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I. V. MATVEYEVA[1, 2], O. I. PONOMARENKO[1], N. B. SOLTANGAZIYEV[1], N. A. NURSAPINA[1], SH. N. NAZARKULOVA[1], A. N. GURIN[1, 2]

[1]Al-Farabi Kazakh national university, Almaty, Republic of Kazakhstan,
[2]RSE Institute of Nuclear Physics, Almaty, Republic of Kazakhstan

HEAVY METALS IN SOILS OF ALMATY REGION (KAZAKHSTAN)

Abstract. The article describes the content of heavy metals in soils of Almaty region (Kazakhstan). Sampling was done at three sampling points: Almaty city, Baitirek village and Avat village. Heavy metals were analyzed in three different forms: water-soluble, mobile and total content. The total content of heavy metals characterizes the overall soil contamination, but does not show the degree of availability of elements for the plant.The content in the soils of plant-accessible mobile forms of heavy metal compounds is determined using ammonium acetate buffer solution with a pH of 4.8. It determines the exchangeable and weakly sorbed forms of metals.The concentration of metals in the aqueous extract shows the degree of mobility of elements in the soil, being the most dangerous and "aggressive" fraction. The content of zinc in all investigated areas should be controlled, especially in Almaty city and Avat village, where increased values for mobile forms were found.

Key words: heavy metals, soils, Almaty region, water-soluble forms, mobile forms, total content.

Introduction. The development of humanity resulted to strong industrialization process, which is strongly represented in mining of different raw materials. Mining-related activities produce large quantities of wastes, which can be in gas, liquid or solid forms [1]. They are dispersed by water and/or wind in the absence of control and result in severe environmental problems [2, 3]. Surveys and monitoring programs focused on heavy metal pollution near mining area in different countries showed accumulation of heavy metals in a variety of environmental media, including air, soil and water [4, 5].

Heavy metal pollution in soil is an increasingly urgent worldwide problem [6]. The soil is the main medium in which heavy metals appear, including from atmosphere and aquaous environment. It serves as a source of secondary pollution of surface air and waters precipitating from it into the oceans. Heavy metals in dust and soil can be easily transferred into human body via three routes: ingestion, inhalation and dermal contact [7-9].Soil is an essential component of ecosystems, with a great capacity to cope with pollution, and so to protect the other components, both abiotic (air and water) and biotic ones (living organisms) [10]. There are many processes that influence on toxicity in soils over time [11]; soil properties largely control themobility, bioavailability and consequently, the potential toxicity of trace elements in the environment. In order to assess the toxicity of heavy metals it is not enough to know only concentration of heavy metals in soils,

but the mobile forms (which can easily migrate and accumulate in living organisms) should be determined. Obviously, the presence of the following heavy metals compounds in the soil should be considered:

– soluble, i.e. free ions and soluble complexes of heavy metals with inorganic anions or organic ligands of various strengths;

– exchangeable, i.e.heavy metals retained mainly by electrostatic forces on clay and other minerals, organic matter and amorphous compounds;

– specifically sorbed, i.e. heavy metals mainly retained by covalent and coordination bonds;

– heavy metals on stable organic matter, i.e. heavy metals retained by complexation and chelation on the actual organic matter or organic matter associated with iron, aluminum, calcium cations, with oxides and hydroxides of iron and aluminum, with clay minerals.

To study the mobility of heavy metals and metabolic processes occurring in the system “soil - plant”, with their participation, the soil of Almaty region was chosen.

MATERIALS AND METHODS

Object description. Three main sampling points were selected for this investigation. The soils are light chestnut.

The first sampling point was in Almaty city (AC), close to operating TPP-1. Almaty city is the largest city in Kazakhstan, with a population of 1,797,431 people, about 8% of the country’s total population.

The second sampling point was in Baiterek village (BV), located in the Enbekshikazakh district of the Almaty region of Kazakhstan (20 km east of Almaty city). The administrative center of Baiterek rural district.

The third sampling point was in Avatvillage (AV), located in Enbekshikazakhsky district of Almaty region of Kazakhstan (17 km west of the city center of Esik on the right bank of the Talgar River). The administrative center and the only settlement of Avat rural district.

Sampling and sample pretreatment. The envelope method was used to collect samples from a ten-centimeter layer of soil in accordance with the generally accepted sampling technique for conducting soil monitoring. The soil was conditioned to air-dry state. Soil samples were averaged by quartering method. The soil was sieved through a sieve with d = 2 mm.

Determination of total content of heavy metals. The total content of heavy metals characterizes the overall soil contamination, but does not show the degree of availability of elements for the plant.

2 g of dry soil was placed in a flask; 2-3 ml of distilled water, 15 ml of concentrated hydrochloric acid, 5 ml of concentrated nitric acid and 10 ml of hydrogen peroxide were added. The resulting suspension was well shaken for 15 minutes. The resulting solution was filteredthrough an acid resistant filter into a 100 ml flask. The precipitate was washed several times with a small amount of

1 M nitric acid and 1 M nitric acid was addedtill the mark[12]. The measurement of content of heavy metals in resulting solution was done by atomic absorption spectrometry.

Determination of mobile forms of heavy metals. The content in the soils of plant-accessible mobile forms of heavy metal compounds is determined using ammonium acetate buffer solution with a pH of 4.8. This method determines the exchangeable and weakly sorbed forms of metals.

5 g of dry soil sample was placed in a flask, 50 ml of ammonium acetate buffer solution was added. The resulting suspension was well shaken for 15 minutes. The resulting solution was filtered, acidified with 1N hydrochloric acid.The measurement of content of heavy metals in resulting solution was done by atomic absorption spectrometry.

Determination of water-soluble forms of heavy metals. The concentration of metals in the aqueous extract shows the degree of mobility of elements in the soil, being the most dangerous and "aggressive" fraction.

4 g of soil was placed in a flask, 20 ml of distilled water was added. The resulting suspension was well shaken.The resulting solution was filtered, acidified with 1N hydrochloric acid.The measurement of content of heavy metals in resulting solution was done by atomic absorption spectrometry.

RESULTS AND DISCUSSION

The results of content of heavy metals in soils are presented in tables 1-4.

Table 1 – Content of lead in soil

	Total content, mg/kg	Mobile forms		Water-soluble forms	
		mg/kg	%	mg/kg	%
AC	46.5	3.9	8.39	0.15	0.31
BV	21.9	2.2	10.0	0.75	3.42
AV	12.3	1.7	13.8	–	–

Lead in all investigated samples is presented in mobile form in small amounts (8.39-13.8%), and water-soluble forms even less than 3.42%, hence it can be characterized as not available for plants and human-beings, so less dangerous.

Table 2 – Content of copper in soil

	Total content, mg/kg	Mobile forms		Water-soluble forms	
		mg/kg	%	mg/kg	%
AC	46.5	3.1	6.67	1.38	2.97
BV	40.0	2.54	6.35	1.80	4.50
AV	32.0	2.88	9.00	1.66	5.19

Copper in analyzed samples occurs in water-soluble forms from 2.97 to 5.19 % and in mobile forms – from 6.35 to 9.00%; more than 85% of copper in analyzed samples are in forms, which cannot easily migrate and accumulate in biological subjects.

Table 3 – Content of zinc in soil

	Total content, mg/kg	Mobile forms		Water-soluble forms	
		mg/kg	%	mg/kg	%
AC	328.0	33.1	10.1	3.1	0.95
BV	149.9	13.1	8.74	4.25	2.84
AV	11.9	4.83	40.6	3.08	25.9

Zinc in samples from Baiterek village and Almaty city has low mobile activity, but for soil from Avat village 25.9% are presented in water-soluble and 40.6% - in mobile forms, so in this case it can easily migrate and be accumulated in plants and hence in bodies of local population. It can be recommend to control the content of zinc in plants and food products produced here.

Table 4 – Content of manganese in soil

	Total content, mg/kg	Mobile forms		Water-soluble forms	
		mg/kg	%	mg/kg	%
AC	555.9	5.9	1.06	0.06	0.01
BV	572.8	21.1	3.68	0.11	0.02
AV	518.2	17.7	3.42	0.14	0.03

Manganese in analyzed samples is presented mostly in immobile form: water-soluble form is less than 0.03% and mobile form is only 3.68%. Therefore, it is evident, that manganese has less migration and accumulation abilities in all investigated samples.

In tables 5-7 the contents of heavy metals in investigated samples, comparing with maximum permissible concentration (MPC) for total content and mobile forms separately are presented.

Table 5 – Content of heavy metals in soils of Almaty city

Metal	Total content, mg/kg		Mobile forms, mg/kg	
	Content in sample	MPC	Content in sample	Content in sample
Lead	46.5	30.0	3.9	6.0
Copper	46.5	55.0	3.10	3.0
Zinc	328.0	100.0	33.1	23.0
Manganese	555.9	1500.0	5.9	600.0

In first sampling point (Almaty city) it was established that total content of lead and zinc was higher (1.55 and 3.28 times, correspondently) than MPC and the content of mobile forms of copper (insignificantly) and zinc was higher (1.03 and 1.44 times, correspondently) than MPC.

Table 6 – Content of heavy metals in soils of Baiterek village

Metal	Total content, mg/kg		Mobile forms, mg/kg	
	Content in sample	MPC	Content in sample	MPC
Lead	21.9	30.0	2.2	6.0
Copper	40.0	55.0	2.54	3.0
Zinc	149.9	100.0	13.1	23.0
Manganese	572.8	1500.0	21.1	600.0

In soils of Baiterek village the total content of zinc is 1.50 times higher than MPC, but in mobile forms it is less than MPC.

Table 7 – Content of heavy metals in soils of Avat village

Metal	Total content, mg/kg		Mobile forms, mg/kg	
	Content in sample	MPC	Content in sample	Content in sample
Lead	12.3	30.0	1.7	6.0
Copper	32.0	55.0	2.88	3.0
Zinc	269.7	100.0	64.9	23.0
Manganese	518.2	1500.0	17.7	600.0

In soils of Avat village also the elevated levels of zinc was found. The total content is 2.70 times higher than MPC and mobile forms are 2.82 times higher than MPC.

In general it is possible to conclude that the content of zinc in all investigated areas should be controlled, especially in Almaty city and Avat village, where elevated values for mobile forms were found.

Conclusion. Lead in all investigated samples is presented in mobile form in small amounts, so it can be characterized as not available for plants and human-beings, so less dangerous. More than 85% of copper in analyzed samples are in forms, which cannot easily migrate and accumulate in biological materials. Zinc in samples from Baiterek village and Almaty city has low mobile activity, but for soil from Avatvillage, it can easily migrate and be accumulated in plants and bodies of local population. Manganese in analyzed samples is presented mostly in immobile form.

In Almaty city it was established that total content of lead and zinc was higher (1.55 and 3.28 times, correspondently) than MPC and the content of mobile forms of copper (insignificantly) and zinc was higher (1.03 and 1.44 times,

correspondently) than MPC. In soils of Baiterekvillage, the total content of zinc is 1.50 times higher than MPC, but in mobile forms it is less than MPC. In soils of Avat village also the elevated levels of zinc was found. The total content is 2.70 times higher than MPC and mobile forms are 2.82 times higher than MPC.

The content of zinc in all investigated areas should be controlled, especially in Almaty city and Avat village, where increased values for mobile forms were found.

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Резюме

И. В. Матвеева, О. И. Пономаренко, Н. Б. Солтангазиев,
Н. А. Нурсапина, Ш. Н. Назаркулова, А. Н. Гурин

АЛМАТЫ ОБЛЫСЫНЫҢ ТОПЫРАҚТАРЫНДАҒЫ АУЫР МЕТАЛДАР (ҚАЗАҚСТАН)

Мақалада Алматы облысы (Қазақстан) топырақтарындағы ауыр металдардың мөлшері сипатталған. Зерттеу нысандарын алу үш сынама алу нүктелерінде: Алматы қаласы, Бәйтерек ауылы және Ават ауылында жүргізілді. Ауыр металдар үш түрлі формада: суда еритін, қозғалмалы және жалпы мөлшері бойынша талданды. Ауыр металдардың жалпы мөлшері топырақтың ластануын сипаттайды, алайда элементтердің өсімдіктер үшін қолжетімділік дәрежесін көрсетпейді. Топырақ құрамындағы өсімдіктер үшін қолжетімді болатын ауыр металл қосылыстарының қозғалмалы формаларын анықтау pH 4,8 тең аммоний ацетатының буферлік ерітіндісін пайдалана отырып жүргізіледі. Ол металдардың ауыспалы және әлсіз сорбцияланған формаларын сипаттайды. Металдардың концентрациясы ең қауіпті және «агрессивті» фракция болып табылатын су экстракциясы, топырақтағы элементтердің қозғалмалы фракциясын көрсетеді. Барлық зерттелген аудандардағы мырыштың мөлшері қадағалануы қажет, әсіресе, қозғалмалы формалар үшін жоғары көрсеткіштер анықталан Алматы қаласы және Ават ауылында тұрақты бақылауда ұстау ұсынылады.

Түйін сөздер: ауыр металдар, топырақ, Алматы облысы, суда еритін формалар, қозғалмалы формалар, жалпы мөлшер.

Резюме

И. В. Матвеева, О. И. Пономаренко, Н. Б. Солтангазиев,
Н. А. Нурсапина, Ш. Н. Назаркулова, А. Н. Гурин

ТЯЖЕЛЫЕ МЕТАЛЛЫ В ПОЧВАХ АЛМАТИНСКОЙ ОБЛАСТИ (КАЗАХСТАН)

Описано содержание тяжелых металлов в почвах Алматинской области (Казахстан). Отбор проб производился в трех точках: г. Алматы, села Байтерек и Ават. Тяжелые металлы анализировали в трех различных формах: растворимые в воде, подвижные и общее содержание. Общее содержание тяжелых металлов характеризует загрязнение почвы, но не показывает степень доступности элементов для растений. Содержание в почвах доступных для растений подвижных форм соединений тяжелых металлов определяют с использованием буферного раствора ацетата аммония с pH 4,8. Он определяет обменные и слабо сорбированные формы металлов. Концентрация металлов в водном экстракте показывает степень подвижности элементов в почве, являясь наиболее опасной и «агрессивной» фракцией. Содержание цинка во всех исследованных районах следует контролировать, особенно в г. Алматы и с. Ават, где были обнаружены повышенные значения для мобильных форм.

Ключевые слова: тяжелые металлы, почвы, Алматинская область, водорастворимые формы, подвижные формы, общее содержание.