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ASSESSMENT OF THE INFLUENCE OF INDUSTRY ON POLLUTION OF SNOW AND SOIL WITH HEAVY METALS IN PAVLODAR

The article investigates soil contamination with heavy metals (zinc, lead, chromium, and manganese) in the snow and soil cover within the influence zone of thermal power plants and facilities of the petrochemical and metallurgical industries. To assess the anthropogenic impact on deposition environments, an analysis of heavy metal content was conducted using various indices and coefficients. The following were utilized: pollution index, enrichment factor relative to Clarke's concentration of the metal in the Earth's crust and in soils, hazard quotient (exceedance of MPC), as well as an adapted coefficient of heavy metal accumulation in soil relative to its content in snow. The main patterns of accumulation and distribution of chemical elements in soil and snow were identified. The study revealed that manganese predominates in terms of the average content of heavy metals in solid snow sediment and soils. Lead shows the lowest values in snow. In the soil cover, the greatest exceedance of MPC pertains to manganese - by 30 times. The content of other metals also exceeds the soil MPC, except for lead. Significant fluctuations in metal content at different sites indicate the influence of various factors such as wind direction, precipitation, and the presence of other industrial enterprises.

Keywords: heavy metals, industrial zone, snow cover, urban soils, pollution index.

Introduction

Thermal power plants (CHPP – Combined Heat and Power Producing) are one of the main sources of environmental pollution, including snow and soil. The primary pollutants from these enterprises are heavy metals, categorized as super-ecotoxicants, possessing mutagenic and carcinogenic properties, as well as the ability to accumulate in environmental objects. The most dangerous in this sense are heavy metals of toxicity classes 1 and 2 (lead, cadmium, mercury, nickel, cobalt, chromium, vanadium, copper and zinc, as well as arsenic, selenium and antimony). Heavy metal pollution from thermal power plants is primarily associated with coal combustion, highlighting the significant impact of industrial activities on the accumulation of heavy metals in the environment [1].

The increasing pollution of natural environments with gaseous, solid, and liquid harmful emissions from thermal power plants leads to the disruption of the self-recovery principle, which is one of the fundamental principles of nature. Of particular interest and practical significance is, on one hand, understanding the mechanisms and regularities of behavior and distribution of heavy metals in the environment. On the other hand, the fact that there are essentially no self-purification mechanisms for them – they merely move from one natural reservoir to another, interacting with various categories of living organisms and leaving negative consequences of this interaction everywhere they go. Such reservoirs include deposition environments: snow and soil covers [2].

Snow cover has the ability to accumulate almost all substances entering the atmosphere from various sources, which makes it an effective indicator of pollution when monitoring air and soil quality in urban areas. One approach to such monitoring is to study the accumulation of pollutants, including heavy metals, in the snow cover, which serves as an important depositing medium [3; 4; 5]. Another accumulating medium that accumulates pollutants is soil. Soil is considered one of the basic resources for the survival of mankind because, by satisfying the food needs of all living organisms, soil performs the function of producing nutrients. Both covers are closely interconnected; snow is not active either chemically or biologically and, therefore, is an indicator of previous atmospheric pollution and future pollution of the soil and hydrosphere, into which water-soluble and solid pollutants migrate during snow melting. The soil, in turn, accumulates heavy metals and contributes to the further accumulation of toxicants in plants.

In this context, heavy metal pollution poses a serious problem worldwide, constituting an issue of environmental safety and sustainable resource management. Therefore, research aimed at identifying the level of pollution and the characteristics of heavy metal distribution in snow and soil covers within the influence zone of thermal power plants is more relevant than ever.

To date, several foreign studies have been carried out on this topic. Research by Yakovlev (2022) [5] revealed that in the zone of influence of a thermal power plant, a very voluminous sediment is formed in the snow cover, which includes soot and other products of coal combustion. The insoluble form of the studied snow contains more metals than the soluble form [5]. In China, in 2021, measurements were taken of the concentrations of heavy metals such as: As, Cd, Cr, Cu, Hg, Mn, Pb and Zn in surface soil layers in the area adjacent to a coal-fired power plant. According to the research results, the degree of contamination varied from severe to moderate. Cd, Hg and As were found to be major contributors to potential environmental risk. The results also showed that wind direction is important for the distribution of heavy metals around a coal-fired power plant [6]. Another study of soil pollution in an area adjacent to a coal-fired power plant in southwest China found that CHP contributed to contamination of nearby soils with Pb, Cd, As, Hg, Cu and Cr, especially mercury. Moreover, soil mercury contamination was caused mainly by fly ash from a coal-fired power plant in Jinsha [7].

In research of Kai Che, 2022 [8] As, Cd, Cr, Cu, Pb, Hg and Ni were analyzed in the flue gases of six power plants. The results showed that the main pollutants in thermal power plants were Cu, Cr and Ni. The average content of Cr, Cu, Pb, Hg and Ni in the surface layer of soil surrounding the coal-fired power plant was 1.16-2.32 times higher than background values. Source analysis showed that emissions from coal combustion contributed the most to the formation of heavy metals in soil around power plants (41.4 %), followed by industrial emissions (23.6 %) and transport emissions (19.6 %) [8].

Based on the examples given, it is obvious that the content of heavy metals in snow and soil around thermal power plants is the subject of extensive research. Statistical analyzes and studies of heavy metals in snow and soil have identified thermal power plants as sources of pollution, highlighting the need for comprehensive monitoring and mitigation strategies [9]. The results of these studies provide valuable information on the sources, distribution and effects of heavy metals, highlighting the need for effective measures to address this environmental problem [10].

This study will analyze heavy metal pollution in the northern industrial zone of the city of Pavlodar. The electric power industry in the city is represented by Pavlodarenergo JSC. Which in the study area includes Pavlodar CHPP-2; Pavlodar CHPP-3 and other facilities. Snow and soil covers were selected as research objects. The purpose of this work is to study technogenic pollution of snow cover and soils with heavy metals.

1)The objectives of our research included:

determination of the concentration of heavy metals in the solid fraction of snow cover in the zone of influence of thermal power plants; 2) identification of the content of heavy metals in the soil in the northern industrial zone of Pavlodar; 3) assessment of heavy metal contamination of the environments under consideration, analysis of the accumulation of toxicants in the soil;

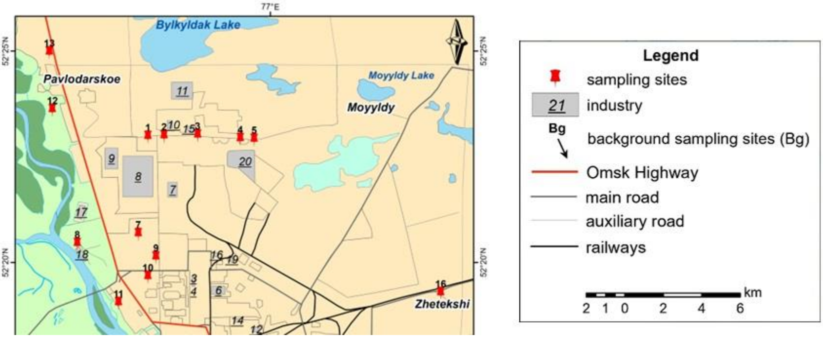
4) comparative assessment of the spatial distribution of heavy metals in snow and soil covers.

Materials and methods

Study area and sample collection

The study of snow cover and soils was carried out in the city of Pavlodar in 2023. Sampling sites were identified (Figure 1). Snow cover sampling was carried out according to Methodological recommendations [11; 12].

Samples were taken on the territory of the northern industrial zone, at various distances from industrial facilities, based on the wind rose. The environmental gradient was taken into account, i.e. gradual reduction of the influence of factories, thermal power plants and other objects. Sampling sites were located at a distance of 100 m, 500 m, 1000 m, 2000 m, 3000 m, 4000 m and 5000 m from Pavlodar Petrochemical Plant JSC, CHPP-2, CHPP-3. Sampling sites also included the vicinity of ash dumps of thermal power plants, residential areas of the city (Lesozavod district), the villages of Zhanaul and Pavlodarskoye, summer cottages, and vegetable gardens of residential areas [13]. A total of 14 snow samples were taken.



Picture 1– Location of the study area and sampling sites in Pavlodar

3 – Pavlodar branch of «KSP Steel» LLP, 4 – Pavlodar branch of «Casting» LLP; 6 – CHPP-2 of «Pavlodarenergo» JSC, 7–CHP-3 of «Pavlodarenergo» JSC; 8 - Pavlodar Petrochemical Plant JSC, 9 – «Neftekhim Company LTD» LLP,

10 – «Kaustik» JSC, 11 – UPNK-PV LLP; 12 – Kazenergokabel JSC, 14 – «Pavlodar Pipe Rolling Plant» LLP, 15 – «PMZ DAMAK» LLP, 16 - Cardboard and Ruberoid Plant, 17 – Pavlodar TcGOS, 18 – JSC «Pavlodar River Port»,19 – «Company of Industrial Materials (KPM)» LLP.

The soil sampling sites coincide with the snow cover sampling sites to determine the pattern of heavy metal content in various environments. During the sampling process, the sampling methodology of the Interstate Standard GOST 17.4.4.02-2017 «Nature Protection (Environmental Protection) – Soils» was employed. Sampling was carried out using the «envelope» method in the upper soil horizon, up to 15 cm deep (the depth of the arable layer) to study the accumulation of heavy metals on the soil surface as a result of melting snow cover and their effect on plants. A total of 14 soil samples were taken.

Laboratory tests were carried out in the laboratory of the branch of the Institute of Radiation Safety and Ecology of the RSE at the National Nuclear Center of the Republic of Kazakhstan of the Ministry of Energy of the Republic of Kazakhstan. The analysis of the content of chemical elements in the solid phase of snow and soil was carried out by mass spectrometry with inductively coupled plasma using an Agilent 7700 X ICP-MS in accordance with the Measurement procedure No. 499-AES/MS MCHA «Methods of quantitative chemical analysis. Determination of the elemental composition of rocks, soils and bottom sediments by atomic emission with inductively coupled plasma and mass spectral with inductively coupled plasma methods" KZ.07.00.03351-2016.

For further analysis of contamination of depositing environment, 4 metals were selected, which are the most toxic and also make a large contribution to the pollution of the city's snow and soil cover. The first hazard class includes zinc (Zn) and lead (Pb), the second – chromium (Cr), and the third class – manganese (Mn).

Statistical processing and coefficient calculations

To assess the pollution of snow and soil covers with heavy metals, the pollution index (PI) was calculated. PI is calculated by comparing the actual (anomalous) content of the pollutant in the natural object to its background level in a similar object.

Pollution index (PI) formula:

$$PI = \frac{Cn}{Bg}, \quad (1)$$

where Cn is the content of heavy metals in the soil, Bg is the content of heavy metals in background samples.

Pollution coefficient relative to MPC (PImpc) - the ratio of the metal content in snow or soil to the maximum permissible metal concentration.

$$PImpc = \frac{Cn}{MPC}, \quad (2)$$

where Cn is the concentration of pollutant in snow or soil;

MPC is the maximum permissible concentration of pollutant i in snow or soil.

Enrichment factor (EFcrust) [14]:

$$EFcrust = \frac{Csample}{Ccrust}, \quad (3)$$

where Csample is the concentration of metal in the soil, according to our study; Ccrust is the concentration of the metal in the earth's crust (clark concentration) [15].

Enrichment factor relative to soil clarke (EFsoil):

$$EFsoil = \frac{Csample}{Csoil\ clark}, \quad (4)$$

Element	Interval	Average content	The oefficient of variation	Background content	Pollution index
Zn	63-800	286.2±55.3	72.2	175	1.6
Pb	26-430	158.5±270.2	64.3	42.5	3.7
Cr	59-1200	316.6±88.9	105.13	755	0.4
Mn	400-1800	638.6±92.7	54.4	560	1.1

where Csample is the concentration of metal in the soil, according to our study; Csoil clark – metal concentration in soil (clark concentration) [16].

The coefficient of heavy metal accumulation in soil (Transfer Factor, TF):

$$TF = \frac{Csoil}{Csnow}, \quad (5)$$

where Csoil is the concentration of heavy metal in the soil;

Csnow is the concentration of heavy metal in snow.

Results and discussion

According to the result of the analysis of environmental reports of Pavlodar enterprises, the main pollutants emitted by enterprises in the northern industrial zone of Pavlodar were identified. The volume of actual emissions of pollutants into the atmospheric air of the petrochemical plant is 22,275.104 tons, Pavlodarenergo JSC – 35,096.751 tons, CHPP-2 – 6,795.546 tons, CHPP-3 - 28,301.205 tons, KSP «Steel» – 2,837 tons . The main volume of emissions comes from inorganic dust with varying silicon content, abrasive, wood and metal dust. The leaders in dust emissions are CHPP-2, CHPP-3, followed by KSP «Steel». According to the results of the study, the amount of heavy metals emitted in pure form is small, but the content of various elements in dust and ash far exceeds these values. Inorganic dust emitted by the city's thermal power plant contains: fireclay, cement, cement production dust - clay, shale, blast furnace slag, sand, clinker, silica ash, coal ash from Kazakhstan deposits. It should be noted that according to the results of industrial environmental monitoring, none of the industrial facilities exceeds the standard indicator for emissions of pollutants.

As a result of the laboratory analysis for the content of heavy metals in snow sediment in the city of Pavlodar, the results presented in Table 1 were obtained.

Table 1– Statistical indicators of the content of heavy metals in solid snow sediment in the zone of influence of the energy industry in Pavlodar, mg/kg

Element	Interval	Average content	The coefficient of variation	Background content	Pollution index
Zn	63-800	286.2±55.3	72.2	175	1.6
Pb	26-430	158.5±270.2	64.3	42.5	3.7
Cr	59-1200	316.6±88.9	105.13	755	0.4
Mn	400-1800	638.6±92.7	54.4	560	1.1

The average content of elements in the samples is presented in the following row: Mn (638.6) > Cr (316.6) > Zn (286.2) > Pb (158.5). The minimum concentrations of zinc, lead and chromium were recorded at site 4.5 - to the north and northeast of the ash dumps, which may be due to the prevailing wind direction [14], and the maximum - at site 13, in the zone of influence of the thermal power plant the content was average. The maximum value of lead is noted at site 2, in the zone of influence of the highway, as well as the chemical industry, which also causes a high content of manganese (max – site 3). The maximum value of chromium was confined to the zone of influence of CHPP-3 and the south of the Pavlodar Petrochemical Plant.

Next, the pollution index relative to the background content of the substance was calculated. Snow samples for background indicators were collected more than 50 km away from the city. The sampling area was 500 m from the main road and 1 km from the nearest village. Thus, the background indicators had an anthropogenic impact, but without the direct influence of urban industry. As a result, pollution indices are low and range from 0.4 to 3.7. Lead and zinc have significant excesses of background concentrations, and chromium has the least.

As a result of statistical analysis of the content of heavy metals in the soils of the northern industrial zone, the following results were obtained (table 2).

Table 2 – Statistical data of the content of heavy metals in the soil cover of Pavlodar, mg/kg

Element	Interval	Average content	The coefficient of variation	Background content
Zn	72-300	140.2±69.7	49.69	192.50
Pb	7-22	13.8±4	29.04	13
Cr	85-195	130.6±28.2	21.59	106
Mn	19000-25000	21607.1±91820.6	8.43	20000

The highest content of elements in soil samples is presented in the following row Mn (21607) > Zn (140,2) > Cr (130,6) > Pb (13,8). As for the spatial distribution of heavy metals in the soil, a strong association with the zone of influence of thermal power plants was not observed. The highest concentrations of metals are confined to industrial areas, and the chromium content is higher at site 5, northeast of the ash dumps of the thermal power plant.

To assess soil contamination with heavy metals, ecological and geochemical indicators were calculated (Table 3), characterizing the excess concentration of metals in the soil of this study relative to the clark in the earth's crust (EFcrust), the clark in the soil (EFsoil) and the pollution index (PI). The pollution indices relative to the clark content in the Earth's crust and soil are used in this study to determine the level of soil pollution with heavy metals relative to the natural content of these metals.

Table 3 – Indices of heavy metal pollution in the soil of the northern industrial zone

Element	Enrichment factor (EFcrust)	Enrichment factor (EFsoil)	Pollution index (PI)
Zn	1.69	2.80	0.73
Pb	0.86	1.38	1.06
Cr	1.57	0.65	1.23

Mn	21.61	25.42	1.08

According to Sutherland (2000) [15], if the enrichment factor is less than 2, then the soils are considered uncontaminated. In our case, the metals zinc, lead and chromium have a low enrichment relative to clarke in the earth's crust, the enrichment of manganese refers to very high contamination. Regarding clarke in soils, zinc is of average enrichment in the soils of Pavlodar and manganese is also highly contaminated. Despite the high values of the enrichment factor, the pollution indices relative to the background data of our study are low, i.e. the content of heavy metals in soils outside the city is only slightly lower than in urban soils.

As can be seen from the results of the study, manganese predominates in soils in all respects. It is known that the natural content of manganese in soils and plants is very high; in our case, its content in the soil is explained by the alkaline environment of the soil and the presence of carbonates in them. According to some studies, manganese is not considered a soil-polluting metal [17].

To assess the potential impact of heavy metals on human health, the maximum permissible concentration of an element in soil was studied, since there are no separate maximum permissible concentrations for snow cover. Since this study studied solid snow sediment after filtration of melt water, it is possible to use and compare the obtained values with the maximum permissible concentration of heavy metals in the soil. For lead and arsenic, MPCs were used according to the Kazakhstan standard [18], for other metals data from literary sources [19] or Russian GOST [20] were used.

As a result, hazard coefficients were obtained, i.e., the exceeding of MPC indicators in soils by the average values of heavy metal content in solid snow sediment and soils, as well as the coefficient of heavy metal accumulation in soil from snow. It is calculated as the ratio of the concentration of heavy metals in the soil to the concentration in the snow cover (Table 4).

Table 4 – Hazard coefficients and accumulation of heavy metals

Element	MPC of heavy metals in soil	Snow cover hazard coefficient, PImpc	Soil cover hazard coefficient, PImpc	Soil accumulation coefficient, Transfer Factor, TF

Zn	55 [20]	5.20	2.55	0.5
Pb	32 [18]	4.95	0.43	2
Cr	100 [19]	3.16	1.31	0.4
Mn	700 [20]	0.91	30.87	34

The highest excess of MPC in snow cover relates to zinc and lead - 5 times, the smallest - to manganese. In the soil cover, the greatest excess of the MPC relates to manganese – 30 times. The content of other metals also exceeds the soil MPC value, except for lead. Thus, the concentrations of heavy metals in snow are much higher than the concentrations in soils and, as a result, have a high excess of the MPC.

To identify the relationship between the content of heavy metals in snow and soil, a correlation analysis was carried out. Among all metals, a correlation within 0.3–0.4 was noted, which indicates that the relationship between these two variables is relatively weak. The content of heavy metals in the soil does not greatly depend on the content of the same metals in the snow cover. For chromium the correlation is negative.

Interesting data is presented by the coefficient of accumulation of heavy metals in the soil. Thus, according to calculations, manganese constantly accumulates in the surface layer of soil in large quantities; it is not washed out or filtered. Zinc and chromium have coefficients of 0.4 and 0.5, their content in the soil is reduced by 2 times compared to snow. The opposite is true for lead; its content in the soil is 11 times less than in the snow cover, which suggests that chromium is washed out from the surface layers of the soil after melting of snow.

To compare the spatial distribution of metals in snow and soil covers, maps of chromium content were compiled (Fig. 2). The maps were compiled using the interpolation method.

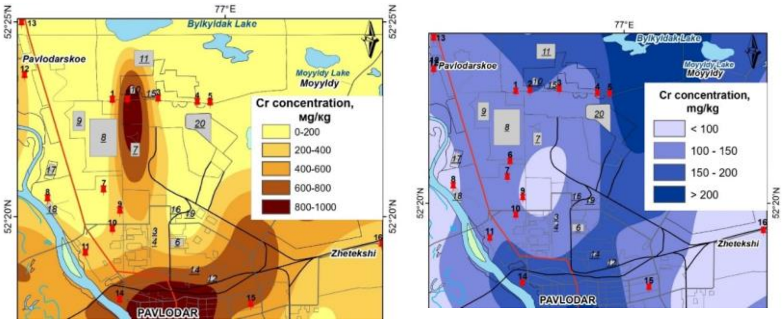


Figure 2 – Spatial distribution of chromium content in urban soils of Pavlodar

Concentrations in snow are much higher than those in soils due to large differences in classes. In the snow, chromium is confined to the Petrochemical Plant and Thermal Power Plant-3 and has the form of concentric areas around these objects. In soils, a smoother distribution of metal is observed with minimal content in the territory of dachas. In most of the northern industrial zone, the chromium concentration ranges from 100 to 150 mg/kg, as well as in the snow cover, most of it corresponds to the class from 0 to 200 mg/kg.

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Conclusions

In the city of Pavlodar, in the northern industrial zone, studies of the content of heavy metals in snow and soil covers were carried out and the coefficients of pollution and accumulation of metals in depositing environments were calculated. The northern industrial zone is of interest as it is within the influence zone of two major thermal power plants in the city, and the identification of the pollution level of this area is the goal of this study. As a result, it was revealed that the highest concentrations of zinc, lead and chromium metals were found in the snow cover (maximum lead – 11 times more), manganese in the soil (34 times more than in snow). Despite the high content of heavy metals, it was revealed that the pollution indices have low values, which is due to low background values. The exception is lead in snow, the excess of which in the city is 3.7 times. However, when determining the hazard coefficient relative to the maximum permissible concentration, all metals in all environments demonstrate an excess of the MPC, except for manganese (0.91) in snow and lead (0.43) in soil. These results highlight the importance of controlling and monitoring heavy metal pollution and the need to take measures to reduce anthropogenic impacts on the natural environment.

The accumulation of heavy metals in soil is a complex problem that requires interdisciplinary research to fully understand its consequences. By studying patterns of accumulation, distribution, and exposure of heavy metals in different environments, researchers can gain valuable information to develop strategies to reduce the risks associated with heavy metal pollution.

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ПАВЛОДАР ҚАЛАСЫНДА ҚАР МЕН ТОПЫРАҚТЫҢ АУЫР МЕТАЛДАРМЕН ЛАСТАНУЫНА ӨНЕРКӘСІПТІҢ ӘСЕРІН БАҒАЛАУ

Мақалада жылу электр станциялары мен мұнай-химия, металлургия өнеркәсібі объектілерінің әсер ету аймағындағы қар мен топырақ жамылғысының ауыр металдармен (мырыш, қорғасын, хром және марганец) ластануы зерттеледі. Қар мен топыраққа антропогендік әсерді бағалау үшін әртүрлі индекстер *мен коэффициенттерді қолдана отырып ауыр элементтердің құрамына талдау жасалды. Пайдаланылды: ластану индексі, кларкқа қатысты байыту факторы жер қыртысындағы және топырақтағы металл концентрациясы, қауіптілік коэффициенті (ШРК-дан асып кету), сондай-ақ топырақта қардан ауыр металдардың жиналу коэффициенті. Топырақ пен қарда химиялық элементтердің жиналуы мен таралуының негізгі заңдылықтары анықталды. Зерттеу барысында ауыр металдардың орташа мөлшері бойынша қардың қатты фракциясында және топырақта марганец басым екені анықталды. Топырақ жамылғысында ШРК-ның ең көп мөлшері марганецке жатады – 30 есе. Қалған металдардың құрамы қорғасынды қоспағанда, топырақтың ШРК мәнінен асып түседі. Әр түрлі учаскелердегі металл құрамының айтарлықтай ауытқуы желдің бағыттары, жауын-шашын және басқа да өнеркәсіптік кәсіпорындардың болуы сияқты әртүрлі факторлардың әсерін көрсетеді.*

Кілтті сөздер: ауыр металдар, өндірістік аймақ, қар жамылғысы, қалалық топырақ, ластану индексі.

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ОЦЕНКА ВЛИЯНИЯ ПРОМЫШЛЕННОСТИ НА ЗАГРЯЗНЕНИЕ СНЕГА И ПОЧВ ТЯЖЕЛЫМИ МЕТАЛЛАМИ В Г. ПАВЛОДАР

В статье исследуется загрязнение почв тяжелыми металлами (цинк, свинец, хром и марганец) снежного и почвенного покрова в зоне влияния ТЭЦ и объектов нефтехимической, металлургической промышленности. Для оценки антропогенного влияния на депонирующие среды была проведен анализ содержания тяжелых элементов с применением различных индексов и коэффициентов.

Были использованы: индекс загрязнения, фактор обогащения относительно кларка концентрации металла в земной коре и в почвах, коэффициент опасности (превышение ПДК), а также адаптированный коэффициент накопления тяжелых металлов в почве относительно содержания в снегу. Выявлены основные закономерности накопления и распределения химических элементов в почве и снегу. В ходе исследования было установлено, что по среднему содержанию тяжелых металлов в твердом осадке снега и почвах преобладает марганец. Наименьшие значения в снегу показывает свинец. В почвенном покрове наибольшее превышение ПДК относится к марганцу - в 30 раз. Содержание остальных металлов также превышает значение ПДК почв, за исключением свинца. Значительные колебания содержания металлов на разных участках указывают на влияние различных факторов, таких как направления ветра, осадки и наличие других промышленных предприятий.

Ключевые слова: тяжелые металлы, промышленная зона, снежный покров, городские почвы, индекс загрязнения.