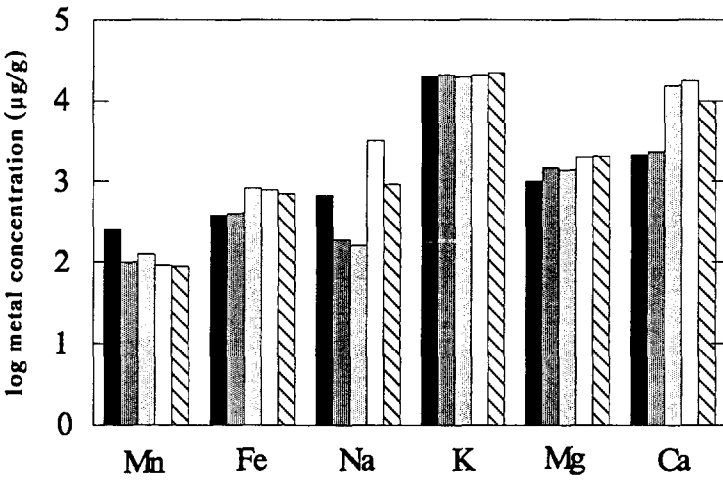
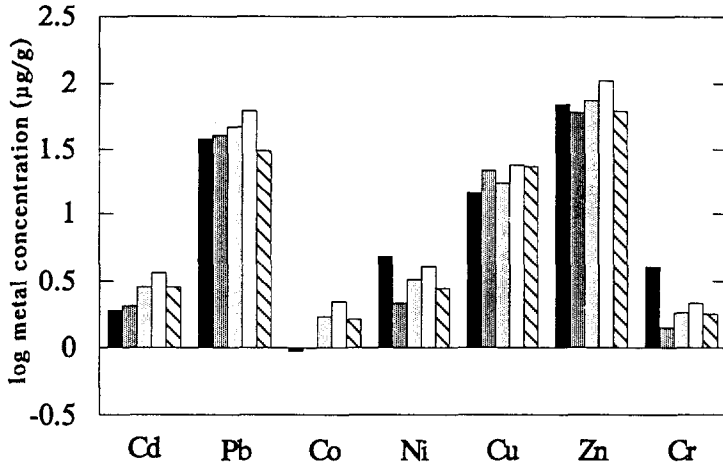


Figure 3. Average metal contents for studied plants.

- *Poa*
- ▨ *Pteridium aquilinum*
- *Diplotaxis*
- ◻ *Plantago lanceolata*
- ▧ *Trifolium repens*

Analytical metal determinations were performed by AAS for most of elements. Na and K were measured by emission spectrometry.

RESULTS AND DISCUSSION

Mean values and standard deviations of total metallic micro and macroconstituents in the selected soils are shown in Table 2. Relative weight proportions of every fraction for the studied metallic elements (Fig. 1) show that macroconstituents like Na, K and Fe and some microconstituents like Co, Cr, Ni and Cu are present in soil mostly in the residual fraction. The exchangeable fraction is considerable for elements like Mg, Ca, Na and Mn.

In Fig. 2, the influence of microconstituents (Cd, Pb, Co, Ni, Cu, Zn, Cr and Mn) has been studied against Fe, Na, K, Mg and Ca content in each speciation fraction. That influence is more remarkable in the fraction associated to Fe-Mn oxides. As far as plant content is concerned, average metal contents for studied plants are show in Fig. 3.

All data obtained in this study will be treated by statistical methods and will be published elsewhere.

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