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M.A. Mukasheva, Sh.M. Nugumanova

Ye.A. Buketov Karaganda State University, Kazakhstan
(E-mail: n_sholpan@inbox.ru)

Status of soil cover on the degree of accumulation of heavy metals in the soil of the industrial region (Karaganda city)

In article the condition of a soil cover of the city of Karaganda is studied. To this end, there have been ranked according to the highest degree of pollution. It was revealed that the dynamics of hygienic indices for 3 years is unfavorable with respect to the soil in the residential area. Against the background of the general tendency to reduce the level of soil pollution in the zone of influence of enterprises, the soil in the industrial area of the city is heavily polluted. The most intensive soils are contaminated with substances belonging to the first and second hazard classes: lead, zinc, copper and nickel. The content of zinc exceeds the MPC by approximately 3 times, lead by 1.5 times, copper by 1.6 times, nickel by 1.3 times. Such differences in the formation of zones of high and low soil polluted cities, to some extent, may be associated with age, the industrial development of the city, which was formed in the past 50–60 years, and much younger.

Keywords: residential area, the soil, lead, method of stripping voltammetry, industrial district, environment, chemical pollution.

In conditions of modern anthropogenic pressure on the environment, the main type of industrial pollution of soils is contamination with heavy metals, the sources of which are industrial enterprises, vehicles, housing and communal services. The most large-scale types of pollution in recent decades include environmental pollution by heavy metals, which are extremely difficult to remove from soil ecosystems.

In addition to direct toxic effects, many heavy metals are characterized by so-called long-term toxicity effects that affect such vital functions of living organisms as reproduction and bioproductivity. Thus, pollution of the environment with heavy metals poses a threat not only to individual organisms, but also to whole generations and populations. Unlike many other pollutants, they are not destroyed and not converted. In nature, in the processes of migration, only the forms of their location and concentration change. For many heavy metals, a cumulative effect is characteristic — the summation of harmful effects from individual pollutants. Monitoring the quality of the urban environment with full coverage of the residential area and taking into account all significant anthropogenic factors in modern conditions will not be implemented to the necessary extent due to the high cost of research. It is necessary to allocate observation zones that reliably reflect the diversity of living conditions of the urban population [1, 2]. From the existing methodological approaches to the ranking of territories according to the level of environmental problems, the most appropriate is the mapping of the territory according to the degree of environmental pollution [3, 4].

In this regard, the state laboratory control soil was held in Karaganda, which allows him to ascertain the environmental status.

Materials and methods

To this end, there have been ranked according to the highest degree of pollution. To this end, we selected soil samples from the various functional areas of the city. The first zone consisted of soil sampling point from the territory located near the industrial plants at a distance of 1000–1500 m. The second zone is the center of the city, where there is not industry, is the big pollution from road transport. Third point selection is «sleeping» area of the city, where there is an extensive highway network and industrial and service enterpris-

es. The metal content in the 750 soil samples was determined by stripping voltammetry. The method is based on the accumulation of ions of analytes on the surface of the working electrode over time, with a yield of ions from the working electrode in a solution under the influence of changes in the working electrode potential. Since each type of ion has a certain output potential, and the movement of ions causes a change in the current in the working electrode circuit, this allows us to detect the current dependence on the voltage applied to the working electrode, to identify the type of ions, proportional to the current to determine the number of ions of the type [5, 6].

The mineralization of samples was carried out in an automated complex sample preparation «TEMOS EXPRESS» TE-1. The automated complex sample preparation «TEMOS EXPRESS» TE-1 is designed for the complete destruction of interfering organic substances, thermal treatment with oxidants (HNO₃, H₂O₂, H₂SO₄ et al.) in the temperature from 50 °C to 650 °C by determining the concentration of toxic elements (Cd, Pb, Zn, Cu, As et al.) in samples of various environmental objects by conducting quantitative chemical analysis by direct and inverse voltammetry, atomic absorption, photometry, etc. Total index of soil contamination (SDRs), calculated using the formula recommended by the F.F. Erisman Moscow Research Institute of Hygiene in 1996.

$$K_{\text{soil}} = C_1 / MPC_1 + C_2 / MPC_2 + C_3 / MPC_3 + \dots + C_n / MPC_n,$$

where K_{soil} — total index of soil pollution; $C_1, C_2, C_3 \dots C_n$ — actual concentration of chemicals in the soil; $MPC_1, MPC_2, MPC_3, MPC_n$ — the maximum permissible concentration of these substances.

Research results

Dynamics of hygienic indicators for 3 years is unfavorable with respect to soil in the residential area. Against the background of the general tendency to reduce the level of soil pollution in the zone of influence of enterprises, the soil remains heavily polluted in the industrial area of the city. In the Oktyabrsky district recorded 66.6 % of non-standard samples in the zone of influence of industrial enterprises. Within a radius of industrial exposure, there are significant excess of MPC in a number of heavy metals. For example, in the area of influence of the foundry «Kazakhmys» corporation, CHP-3 content of salts of heavy metals — copper, zinc, lead, nickel — ranging from 1.8 to 7.5 MPC. In the central area of the city (Kazybek bi), 100 % of the samples taken in the area of influence of transport highways registered concentrations exceeding the standards for heavy metals (lead — from 2 to 10, MPC, nickel — from 4.6 to 6.3 MPC). In the South-Eastern area of influence of highway industrial enterprises in 100 % of cases, the sampling of lead content exceeds the norm of up to 3 MPC; zinc — 1.7 MPC; nickel — to 1.8 MPC.

During the period 2012–2015 in the city a special eco-hygienic survey of soils was carried out by soil Center of Sanitary Inspection. Evaluation of soil contamination level was carried out by 17 indicators, including heavy metals.

It may be noted that the most heavily contaminated soil substances belonging to the first and second classes of hazards: lead, zinc, copper and nickel.

The most unfavorable is the situation on pollution by lead and zinc soil. The proportion of unsatisfactory samples for these indicators amounted respectively to 19.3 % and 15.5 %, and the frequency of the MPC for copper and nickel, respectively, 7.3 % and 7.6 %.

One of the most contaminated areas is — Kazybek bi, where 40 % of the samples revealed lead in quantities exceeding maximum concentration limit in 46 % of samples — zinc, 26.7 % — nickel. The share of non-standard analyzes for copper was the highest in 2007 in the Oktyabrsky district, but in 2005 the Kazybek bi district was in the lead.

The long-standing industrial pollution of the soil cover of the city, represents the city of Karaganda in a single biogeochemical province. In studying the table we observe that the subject areas on the total figure is almost aligned with each other.

The lead content of the soil cover ranges from 22 mg/kg to 53 mg/kg (Table 1, Fig. 1).

Table 1

Heavy metals in soils of Karaganda (mg/kg)

№	Cu	Pb	Zn	V	Cr	Co	Ni	Mn	Be	SDRs
1	53	22	115	71	98	17	27	607	2,1	6,7
2	26	24	150	50	51	23	14	280	1,8	4,7
3	21	53	60	67	68	22	22	1447	1,6	5,54

Note. 1 — area with high anthropogenic load; 2 — average anthropogenic impact; 3 — relatively clean area.

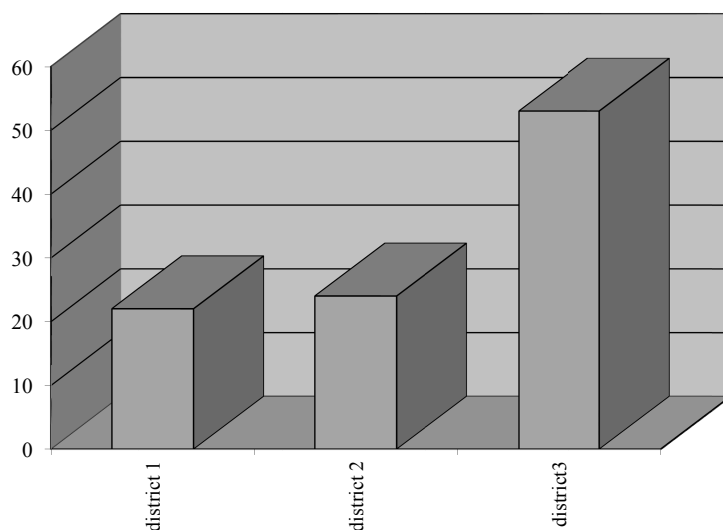


Figure 1. The content of Pb in the soils of Karagandy (mg/kg)

Lead contaminated territories of all areas of the city, most content from leading motorways (Fig. 2). For copper characterized by localization in the upper layer of soil (10–15 cm from the surface) which reflects its bioaccumulation and modern anthropogenic influence. Contamination of soil copper compounds is the result of contributions from industrial sources. Possible occurrence of local copper anomalies in soils as a result of corrosion of structural materials containing copper alloys (electrical wires, pipes).

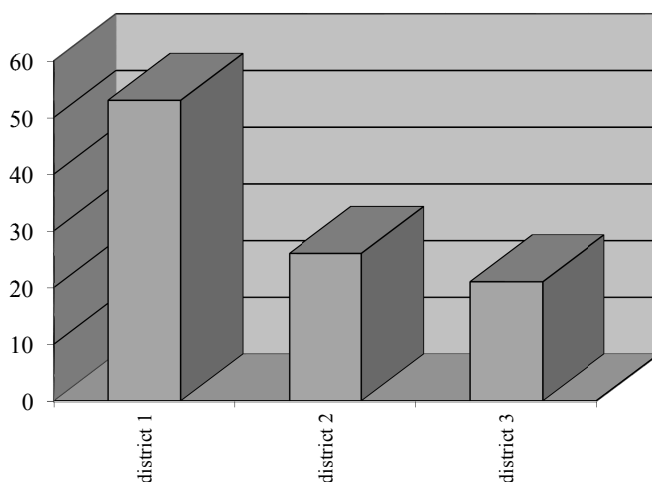


Figure 2. The content of Cu in the soils of Karagandy (mg/kg)

The variability of copper concentration in the city was 21 mg/kg — 53 mg/kg (Fig. 2). Manganese accumulation usually occurs in the subsoil, and 60–90 % of the manganese is found in sandy soil fractions. In soils of the city there is a wide distribution of manganese in concentrations from 607 to 1447 mg/kg (Table 1). This is due to the fact that emissions of many enterprises of the city contain manganese oxide. The reason for the low manganese content in the upper layers of the soil can be a large radius of its dispersion and exceeding the solubility in the presence of pH-lowering humic acids.

Nickel is found in the town soil cover in concentrations of 22 mg/kg to 27 mg/kg (Fig. 3). The high concentrations are determined in the territories of all districts of the city. Accumulation of nickel in soil is due to the ability of the cell adsorbed manganese oxides and organic forms of iron.

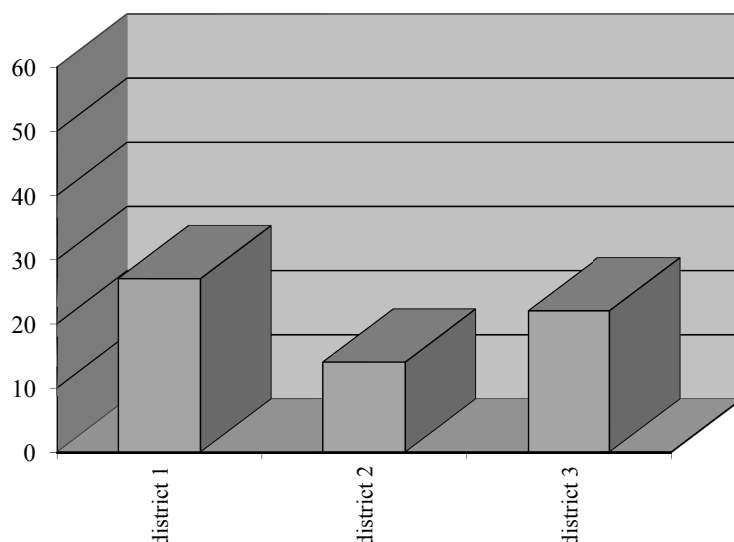


Figure 3. The content of Ni in the soils of Karagandy (mg/kg)

The range of concentration of beryllium in the city of 1.6 mg/kg — 2.1 mg/kg, which contributes to shift the pH toward alkaline sides. The chromium coming from technogenic sources usually accumulates in a thin surface layer of soils. The range of oscillations is 68–98 mg/kg (Table 1). Chromium is from 68 to 98 mg/kg. Increased chromium content is registered in the individual samples. The presence of chromium in soils indicates its technogenic nature. Chromium accumulation in soil associated with the pH of the medium and large amounts of organic complexes [7, 8].

Revealed several territorial areas of the city (district № 2 — the average man-caused load), where there is extensive contamination of soil, including: Avenue Bukhar-Zhyrau (lead — 2.3 MPC, copper — 5.5 MPC); Prospect Builders (lead MPC — 2.5); Bus South-East (lead — 2,9 MPC); area CHP-3 (copper — 7.5 MPC; nickel — 6 MPC); zone of «Kazakhmys» in the October district (lead — 2 MPC, copper — 3,7 MPC, zinc — 1,7 MPC).

High lead contamination of soil from the exhaust gases of vehicles registered in the quarter of 45, str. Yazev, str. Gogol, Avenue N.Abdirova reaching 2 to 10 MPC (Table 2).

Table 2

Excess of heavy metals in the soil relative to the MPC residential areas

Zone	2013 y.				2014 y.				2015 y.			
	Cu	Zn	Pb	Ni	Cu	Zn	Pb	Ni	Cu	Zn	Pb	Ni
1	1.8	2	3.2	4	2	3.4	5	7	2.3	5	6	7.5
2	2	2	4	4	3	3.4	6	6.5	7.5	4.2	7.2	6
3	5.4	—	2	4.6	—	—	6	5.4	—	—	8	6
4	5.5	—	3	4.2	—	—	8	5.7	—	—	10	6.3
5	2.5	—	2.5	1.3	—	—	1.6	1.2	—	1.2	1.7	1.2
6	—	—	2.9	1.2	—	—	1.7	1.2	—	—	1.5	1.2

Note. 1, 2 — Oktyabrsky district; 3, 4 — Kazybek bi; 5, 6 — South-East.

In terms of oil pollution, the most polluted are Kazybek bi and southeastern regions, where the average annual concentration of 735–737 mg/kg. These laboratory monitoring of soil pollution by pesticides indicate their absence in the soil.

Monitoring of territories clinics residential areas on the total level of soil contamination has revealed that similar to the total index of air pollution the highest soil pollution with heavy metals is observed in the service area of a polyclinic № 2 (Kazybek bi). Soil pollution is noted on the territory of the polyclinic № 3 (South-East). Pollution 13 and 15 districts (Maikuduk) territory clinic № 4 and 7 Oktyabrsky district (an average SDRs of the city — 2.08).

By calculating the average levels of soil contamination with heavy metals in the service areas of polyclinics, some sharply differing values of the indicators (abnormal values) characterizing analyzes of soil

samples either on motorways or in the immediate vicinity of industrial facilities were excluded from treatment. Of course, by sampling soil samples, the zones of influence of enterprises and highways were not completely avoided, residential areas were affected selectively, however, the main regularities of the differences in soil pollution of the city were fixed quite objectively.

Thus, the highest level of pollution and accumulation of elements of I and II classes of danger, such as lead, zinc, copper, nickel, based on the share of non-standard samples is Kazybek bi area and the area of the foundry «Kazakhmys» corporation.

City Karaganda receives heat and hot water mainly from CHP-3, which also contributes to the pollution of the regional center [3, 9]. The table shows that the accumulation of the studied elements in the soil adjacent to the territory of CHP-3 at doses exceeding the maximum permissible concentration in a few times (Table 3).

Since the zinc content exceeds the MPC is about 3 times in all sampling points. The lead content exceeds MPC by 1.5 times in all sampling points. The copper content exceeds MPC by 1.6 times. The nickel content exceeds MPC by 1.3 times. MPC cobalt content exceeds 0.6 times at a distance of 500–1000 m, in other points of the content selection is within the MPC, but greater than the background by more than 10 times. We also spread the soil pollution of heavy metal salts was determined (in terms of the SDR). Effects observed in the radius of the motorway on the territory of 45 quarters (Kazybek bi district) and the main part of the prospectus of Builders of South-Eastern District. Similarly, atmospheric pollution regularly highlighted «conditionally clean» zone — Gulder community-1 and Mikhailovka area (Kazybek bi district).

Table 3

The distribution of heavy elements in the soils of the area CHP-3 Karaganda (mg/kg)

Chemical element	Background	MPC	Subject distance		
			500–1000 m	1500–3000 m	3000–10000 m
Zinc	41.5±2.33	100	328.6±18.26	299.1±34.88	285.46±21.0
Lead	15.6±0.89	60	85.5±4.22	82.3±5.85	84.87±10.34
Copper	18.2±2.21	100	168.4±7.11	162.3±12.75	161.5±8.12
Cobalt	3.8±0.56	50	56.5±11.50	46.9±6.33	43.2±7.14
Nickel	12.2±1.54	70	95.5±23.96	89.6±9.74	88.3±11.25

Such differences in the formation of zones of high and low soil polluted cities, to some extent, may be associated with age, the industrial development of the city, which was formed in the past 50–60 years, and much younger.

Thus, to increase the effectiveness of the monitoring of chemical elements in samples of natural environments that require surveillance organization dynamics.

References

- 1 Мукашева М.А. Оценка техногенного загрязнения почвы на примере промышленного города / М.А. Мукашева, Д.В. Суржигов, Г.М. Тыкежанова и др. // Вестн. Караганд. ун-та. Сер. Биология. Медицина. География. — 2013. — № 1(69). — С. 77–81.
- 2 Мукашева М.А. Загрязнение почвенного покрова территории промышленного города тяжелыми металлами / М.А. Мукашева, А.М. Айткулов, З.Т. Кыстаубаева, Ш.М. Нугуманова // Вестн. Челябинского гос. ун-та. — 2013. — № 7(298). — С. 152–155.
- 3 Mukasheva M.A. Monitoring of distribution of heavy metals in TEC-3 vicinities by means of plants-indicators / M.A. Mukasheva, S.S. Shorin, A.M. Pudov, I.M. Pudov // European Researcher. — 2013. — Vol.(40). — No. 2–1. — P. 233–237.
- 4 Мукашева М.А. Основы биомониторинга для экологической безопасности населения (натурные и экспериментальные исследования) / А.М.Мукашева.А., А.М. Айткулов. — LAP LAMBERT Academic Publishing, 2012. — 281 с.
- 5 Мукашева М.А. Определение тяжелых металлов в объектах окружающей среды на аналитическом вольтамперометрическом комплексе «СТА»: Метод. рекомендации / М.А. Мукашева, А.М. Пудов, И.М. Пудов и др. — Караганда, 2013. — 37 с.
- 6 Мукашева М.А. «СТА» аналитикалық вольтамперометриялық кешенінде қоршаған орта нысандарындағы ауыр металдарды анықтау: Әдістемелік нұсқаулар / М.А. Мукашева, И.М. Пудов, Р.З. Қасенов. — Караганда: ҚарМУ баспасы, 2013. — 40 б.
- 7 Мукашева М.А. Мониторинг накопления тяжелых металлов в почвах селитебных ландшафтов / М.А. Мукашева, А.М. Айткулов, Г.М. Тыкежанова // Здоровье и болезнь. — 2008. — № 10(76). — С. 55–58.

8 Мукашева М.А. Обоснование принципов моделирования поведения тяжелых металлов в почве: Междунар. журн. эксперимент. образования / М.А. Мукашева, А.М. Айткулов, Г.М. Тыкежанова, Ш.М. Нугуманова. — М., 2009. — № 3. — С. 22–23.

9 Мукашева М.А. Методология комплексной оценки антропогенных факторов в прогнозе канцерогенного риска / М.А. Мукашева, А.М. Айткулов, Т.В. Бенц и др. // Успехи современного естествознания: Материалы Всероссийской выставки-презентации учеб.-метод. изданий. — М., 2010. — № 2. — С. 142 — 143.

М.А. Мукашева, Ш.М. Нугуманова

Өндіріс аумағы топырағында ауыр металдардың жинақталу деңгейі бойынша топырақ жамылғысының жағдайы (Қарағанды қаласы)

Мақалада Қарағанды қаласының әртүрлі функционалды аумақтарының топырақ жамылғысының жағдайы зерттелді. Топырақтың ауыр металдармен ластануына байланысты экологиялық жағдайдың деңгейі бойынша қала аумағының жіктелуі жүргізілді. Селителік аумақтағы топырағының 3 жылдық гигиеналық көрсеткіштердің жағымсыз динамикасы анықталды. Өндіріс аумағы топырағының жоғары мөлшерде ластануы дәлелденді. Топырақ қарқынды түрде қауіптіліктің бірінші және екінші класына жататын мырыш, мыс, никель және тағы басқа заттармен ластанған. Мырыш мөлшері ШРК мөлшерінен 3 есе, мыс 1,6 есе, никель 1,3 есе жоғары. Қала топырағының жоғары және төмен деңгейде ауыр металдармен ластануы соңғы 50–60 жылдар бойы қалыптасқан өндіріс құрылыспен байланысты болуы мүмкін.

Кілт сөздер: селителік аумақ, топырақ, мырыш, мыс, инверсиялық вольтамперометрия тәсілі, өндіріс аумағы, қоршаған орта, химиялық ластану.

М.А. Мукашева, Ш.М. Нугуманова

Состояние почвенного покрова по степени накопления тяжелых металлов в почве промышленного региона (город Караганда)

В статье изучено состояние почвенного покрова города Караганды с различных функциональных зон. Проведено ранжирование территорий города по степени направленности экологической ситуации, связанной с загрязнением почвы тяжелыми металлами. Выявлено, что динамика гигиенических показателей за 3 года неблагоприятна по отношению к почве в селителной зоне. На фоне общей тенденции к снижению уровня загрязнения почвы в зоне влияния предприятий в промышленном районе города почва сильно загрязнена. Наиболее интенсивно почвы загрязнены веществами, относящимися к первому и второму классам опасности: свинцом, цинком, медью и никелем. Содержание цинка превышает ПДК примерно в 3 раза, свинца — в 1,5 раза, меди — в 1,6 раза, никеля — в 1,3 раза. Подобные различия в формировании зон высокой и низкой загрязненности почв города в определенной мере могут быть связаны с возрастом промышленной застройки города, которая сформировалась в последние 50–60 лет (и значительно моложе).

Ключевые слова: селителные территории, почва, свинец, цинк, медь, никель, метод инверсионной вольтамперометрии, промышленный район, окружающая среда, химическое загрязнение.

References

1 Mukasheva, M.A., Surzhikov, D.V., & Tykezhanova, G.M. (2013). Otsenka tehnogeno zahriazneniia pochvi na primere promyshlennogo horoda [Assessment of technogenic pollution of the soil on the example of the industrial city]. *Vestnik Karahandinskogo universiteta — Bulletin of the Karaganda University*, 1(69), 77–81 [in Russian].

2 Mukasheva, M.A., Aytkulov, A.M., & Kystaubayeva, Z.T. (2013). Zagriazneniie potschvenoho pokrova territorii promyshlennogo horoda tiazholyimi metallami [Pollution of a soil cover of the territory of the industrial city by heavy metals]. *Vestnik Chelyabinskogo gosudarstvennogo universiteta — Bulletin of the Chelyabinsk State University*, 7(298), 152–155 [in Russian].

3 Mukasheva, M.A., Shorin, S.S., Pudov, A.M., & Pudov, I.M. (2013). Monitoring raspredeleniia tiazhelykh metallov v okrestnostiakh TETs-3 s pomoshchiu rastenii-indikatorov [Monitoring of distribution of heavy metals in TEC-3 vicinities by means of plants-indicators]. *Yevropeiskiiye issledovaniia — European Research*, 40, 1, 233–237 [in Russian].

4 Mukasheva, M.A., & Aytkulov, A.M. (2012). *Osnovy biomonitorinha dlia ecolohitscheskoi bezopasnosti naseleniia (naturnyie i eksperimentalnyie issledovaniia)* [Biomonitoring bases for an ecological safety of the population (natural and pilot studies)]. LAP LAMBERT Academic Publishing [in Russian].

5 Mukasheva, M.A., Pudov, A.M., & Pudov, I.M. (2013). *Opređenje tiazhelich metalov v objektach okruzhauschei sredi na analititscheskom woltampericheskom komplekse «HUNDRED»* [Determination of heavy metals in environment objects on the «HUNDRED» analytical voltammetric complex]. Karaganda [in Russian].

6 Mukasheva, M.A., Pudov, I.M., Kasenov, R.Z. (2013). «HUNDRED» *analitikalik voltamperimetriialik kescheninde korschagan orta nisandarindagi auir meteldardi aniktau* [Determination of heavy metals in environment objects on the «HUNDRED» analytical voltammetric complex]. Karaganda [in Kazakh].

7 Mukasheva, M.A., Aytkulov, A.M., & Tykezhanova, G.M. (2008). *Monitorinh nakopleniia tiazhelich metalov v potschvach selitebnich landshaftov* [Monitoring of accumulating of heavy metals in soils the seliteb landscapes]. *Zdorovie i bolezni — Health and disease*, 10, 55–58 [in Russian].

8 Mukasheva, M.A., Aytkulov, A.M., & Tykezhanova, G.M. (2009). *Obosnovaniie principov modelirovaniia povedeniia niazhelich metalov v pochve* [Reasons for the principles of behavior modeling of heavy metals in the soil]. *Mezhdunarodnyi zhurnal eksperimentalnoho obrazovaniia — International magazine of experimental education*, 3, 22–23 [in Russian].

9 Mukasheva, M.A., Aytkulov, A.M., & Benz, T.V. (2010). *Metodolohiia kompleksnoi otsenki antropohennykh faktorov v prohnoze kantserogenного riska* [Methodology of complex assessment of anthropogenous factors in the forecast of cancerogenic risk]. *Uspekhi sovremennykh estestvennykh nauk — Achievements of modern natural sciences*, 2, 142–143 [in Russian].