EXTRACTION OF TOXIC HEAVY METALS FROM POLLUTED SOILS IN FORM OF CHELATES

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INTRODUCTION

Heavy metals as essential microelements and hazardous, toxic soil pollutants interact with the components of soil. They can be incorporated into different parts of the plants from the soil solution and they get into the food chain. Environmental protection requires the removal of toxic heavy metals from contaminated soils. The two most frequently applied methods are a/ treatment of soils with chemicals; (b/ applying micro-organisms with metal accumulating properties.

In the laboratory practice the most frequently used chemical possibility of removal is the extraction method (using a suitable extractant, e. g. a strong acid or a suitable complexing agent at a given pH). Complexing agents are widely used in the practice of soil science. The three most frequently applied possibilities are the following:

–Polyamine-polyacetate chelating compounds as metal carriers have been used for about 40 years as microelement fertilisers to supply essential microelements (Fe, Mn, Zn and Cu) to plants. The efficiency of the chelating agents depends on their ability to keep the trace elements in soluble form *(Hargitai-Tóth et al.).*

–Knowledge of the total trace element concentrations of the soil samples (for example determining with mixture of concentrate strong acids in Teflon bomb) provides only limited information about the their plant availability, toxic effects, mobility and transport properties. Although there is no existence of an universal extractant which is suitable for simultaneous determination of the plant availability of all the known microelements; chelating agents (at a given pH) are effectively employed to extract the bio-available forms *(Lakanen and Erviö 1971, Lindsay and Norwell 1978, Li and Shuman 1996, Norwell 1984, Quewauviller et al. 1996, Soltanpour and Shwab, 1977).*

–Chelating agents are often used to remove toxic heavy metals from contaminated soils and this topic is a highly important issue in environmental protection *(Peters and Shem 1992).*

The objectives of this study were:

(1)to investigate the effect of some extractants (containing EDTA or DTPA chelating agents) on the extractability of Cd, Pb and Cr from artificially polluted soils;

(2)to examine the effect of pH on the extraction in the presence of EDTA or without EDTA;

(3)finally we considered to study the time-dependence of the extraction of the examined heavy metals from artificially polluted soils using EDTA (pH=4,65).

In this paper we give a qualitative interpretation of the extraction in terms of previous suggestions.

MATERIALS AND METHODS

In the experiments three different soils: a humus alluvial soil from Tiszavasvári, a chernozem soil from Tiszalök and a sandy soil from Nyíregyháza (East Hungary) were used. Some chemical characteristics of these soils are shown in Table I.

Table I. **Some characteristics data of the soils**

	Humus alluvial soil	***Chernozem soil***	***Sandy soil***
pH (KCl)	7,40	7,67	6,2
Org. C (g/kg)	19,1	13,3	5,8
Carbonate %	14,1	6,69	-

Artificial pollution of soils. Soils were thoroughly shaken with solutions of $Cd(NO_3)_2$, $Pb(NO_3)_2$ and $Cr(NO_3)_3$. Each soil contained $2 \cdot 10^{-5}$ mol/g Cd (2248 mg/kg), Pb (4144 mg/kg) or Cr (1040 mg/kg). After half an hour of shaking the homogeneous suspensions were transferred into plastic dishes and kept in a room, for more than 3 years. In the course of time the soil samples lost their water content. The experiments were made three years after the pollution.

In the first part of the experiments the effect of three extraction procedures was investigated on the removal of Cd, Pb and Cr from artificially polluted humus alluvial, chernozem and sandy soils:

–0,005M DTPA/ 0,01M $CaCl_2$/ 0,1M trietanol-amin (TEA) (pH=7,30), [*Lindsay and Norwell 1978],*

–0,005M DTPA/ 1 M NH_4HCO_3 (pH=7,60), [*Soltanpour and Shwab,1977*],

–0,02 M EDTA/ 0,5 M $NH_4OOC\text{-}CH_3$ (pH=4,65), [*Lakanen and Erviö, 1971*].

Secondly we investigated the effect of pH on the extraction of Cd, Pb and Cr from artificially polluted humus alluvial and chernozem soils in presence of EDTA or without EDTA. Two parallel experiments were carried out. In one of the runs the samples were mixed with solutions contained appropriate concentrations of HNO_3 or NaOH to adjust the pH. In the other run the solutions contained EDTA too. The ratio of solid : liquid was 1:40 and the molar ratio of heavy metal : ligand was 1:50. The pH of the solutions was measured and the heavy metal concentrations in the liquid phase were determined by AAS.

Finally we have studied the time-dependence of extraction of Cd, Cr, Pb from polluted humus alluvial and chernozem soils using EDTA as extracting agent. Before carrying out the experiment bidistilled water was added to the soil samples and the mixtures were stirred for 30 min. This time proved to be enough to reach equilibrium between the phases. After 30 min. the pH was adjusted to 4,65. At time zero EDTA was added to the samples and the suspensions were stirred vigorously. The ratio of solid : liquid was 1:40, the molar ratio of heavy metal : ligand was 1:50 and pH was kept at a constant value of pH=4,65 by adding a few drops of 2M HCl or 2M NaOH if it required. Reaction periods varied from 0,5 min to 3 days. The temperature was 25 °C. Then 10 cm^3 portions of the suspensions were withdrawn and the phases were separated by colloid membrane filtration. The concentrations in the liquid phase were determined by AAS.

RESULTS AND DISCUSSION

Three extraction procedures (DTPA/$CaCl_2$/TEA; DTPA/NH_4HCO_3; EDTA/$NH_4OOC\text{-}CH_3$) were compared in Fig. 1 to evaluate the extractability of Cd, Pb and Cr from polluted soils. The extractants contained salts ($CaCl_2$, NH_4HCO_3 and $NH_4OOC\text{-}CH_3$). The effect of salts on extraction was to improve the removal processes since salt solutions have also been used as extracting agents. The improvement is probably due to cation exchange reaction, which play an important roll in adsorption and desorption processes.

EDTA was the most effective extractants for Cd and Pb. This extraction removed more than 90% Cd and 63-75% Pb for the three different types of soils (Fig.1A). The percentages of DTPA extractable heavy metal ions (32-40% for Cd and 12-36% for Pb, according to the methods of both *Lindsay et al.* and *Soltanpour et al.*) were much lower (Fig.1B) than those for EDTA (according to *Lakanen et al.*). Extracting metals more

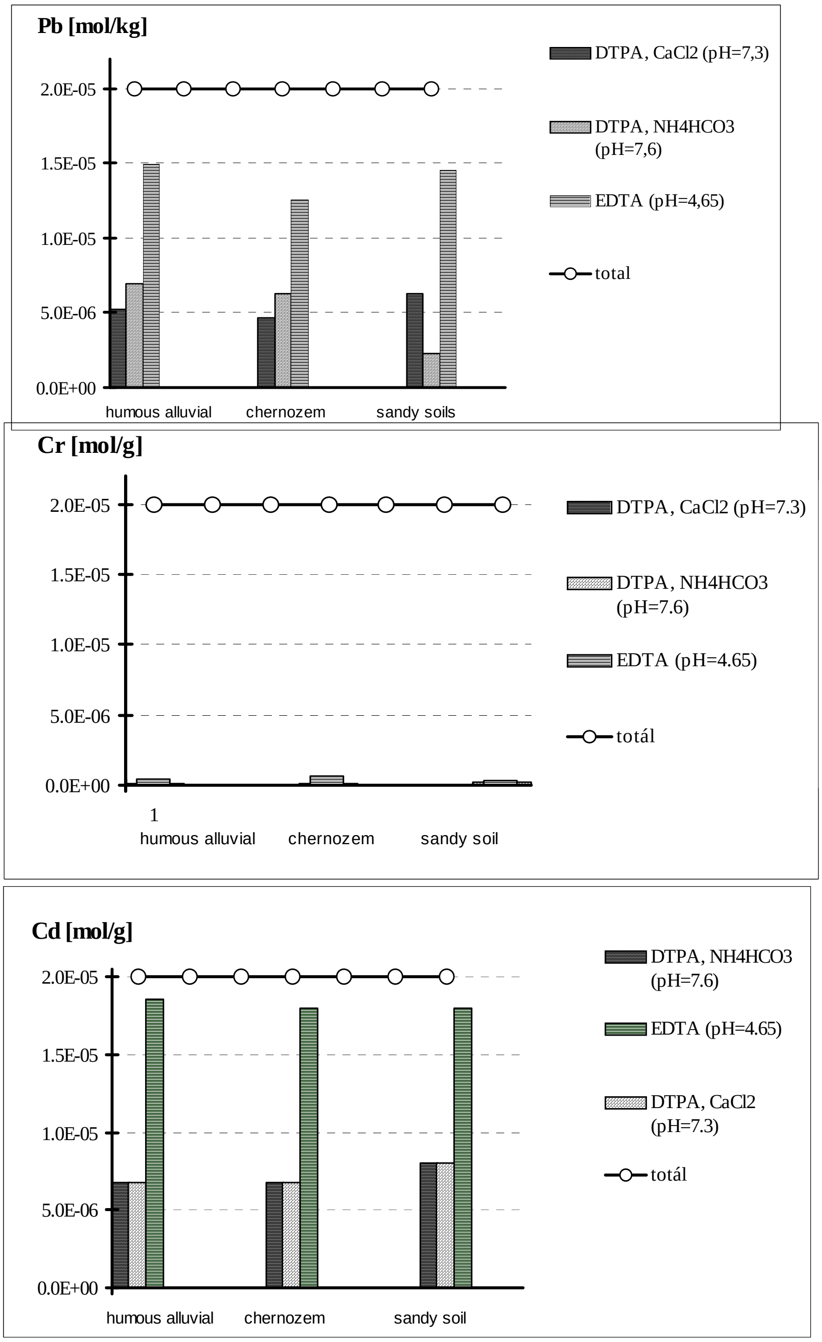

*Fig.1: Comparison of Pb (**A**), Cd (**B**) and Cr (**C**) extracted by three chelating extractants from humus alluvial, chernozem and sandy soil.*

effectively from polluted soils may require higher concentrations of chelating agent (DTPA) or higher extractant : soil ratio. The concentration of EDTA (0,02 M) was four times higher than the concentration of DTPA. The amount of extracted chromium was very low (less than 4%) for all the three extractants as was shown on Fig.1C. The reason for the slight removal results of Cr may be the rather immobile species of Cr(III) that can be present in different compounds or lattice structures of great binding strength.

Changes in percentages of extracted Cd, Pb and Cr versus pH are shown in Fig.2 for the chernozem soil. There were no meaningful differences between the soils. The extracted amounts of heavy metal ions at a given pH followed the order: Cd > Pb >> Cr. At pH 1 about 20% of Cr, 60-70% of Pb and more than 90% of Cd appeared in the solution. As the pH increased the efficiency of extractability sharply decreased. Practically there were no Cr^{3+}-ions at pH >2,5; Pb^{2+}-ions at pH>3 and Cd^{2+}-ions at pH >7,5 in the solution.

At low pH the most important effects of H^+-ions were the following:

–Heavy metal cations on the surface of clays, other minerals (oxides and hydroxides of Fe, Mn, Al, Si, etc.) and humus substances were exchanged;

–H^+-ions could cause serious damage in the soil structure by changing the interaction between the soil particles;

–It can be suggested that mainly carbonates and Fe-, Mn-oxides coatings of the alumino-silicate-matrix were dissolved (together with the previously chemisorbed or precipitated toxic, polluting heavy metal ions on their surfaces) and the matrix remained relatively unharmed.

In Fig. 3 the efficiency of extraction with Cd, Pb and Cr in percentages as a function of pH for the chernozem soil can be seen in presence of EDTA. The most favourable conditions for removal of Cd and Pb were in pH range 3-5,5. In this range the extractability of heavy metals remained almost constant. The removal efficiency for Cd was approximately 75% (chernozem as well as humus alluvial soil); for Pb 65% (chernozem soil) and 75% (humous alluvial soil). The extraction of Pb above pH 7 depended better on pH than Cd. The ability of EDTA to enhance the extractability of Cr(III) was very low (less than 5%) over the entire examined pH range.

Changes in percentage of Cd, Pb and Cr during a 3-day experimental period - that is the removal with EDTA, - are shown in Fig. 4 for the chernozem soil. There were no significant differences between the soils. Extraction of Cd and Pb was faster than that of Cr. Approximately 1 day was required to reach the equilibrium. It can be seen on Fig.4 that the removal processes for Cd and Pb could be divided into two groups: the rapid reactions taking

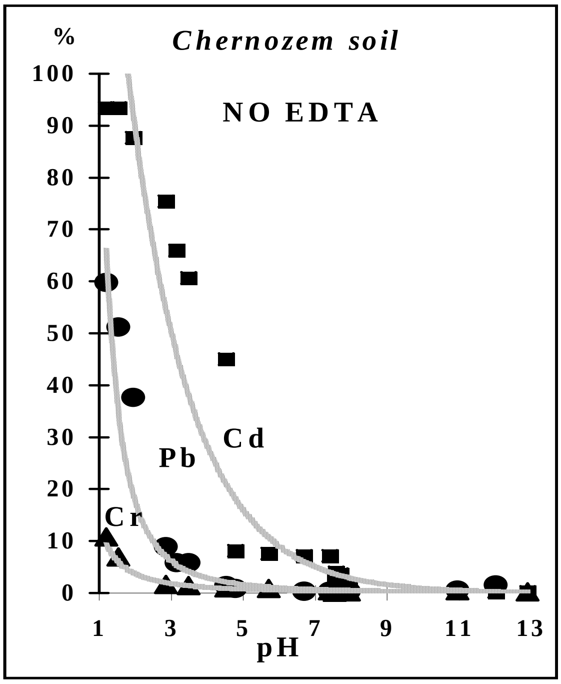

Fig.2. Changes with pH in the percentages of extracted Cd, Pb and Cr with polluted chernozem soil without EDTA.

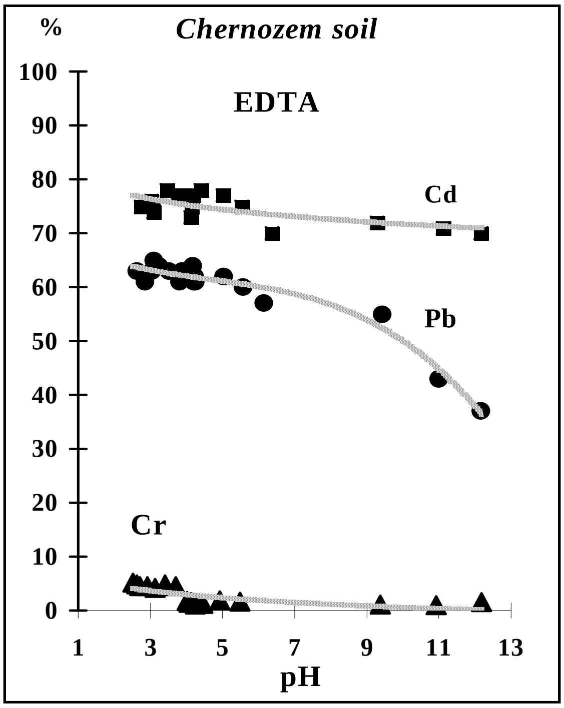

Fig.3. Changes with pH in the percentages of Cd, Pb and Cr extracted with EDTA with polluted chernozem soil.

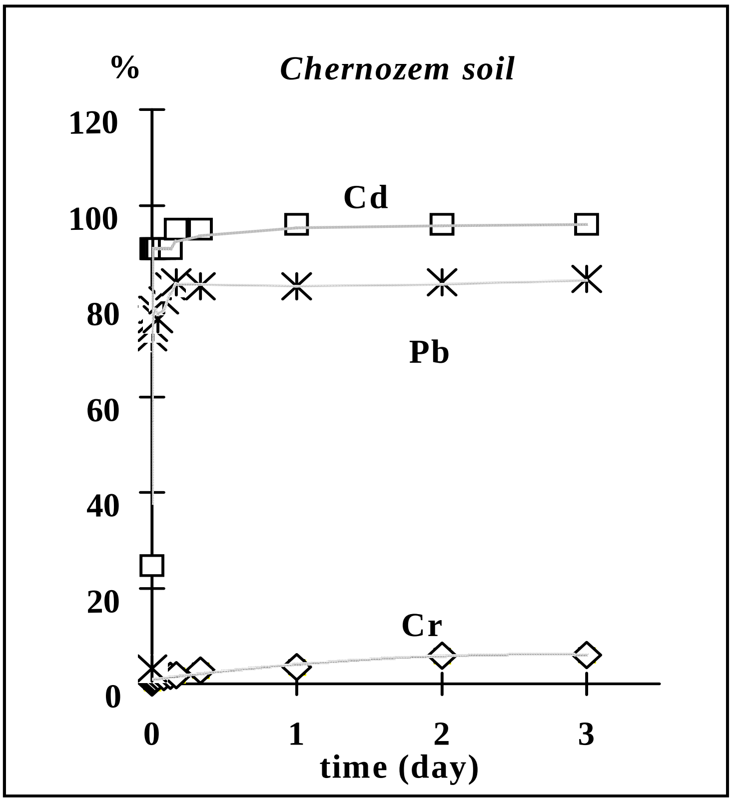

Fig. 4. Changes with time in the percentages of Cd, Pb and Cr extracted with EDTA with polluted chernozem soil (pH=4,65).

place within two minutes and the slow reactions requiring about one day. Due to the fast reaction about 90% (both soils) of Cd and 72% (chernozem), 86% (humus alluvial soil) of Pb appeared in the solution. The efficiency of the extraction after one day was for Cd 96% (chernozem soil), 99% (humus alluvial soils) and for Pb 85 % (chernozem soil), 99 % (humus alluvial soil). Therefore it is not possible to describe the extraction with a single-reaction because the heavy metals are fixed on a variety of soil components (clay minerals, hydrous oxides of silicon, aluminium, manganese, humic substances, etc.) whose affinity and binding strength are very different. For this reason many types of reactions occur during the extraction (dissolution, ion-exchange, desorption, decomplexation, surface precipitation, diffusion from the inner sites of the soil matrix, etc.).

In case of Cr the processes of removal was much slower. The efficiency of extraction was only 6,1% (chernozem) and 3,4% (humus alluvial soil) after three days and this time was not enough to reach the equilibrium. The slow extraction partly can be attributed to slow irreversible processes (e.g. diffusion from the internal lattice sites). Moreover it is possible that the forward steps (e.g. desorption) of the reversible processes of the removal are much slower than the backward steps (e.g. adsorption) because of the great binding strength of chromium(III) fixation on the soil components. Because strong bonds must be broken, desorption always requires much higher activation energy than chemisorption consequently removal much slower than chemisorption. The slow extraction partly can be explained in terms of kinetic inertnes of Cr(III)-complexes, mainly the slow decomplexation reaction of Cr(III)-humus complexes.

ABSTRACT

We have studied the extraction of some heavy metals from artificially polluted soils. First we investigated the effect of three different extraction procedures (containing chelating agents) on the extractability of Cd, Pb and Cr. EDTA/NH_4OOC-CH_3 (pH=4,65) was a more effective extractant for Cd and Pb than DTPA/$CaCl_2$/TEA (pH=7,30) or DTPA/NH_4HCO_3 (pH=7,60). The extractability of Cr was very slight. Secondly we investigated the effect of pH on the extraction. Without presence of EDTA at pH 1 about 20% of Cr, 60-70% of Pb and more than 90% of Cd appeared in the solution. As the pH increased the efficiency of extractability sharply decreased. In presence of EDTA the most favourable conditions for removal of Cd and Pb were in pH range 3-5,5. The removal efficiency with Cd was approximately 75%, with Pb 65% -75% and with Cr <5%. Finally we studied the time-dependence of extraction using EDTA (pH=4.65) as a chelating agent. Approximately 1 day was required to reach the equilibrium for removal of Cd and Pb. The efficiency of the extraction after one day was for Cd 96% - 99% and for Pb 85% - 99 %. In case of Cr the processes of removal was much slower. The efficiency of extraction was only 3,4%-6,1% after three days and this time was not enough to reach the equilibrium. The concentrations in the liquid phase were determined by AAS.

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