

Managing Heavy Metals Translocation Based on Variation of Composition and Properties of the Upper Soil Horizon

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Abstract: The composition, structure and properties of humic substances (humic and fulvic acids) evolved from saline black soil, chestnut and gray soils of Kazakhstan have been studied. A determining role has been revealed in the distribution of heavy metals (Cu, Pb, Cd and As) in the soil continuum of the granulometric texture, content of humic substances, namely, the mass ratio of humic and fulvic acids, pH and redox potential of the soil environment. Based on the experimental data, it has been shown the availability of opportunity for using the mixtures of humic acids, calcium peroxide and bentonite to detoxify soils contaminated with heavy metals. In this case, the mixture acts both as ameliorant and geochemical barrier preventing the heavy metals translocation process in soil-plant system.

Key words: Translocation of heavy metals into the clover • Heavy metals toxicity • Humic acids, fulvic acids • Geochemical barrier • Calcium peroxide • Bentonite • Lead • Cadmium • Mercury • Arsenic • Determination of heavy metals based on atomic absorption

INTRODUCTION

The problem related to determination of toxicants behavior patterns in specific ecosystems and the biosphere as a whole is one of the most topical issues among the challenges that are of essential importance both for theoretical justification of the ways to preserve the biosphere and for the successful application of appropriate environmental measures.

Heavy metals (HM) are among the common and highly toxic environmental pollutants [1-2]. Some of HM, such as Cu, Zn, Mo, Fe and Mn, called, if in small quantities, as microelements, are vital for plants, animals and humans. At high concentrations, they have a negative impact on the biota. Large amount of these compounds comes to the environment through the atmosphere. Arsenic, mercury, lead and cadmium, even in small quantities, are most dangerous for the biota [3-5].

The study of HM translocation from soil to plants is of great scientific and practical interest for industrial areas with significant anthropogenic pressure on the environment. As known, the physical and chemical properties of soil and agro-chemical and biological

characteristics of plants along with HM specification in the soil (soluble, insoluble, sorbed, etc.) have an impact on the translocation ability of HM in the "soil-plant" system [6]. Due to small amount of information and its fragmentary character, it is necessary to conduct studies on the impact of various factors on the process at issue in order to determine how to manage it. Continuously growing metal pressing is one of the permanent environmental factors, as a progressive contamination of vegetation mantle by chemical elements reduces its environmental, economic and aesthetic value.

The soil is an object accumulating the basic amount of HM. Therefore, as long as they are in the soil system in undissolved and inaccessible state, the negative impact of HM will be negligible. The danger occurs when HM transfer from insolubilization state into solubilization state. In that case there is the possibility of HM to translocate from soil solution into the plants and later into animals and humans, respectively, consuming these contaminated plants.

One of the major topical areas of detoxification and remediation of soils contaminated with HM is development of the ways to reduce the mobility of the

HM, fixation them in the soil in order to reduce the availability to plants, toxicity removal and less accumulation in plant biomass.

The goal of the work was to conduct a comparative study of HM (As, Pb, Cd and Cu) in different types of soils and to develop the ways of management the processes of their translocation based on variations in the composition and properties of the fertile soil layer.

Objects and Research Methodology: Soils from different regions of Kazakhstan, namely black soil (taken near the Almaty-1 railway station), chestnut soils (Dzhezkazgan, copper smeltery area) and gray soils (Shymkent lead plant area) subjected to various man-made impact, were used for tests.

The clover was selected as a testing plant. This plant is able to accumulate large amounts of lead and other HM and is sensitive to HM toxic concentrations in the soil [7].

The mixture of bentonite, humic acid and calcium peroxide was chosen as a sorbent due to their availability, possession of valuable process characteristics and, to a certain degree, because of scrutiny of the first two soil components [7-8].

Bentonite is a natural material and calcium peroxide is produced on an industrial scale. Humic acid can be obtained from waste coal or as biohumus from various agricultural wastes.

The following portions of compounds were used: calcium peroxide - 25 g/kg, bentonite clay: 40 g/kg (grain size: less or equal to 1 mm), humic acid (HA): 1 g/kg of soil. HM were introduced in the form of nitrate. Clover was used as a testing plant. The experiments were conducted in wooden boxes of 50 cm height and 30x50 sq. cm in area.

Detection of HM in soil and plant matter (after dry calcination) was carried out using the atomic absorption spectrophotometer SF-56. The most sensitive resonance absorption lines of the elements were used at the following wavelengths: Pb-283.3, or 217.0 nm, Cu-324.7 nm, Cd-228.8 nm and As-193.7 nm. The sample solutions were sprayed into the flame of acetylene-air mixture where the light was emitted from the hollow cathode lamp [9].

Factor pH of the aqueous extracts from the soil was measured using the pH-340 device.

Humus content in the soil was measured based on the optical density of the solutions in the spectrophotometer at 590 nm. Humic acids (HA) were extracted from the soil by the Kononova and Belchikova method [10]. Electronic absorption spectra in the visible

region was recorded to explore the changes in the structural state of HA and their nature. The extinction coefficients ratio E₄:E₆ characterizing the relative degree of condensability (aromaticity) of HA [11-12] was calculated based on the dependency of optical density of humic and fulvic acids (FA) on the wavelength. The concerned ratio was independent of the solution concentration and the thickness of the absorbing layer.

Statistical processing of the investigation results was performed using the "Statistics" software code.

RESULTS AND DISCUSSION

As is well known, the physical and chemical adsorption, or exchangeable adsorption, called cation exchange capacity, plays the most important role in chemical sealing and cation adsorption. It identifies the important physical and physico-chemical properties of the soil, namely structural condition, the reaction and the buffering capacity. In this connection we have conducted studies to determine these soil properties (Table 1).

The results of experimental studies have shown an increase in cation exchange capacity in all the studied soil types when introducing a bentonite clay, calcium peroxide and humic acid both individually and as a mixture. Accordingly, both the negative charge and the exchange capacity of the soil to absorb cations increase. Humic acid (HA) makes a significant contribution to the change in cation exchange capacity along with bentonite containing montmorillonite, the secondary (clay) mineral that is caused by carboxyl (COOH) and phenolic hydroxyl (OH) groups.

Below are the results of experimental studies to determine the total content of humus (humic and fulvic) acids in different grain-size soil fractions (Table 2) and the data on concentration distribution of HM (Table 3).

The composition and structure of HA makes a significant contribution to the mobility of HM. In this connection, we have carried out special studies to determine the group composition of humus both in soils and their clay fractions (Table 4).

The data presented in Table 4, shows that for gray soils being under the influence of technogenesis, the humus is of fulvic type (HAC/FAC <0.5), for the chestnut soils it is of humate-fulvic type, whereas for black soils it is of fulvate-humate type. In all cases, regardless of the soil type being under the impact of technogenesis, the content of fulvic acid increases, while the fraction of humic acid decreases. The observed change in HA to FA ratio (HAC/FAC) should be

Table 1: Properties of the investigated soils.

Options and soil types	pH_{H_2O}	pH_{KCl}	Humus, %	Cation exchange capacity, mg-eq./100 g
<i>Gray soil (control)</i>	7.0	7.1	1.27	8.23
+ CaO ₂	8.0	8.1	1.32	10.14
+ CaO ₂ +ΓK	7.5	7.7	3.40	47.95
+ bentonite	7.4	7.6	1.30	97.3
+ bentonite + CaO ₂ +ΓK	7.8	7.9	3.45	120.4
<i>Black soil (control)</i>	5.6	5.8	10.5	66.3
+ CaO ₂	7.4	7.5	10.7	72.5
+ CaO ₂ +HA	7.0	7.1	13.1	102.4
+ bentonite	7.7	7.9	11.4	99.8
+ bentonite + CaO ₂ +HA	7.6	7.8	14.6	131.5
<i>Chestnut soil (control)</i>	6.8	7.0	5.1	44.7
+ CaO ₂	7.5	7.8	5.0	48.3
+ CaO ₂ +ΓK	7.0	7.1	7.4	97.6
+ bentonite	7.3	7.5	5.3	110.1
+ bentonite + CaO ₂ +HA	7.7	8.0	7.9	122.8

Table 2: The content of humus in the soil grain-size fractions, % (sampling depth of 0-30 cm).

Soil	Fractions grain-size, mm					
	0.1-0.25	0.05-0.1	0.01-0.05	0.005-0.01	0.001-0.005	< 0.001
Black soil	3.9	4.3	4.9	5.2	8.1	13.5
Chestnut soil	2.7	2.8	3.2	3.3	4.0	6.9
Gray soil	0.2	0.2	0.3	0.4	0.6	1.2

Table 3: Total content of HM in different types of soils and their fractions (<0.01 mm) (numerator: content in the soil, the denominator: in the fraction).

Metals	Content of HM in soils, mg/kg		
	Black soil	Chestnut soil	Gray soil
Pb	187.8±0.5	129.6± 0.4	92.3± 0.3
	94.6±0.8	63.2±0.2	55.4±0.4
Cd	2.8±0.04	0.8± 0.02	0.7± 0.03
	1.1± 0.02	0.3± 0.01	0.5± 0.01
As	2.7±0.04	0.9± 0.01	1.8± 0.02
	1.4± 0.02	0.2 ±0.04	0.7± 0.04
Cu	2.9±0.05	1.8± 0.03	1.3± 0.01
	1.5 ±0.03	0.7 ±0.05	0.7± 0.01

Table 4: The group composition of humus in soils and their clay fractions (0-25 cm).

Subject title	$C_{total}, \%$	Content C (% to C_{total}) _B			
		HA	FA	In nonhydrolyzed residue	$C_{HA} C_{FA}$
Gray soil	0.40	8.1	23.2	68.7	0.35
Fraction < 0,001	0.33	11.2	39.6	49.2	0.28
Chestnut soil	1.19	32.0	28.9	39.1	1.1
Fraction < 0,001	1.01	36.4	43.2	20.4	0.84
Black soil	4.20	31.19	15.9	52.92	1.57
Fraction < 0,001	3.15	36.0	22.3	41.7	1.32

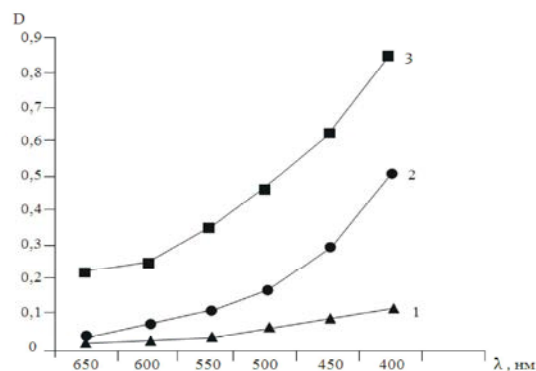


Fig. 1: The optical density of HA extracted from different soil types: 1 - gray soil, 2 - chestnut soil, 3 - black soil.

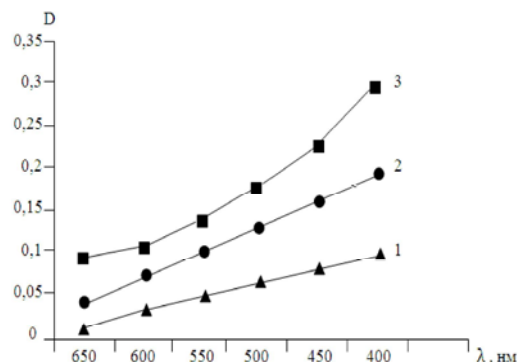


Fig. 2: The optical density of FA extracted from different soil types: 1 - gray soil, 2 - chestnut soil, 3 - black soil.

Table 5: The content of HM in the studied subjects, mg/kg.

The name of the investigated object	Containment of metals, mg/kg				
	Without introducing sorbents		In clever when introducing sorbents		
	In soils Gray and black soils	In plant Gray and black soils	Bentonite Gray and black soils	Bentonite and HA Gray and black soils	Bentonite, CaO ₂ and HA Gray and black soils
	Lead				
Clever	60.2/77.8	16.4/0.5	1.4/0.2	0.4/0.2	not found
Clever	150.5/168.1	69.1/1.3	0.6/0.5	0.6/0.4	0.1/0.02
Clever	200.5/218.1	72.6/1.3	0.6/0.4	0.7/0.4	0.2/ not found
Clever	500.2/518.4	80.3/1.1	1.2/0.4	0.8/0.3	0.3/ not found
	Cadmium				
Clever	2.5/2.7	1.1/0.4	0.05/0.03	0.04/0.03	0.01/ not found
Clever	5.0/5.0	1.7/0.4	0.06/0.03	0.03/0.03	0.01/ not found
	Copper				
Clever	100.0/120.5	20.5/19.1	16.6/15.7	9.8/15.2	0.3/0.2
Clever	250.0/270.6	22.8/19.2	9.1/6.8	5.9/6.6	4.2/1.2
	Arsenic				
Clever	2.2/2.2	1.9/0.7	0.06/0.03	0.05/0.03	not found
Clever	40.0/10.3	17.7/8.9	6.9/2.7	5.5/2.5	not found

considered as a negative environmental effect, because lower share of HA creates better conditions for the translocation of HM into plants.

The measurement results of the optical density of humic specimen taken from gray soils, chestnut soils and black soils showed lower optical density (condensation) of HA in the soil located in the areas of acute industrial pollution (Figures 1-2).

Reduction of HA share and decrease of their molecules complexity in connection with the areas of sever industrial impact can be explained to some extent by inhibition of the microbiological activity of soils in the presence of HM.

Reduction of soil microbial activity slows down the "maturation" processes of humic substances, i.e. polycondensation processes. A significant part of humic substances is represented by more mobile FA and relatively simple forms of HA.

It was thus established that most of HM are accumulated in the fine particles, which contain the bulk of the clay minerals and HA (Table 2). The role of clay minerals and humic substances in the accumulation of HM has been studied insufficiently. In this regard, a comprehensive study of the accumulation process of HM in the soil is of particular interest both on scientific and practical level. Accumulation of HM in the soil is an

important environmental specification, since the properties of the soil components determine the migration of elements into plants and animals. In addition, the enrichment of soil microdisperse particles with HM pose a real threat to the health of the urban population as HM can penetrate into the human body with the dust through the respiratory system, that leads to various diseases.

The translocation of HM from the contaminated soil into plants has been studied on the example of gray and black soils (Table 5).

As it is seen from an experimental data (Table 5), translocation of HM is highly dependent on the availability of bentonite clay, calcium peroxide and humic acid. Moreover, a sharp inhibition of HM transition from the soil into the plant is observed when introducing humic acid mixture and bentonite.

One of the main reasons why the amount of HM translocating from the soil into the plant decreases, is their involvement in the complexation reactions with humic acid, leading to the formation of stable chelates, which are further secured by adsorption on the surface of bentonite clays. On the other hand, binding of HM occurs due to the ability of clay minerals to ion exchange. Since bentonite clay and HA of the soil have cation-exchanged centers and large total quantity of negative charge, the positively charged particles of heavy metal ions are adsorbed more strongly and thus by such accumulation, the translocation process of HM into plants in the soil environment reduces drastically.

Comparing the experimental data obtained when introducing bentonite and its mixture with humic acid into the soil system, it has been established that the translocation process of Cd into the plant is independent on availability of humic acid. Amount of Cd in the plant was virtually the same both in the presence of humic acid and without it, that can be explained by the absence of chemical interaction between cadmium and humic acid.

Adding bentonite and its mixture with HA differently affects on transfer of investigated elements into the clover in terms of their quantity. For example, for lead and cadmium, the damping effect is higher than that for copper. Distribution of Pb into the clover is reduced by 85-97%, Cu - by 23-48% and Cd - by 97-98%.

Distribution of calcium peroxide together with HA mixture and bentonite led to significant fixation of HM, particularly lead. Thus the amount of lead and other metals translocated into the studied culture of clover in the presence of bentonite clay+HA+calcium peroxide mixture did not exceed the standard level even in highly

contaminated soil (in food plants, the allowable level of concentration for lead is 0.5 mg/kg, cadmium - 0.1 mg/kg and copper - 10.0 mg/kg). When introducing the above mixture into the soil, the translocation of arsenic into the clover is inhibited completely both in gray soil and black soil. This can be explained by oxidation of arsenic (III) to arsenic (V) and the formation of calcium arsenate $\text{Ca}_3(\text{AsO}_4)_2$ insoluble in soil solution.

The conceptual framework of soil sorption detoxification concludes in sufficiently rapid transfer of HM from the soil solution into the sorbed state impermeable for plants. Their subsequent gradual release (desorption) can only occur in concentrations not exceeding the self-purification capability of soils: soil microbial flora is capable to decompose so small amounts of pollutants into non-toxic compounds.

CONCLUSION

The research results presented in this paper testify that the following important tasks can be solved simultaneously:

- Environmental task, aimed at creating artificial geochemical barrier to inhibit the translocation process of HM (Cu, Pb, Cd and As) in soil-plant system;
- Technological task, allowing to extend the list of sorption materials having high adsorption activity with respect to ions of HM and other toxicants;
- Rehabilitation of producing properties of polluted agricultural lands adjacent to industrial facilities and getting environmentally clean products.

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