*Acta Mineralogica-Petrographica, Szeged 2006–2007, Vol.* ***47****, pp. 53-59*

ACTA
Mineralogica
Petrographica

# MOBILIZATION CONDITIONS OF LEAD IN FOREST SOILS FROM THE CSERHÁT MTS., NE HUNGARY

PÉTER SIPOS

Institute for Geochemical Research, Hungarian Academy of Sciences H-1112 Budapest, Budaörsi út 45., Hungary
e-mail: sipos@geochem.hu

## ABSTRACT

The possible mobilization conditions of lead compared to other heavy metals (Zn and Cr) in four forest soil profiles was studied by sequential extraction to verify the relatively high lability of lead in soils at the woodlands of an undisturbed area (Cserhát Mts., NE Hungary).

The results show that lead can be mobilized in a wide range of environmental conditions. The most significant amount of lead can be bound to the residual fraction (26-57%), but the role of organically bound fraction (16-49%) and amorphous oxide bound fraction (11-28%) is also important in binding Pb. Contrarily, the mobilization of the other studied metals is restricted in these profiles.

Metal/Ti ratios show that lead has been significantly redistributed during the soil formation and it is presented in more labile form as compared to the other studied metals in the profiles. These differences can be resulted by the different source minerals of the studied metals on one hand, or by an external lead source on the other.

***Key words:*** lead, lability, sequential extraction, forest soils, Cserhát Mts.

## INTRODUCTION

Lead is widely distributed in the environment, primarily because of anthropogenic contamination. The largest lead emissions to the atmosphere occurred between 1950 and 1990 because of its combustion in Pb-containing petrol, but many other anthropogenic sources contribute to the lead distribution, such as metal smelting, coal burning, or the using of sewage sludge and commercial fertilizers in agriculture (Adriano 1986). In addition, there are natural sources of Pb deposition, as well, such as windborne soil particles, volcanic dust, sea spray, forest foliage and several biogenic processes (Settle and Patterson 1980).

Most recent results on atmospheric heavy metal deposition (Ötvös et al. 2003) show relatively low atmospheric Pb deposition in Hungary as compared to the other European countries (14.8 mg/kg on mosses). Higher concentrations (up to 126.7 mg/kg) were measured only close to industrial areas and roads characterized by intense traffic. Szalai (1998) found an approximate 1-3% increase per year in the Pb content of the topsoil on the Isle of Háros, Budapest. As compared to the results of other studies referring to Middle-Europe (e.g. Friedland et al. 1984, Sturges and Barrie 1989) 2-3 times lower atmospheric lead deposition were measured in Hungary (81 g/ha per year and 77 g/ha per year by Molnár et al. (1993) and Mészáros et al. (1993), respectively) showing its spatial and temporal heterogeneity. The enhanced lead concentrations of anthropogenic origin may result in

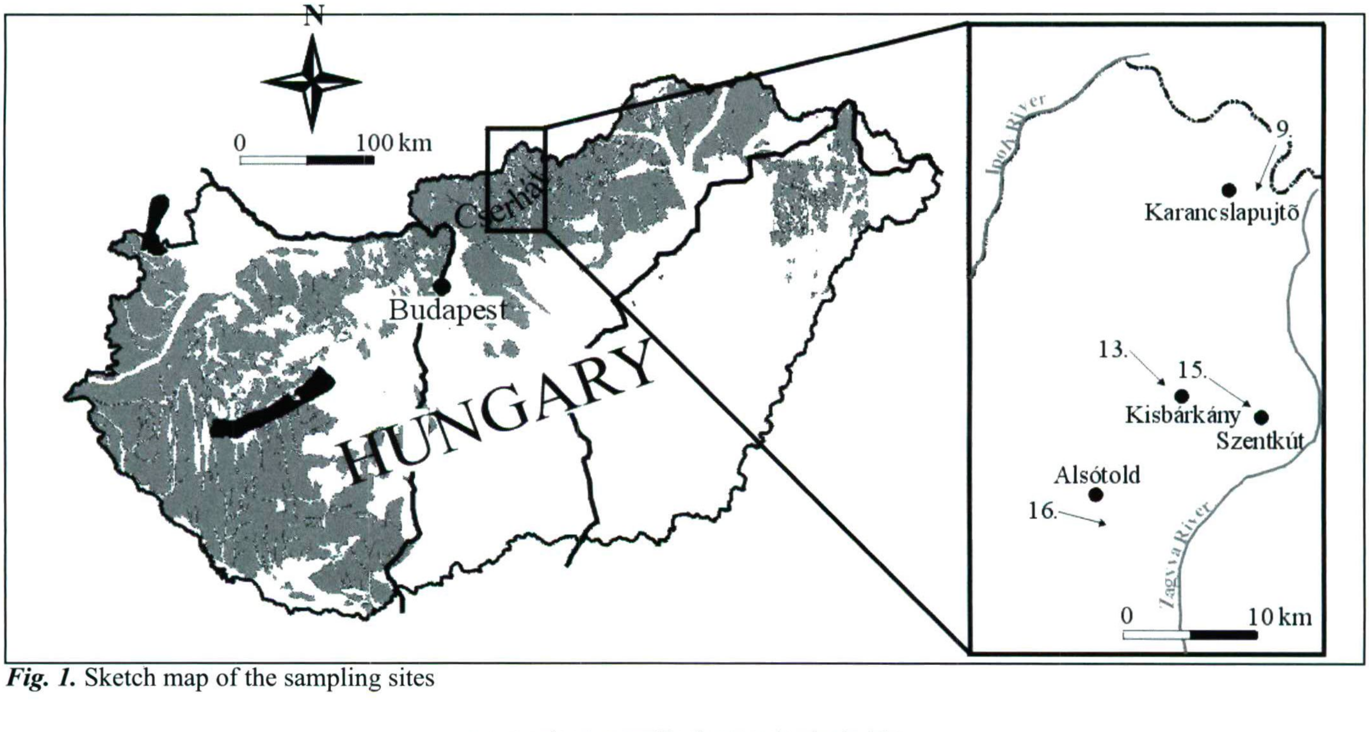

***Fig. 1.*** Sketch map of the sampling sites

changes of lability and bioavailability of this element in soils (Asami et al. 1995).

In forest soils of the Cserhát Mts., Sipos (2003) found a relative high bioavailability of lead as compared to other trace metals, such as Cu, Ni and Zn. In this paper the possible mobilization conditions of lead is studied as compared to a relatively mobile (Zn) and also to an immobile (Cr) heavy metal to verify the relatively high lability of lead in soils at the woodlands of an undisturbed area. Soil profiles developed from different parent materials were sampled to avoid the similarities in mineralogical and chemical compositions of the studied soils.

## MATERIALS AND METHODS

Four forest soil profiles were sampled to study the mobilization conditions of Pb as well as Zn and Cr. All of the studied profiles are Luvisols (Driessen et al. 2001) with silt loam texture, and are found in the Cserhát Mts., NE Hungary in short distance from each other (Fig. 1). The detailed characterization of the studied soil profiles can be found in Table 1 and also in the papers by Sipos (2003 and 2004). The variation of Ti/Zr ratios (Milnes and Fritzpatrick 1989) in the studied soil profiles with depth show the homogeneity of soils and parent materials.

Sequential extraction method after Li et al. (1995) was used to characterize the possible mobilization conditions of metals in the studied profiles. Five fractions were separated in five steps as follows: (1) exchangeable with $MgCl_2$ (EX); (2) bound to carbonates or specifically adsorbed, extracted by NaOAc (SAC); (3) bound to Fe-Mn oxides, extracted by $NH_2OH{\cdot}HCl$ (OX); (4) bound to organic matter and sulphides, extracted by $H_2O_2$ and $HNO_3$ (ORG); and (5) residual, extracted by $HNO_3$, $HClO_4$ and HF (RES). Concentrations of the studied metals in the solutions were analyzed by ICP-AES method (Jobin Yvon Ultima 2 Sequential ICP).

According to Johnson and Petras (1998) the EX, SAC, OX and ORG fractions can be interpreted as being pedogenic and labile. On the other hand metals in RES fraction are tightly bound in silicate mineral lattices or in crystalline oxide minerals. Metals released through weathering or deriving from anthropogenic sources are assumed to be soluble initially and it can not be added to the crystalline fraction, therefore they enter to the EX and SAC soil pool (Han et al. 2001). Based on these assumptions, we estimated the mobilization of metals by the estimating the depletion of metals from the crystalline fraction (RES). According to the suggestion of McBride et al. (1999), it can be estimated by using a relatively immobile element as an index, such as Ti. The total concentrations (TOT) and the amounts in RES fraction of metals were "normalized" as follows: $(M_{\text{TOT or RES}})N = (M_{\text{A or E or B}}/M_C)\text{-}(Ti_{\text{A or E or B}}/Ti_C)$, where M is metal concentration (Pb, Zn, Cr) and A, E, B, C are genetic soil horizons. The Ti and Zr contents of samples were determined by a Philips PW1410 X-ray fluorescence spectrometer.

## RESULTS AND DISCUSSION

### *Total metal contents and their distribution in the studied soil profiles*

The mean total lead content of the studied soil samples is 30.6 ± 7.5 mg/kg, which is in the range observed world-wide in different soils (Siegel 2002). Highest concentrations were found in the soil over andesite (P16) with a relatively small deviation (33.6 ± 2.8 mg/kg), while the soil over siltstone (P13) and calcareous sandstone (P15) are characterized by similar lead concentrations with relatively high deviation

***Table 1.*** Some physico-chemical properties of the studied soil profiles.

| Profile | Horizon | Depth | Munsell | pH | TOC* | Carb* | Texture* | | | Ti | Zr | Ti/Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Bedrock | | cm | color | ($H_2O$) | % | % | Sand | Silt | Clay | mg/kg | | |
| P09<br>calcareous<br>siltstone | A | 0-5 | 10YR3/4 | 5.66 | 6.74 | - | 41 | 51 | 8 | 4 495 ± 61 | 302 ± 11 | 15 |
| | E | 5-20 | 7.5YR5/8 | 6.39 | 0.92 | - | 38 | 55 | 7 | 5 195 ± 32 | 252 ± 12 | 21 |
| | B | 20-40 | 10YR5/8 | 6.85 | 0.39 | - | 26 | 62 | 12 | 4 512 ± 30 | 323 ± 13 | 19 |
| | BC | 40-60 | 10YR6/8 | 8.08 | <0.10 | 10 | 37 | 54 | 9 | 3 962 ± 60 | 194 ± 6 | 20 |
| | C | 60-75 | 2.5YR6/4 | 8.41 | <0.10 | 25 | 43 | 50 | 7 | 2 792 ± 55 | 155 ± 4 | 18 |
| P13<br>siltstone | A | 0-45 | 10YR4/2 | 5.49 | 2.31 | - | 15 | 75 | 10 | 5 679 ± 47 | 403 ± 2 | 14 |
| | E | 45-60 | 2.5YR5/2 | 5.05 | 0.25 | - | 9 | 77 | 13 | 5 485 ± 123 | 288 ± 3 | 19 |
| | B | 60-150 | 7.5YR5/2 | 5.05 | 0.20 | - | 8 | 74 | 18 | 4 730 ± 14 | 252 ± 2 | 19 |
| | C | 150-200 | 2.5YR6/2 | 5.41 | 0.14 | - | 8 | 79 | 13 | 4 773 ± 8 | 253 ± 4 | 19 |
| P15<br>calcareous<br>sandstone | A | 0-30 | 10YR3/3 | 5.27 | 3.48 | - | 29 | 61 | 10 | 5 340 ± 44 | 401 ± 12 | 13 |
| | E | 30-40 | 7.5YR4/4 | 5.27 | 1.06 | - | 10 | 77 | 13 | 5 532 ± 18 | 350 ± 3 | 16 |
| | B | 40-100 | 10YR5/4 | 5.67 | 0.78 | - | 7 | 76 | 17 | 5 198 ± 23 | 343 ± 10 | 15 |
| | C | 100-120 | 10YR6/4 | 7.84 | <0.10 | 40 | 31 | 60 | 9 | 2 368 ± 38 | 160 ± 4 | 15 |
| P16<br>andesite | A | 0-40 | 10YR3/3 | 5.84 | 2.29 | - | 24 | 67 | 9 | 7 133 ± 186 | 439 ± 2 | 16 |
| | E | 40-60 | 7.5YR4/2 | 6.30 | 1.05 | - | 4 | 87 | 9 | 7 301 ± 160 | 522 ± 11 | 14 |
| | B | 60-130 | 10YR5/6 | 6.03 | 0.35 | - | 4 | 82 | 14 | 6 093 ± 88 | 362 ± 10 | 17 |
| | C | 130-150 | 2.5YR5/4 | 6.12 | <0.10 | - | 6 | 82 | 12 | 6 340 ± 54 | 370 ± 13 | 17 |

*TOC was analyzed by Rock-Eval method (Delsi Oil Show Analyzer), carbonate (carb) content by XRD analyses (Philips 1710), texture by the pipette method, Ti and Zr concentrations by XRF analyses

(31.7 ± 6 and 30.5 ± 12 mg/kg, respectively), and the lowest lead contents were measured in the soil over calcareous siltstone (P9) with a relatively high deviation (25.1 ± 9.6 mg/kg). The similar lead concentrations of these soils developed on different litholgies shows that the parent rock does not influence the concentration of lead in the studied profiles significantly.

The variation of lead concentration in the studied profiles show in each case the same distribution: the amount of this metal decreases with depth (from 34.3 to 15.2 in P9, from 40.0 to 32.4 in P13, from 41.9 to 18.1 in P15, and from 37.4 to 31.4 mg/kg in P16), in spite of the fact that in the studied soils the downward leaching is the most significant pedogenic process resulting an accumulation in the B horizon. The amount of this metal in the surface horizon can be as high as twice of the value in the C horizons. The downwards decreasing lead content suggests the strong association of Pb to soil organic matter or its potential enrichment from external sources, which corresponds with the observations of Johnson and Petras (1998) and Sanchez-Camazano et al. (1998), as well as Fujikawa et al. (2000). According to Hansmann and Köppel (2000) the often considerably high Pb content of surface soil horizons is attributed to organic matter accumulation on the surface due to plant dry matter recycling rather than anthropogenic sources. However, Pb of anthropogenic origin exhibits the same accumulation pattern on the surface layer.

The mean total zinc (70.1 ± 11.4 mg/kg) and chromium (75.7 ± 14 mg/kg) content of the studied soils are also in the range reported for soils by other studies (Siegel 2002). There are only little differences among the Zn and Cr content of the studied profiles, which is also shown by the small relative deviations. The distribution of these metals with depth is mostly uniform, only a weak depletion in the C horizons of soils developed on calcareous parent material, as well as a weak enrichment on andesite was found showing the effect of parent materials. The uniform distribution type suggests the presence of these metals in minerals highly resistant to weathering.

*Mobilization conditions of heavy metals in the studied soil profiles*

Sequential extraction studies were performed on three parallel samples from each of the different genetic horizons of the four studied profiles (Table 2. and Fig. 2.). The results show that the most significant amount of metals can be bound to the RES fraction (26-62% of lead, 75-91% of zinc

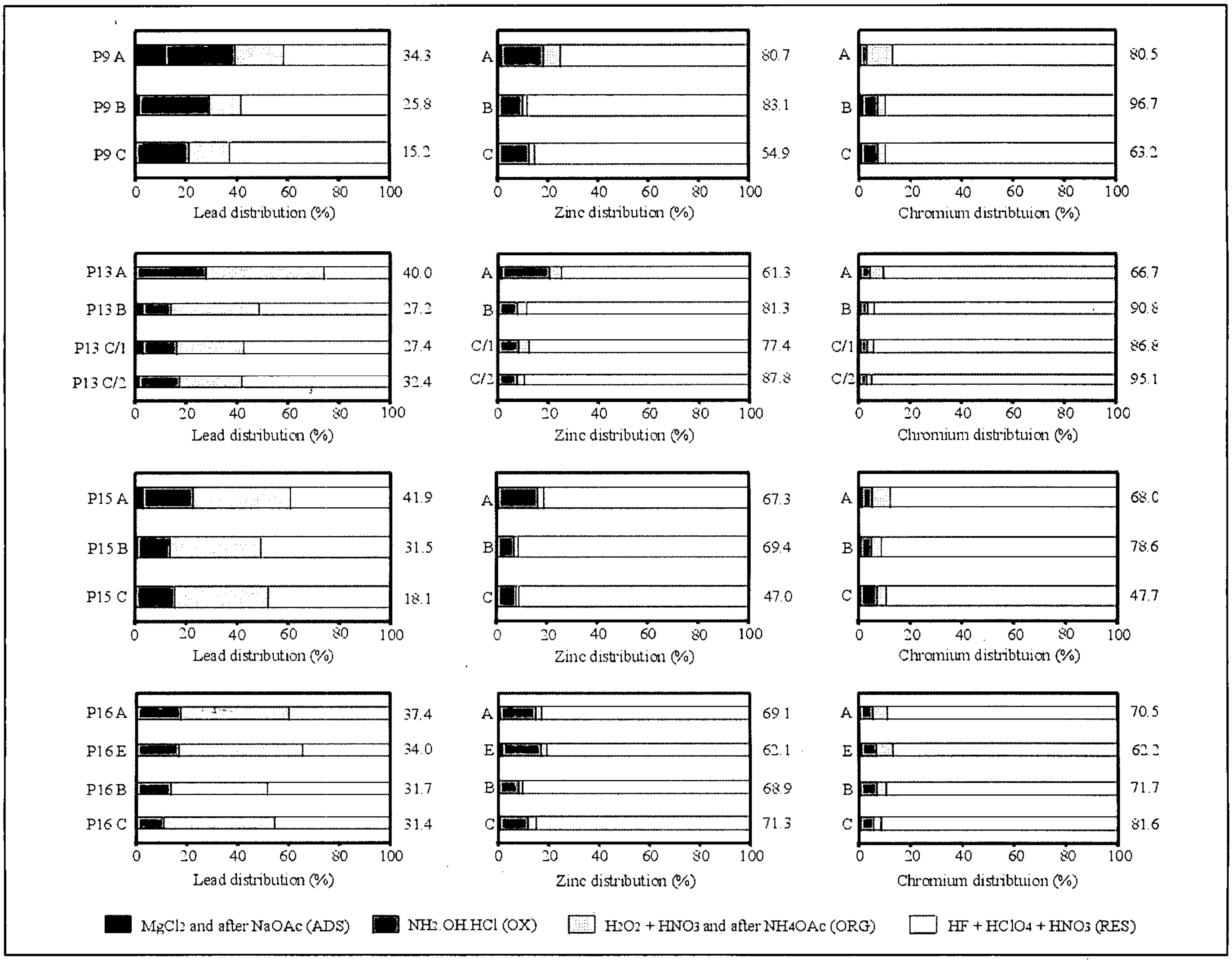

**Fig. 2.** Distribution of the studied metals among the different extracted fractions (ADS = adsorbed, OX = amorphous oxide bound, ORG = organically bound, RES = residual). The figure also shows the total metal contents of the studied samples in mg/kg.

*Table 2.* Results of sequential extractions and the titanium content of the studied soil samples.

| Element | Step | Profiles/Horizons | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | P9 | | | P13 | | | | P15 | | | P16 | | |
| | | A | B | C | A | B | C/1 | C/2 | A | B | C | A | E | B | C |
| Pb | 1 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| | 2 | 3.9 ± 0.3 | 0.6 ± 0.2 | <0.28 | <0.28 | 1.2 ± 0.2 | 1.1 ± 0.2 | 0.6 ± 0.2 | 1.6 ± 0.2 | 0.4 ± 0.2 | <0.28 | <0.28 | <0.28 | <0.28 | <0.28 |
| | 3 | 9.2 ± 0.5 | 6.5 ± 0.2 | 3.7 ± 0.2 | 16.7 ± 0.8 | 4.2 ± 0.1 | 4.4 ± 0.1 | 6.6 ± 0.2 | 10.1 ± 0.6 | 5.7 ± 0.4 | 4.1 ± 0.2 | 9.4 ± 0.8 | 9.2 ± 0.1 | 6.3 ± 0.1 | 5.4 ± 0.3 |
| | 4 | 6.4 ± 0.3 | 1.9 ± 0.1 | 0.6 ± 0.01 | 7.9 ± 0.2 | 2.4 ± 0.1 | 2.8 ± 0.2 | 2.6 ± 0.6 | 9.2 ± 0.7 | 3.1 ± 0.3 | 0.9 ± 0.05 | 6.6 ± 0.04 | 6.1 ± 0.3 | 3.5 ± 0.3 | 3.4 ± 0.1 |
| | 5 | 14.8 ± 1.7 | 16.8 ± 3.0 | 10.9 ± 0.3 | 15.4 ± 1.1 | 19.5 ± 0.1 | 19.1 ± 1.3 | 22.6 ± 1.7 | 21.1 ± 0.6 | 22.4 ± 2.4 | 13.0 ± 1.3 | 21.4 ± 1.2 | 18.8 ± 1.1 | 21.9 ± 2.5 | 22.5 ± 1.1 |
| | Sum | 34.3 ± 2.9 | 25.8 ± 3.5 | 15.2 ± 0.5 | 40.0 ± 2.0 | 27.2 ± 0.7 | 27.4 ± 1.9 | 32.4 ± 2.5 | 41.9 ± 2.1 | 31.5 ± 3.3 | 18.1 ± 1.5 | 37.4 ± 2.0 | 34.0 ± 1.5 | 31.7 ± 2.9 | 31.4 ± 1.5 |
| Zn | 1 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| | 2 | 1.9 ± 0.7 | 0.3 ± 0.2 | 0.1 ± 0.1 | 0.9 ± 0.5 | 0.03 ± 0.03 | 0.3 ± 0.3 | 0.3 ± 0.2 | 0.5 ± 0.4 | 0.9 ± 0.2 | <0.02 | 0.6 ± 0.5 | 1.1 ± 0.1 | 0.1 ± 0.1 | 0.3 ± 0.3 |
| | 3 | 13.4 ± 0.4 | 8.4 ± 0.3 | 7.1 ± 0.1 | 11.6 ± 0.2 | 6.6 ± 0.05 | 6.5 ± 0.3 | 7.0 ± 0.5 | 10.5 ± 0.3 | 4.7 ± 0.3 | 3.7 ± 0.1 | 9.7 ± 0.4 | 9.6 ± 0.4 | 5.7 ± 0.3 | 8.0 ± 0.4 |
| | 4 | 5.4 ± 0.3 | 1.7 ± 0.5 | 1.2 ± 0.1 | 3.2 ± 0.6 | 2.9 ± 0.3 | 3.1 ± 0.2 | 2.7 ± 0.3 | 1.7 0.1 | 1.2 ± 0.6 | 0.6 ± 0.4 | 1.8 ± 0.4 | 1.6 ± 0.4 | 1.4 ± 0.6 | 2.4 ± 0.8 |
| | 5 | 60.1 ± 2.3 | 72.7 ± 5.4 | 46.5 ± 1.1 | 45.6 ± 1.3 | 71.8 ± 3.1 | 67.5 ± 1.5 | 77.8 ± 3.2 | 54.7 0.4 | 62.6 ± 2.5 | 42.8 ± 0.2 | 57.1 ± 0.4 | 49.8 ± 1.3 | 61.8 ± 2.5 | 60.5 ± 0.4 |
| | Sum | 80.7 ± 3.8 | 83.1 ± 6.5 | 54.9 ± 1.4 | 61.3 ± 2.6 | 81.3 ± 3.8 | 77.4 ± 2.5 | 87.8 ± 4.4 | 67.3 1.4 | 69.4 ± 3.6 | 47.0 ± 0.7 | 69.1 ± 1.7 | 62.1 ± 2.2 | 68.9 ± 3.5 | 71.3 ± 1.9 |
| Cr | 1 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 |
| | 2 | 0.6 ± 0.04 | 1.7 ± 0.7 | 0.7 ± 0.1 | 0.6 ± 0.05 | 0.6 ± 0.02 | 0.5 ± 0.03 | 0.4 ± 0.02 | 0.9 0.1 | 0.7 ± 0.2 | 0.4 ± 0.04 | 0.6 ± 0.05 | 0.7 ± 0.1 | 0.6 ± 0.03 | 0.7 ± 0.05 |
| | 3 | 2.0 ± 0.1 | 5.7 ± 0.3 | 4.0 ± 0.1 | 2.5 ± 0.1 | 2.9 ± 0.01 | 2.7 ± 0.05 | 2.8 ± 0.1 | 2.7 0.1 | 3.3 ± 0.2 | 3.1 ± 0.01 | 3.4 ± 0.2 | 3.8 ± 0.2 | 4.1 ± 0.1 | 4.1 ± 0.1 |
| | 4 | 8.0 ± 0.7 | 2.8 ± 0.04 | 1.8 ± 0.02 | 3.4 ± 0.1 | 2.3 ± 0.1 | 2.1 ± 0.1 | 2.0 ± 0.04 | 4.8 0.3 | 3.0 ± 0.04 | 1.6 ± 0.1 | 3.9 ± 0.1 | 4.2 ± 0.4 | 3.0 ± 1.1 | 2.3 ± 0.1 |
| | 5 | 69.9 ± 1.2 | 86.5 ± 0.9 | 56.7 ± 3.7 | 60.3 ± 2.9 | 85.0 ± 5.3 | 81.5 ± 10.6 | 89.9 ± 2.0 | 59.6 2.7 | 71.7 ± 2.8 | 42.7 ± 2.0 | 62.7 ± 5.1 | 53.5 ± 7.7 | 64.1 ± 9.5 | 74.5 ± 1.4 |
| | Sum | 80.5 ± 2.0 | 96.7 ± 2.0 | 63.2 ± 3.9 | 66.7 ± 3.1 | 90.8 ± 5.4 | 86.8 ± 10.7 | 95.1 ± 2.1 | 68.0 3.1 | 78.6 ± 3.2 | 47.7 ± 2.2 | 70.5 ± 5.4 | 62.2 ± 8.5 | 71.7 ± 0.8 | 81.6 ± 1.6 |

Sum = total metal concentrations summarized from the 1-5 extraction steps

***Table 3.*** The normalized values of the total and residual lead, zinc and chromium concentrations.

| Profile | Horizon | $(Pb_{TOT})N$ | $(Pb_{RES})N$ | $(Zn_{TOT})N$ | $(Zn_{RES})N$ | $(Cr_{TOT})N$ | $(Cr_{RES})N$ |
|---|---|---|---|---|---|---|---|
| P9 | A | -0.2547 | 0.6433 | -0.3179 | -0.1383 | -0.3764 | -0.3361 |
| | B | -0.0844 | 0.0726 | -0.0552 | -0.1042 | -0.0927 | -0.0885 |
| | C | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| P13 | A | -0.5149 | 0.0371 | -0.6099 | -0.4972 | -0.5248 | -0.4942 |
| | B | -0.1351 | -0.1574 | -0.0725 | -0.0693 | -0.0498 | -0.0416 |
| | C/1 | -0.1659 | -0.1652 | -0.1431 | -0.1290 | -0.1034 | -0.0976 |
| | C/2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| P15 | A | -0.7560 | 0.0598 | -0.9772 | -0.8228 | -0.8574 | -0.8318 |
| | B | -0.5210 | -0.4536 | -0.7309 | -0.7178 | -0.5157 | -0.5484 |
| | C | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| P16 | A | -0.1745 | 0.0689 | -0.1820 | -0.1548 | -0.2836 | -0.2613 |
| | E | -0.3155 | -0.0660 | -0.3287 | -0.2803 | -0.4342 | -0.3899 |
| | B | 0.0100 | 0.0489 | 0.0600 | 0.0058 | -0.1008 | -0.0825 |
| | C | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

and 87-94% of chromium). The role of RES fraction in binding heavy metals increases with depth in each studied profile showing the increasing effect of soil parent material on the distribution of metals. Similar phenomenon was found both in natural (Arunachalan et al. 1996, Palumbo et al. 2000) and contaminated (Li et al. 2000) soils. According to the metal proportions bound to the RES fraction it can be stated that Pb is more labile than Zn or Cr. As compared to other studies (Tyler 1978, Plant and Raiswell 1983, Fujikawa et al. 2000) the lead shows unexpected high lability, this may be due to the different sources of the studied metals. In general, metals of anthropogenic origin are mostly found in labile fractions of soil as compared to metals inherited from the soil parent material (Asami et al. 1995).

The role of ORG fraction in binding metals is the most important in the case of lead (16-49% of total lead can be bound to it), while only a few percent of zinc and chromium can be bound to this fraction. In general, the amounts of Pb in this fraction decrease with depth in the studied soil profiles suggesting the relation between lead and organic matter. However, the highest metal amounts in ORG fraction are not always in the horizons having the highest organic matter content. The metal adsorption capacity of soil organic matter depends not only on its quantity but also on its quality (Fujikawa and Fukui 2001). For example humic acid is highly resistant to weathering, and its proportion in the soil organic matter highly influences the adsorption capacity (Schnitzer 1995).

Significant amount of lead (11-28%) and zinc (7-19%) can be bound to OX fraction, while in the case of chromium its role is secondary, only 1-6% of this metal is bound to this fraction. The co-precipitation and the subsequent adsorption of heavy metals by amorphous iron and manganese oxides is a well known phenomenon in soils (Taylor and McKenzie 1996, Maskall and Thornton 1996 etc.). The role of SAC fraction in binding the studied metals is negligible. Significant lead amount (12%) can be only bound to this fraction in the A horizon of soil P9.

The mobilization conditions of the studied metals shows similarities in the different soil profiles suggesting similar effects forming their distributions in these soils. The high lability of lead is unexpected; in addition this metal can be mobilized in a wide range of environmental conditions. These results suggest significant redistribution of lead during the pedogenic processes as compared to zinc and chromium. The lack of this kind of redistribution in the case of zinc (which is known as a mobile metal in soil conditions) rises the differences in source minerals of the studied metals or the presence of an external lead source, which comes the lead in phases weakly resistant to weathering from.

*Normalized distribution of the different metal fractions in the studies profiles*

The Ti-normalized metal concentration values show the degree of redistribution of metals in soil. These values were calculated for the total metal amounts and for the metal concentrations in RES fraction, as well (Table 3). The normalized distribution of chromium and zinc concentrations, as well as of the residual lead amount show a decreasing mobilization with depth in each studied profile (Fig. 3). In the P16 profile the highest depletion of the studied metals has been found in the E horizon due to the intense leaching from this horizon. This trend corresponds to the increasing effect of soil parent material downwards, and inversely, to the increasing effect of weathering and pedogenic processes upwards. The similarity of the normalized total and residual concentration values indicates that the mobilization of Zn and Cr is restricted in these profiles, and the weathering of phases containing these metals is not in advanced stage. The zinc shows a slight mobilization only in the case of profile P9.

The normalized distribution of $Pb_{TOT}$ shows a different trend as compared to the other metals. The total lead concentration shows relative enrichment in the upper horizons of all the studied soil profiles. This enrichment is the most significant in the case of P9 profile, where this phenomenon is present in the B horizon, as well. However, there is only a slight lead enrichment in the other three profiles. These differences can be due to the erosion of the upper soil horizons, or, in the case of an external lead source its heterogeneity.

Variation of metal/Ti ratios shows that lead has been significantly redistributed during the soil formation and it is presented in more labile form as compared to the other studied metals in the profiles. These differences can be resulted by the different source minerals of the studied metals on one hand, or by an external lead source on the other. In the first case, the detailed chemical characterization of soil minerals should be performed to determine the source phases of the studied metals, e.g. by heavy mineral separation. In general, Pb occurs in soils as discrete minerals, but since it can replace K, Sr, Ba and even Ca and

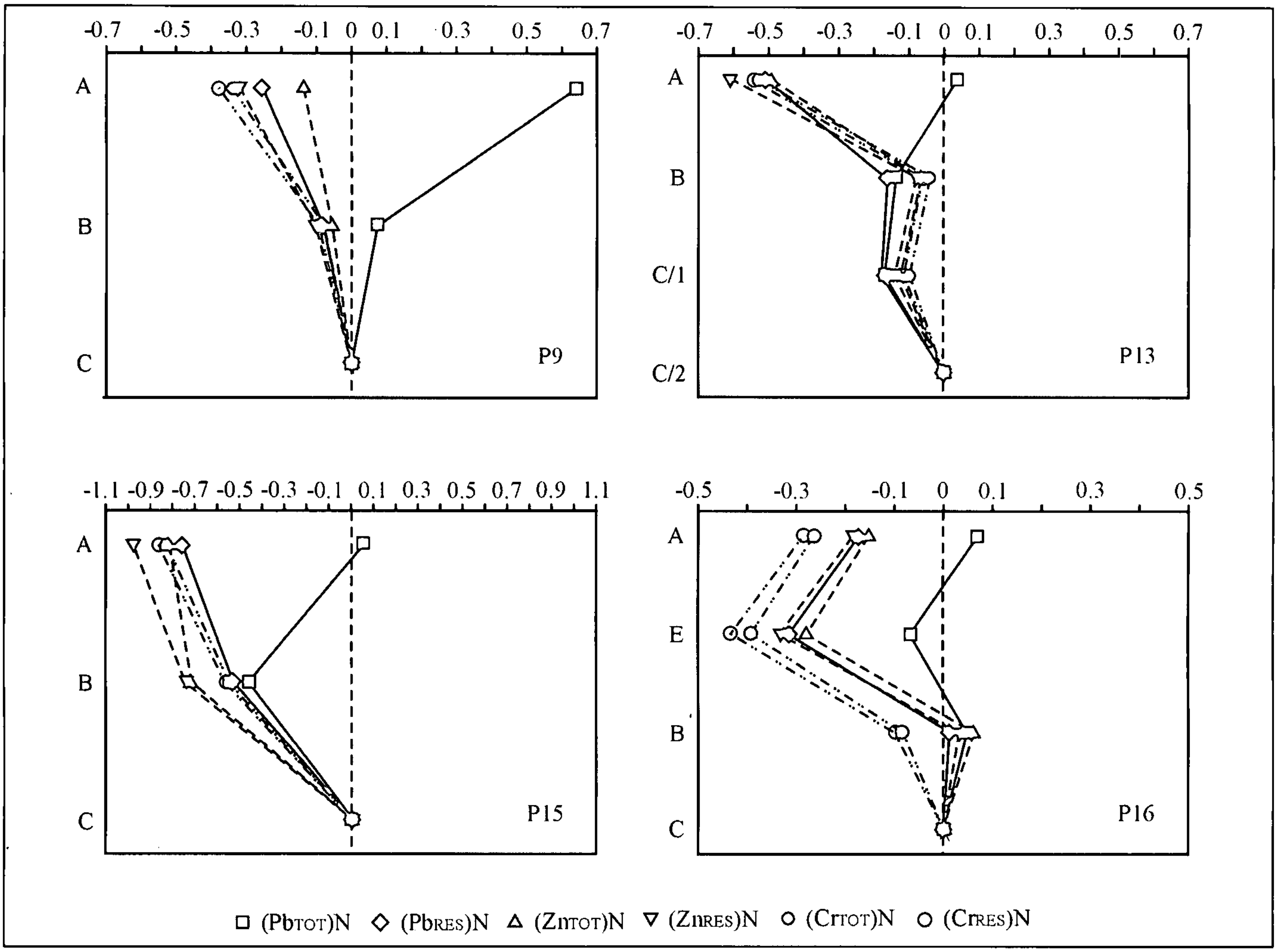

*Fig. 3.* Normalized distributions of total and residual metal concentrations in the studied soil profiles. P9, P13, P15 and P16 are the numbers of the studied profiles

Na, it can be fixed in the mineral lattice of silicates, which can be also weakly resistant to weathering (such as feldspars) (Nriagu 1978). Taking the geological and pedological characteristics of the study area into account, in the case of an external lead source, the natural origin of mobile lead is not probable. However, the verification of anthropogenic lead and the determination of its ratio to natural lead content of these soils need further studies, which may be based on lead isotope analyses (Erel et al. 1997, Weiss et al. 1999).

## CONCLUSIONS

The lead presents unique distribution type and redistribution characteristics in the studied soil profiles. The results show that the effect of soil parent material on the concentration and distribution of lead was significantly overwritten by pedogenic processes (or even anthropogenic influences).

The enrichment of lead in the upper horizons of these soils, its unexpected high lability (or extractability) and intense redistribution and mobilization as compared to other heavy metals (primarily to zinc) all suggest the presence of different lead source.

These differences can be resulted by the different source minerals of the studied metals on one hand, or by an external lead source on the other. The determination of the exact reason of the increased lability and bioavailability of this highly toxic heavy metal needs further studies.

## ACKNOWLEDGEMENTS

This study was financially supported by the Hungarian National Research Found (OTKA No. T-043445). The author is grateful to Dr. Chung Choi (University of Bristol) for the ICP analyses as well as for his help at sequential extractions. Use of analytical facilities at the Department of Earth Sciences, University of Bristol was funded by the European Community Access to Research Infrastructure action of the Improving Human Potential Programme, contract HPRI-CT-1999-00008, awarded to Prof. B. J. Wood (EU Geochemical Facility, University of Bristol). Dr. Béla Raucsik and Dr. Géza Szendrei are also thanked for their helpful reviews.

## REFERENCES

ADRIANO, D.C. (1986): Trace elements in the terrestrial environment, Springer-Verlag, New York, 219–262.

ARUNACHALAM, J., EMONS, H., KRASNODEBSKA, B., MOHL, C. (1996): Sequential extraction studies on homogenized forest soil samples. The Science of the Total Environment, **181**, 147–159.

ASAMI, T., KUBOTA, M., ORIKASA, K. (1995): Distribution of different fractions of cadmium, zinc, lead and copper in unpolluted and polluted soils. Water, Air and Soil Pollution, **83**, 187–194.

DRIESSEN, P., DECKERS, J., SPAARGAREN, O., NACHTERGAELE, F. (2001): Lecture notes on the major soils of the world, FAO, Rome.

EREL, Y., VERON, A., HALICZ, L. (1997): Tracing the transport of anthropogenic lead in the atmosphere and in soils using isotopic ratios. Geochimica et Cosmochimica Acta, **61**, 4495–4501.

FRIEDLAND, A.J., JOHNSON, A.H., SICCAMA, T.G. (1984): Trace metal content of the forest floor in the Green Mountains of Vermont – Spatial and temporal patterns. Water, Air and Soil Pollution, **21**, 161–170.

FUJIKAWA, Y., FUKUI, M., KUDO, A. (2000): Vertical distributions of trace metals in natural soil horizons from Japan. Part 1. Effect of soil types. Water, Air, and Soil Pollution, **124**, 1–21.

FUJIKAWA Y., FUKUI, M. (2001): Vertical distributions of trace metals in natural soil horizons from Japan. Part 2: Effects of organic components in soil. Water, Air, and Soil Pollution, **131**, 305–328.

HAN, F. X., BANIN, A., TRIPLETT, G. B. (2001): Redistribution of heavy metals in arid-zone soils under a wetting-drying cycle soil moisture regime. Soil Science, **166**, 18–28.

HANSMANN, W., KÖPPEL, V. (2000): Lead-isotopes as tracers of pollutants in soils. Chemical Geology, **171**, 123–144.

JOHNSON, C.E., PETRAS, R.J. (1998): Distribution of zinc and lead fractions within a forest Spodosol. Soil Science Society of America Journal, **62**, 782–789.

LI, X., COLES, B.J., RAMSEY, M.H., THORNTON, I. (1995): Sequential extraction of soils for multielement analysis by ICP-AES. Chemical Geology, **124**, 109–123.

LI, X., SHEN, Z., WAI, O., LI, Y. (2000): Chemical partitioning of heavy metal contaminants in sediments of the Pearl River Estuary. Chemical Speciation and Bioavailability, **12**, 17–25.

MASKALL, J., THORNTON, I. (1996): The distribution of trace and major elements in Kenyan soil profiles and implications for wildlife nutrition. In Appleton, J.D., Fuge, R., McCall, G.J.H. (eds.): Environmental geochemistry and health. Geological Society Special Publication No. **113**, 47–62.

MCBRIDE, M.B., RICHARDS, B.K., STEENHUIS, T., SPRIES, G. (1999): Long-term leaching of trace elements in a heavily sludge-amended silty clay loam soil. Soil Science, **164**, 613–623.

MÉSZÁROS, E., MOLNÁR, A., HORVÁTH, ZS. (1993): Atmospheric wet deposition of microelements in Hungary (in Hungarian). Agrokémia és Talajtan, **42**, 221–228.

MILNES, A.R., FRITZPATRICK, R.W. (1989): Titanium and zirconium minerals. In Dixon, J.B., Weed, S.B. (eds.): Minerals in soil environments. Soil Science Society of America Book Series, Madison, 1131–1205.

MOLNÁR, A., MÉSZÁROS, E., BOZSÓ, L., BORBÉLY-KISS, I., KOLTAY, E., SZABÓ, GY. (1993): Elemental composition of atmospheric aerosol particles under different conditions in Hungary. Atmospheric Environment Part A, **27**, 2457–2461.

NRIAGU, J.O. (1978): The biogeochemistry of lead in the environment, Elsevier, Amsterdam.

ÖTVÖS, E., PÁZMÁNDI, T., TUBA, Z. (2003): First national survey of atmospheric heavy metal deposition in Hungary by the analysis of mosses. The Science of the Total Environment, **309**, 151–160.

PALUMBO, B., ANGELONE, M., BELLANCA, A., DAZZI, C., HAUSER, S., NERI, R., WILSON, J. (2000): Influence of inheritance and pedogenesis on heavy metal distribution in soils of Sicily, Italy. Geoderma, **95**, 247–266.

PLANT, J.A., RAISWELL, R. (1983): Principles of environmental geochemistry, In Thornton, I. (ed.): Applied environmental geochemistry. Academic Press, London–New York, 1–39.

SANCHEZ-CAMAZANO, M., SANCHEZ-MARTIN, M.J., LORENZO, L.F. (1998): Significance of soil properties for content and distribution of cadmium and lead in natural calcareous soils. The Science of the Total Environment, **218**, 217–226.

SCHNITZER, M. (1995): Organic-inorganic interactions in soils and their effects on soil quality. In Huang, P. M., Berthelin, J.M., McGill, W.B., Page, A.L. (eds.): Environmental impact of soil component interactions. Lewis Publishers, Boca Raton, Florida, 3–19.

SETTLE, D.M., PATTERSON, C. (1980): Lead in Albacore: guide to lead pollution in Americans. Science, **207**, 1167–1176.

SIEGEL, F.R. (2002): Environmental geochemistry of potentially toxic metals, Springer-Verlag, Berlin Heidelberg.

SIPOS, P. (2003): Distribution of Cu, Ni, Pb and Zn in natural brown forest soil profiles from the Cserhát Mts., NE Hungary. Acta Mineralogical-Petrographica, Szeged, **44**, 43-50.

SIPOS, P. (2004): Geologic and pedogenic effects on heavy metal distributions in forest soils from the Cserhát Mts. and the Karancs area, NE Hungary. Acta Geologica Hungarica, **47**, 411–429.

STURGES, W.T., BARRIE, L.A. (1989): Stable lead isotope ratios in arctic aerosols: evidence for the origin of arctic air pollution. Atmospheric Environment, **23**, 2513–2519.

SZALAI, Z. (1998): Determination of heavy metal deposition through the analysis of soil and vegetation samples (Budapest, Isle of Háros). Földrajzi Értesítő, **47**, 515–522. (in Hungarian)

TAYLOR, R.M., MCKENZIE, R.M. (1966): The association of trace elements with manganese minerals in Australian soils. Australian Journal of Soil Research, **4**, 29–39.

TYLER, G. (1978): Leaching rates of heavy metal ions in forest soils. Water, Air, and Soil Pollution, **9**, 137–148.

WEISS, D., SHOTYK, W., KEMPF, O. (1999): Archives of atmospheric lead pollution. Naturwissenschaften, **86**, 262–275.

*Received: August 30, 2007; accepted: November 30, 2007*