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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. Well adjusted system of monitoring by estimates of accumulation of metals in objects of a surrounding medium is necessary for carrying out the bioremediation of actions. The developed system will allow to determine consistent patterns of formation of technogenic load of the soil with a sufficient degree of accuracy. In the analysis of accumulation in the soil, it is necessary to take into account the frequency and the dynamics of the research, the number of points of comparison. In addition, to assess bioremediation measures must take into account views of the environment, the amount, location and frequency of sampling, certain requirements for the methodological and technical support.

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

The city of Karaganda is a major regional center of the Republic of Kazakhstan, industrial industrial center, the level of development of the industry occupies a leading position in Kazakhstan. On its territory are located dozens of industrial enterprises technogenic Profile, energy companies [1, 2]. Is developed intense inter-city transport network. In the city as a priority pollutant consistently carry heavy metals. During the ecological and hygienic assessment of soil and air pollution by heavy metals (lead, cadmium, nickel, zinc, copper) recorded the maximum air pollution levels of lead — 3.57 ug/m ^{3}, which exceeded the MPC by 12 times. The share of heavy metals on the total air pollution index accounted for between 5 and 76 %. What characterizes them as priority pollutants of the urban environment [3, 4].

The important role in the circulation of chemicals in large industrial cities belongs to the soil. Being the key environment and the universal adsorbent, the soil reflects the level of long-term anthropogenous influence. That consideration of the specific formation of the soil quality and the variety of criteria evaluation, the relationship between the integral and specific indicators will develop approaches to bioremediation measures. The effectiveness of the research program for the implementation of bioremediation measures will be successful only if will take into account all the sanitary and environmental contamination of soil criteria and ranking areas for these indicators.

One of the most important problems of monitoring of pollution of soils is the choice of priority ingredients for monitoring determined by a number of conditions and parameters. For example, a control sequence of the ingredients of technogenic origin located at the first stage of the chemical elements such as hydrargyrum, lead, cadmium, nickel, cobalt, molybdenum, vanadium, copper, fluorine, arsenic, zinc, chromium, antimony, selenium [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

For the organization of bioremediation measures necessary quantitative characteristic distribution of metals in soils. To this end, there have been ranked according to the degree of territories of the environmental situation of tension related to soil pollution with heavy metals. 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 enterprises. The metal content in the 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, proportional to the current to determine the number of ions of the type [5, 6].

The mineralization of samples was carried out according to methodical instructions [5, 6] in an automated complex sample preparation «TEMOS EXPRESS» TE-1, which is designed for the complete destruction of interfering organic substances, thermal treatment with oxidants (HNO_3, H_2O_2, H_2SO_4 et al.) in the temperature from 50 °C to 650 °C, in determining the concentration of Cd, Pb, Zn, Cu, As , et al. samples.

Total index of soil contamination (SDRs), calculated using the formula recommended by the Moscow Research Institute of Hygiene them. F.F.Erismana 1996

$$_{\text{the soil}}K = C_{1}/MPC_{1} + C_{2}/MPC_{2} + C_{3}/MPC_{3} + \dots C_{n}/MPC_{n}$$

where $_{\text{the soil}}K$ — total index of soil pollution; C_1, C_2, C_3 ... 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

Based on these results we analyzed the results, showing the level of heavy metals in soil samples. The dynamics of health indicators, shown in the background of the general trend to reduce soil pollution that 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. 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 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.

A special ecological and hygienic inspection of 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.

These studies have relevance, as an intermediate step in the environmental monitoring, the purpose of which is to optimize nature management aimed at reducing damage to the environment and economic efficiency. Taking into account the above listed, the soil cover is a unique object for study.

Extensive use is made of the complex characteristics of the quality of soil, where the conditional indicator of the degree of air pollution, soil pollution one to the index. The need for continuous monitoring of the soil due to the fact that he is the ultimate receiver of most man-made chemicals involved in the biosphere. Representing a geochemical barrier to the migration of pollutants, soil cover protects the adjacent environment from anthropogenic impacts. However, the capacity of soil as a buffer system are not unlimited. Accumulation their transformation products in the soil causes a change in its chemical, physical and biological conditions, degradation and, ultimately, the of destruction [7–11].

Identification of the basic laws of the spatial distribution of heavy metals showed that a small amount of precipitation and severe aridity of the climate led to the formation of light-brown soils of the subzone. Agrochemical indexes of the studied soils revealed the following: the humus content — 1.45 %, pH — 6.79, the amount of absorbed bases — 5.4 mg-Eq per 100 grams of soil, the amount of sesquioxides of iron and aluminum oxides was — 1 %. These indicators, which determine the mobility of heavy metals in soil, possible to calculate the index of the protective capacity of the soil from pollution - buffering capacity of the soil, as the average.

As a result of the work, it found that 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 %.

In all of the above ingredients, 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 tests for copper was the highest in the Oktyabrsky district.

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 1 we observe that the subject areas on the total figure is almost aligned with each other.

Table 1

Heavy metals in soils of Karaganda (mg/kg)

Area	Cu	Pb	Zn	V	Cr	Co	Ni	Mn	Be	SDRs
Area with high anthropogenic load	53	22	115	71	98	17	27	607	2.1	6.7
Average anthropogenic impact	26	24	150	50	51	23	14	280	1.8	4.7
Relatively clean area	21	53	60	67	68	22	22	1447	1.6	5.54

For copper characterized by localization in the upper layer of soil (10–15 cm from the surface). The variability of the concentration of copper in the city was 21 mg/kg — 53 mg/kg, which reflects its bioaccumulation and modern anthropogenic influence. Contamination of soil copper compounds, possibly the result of contributions from industrial sources as a result of corrosion of structural materials containing copper alloys (eg, electrical wires, pipes).

The lead content of the soil cover ranges from 22 mg/kg to 53 mg/kg. Lead contaminated territories of all areas of the city, most content from leading motorways.

In soils of the city there is a wide distribution of manganese in concentrations up to 1447 mg/kg. We attribute this to the fact that industrial emissions of many companies contained manganese oxide. Manganese accumulation usually occurs in the subsoil, and 60–90 % of the manganese is found in sandy soil fractions.

Accumulation of nickel in soil is due to the ability of the cell adsorbed manganese oxides and organic forms of iron.

Nickel is found in the town soil cover in concentrations of 22 mg/kg to 27 mg/kg. High concentration of beryllium in the city of 1.6 mg/kg — 2.1 mg/kg, which contributes to shift the pH toward alkaline sides.

Coming from industrial sources chromium is from 68 to 98 mg/kg. Increased chromium content is registered in the individual samples. 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 Bukhara-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
Oktyabrsky	1.8	2	3.2	4	2	3.4	5	7	2.3	5	6	7.5
Oktyabrsky	2	2	4	4	3	3.4	6	6.5	7.5	4.2	7.2	6
Kazybekbi	5.4	-	2	4.6	-	-	6	5.4	-	-	8	6
Kazybekbi	5.5	-	3	4.2	-	-	8	5.7	-	-	10	6.3
South-East	2.5	-	2.5	1.3	-	-	1.6	1.2	-	1.2	1.7	1.2
South-East	-	-	2.9	1.2	-	-	1.7	1.2	-	-	1.5	1.2

In terms of oil pollution, the most polluted are Kazybekbi 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.

It follows from the above that the ecological functions of soils related to their chemical and physico-chemical properties, provide absorption capacity of soil (sorption of mineral and organic matter), the possibility of degradation and mineralization biophilic elements and enzymes in the soil [1]. By alkaline reaction, a high organic matter content, soil character occurs fixation of heavy metals in the upper soil layers, resulting in the migration capacity of toxicants in the soil profile is sharply reduced.

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 (Kazybekbi). 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).

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 Kazybekbi 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).

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

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 (Kazybekbi 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 (Kazybekbi District).

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.

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Өндіріс аймағының топырағында ауыр металдардың жинақталу дәрежесіне байланысты топырақ қабатының жағдайы (Қарағанды қаласы)

Мақалада Қарағанды қаласының топырақ қабатының жағдайы зерттелген. Биоремедиациялық шараларды жүргізу үшін қоршаған орта объектілерінде металдардың жинақталуын бағалаудың жақсы ұйымдастырылған мониторингтік жүйе болуы тиіс. Құрастырылған жүйе топыраққа техногенді жүктеменің қалыптасу заңдылықтарын жеткілікті дәрежеде орнатуға мүмкіндік береді. Топырақтағы кумуляцияны талдау барысында зерттеудің кезеңдері мен динамикасын, салыстыру нүктелерінің санын ескеру қажет. Сонымен қатар биоремедиациялық шараларды бағалау үшін қоршаған орта объектілерінің түрлерін, көлемін, үлгілерді жинау орны мен уақытын, әдістемелік және техникалық қамсыздандырылуға қойылатын белгілі бір талаптарды ескеру керек.

Кілт сөздер: селитебті аймақтар, топырақ, қорғасын, инверсиялық вольтамперометрия әдісі, өндіріс ауданы, қоршаған орта, химиялық ластану.

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

В статье изучено состояние почвенного покрова города Караганды. Для проведения биоремедиационных мероприятий необходима хорошо налаженная система мониторинга по оценкам накопления металлов в объектах окружающей среды. При анализе кумуляции в почвах необходимо учитывать периодичность и динамику исследований, количество точек сравнения. Кроме того, для оценки биоремедиационных мероприятий нужно учитывать виды объектов окружающей среды, объем, место и периодичность отбора проб, определенные требования к методическому и техническому обеспечению. Разработанная система позволит с достаточной степенью точности устанавливать закономерности формирования техногенной нагрузки на почву.

Ключевые слова: селитебные территории, почва, свинец, метод инверсионной вольтамперометрии, промышленный район, окружающая среда, химическое загрязнение.

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