MAIN SOIL PARAMETERS GOVERNING HEAVY METAL ADSORPTION AND DESORPTION PROCESSES

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Abstract

Heavy metals are distributed within soil profile according to their chemical state, transferred by hydrological flows and taken up by organisms through trophic pathways. Persistent pollutants include Zn, Cu, Pb, Cd and Ni, which cannot be removed or destroyed, leading to bioaccumulation. In soil, the maximum permissible limit for the European Union are 100 mg/kg Cu, 300 mg/kg Zn, 50 mg/kg Ni, 3 mg/kg Cd, 250 mg/kg Pb. Adsorption and desorption take place through the exchange of molecules and ions between the solid phase of heavy metals and the liquid phase of the soil, and are in accordance with the soil components: colloidal clay content, pH, organic matter, amount of carbonates and salts. The paper aim is to characterized two soil profiles up to 110 cm depth, collected from Agromixt Spineni Farm, Iasi which govern heavy metal adsorption and desorption process. The results present a neutral to alkaline (pH up to 8.81) soil pH, a carbonate content between 0.56% - 19.62% and salt content from 52-554 mg/100g soil. The results indicate that heavy metals are deposited and accumulated in the surface soil layers 0-30 cm depth. The solubility of carbonates and the presence of salts in high concentrations can retain copper (3.1 mg/Kg), nickel (1.5 mg/Kg) and lead (6.8 mg/Kg). The increased content of organic matter, weakly acidic or neutral pH values allow an increase in the mobility of zinc (15.5 mg/Kg) and cadmium. (1.0 mg/Kg). The accessibility of heavy metals can be reduced in alkaline media by desorption phenomenon, and their effect on the environment will be low and pose no risk to human health.

Key words: soil, heavy metals, adsorption, desorption.

The objective of this work was to follow the adsorption and desorption processes of heavy metals in Agromixt Spineni Iasi Farm, as well as the chemical and physical parameters that influence these phenomena. The category of toxic metals includes a number of chemical elements that are highly toxic to living organisms, such as Ni, Pb, Cd, their toxic effect does not diminish over a long period of time. Depending on the chemical, physical and electrochemical properties of the metals and the organisms subject to contamination, a differentiated toxicity can be established (Duffus *et al*., 2002). The mobility of heavy metals is directly influenced by their "chemical speciation" (free metal ions, dissolved or coprecipitated metal complexes) which directly influences their behaviour and toxicity in the environment (Fairbrother *et al.*, 2007).

Both adsorption and desorption are an exchange of atoms and ions or molecules that takes place between the solid phase of heavy metals in the soil and the soil solution. Adsorption is a process of accumulation of ions at the solid-liquid interface where the colloidal part of the soil participates and desorption takes place when changes occur in an equilibrium situation, occurs at the surface and controls the accessibility and mobility of heavy metals.

An equilibrium is established between the ions in solution and the solid phase, which is constantly changing due to external intervention (base amendment, improper fertilization, acid rain). The most important soil parameters driving the adsorption and desorption processes are: pH and Eh values, organic matter, content of grain size fractions, oxides and hydroxides especially of Al, Mn and Fe, formation of insoluble salts, carbonate content and microorganisms (Kabata-Pendias, 2001).

Zinc is an essential microelement for all plants and has a nutritive effect, but in excessive quantities it becomes toxic. In Romanian soils, zinc content varies between 10 and 300 ppm**.**

Cadmium is a non-essential metallic element, but due to its increased mobility and availability it easily accumulates in plants, which is why it is one of the most dangerous pollutants. In Romania, the maximum limit for Cd in soil is 1.0 mg/kg, which can enter the atmosphere from volcanic eruptions and forest burning, and sewage sludge contains a high load of cadmium.

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Copper is a microelement involved in some sequences of the nitrogen circuit and plays an enzymatic role. Copper retention in soil increases in proportion to the organic matter content and co-precipitates with oxides in the soil material. The normal value of Cu in soil is 20 ppm and the intervention threshold is 100 ppm.

According to the Order 756/1997 issued by the Ministry of Water, Forests and Environmental Protection, the maximum limit for lead content in soil is 100 mg/kg and the average content for plants is between 0.5 and 3 ppm.

Nickel is a transition metal, it associates with Co, Cu, and Pt. According to Order no. 756/1997 issued by the Romanian Ministry of Water, Forests, and Environmental Protection, the maximum permissible limit for the total content of nickel in soil is 50 mg/kg. The risk of soil contamination with heavy metals either directly or indirectly, occurs under conditions of high acidity, when the soil has a low carbonate content. In alkaline soils rich in carbonates and salts, heavy metals are adsorbed and fixed by soil colloids. Some researchers believe that an ion exchange reaction may occur and that calcium carbonate has a buffering effect (Liu *et al*., 2011).

The electrochemical series of metal voltages characterize the behaviour of metals and their salts in aqueous solutions. All metals to the left of hydrogen are able to replace from saline solutions those metals that are in the metal stress series after it, except for alkaline earth metals.

MATERIAL AND METHOD

In order to study the behaviour of heavy metals Cd, Zn, Pb, Ni, Cu on two profiles from Spineni - Andriseni (cambic cernozite) showing a neutral and alkaline reaction, it was necessary to determine the total and plant-accessible forms. Solubility and mobility of heavy metals is closely related to adsorption, desorption, complexation, oxidation-reduction, precipitation and dissolution processes. (Barman *et al.* 2000, Quartacci *et al.,* 2005)

The whole mechanism of adsorption and desorption of heavy metals is related to soil components, therefore the ability of clay and calcium carbonate to accumulate heavy metals, soil reaction, salt and humus content were evaluated.

In the laboratory the soil samples (dry and wetted) were analyzed potentiometrically on a WTW multi-carrier for pH determination in aqueous extract in soil water ratio of 1: 2.5 The determination of organic carbon and humus content was performed by the Walkley-Black method in the Gogoaşă modification by wet mineralization of soil samples and titration with

Mohr salt. Organic carbon multiplied by the constant 1.724 leads to the humus value. The determination of grain size fractions was carried out by the classical Kacinski method by differential treatment of samples with or without carbonates. Coarse sand is determined by wet sieving and the pipetting of grain size fractions of fine sand, dust, colloidal clay and physical clay is performed using Kubiena pipette.

The phenomenon of soil enrichment in salts occurs with the help of humid air masses loaded with soluble salts followed by their dissolution, accumulation and transport by water. In order to assess the salinization intensity, it was necessary to obtain an aqueous extract with a soil-water ratio of 1:5 and to determine the content of soluble salts by a conductometric method.

The content of heavy metals in total form was carried out by wet disaggregation with a mixture of acids (nitric, hydrochloric and perchloric) according to the ICPA Bucharest method and the determination of metals by the Flame Atomic Absorption Spectrometer (AAS) 700. The determination of the mobile contents of microelements takes place by an extraction in a solution of EDTA-ammonium acetate.

RESULTS AND DISCUSSIONS

Research has shown that in soil all heavy metals undergo a rapid initial reaction, followed by slower reactions when the metal is removed from the soluble pool. This process increases the fixed fraction, which cannot be easily changed in the solution phase.

Due to the need to integrate the principles of accumulation, transfer and blocking or removal of heavy metals under certain conditions, the soil taken from Spineni Andriseni Farm was chemically and physically analyzed *(table 1, table 2)*. By comparison the two profiles 8 and 15 showed the adsorption-desorption phenomenon.

Table 1

Profile characteristics (profile 8)

Type	pH	CaCO₃ (%)	Salt content (mg/100 g)	Humus (%)	Colloidal Clay (%)
A	6.85	-		4.22	41.7
A	7.05	-		3.73	42.4
A	7.20	-		3.05	41.8
AB	7.38	-			40.3
B	7.60	0.56	52		41.1

In order to characterize the state of the soil and to correlate its characteristics with the heavy metal content, it was necessary to determine the concentration of heavy metals in total and accessible form (up to a depth of 60 cm in profile 8 and 80 cm in profile 15). The values obtained for heavy metals in soil were compared with the

standard reference values imposed by the Romanian legislation - Order 756/1997.

Table 2

Physical and chemical characteristics (profile 15)

Type	pH	CaCO₃ (%)	Salt content mg/100g	Humus (%)	Colloidal Clay (%)
A	7.90	5.23	220	2.80	53.3
C	8.24	10.22	544	0.89	52.1
C	8.61	19.62	393		51.3
CG	8.50	18.30	554		55.4
G	8.81	17.50	456		56.2

Clay includes aluminosilicates and hydrated metal oxide, exhibits cation exchange and surface characteristics, therefore adsorption of heavy metals occurs, clay being an active adsorption component of soil. Organic matter consists of living organisms, soluble biochemical compounds, and insoluble humic substances. All of these provide sorption sites for metals and participate in the exchange capacity of the soil. The results show that of all the metals analyzed, copper is the most strongly retained on organic matter. (Wu *et al*., 2018). An important parameter that directly influences adsorption and desorption processes or heavy metal precipitation/dissolution phenomena is the soil reaction (*figure 1)*. A decrease in the activity of metals in both total and accessible forms is observed with increasing pH values. Under acidic conditions and neutral pH values, heavy metals have a higher activity, which makes them more easily adsorbed by plants.
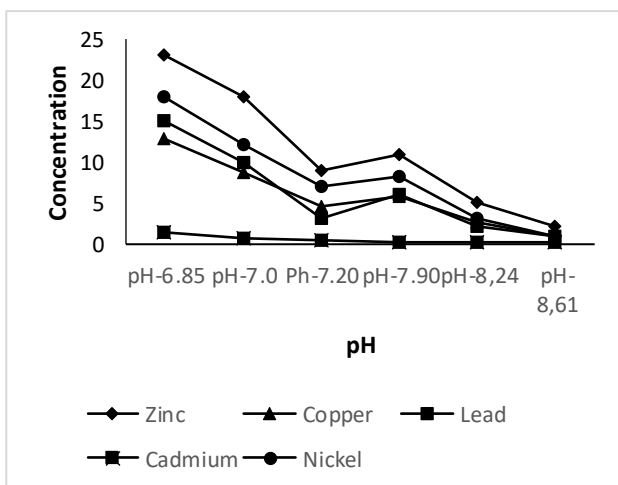

Figure 1 - **Variation diagram of heavy metal concentration (total forms) as a function of soil reaction**

The presence of calcium in the soil can increase the mobility of some metals, triggering a competition for sorption centres between calcium and heavy metal Cations (*figure 2)*. In this situation cation exchange reactions become predominant and occur when there is compatibility

with the metal element in the host mineral. In alkaline, CaCO₃ - rich soils, heavy metals form insoluble carbonates, hydrated hydroxides or are adsorbed and fixed by soil colloids. It is noted that in the lower carbonate soil the metals were retained by cation exchange reactions, whereas in the higher carbonate soil the heavy metals were retained by specific adsorption on calcium carbonate. In this case desorption occurs, which can significantly reduce exchangeable and carbonate-bound metals. (Liu *et al*., 2021)

The affinity of metals for the soil solid phase is dependent on their concentration, a hypothesis supported by the results obtained and by previous studies (O'Connor *et al*., 1984).
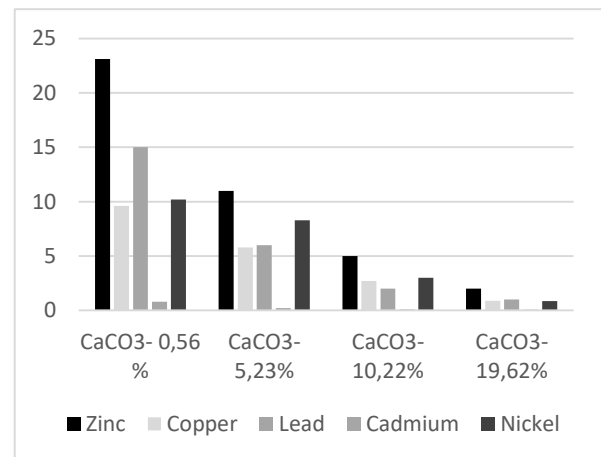

Figure 2 **Exchange reactions between carbonates and heavy metals**

The retention processes of heavy metals in soil involve sorption and precipitation processes. Adsorption is an accumulation of ions at the surface and by precipitation the metals form new compounds. Desorption studies provide information on the strength of the association that is made between a metal and soil and are carried out to determine the reversibility of sorption reactions. The behaviour of metals in soil is determined by sorption-desorption processes in which they participate with other soil components. The total and accessible forms of microelements in the two profiles analyzed are shown in *tables 3* and *4.*

Table 3

Heavy metals in total (T) and accessible (Ac) (profile 8)

Zn mg/Kg		Cu mg/Kg		Pb mg/Kg		Ni mg/Kg		Cd mg/Kg	
T	Ac	T	Ac	T	Ac	T	Ac	T	Ac
23.1	15.5	12.8	3.1	16.0	6.8	10.1	1.5	1.3	0.5
18.7	8.0	8.8	1.7	10.3	4.1	7.4	0.9	0.6	0.2
9.2	2.5	4.6	0.6	3.8	0.4	2.6	0.1	0.3	0.1

The mobility of metals is directly influenced by their "chemical speciation" which determines their behaviour and toxicity in the environment (Fairbrother *et al*., 2007). Speciation therefore refers to the occurrence of metals in different chemical forms such as: metal complexes

dissolved in solutions and adsorbed on solid surfaces or metal species that have co-precipitated in their own or other metals' solid phases at much higher concentrations or free metal ions (Qin Yu *et al.,* 2010).

Table 4

Heavy metals in total (T) and accessible (Ac) (profile 15)

Zn mg/Kg		Cu mg/Kg		Pb mg/Kg		Ni mg/Kg		Cd mg/Kg	
T	Ac	T	Ac	T	Ac	T	Ac	T	Ac
11.7	4.7	5.8	1.8	6.8	2.0	7.0	0.6	0.2	0.02
5.2	1.5	2.7	0.9	2.5	0.6	3.7	0.1	0.1	0.01
2.1	0.9	0.9	0.2	1.4	0.07	0.9	0.02	-	-

Speciation of a metal alters both its toxicity and certain chemical processes. The results led to the conclusion that heavy methylated metals were strongly retained in the soil over an increased carbonate content but only 10-15% of the total were converted to mobile forms. In neutral soils, of the total only some of the metal was trapped and the rest became accessible to plants.

The electrochemical voltage series of metals is the descending order of their reactivity and characterizes the behaviour of metals and their salts. It represents a series of voltages for the most important metals and hydrogen.

Mg,Al,Mn,Zn,Cr,Fe,Cd/Ni,Sn,Pb/**H**/Cu,Hg,Ag,Pt

Relative to the $H_2 / 2H^+$ system, some substances will behave as oxidizing agents, others as reducing agents. The heavy metals analyzed can replace hydrogen, except for copper. In the case of saline soils, each metal, can displace those metals that are in the metal stress series after hydrogen. When organic ligands are trapped in the soil by complexation, heavy metals tend to lock up.

CONCLUSIONS

In general, sorption studies are carried out in order to assess the intensity of metal retention phenomena in the soil and on different soil constituents. Sorption occurs at the solid-liquid interface and represents an accumulation of ions. Desorption is an important process that controls to some extent the accessibility and mobility of heavy metals in polluted soils. The affinity of metals for the solid phase of the soil depends on the properties of the metal, its concentration and the nature of the soil surface. Of the cations studied, copper had the lowest mobility and zinc the highest. Soils with higher reaction values and increased carbonate content retained and trapped heavy metals much better than those with neutral pH. It was found that organic matter and clay content are parameters that have a great influence on the adsorption phenomenon. An increase in the mobility of heavy metals through the formation of soluble complex combinations dependent on the soil reaction was observed and it was shown that adsorption intensifies with increasing pH. In the case of saline soils each metal, can replace those metals that are in the metal tension series after hydrogen. If compatibility occurs between the host mineral and the metal element, a uniform substitution takes place which favours cation exchange. The processes of mutual displacement of metals in solutions and their precipitation at the surface are considered as manifestations of transmutation of elements.

The harmful effects of heavy metals depend on their mobility, i.e. their solubility in soil. Therefore, in the case of soils polluted with heavy metals, the first remediation measures will aim to create conditions that allow the heavy metals to pass from the soil solution into stable forms bound to different constituents.

ACKNOWLEGMENTS

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