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Heavy Metals Contamination in Snow Cover of Pavlodar (Kazakhstan)

A study of the concentration of heavy metals in snow cover was carried out in Pavlodar in the area of influence of the Pavlodar Petrochemical Plant and other industrial facilities. Significant excesses of background concentrations of manganese, chromium, vanadium and other metals were detected. The distribution of metals in the snow cover showed that the elements have high values near the oil refinery and decrease at a distance of 700 m. The possible influence of other industrial enterprises and the direction of winds from CHP-3 are also noted. Manganese and barium show more stable values, and chromium, zinc, lead and cadmium have increased concentration near JSC "Kaustik". The total concentration of manganese, strontium, cobalt and arsenic varies slightly across all sites, indicating uniform contamination by these substances. Lead is highest in industrial areas and in populated areas with highways. Aluminum and iron are widespread, with the lowest values in the Zhanaul village at a distance of 3 km from the Petrochemical Plant. The results of the study highlight the importance of controlling and monitoring heavy metal pollution and the need to take measures to reduce anthropogenic impacts on the natural environment.

Keywords: heavy metals, industrial zone, snow cover, total pollution, dispersion, deposition.

Introduction

Pavlodar city is one of the industrial centers of Kazakhstan. Almost all industries are represented in the city. The main part of the industry is in metallurgy — 42.6 %, the second place is electric power — 17.8 %, the share of petroleum products production is 13.3 %. The city also has a developed mechanical engineering and chemical industry.

The high productive capacity of the factories in Pavlodar determines the successful economic development of the region, but the downside of this development is the consequences of the impact of production on the environment. Every year, tons of pollutants are released into the air, including heavy metals, which have a negative impact on the health of city residents.

Industrial activities result in the release of a large number of elements into the atmosphere, including metals of various hazard classes. These elements settle on the surface of the earth, polluting the soil, vegetation and water bodies. They can also enter the body of humans and animals, which poses a serious danger. The most toxic are heavy metals of classes 1 and 2 (lead, cadmium, mercury, nickel, cobalt, chromium, vanadium, copper, zinc, arsenic, selenium and antimony) [1].

The most polluted areas are near metallurgical plants and roads, and wastewater, slag and exhaust gases from smelting operations contain high levels of heavy metals. Various [1–4] studies provide evidence of extensive pollution in surrounding areas, reaching 40–70 % of the area. A study examining heavy metal pollution in agricultural land around a smelter in China found that smelting activities were the main source of metal pollution in the surrounding area, accounting for 48.62 % of the total pollution [2].

Also, due to the large amount of industrial emissions and traffic in the city, industrial areas and areas along city roads suffer the most [3]. In particular, metals are emitted from brake linings, tire rubber, exhaust emissions, lubricants and oils, gasoline and diesel fuel, and asphalt pavements [4]. Cumulative heavy metal pollution depends on factors such as climate, road design, traffic volume, distribution of vehicles into different classes and road maintenance, which is especially important in cool temperate climates with seasonal snow [5].

The environmental impact of heavy metals on the environment is determined by many factors, including their behavior in the atmosphere. Chemical transformations in the atmosphere can lead to the formation of more or less toxic forms of elements than those originally emitted, as well as affect the mechanism and rate of their discharge from the atmosphere [3].

Atmospheric metals are absorbed by particulate matter, migrate as particulate matter moves, and then settle in various ecosystems through wet (precipitation) and dry deposition [6–8].

For example, during deposition with precipitation, metals are mainly in a soluble state, their percentage being 30–100 %. Analysis of sediment samples in some studies showed that the average percentage of water-soluble Cr, Cd and Pb reached 80 %, 87 % and 93 %, respectively [9, 10]. In addition, the bioavailable fraction of trace metals from recent metal deposits was found to be higher than the fraction of metals previously present in the soil, suggesting that recently deposited metals have a greater impact on terrestrial ecosystems.

Aerosol particles are an important factor influencing the behavior of heavy metals in the atmosphere. Their chemical composition and size determine how long heavy metals remain in the atmosphere and how far they can spread [3]. The transmission distance of atmospheric metals depends mainly on meteorological conditions and particle size, as well as on the physicochemical properties of aerosols. The impact of air pollution varies greatly between urban and rural areas [11]. Metals from precipitation have an impact on urban neighborhoods or remote areas due to their widespread distribution. The main factor in air pollution is related to distance, and the closer to the source, the higher the degree of pollution. The main effect of atmospheric metals is their wide transport range and their ability to migrate [12].

Factors influencing long-range transport of metals are complex and depend on emission sources, particle size, meteorological conditions and terrain. Sources of emissions and their remoteness are the main factors determining the supply of microelements to remote areas.

Solid precipitation does not infiltrate into the soil or enter water bodies, but accumulates pollutants that enter the atmosphere from precipitation, gases, aerosols, and particulate matter. The chemical composition of melt water reflects the degree of air pollution in the most soluble forms of elements. This makes the eco-geochemical assessment of snow cover pollution an important tool for environmental monitoring [1].

The chemical composition of atmospheric aerosols in snow can be used to track the paths of air masses, as well as the sources and intensity of emissions of certain chemical components [13–18].

The safety of agricultural land is critical to human health, but metals have become an important source of pollution in many agricultural areas [19, 20]. According to statistics, more than 50 % of the total load of As, Cd, Cr, Hg and Pb in agricultural soils over the past decade was due to atmospheric deposition of metals. Whether from natural or anthropogenic sources, elevated concentrations of heavy metals in the environment worldwide pose a threat to human health [21–23].

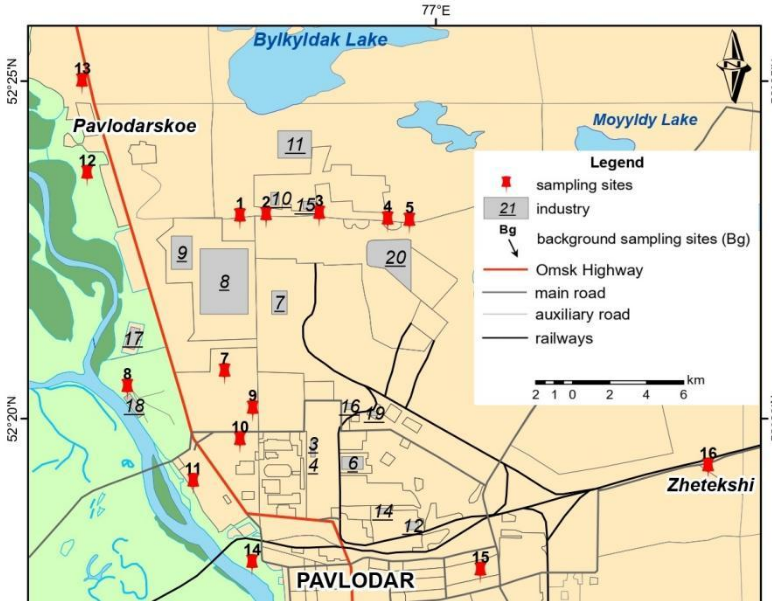
Excess metals in soil can affect crop growth and soil ecology and can also lead to soil degradation. Therefore, highly contaminated areas (near smelters, along roads) must be managed in a sensible and effective manner, such as waste disposal, fencing off the contaminated area, and identifying environmental risks within the contaminated area [3]. In other areas, mainly agricultural land, the soil needs to be monitored to ensure that metal concentrations are below the risk value, preventing them from entering the human body through the food chain and thus affecting human health.

This study will analyze heavy metal pollution in the northern industrial zone of the city of Pavlodar. Snow cover was chosen as an object of research as one of the depositing medium, capable of accumulating pollutants and being very informative about real pollution in a certain period of time (snow accumulation).

Experimental

The snow cover study was carried out on the territory of the city of Pavlodar. The entire city was divided into squares, taking into account industrial and residential areas [3]. Further, sampling points were identified (Fig. 1). The choice of sites was determined by the presence of industrial facilities, their type, and distance from the source of pollution. Thus, the northern industrial area with the metallurgical industry was allocated in the city; energy industry; chemical industry; mechanical engineering and other industries.

Samples were taken at various distances from industrial facilities, in the eastern, southern and northeastern and southeastern directions of the wind, based on the wind rose to determine the boundary of the object's zone of influence on the atmosphere. The wind rose was constructed based on Kazhydromet data for 2022 (Fig. 2). The main wind direction for the entire 2022, according to the plotted schedule, is south. Western and southeastern also predominate. Thus, sampling points were selected according to the direction of the prevailing winds. In addition, the direction of the wind in winter was taken into account, that is, during the accumulation of snow cover (Fig. 3).



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

Figure 1. Map of the city of Pavlodar indicating the study area

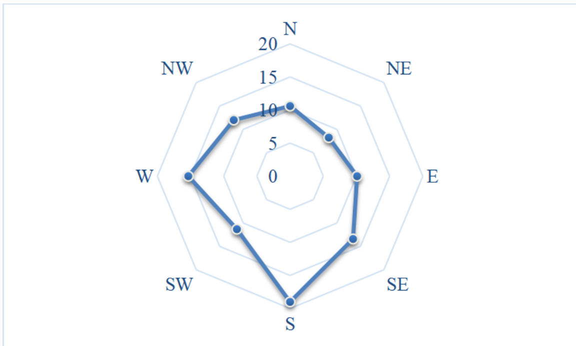


Figure 2. Wind rose for the city of Pavlodar (2022), constructed by the authors based on data from the Meteorological database of the RSE "Kazhydromet" [24]

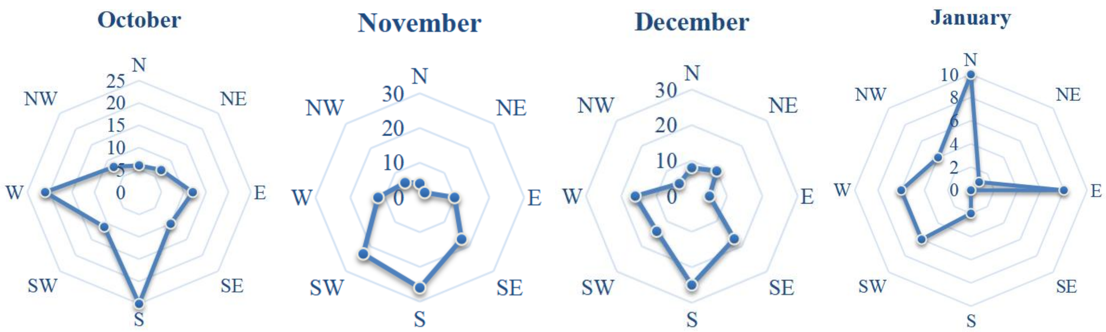


Figure 3. Wind rose for the city of Pavlodar (October, November, December 2022), constructed by the authors based on Kazhydromet data

The beginning of the accumulation of snow cover usually occurs in October, when the southern and western directions predominated; in November and December — the southern, southwestern, and southeastern directions. Thus, the main air masses and, accordingly, pollutants were directed away from the city, but reached the northwestern direction of the Pavlodar region (the village of Pavlodarskoye — 3–5 km from the industrial plant), where samples were taken for analysis. To the east of the city, at a distant distance (13 km) in the village of Zhetekshi, sampling was also carried out.

The distance between samples varied from 100 m, the further sampling point was 13 km from industrial facilities, the background (lowest impact) points were located at a distance of 56 km. Due to the fact that the background indicators of our study had high indicators due to the proximity of the settlement, in this study we also used the background values obtained in previous studies [3] conducted in the city of Pavlodar, for those values that were not presented in these sources, our background values were used.

The environmental gradient was taken into account, i.e. gradual reduction in the influence of factories, thermal power plants and other objects. Sampling points 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, "KSP Steel" LLP, CHP-2, CHP-3, since these objects are leading environmental factors. Sampling locations also included the vicinity of ash dumps of thermal power plants, residential areas of the city (Lesozavod district), the villages of Zhanaul and Pavlodarskoye, suburban area with cultivation vegetables and fruits for own use (dacha), and vegetable gardens of residential areas. Dacha plots were allocated because the main goal of the study is to determine the impact of pollutants on the quality of plant products grown in the immediate vicinity of the industrial zone. In order to reduce the impact of automobile exhaust on the samples, samples were taken at least 25 m from the road route, according to literature sources [25–27].

Sampling was carried out in January, with an average snow cover height of 60 cm. The methods used for sampling were the pit method: the pit (depth, width, height) in the snow cover was measured. Snow was collected in plastic bags; the average sample weight was 6 kg.

Next, the snow was processed under laboratory conditions, and the snow melted under natural conditions within 8–12 hours.

Melt water was filtered through ash-free "Blue Ribbon" filters, specialized filters for separating fine-crystalline sediments such as cold-precipitated barium sulfate, copper oxide, etc. from the solution. The resulting sediment, after filtering the melt water, was dried, weighed and packaged for further work on determining the concentration of heavy metals. Laboratory tests were carried out in the laboratory of the branch "Institute of Radiation Safety and Ecology" of the RSE on PVC "National Nuclear Center of the Republic of Kazakhstan" of the Ministry of Energy of the Republic of Kazakhstan.

The analysis of the concentration of chemical elements in the solid phase of snow was carried out by mass spectrometry with inductively coupled plasma using an Agilent 7700 X ICP-MS according to: Measurement procedure No. 499-AES/MS MKHA "Methods of quantitative chemical analysis. Determination of the elemental composition of rocks, soils, soils and bottom sediments by atomic emission with inductively coupled plasma and mass spectral with inductively coupled plasma methods" KZ.07.00.03351–2016.

The concentration coefficient of a chemical element, K_c, is calculated based on the ratio of the real (anomalous) concentration of the pollutant in a natural object (C) to its background level (C_{bg}) in a similar object:

$$K_c = \frac{C}{C_{bg}}. \quad (1)$$

The total pollution indicator Z_c is equal to the sum of the concentration coefficients K_c of chemical elements concentration of which exceeds background values, and is expressed by the following formula:

$$Z_c = \sum K_c - (n-1), \quad (2)$$

where: n is the number of anomalous elements taken into account.

Results and Discussion

As a result of the analysis of environmental reports of Pavlodar enterprises, the main pollutants emitted by industrial enterprises in Pavlodar were identified. The volume of actual emissions of pollutants into the atmospheric air of Pavlodar Petrochemical Plant JSC — 22275.1 tons, "Pavlodarenergo JSC — 35096.8 tons, CHP-2 of "Pavlodarenergo" JSC — 6795.5 tons, CHP-3 of "Pavlodarenergo" JSC — 28 301,2 tons, "KSP Steel" — 2837 tons (Table 1).

Table 1

Emissions of pollutants from industrial enterprises Northern industrial zone of Pavlodar (kg/year)

Name of pollutant	Petrochemical Plant	CHP-2	CHP-3	"KSP Steel"	"Casting" LLP	"Neftekhim LTD"	JSC "Caustic"
Iron	1.1	5.2	2176.3	16915.4	1450.8	6.0	265.01
Manganese and its compounds	0.1	11,5	50,6	18000.84	5.29	1.0	5.56
Aluminum	78877.7			1322.7			0.0037
Chromium	0.1	0.3	1.46	6.0	0.04		0.03
Chlorine							175.2
Nickel oxide	0.005	0.2	0.01	0.0003	0.0039		0.0029
Lead		0.02		0.002			0.0004
Copper		1.7	20.92	0.05			0
Zinc		0.03		313.5			0
Petrol	48740.9		50.77	35.2			675.9
Kerosene		5.6		14.2	81.5		0
Inorganic dust	188 492	1177692	4 885 213	304247.2	220000	790	1436.55 (+ suspended solids)
Abrasive dust	1,1	65.42	150.66	3080.8	33.36	1	209.72
Wood dust		76.71	563.8	6741.1			191.46
Rubber dust				10.3			
Metal dust		165.68	456.1				

Information on the volume of actual emissions of pollutants into the atmospheric air of industrial enterprises from January 1 to December 31, 2020 is presented in the table. For research purposes, only emissions of heavy metals were isolated, because of interest is their accumulation in the snow cover.

As a result of the analysis, it was revealed that the maximum emissions of interest in this study occur at CHP-3 4888.68 t/year, "KSP Steel" — 350.7 t/year and Pavlodar Petrochemical Plant — 316.1 ton/year. The main volume of emissions comes from inorganic dust with varying silicon concentration, abrasive, wood and metal dust. The leaders in dust emissions are CHP-2, CHP-3, followed by "KSP Steel". Next, in terms of emissions, follows aluminum — 78.877 t/year, petrol — 48.74 t/year, emitted by Pavlodar Petrochemical Plant, manganese — 18 t/year, iron — 16.915 t/year, emitted by "KSP Steel", as well as 1.45 t/year of iron emitted by "Casting" LLP. The largest volumes of chromium (6 t/year), zinc (0.3135 t/year), and wood dust (6.741 t/year) come from the pipe rolling plant. JSC "Kaustik" (chemical plant) emits 0.175 t/year of chlorine. 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 can be seen from the table, the amount of heavy metals emitted in pure form is small, but the concentration of various elements in dust and ash far exceeds these values. According to research [3], the chemical composition of ash and dust from Pavlodar CHP is: lead — 2.86 mg/kg; cadmium — 0.23 mg/kg; mercury — 6.59 mg/kg; arsenic — 0.28 mg/kg; fluorine — 10.0 mg/kg; antimony — 0.37 mg/kg; beryllium — 0.017 mg/kg; selenium — 0.53 mg/kg; tellurium — 0.1 mg/kg.

As a result of the laboratory analysis for the concentration of heavy metals in snow sediment in Pavlodar, the results presented in Table 2 were obtained.

Among the concentration of elements of hazard class 1, there is quite a wide variability; the coefficient of variation in all cases exceeds 50 %, in all classes exceeds 30 %. Thus, it can be assumed that contamination with these substances is confined to specific objects. V, Cr, Cu have the greatest variability. The variation series is represented by the following order:

$$V_{119}>Cr_{105.13}>Cu_{87}>Cd_{82}>Zn_{72}>Pb_{64}>Mn_{54}>As_{538}>Ba_{42}> >Mo_{40}>Co_{37}>Sr_{31}>Ni_{30}.$$

The highest concentration of elements in the samples is presented in the following row

$$Ba_{1076.4}>Mn_{638.1}>Cr_{316.6}>Zn_{286.2}>Sr_{267.1}>Pb_{158.5}>V_{141.7}>Cu_{127.2}>Ni_{32.9}>As_{14}>Co_{11.8}>Mo_{2.5}>Cd_{1.67}.$$

However, other trends prevail among the classes, for example, among the elements of the first hazard class, zinc (286.2 mg/kg) and lead (158.5 mg/kg) are of greatest importance, which apparently is associated with vehicle emissions. In the second class, chromium (316.6 mg/kg) and copper (127.3 mg/kg) predominate, in the third class the leaders are barium (1056.4 mg/kg) and manganese (638.6 mg/kg).

Table 2

Statistical indicators of the concentration of chemical elements in solid snow filtrate (SSF) Pavlodar-Northern industrial zone, mg/kg

Element	Concentration range	Mean	STD	The coefficient of variation	Background concentration of metal. Data of this study/literature sources [3]	Concentration coefficient of this study/literature sources [3]
Toxicity class 1						
Zn	63–800	286.2±55.3	206.8	72.2	175/48.3	1.6/5.9
As	7–37	14±1.99	7.5	53.4	7/	2/
Cd	0.3–6.1	1.7±0.36	1.37	81.89	0.8/0.16	2/10.49
Pb	26–430	158.5±2702	101.9	64.3	42.5/23.2	3.7/6.8
Toxicity class 2						
Cr	59–1200	316.6±88.9	332.8	105.13	755/18.4	0.4/17.2
Co	7–22	11.8±1.18	4.42	37.45	7.5/7.9	1.6/1.49
Ni	15–49	32.9±2.71	10.1	30.8	20.5/21.1	1.6/1.56
Cu	35–430	127.3±29.7	111.4	87.5	70/20.5	1.8/6.2
Mo	1–4.2	2.5±0.26	0.9	39.5	1.1/0.29	2.3/8.7
Toxicity class 3						
V	70–720	141.7±45	168.6	119	64/9.8	2.2/14.5
Mn	400–1800	638.6±92.7	347.1	54.4	560/24.3	1.1/26.3
Sr	200–490	267.1±22.2	82.9	31	205/29.8	1.3/8.9
Ba	570–2200	1076.4±120.4	450.7	41.8	990/	1.08/

Note – The sample size is 15 sampling sites. Mean is the arithmetic mean of the content of heavy metals at 15 sampling sites and error

Next, the concentration coefficient was calculated relative to the background concentration of the substance. Snow samples for background indicators were collected at a distance of 40 km from the city border. Thus, the background indicators had an anthropogenic impact, but without the direct influence of urban industry. As a result, concentration coefficients are low and range from 0.4 to 3.7. The concentration coefficient series represents:

$$Pb_{3.7}>Mo_{2.3}>V_{2.2}>Cd_{2.09}>As_{2}>Cu_{1.8}>Zn_{1.6}>Ni_{1.6}>Co_{1.57}>Sr_{1.3}>Mn_{1.14}>Ba_{1.08}>Cr_{0.42}.$$

Lead, molybdenum and vanadium have the greatest difference in metal concentration in the city and in the background area; other elements gradually reduce the difference. According to these results, we can assume 2 options: first — pollution of snow cover in the city and in the northern industrial zone depends on the location of industrial enterprises, and pollutants are carried away and dispersed by the wind according to the wind rose; second — the main pollution in winter is emissions from coal combustion during heating of private houses, as well as vehicles.

To compare the data obtained in the study, data on the background concentration of heavy metals from literary sources were used [3]. Thus, in 2002-2003, similar studies were carried out in the city of Pavlodar; the background sites were located 80 km from the city in the opposite direction from the wind rose, where there were no anthropogenic sources of pollution. Comparing our concentrations with background data, the following results were obtained.

The series by concentration coefficient, constructed on the basis of literary sources of background concentrations, has the following form:

$$Mn_{26}>Cr_{17.2}>V_{14.6}>Cd_{10.5}>Sr_{8.9}>Mo_{8.71}>Pb_{6.83}>Cu_{6.2}>Zn_{5.9}>As_{2}>Ni_{1.56}>Co_{1.49}>Ba_{1.08}.$$

Thus, the magnesium concentration in the city's snow is 26 times higher than the background value. This is followed by chromium, vanadium, cadmium with indicators of more than 10 times, the lowest value is barium, the urban concentration of which exceeds the background level by only 4.9 times. Analyzing the hazard classes, it is clear that in the first class cadmium (10.49) in the urban environment is many times higher than the background one, in the second class — chromium (17.2), and in the third — manganese (26.3) and vanadium (14.5) have high concentration coefficients.

Thus, a completely different picture emerges. Manganese, chromium, vanadium, etc. have significant excesses of background concentrations. Comparing how many times the concentration in the background area with the anthropogenic impact (40 km) differs from the concentration in the background area without anthropogenic intervention (80 km), the following data were obtained. The difference in the concentration coefficient of chromium is 40 times, manganese is 23 times, i.e. these metals are a direct indicator of pollution from anthropogenic sources, industry, and vehicles. Next, in descending order, are vanadium (7 times), strontium (6.6 times), cadmium (5 times). The concentration coefficients for nickel and cobalt are practically the same in both studies, which indicates background contamination with these metals.

To determine the impact of industrial facilities on the spread of pollutants, the concentration of heavy metals in snow depending on the distance from the source of pollution (Pavlodar Petrochemical Plant). A total of 5 sites are presented, located at different distances from the Pavlodar Petrochemical Plant (Table 3).

Table 3

Characteristics of snow sampling sites

Site number	Site name	Coordinates		Altitude above sea level, m
		Latitude	Longitude	
1	North of Pavlodar Petrochemical Plant	52.3828782	76.9209185	166
2	JSC "Caustic"	52.3832968	76.9319969	122
3	"PMZ DAMAK" LLP	52.3833187	76.9534616	124
4	North of the ash dump	52.3819332	76.9806923	127
5	Northeast of the ash dump	52.3818403	76.9898166	128

Thus, a correlation analysis was carried out for all elements; the most correlated elements were selected and placed together for ease of analysis (Fig. 4).

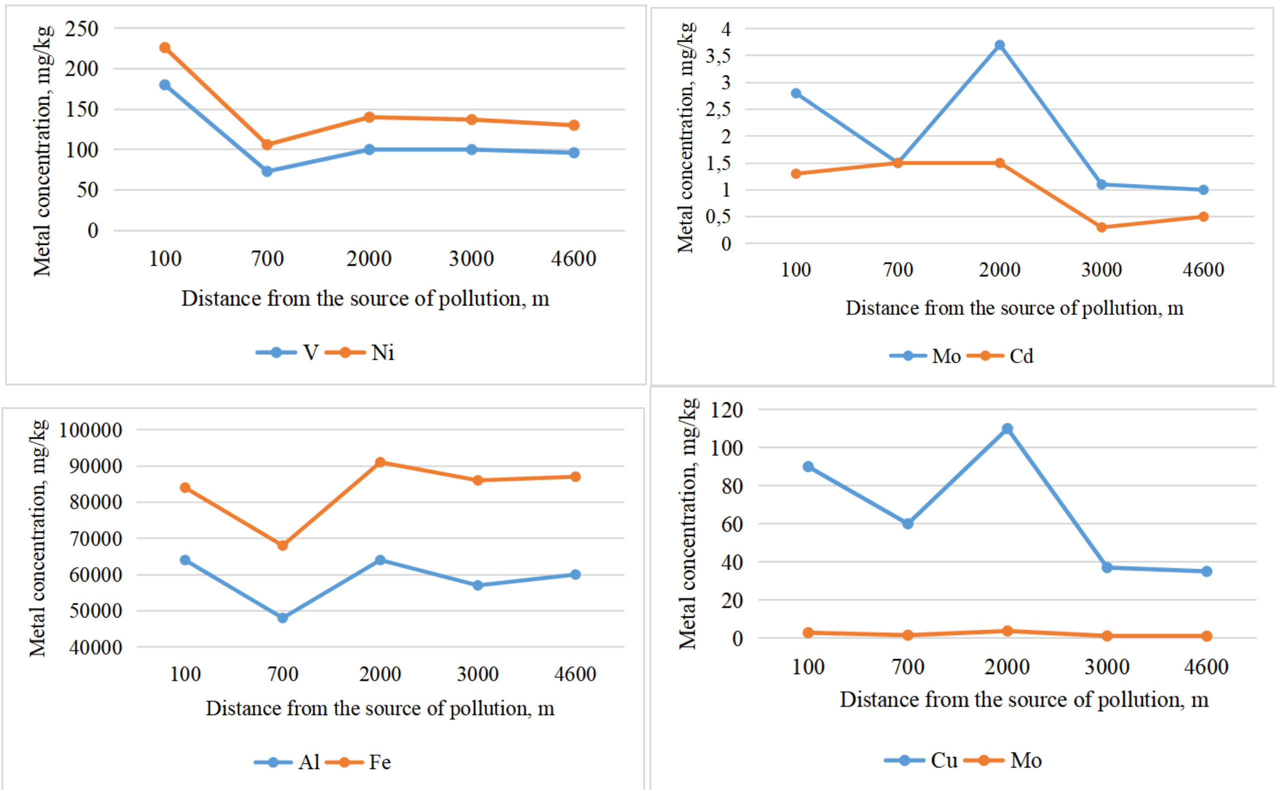


Figure 4. Concentration of heavy metals in solid snow sediment at different distances from the Pavlodar Petrochemical Plant

Substances V, Ni, Mo, Cd, Cu, Mo, Fe and Al have a similar distribution trend. All elements in the immediate vicinity of the Pavlodar oil refinery have high indicators, further, a decrease is at a distance of 700 m. Emissions of aluminum and iron, and, accordingly, their presence in solid snow sediment indicates general contamination of the northern industrial zone with these elements, i.e. the values are always at a high level. All substances have a sharp rise at a distance of 2000 m from the plant (Fig. 5). This may be due to the natural transfer and sedimentation of pollutants, but it can be assumed that this is also influenced by the overlap of the zone of influence by other industrial enterprises — JSC “Kaustik” — chemical production, LLP “Pavlodar Mechanical Plant “DAMAK”, and also this area lies in the direction of the prevailing winds from CHPP-3. With distance from sources of pollution, the concentration of elements in the snow cover also decreases. At a distance of 4500 m from the Pavlodar Petrochemical Plant, a slight increase in indicators is observed, which may also be due to the transfer and sedimentation of particles, as well as the location of the thermal power plant ash dumps to the south.

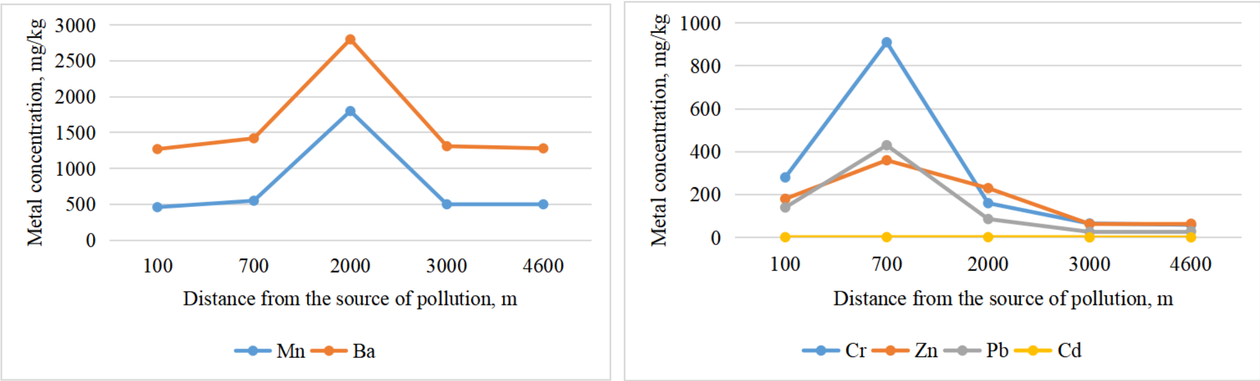


Figure 5. Concentration of heavy metals in solid snow sediment
at different distances from the Pavlodar Petrochemical Plant

The heavy metals Mn and Ba behave differently; at all sample collection points they show more or less the same value, except for the point at a distance of 2000 m, where all elements have extremely high values. The elements Cr, Zn, Pb, Cd have an increased concentration 700 m from the Pavlodar Petrochemical Plant, but in close proximity to JSC Kaustik.

Of interest is the distribution of elements in general across the sampling points presented in Figures 6, 7.

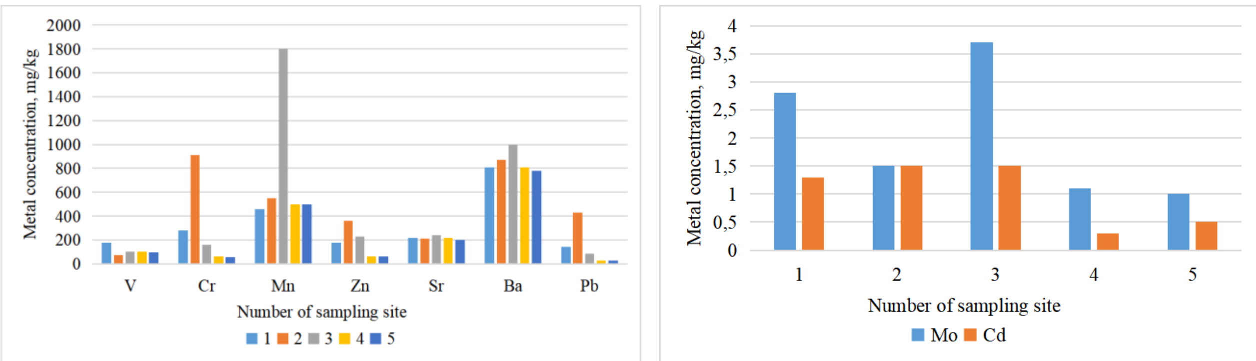


Figure 6. Concentration of heavy metals in solid snow sediment
at different distances from the Pavlodar Petrochemical Plant

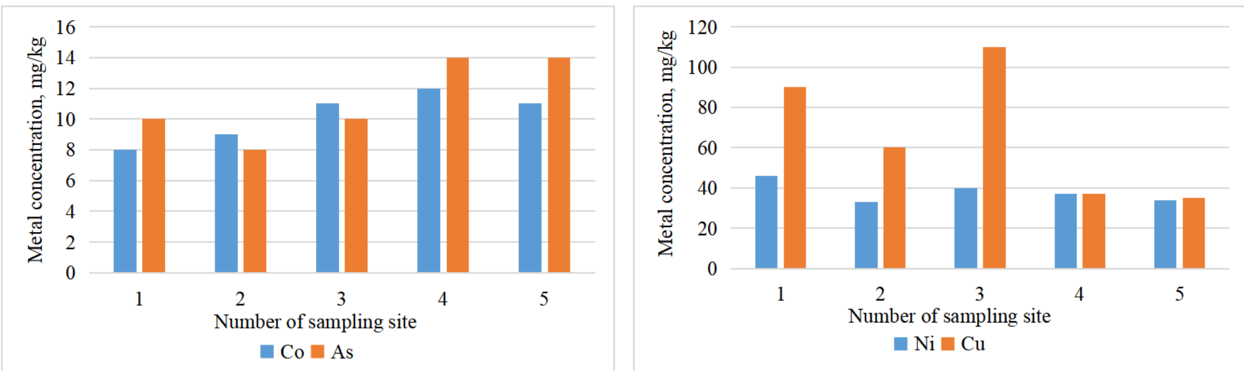


Figure 7. Concentration of heavy metals in the solid phase of snow at sampling sites
in the northern industrial zone of Pavlodar

The concentration of manganese (except for point 3), strontium, cobalt and arsenic in all areas does not differ very much. It follows from this that contamination by these substances is uniform.

The concentration of other heavy metals varies from site to site.

The highest concentration of vanadium is observed in site 6 and amounts to 720 mg/kg; in other sites the concentration varies about 100 mg/kg. An increased concentration of chromium Cr is observed in sites adjacent to the Pavlodar Petrochemical Plant, as well as JSC “Kaustik”, in other sites it varies, reaching the lowest values at sites 4 and 5, near the ash dumps at a distance of about 5 km from the sources, as well as in the northern direction from the Petrochemical Plant — in the village Pavlodarskoye (5 km).

The value of nickel is approximately uniform at all sampling sites; the lowest values are observed in the dacha sites south of the oil refinery. The maximum value of magnesium Mn concentration was found at the 5th site, the ash dump, which is anomalous and amounts to 1800 mg/kg, with average values of 400–600 mg/kg for uniformly contaminated remaining areas. Cobalt shows values from 7 to 22 mg/kg, the lowest values in industrial areas (1, 2, 6, 7, 3, 4 sites), while in sites of populated areas the cobalt concentration has the highest values. The concentration of copper also does not depend on the location of industrial facilities; dacha sites and vegetable gardens of populated areas have high values of this metal, which may be associated with pollution from vehicles. The presence of zinc in the snow cover is ubiquitous, the highest value is in remote eastern areas, while the highest value is noted in the northeast direction (the village of Pavlodarskoye), which may be due to the prevailing southern winds. Arsenic has values in the solid fraction of snow on average from 8–14 mg/kg, the highest value is 37 mg/kg in the urban area of the Lesozavod (large amount of transport, stove heating), also, in this area there is a large amount of strontium 490 mg/kg, with an average concentration of 200–250 mg/kg. Molybdenum concentration in snow cover varies significantly at each site (from 1.1 to 4.2 mg/kg), which makes it difficult to identify patterns in the distribution of this heavy metal. The highest lead concentration is confined to the industrial areas of the territory of Pavlodar Petrochemical Plant, JSC “Caustic” — 430 mg/kg, as well as settlements with large highways, on average 180–200 mg/kg, with minimum values — 26 mg/kg. Aluminum and iron are ubiquitous and have high values; the village of Zhanaul, located in the south-west direction, at a distance of 3000 m from the Pavlodar Petrochemical Plant, has the lowest values of these metals.

Figure 8 presents the results of a study of the concentration of heavy metals in the snow cover of the city of Pavlodar in a cartographic representation. Here are the elements that have the most pronounced association with industrial facilities.

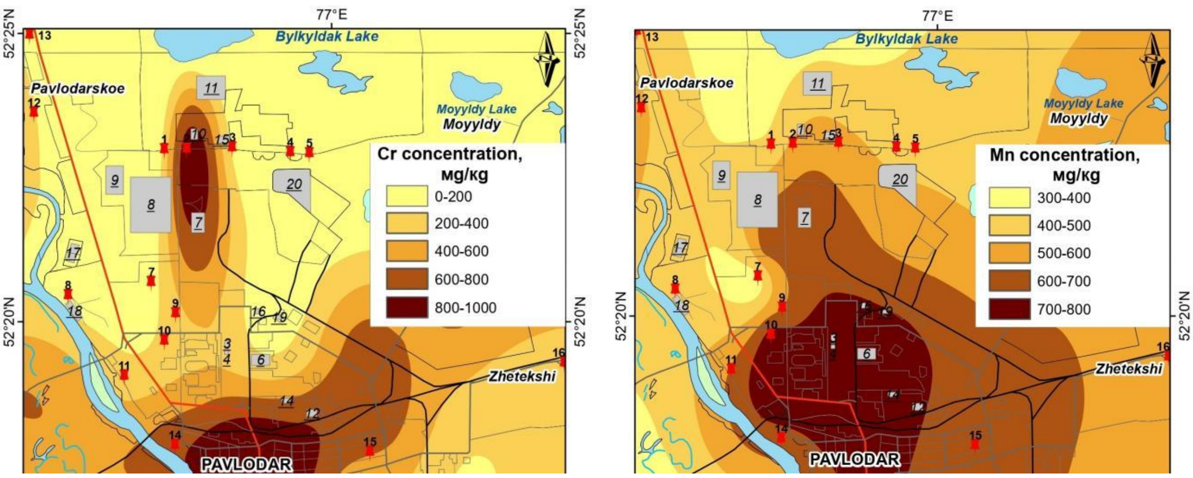


Figure 8. Map of the concentration of heavy metals in the solid phase of snow in Pavlodar

The increased chromium concentration is clearly visible in the southern direction from the factories, along the transport road. Chromium contamination is observed everywhere despite the location of dacha sites, in contrast to lead and zinc, the contamination of which is also linear in nature, but with low concentrations in dachas. Manganese pollution is confined to the city center and the concentration of harmful substances decreases towards the north.

There are no separate maximum permissible concentrations for snow cover. However, its contamination needs to be analyzed according to contamination standards. 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 (MPC) of heavy metals in the soil. For lead and arsenic, MPCs were used in accordance with the Kazakhstan standard; for other metals, data from literary sources or Russian State Standard were used [28] (Table 4).

Table 4

Exceeding the maximum permissible concentration (MPC) values of soils by the average values of the concentration of heavy metals in solid snow sediment in the Northern industrial zone

Metal	Metal concentration in solid snow sediment	The maximum permissible concentration of heavy metals in soil	Exceeding the MPC value
Pb	6.83	32	4.95
As	14	2.0	7
V	141.7	150 [28]	0.94
Cr	316.57	100 [3]	3.16
Mn	638.57	700 [28]	0.91
Co	11.82	5 [28]	2.36
Ni	32.92	20 [28]	1.64
Cu	127.28	33 [28]	3.85
Zn	286.21	55 [28]	5.20
Sr	267.14	10 [3]	26.71
Mo	2.52	5 [3]	0.5
Cd	1.67	0.5 [28]	3.35

According to the Table 4, the greatest excess of MPC relates to strontium — 26 times, arsenic — 7 times, zinc — 5 times, lead — 5 times. The concentration of other metals also exceeds the soil MPC value, except for molybdenum, vanadium and manganese, which do not exceed the maximum permissible soil concentration. Thus, we can conclude that the concentrations of heavy metals in the soil are high and their levels are many times higher, because the depositing medium retains solid sediment every year. Some of the heavy metals are washed out with precipitation during melting and rain, some are absorbed by the soil and penetrate into deeper layers, and some of the metals are concentrated in plants, which poses a threat especially in summer cottages where the population grows plant products. The study of the migration of heavy metals in these environments is the subject of further study within the framework of this study.

To determine the total pollution of the Northern industrial zone of Pavlodar, pollution coefficients for each element were calculated in accordance with the background data of this study and literature sources [3]. As a result, the total pollution of this study was 10.9, which corresponds to a low level of pollution, but some authors attribute values from 16–24 to the general urban pollution level. However, such a low index of the total industrial area may indicate high values of the background concentration of heavy metals, i.e. the area for collecting background samples was influenced by anthropogenic factors. In calculations used in literature sources (without anthropogenic intervention), the coefficient of total snow cover pollution was101.28, which corresponds to an average moderately hazardous level of pollution (Zc 64–128). Also in published studies [29] there is data on the total pollution of the eastern industrial zone of Pavlodar. The eastern industrial region is characterized by the metallurgical industry: Aluminum of Kazakhstan JSC, Kazakhstan Electrolysis Plant JSC. Zc is 18.2, which is higher than the value of the northern industrial zone, but also relates to the general urban pollution level. Also, Zc calculated from literature studies exceeds that of the northern industrial zone and is 127.7.

Conclusion

Thus, we can conclude that the pollution of the snow cover of the northern industrial zone occurs due to emissions into the atmospheric air from industrial enterprises, as well as widespread pollution from motor vehicles. There is an excess of the maximum permissible concentration in the soil of the snow filtrate, because when the snow melts, all the sediment will end up in the soil; accordingly, it will deposit heavy metals and large concentrations in the soil are predicted.

The concentration of chromium and lead, according to interpolation from data from research points, corresponds to the location of petrochemical production plants at a distance of dispersion and sedimentation. Large concentrations of manganese are confined to ferrous and non-ferrous metallurgy; steelmaking and ferroalloy production make a special contribution.

The magnesium concentration in the city's snow is 26 times higher than the background (natural) indicator. This is followed by chromium, vanadium, cadmium with indicators of more than 10 times, the lowest value is barium, the urban concentration of which exceeds the background level by only 4.9 times.

All heavy metals show a tendency to decrease their concentration in snow at a distance of up to 2000 m, then an increase in concentration is observed, which may be due to the deposition of polluting particles, or cross-contamination with other industrial enterprises.

From the presented data the following conclusions can be drawn:

Manganese, chromium, vanadium, strontium, cadmium and arsenic are direct indicators of anthropogenic impacts associated with industry and motor vehicles.

Distance from the source of pollution affects the concentration of heavy metals in snow. Proximity to industrial facilities leads to increased concentration of many metals and a further decrease in concentration at a distance of 2 km.

Some metals, such as nickel, cobalt, copper, aluminum and iron, have a uniform distribution and are not dependent on a specific source of contamination.

Significant variations in metal concentration at different sites indicate the influence of various factors such as wind directions, precipitation and the presence of other industrial plants.

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.

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Павлодар қаласында қар жамылғысының ауыр металдармен ластануы

Қар жамылғысындағы ауыр металдардың құрамын зерттеу Павлодар қаласындағы Павлодар мұнай-химия зауытының (ПМХЗ) және басқа да өнеркәсіптік объектілердің әсер ету аумағында жүргізілді. Марганец, хром, ванадий және басқа металдардың фондық концентрациясының айтарлықтай асып кетуі анықталды. Қар жамылғысындағы металдардың таралуы элементтердің мұнай өңдеу зауытының жанында жоғары мәндерге ие екендігін және 700 м қашықтықта төмендейтіндігін көрсетті. Басқа өнеркәсіптік кәсіпорындардың ықтимал әсері және ЖЭО–3-тен желдің бағыты да анықталды. «Каустик» АҚ маңында марганец пен барий тұрақты мөлшерді көрсетті, ал хром, мырыш, қорғасын және кадмий жоғары мөлшерге ие болды. Марганец, стронций, кобальт және мышьяктың жалпы мөлшері барлық жерлерде біркелкі ластануын көрсетеді. Қорғасынның ең үлкен мөлшері өнеркәсіптік аудандарда және автомобиль жолдары бар елдімекендерде кездеседі. Алюминий мен темір кеңінен таралған, ең төменгі мөлшері Мұнай-химия зауытынан 3 км қашықтықта орналасқан Жаңааулы ауылында кездесті. Зерттеу нәтижелері қоршаған ортаның ауыр металдармен ластануын бақылау мен бақылаудың маңыздылығын және қоршаған ортаға антропогендік әсерді азайту үшін шаралар қабылдау қажеттілігін көрсетеді.

Кілт сөздер: ауыр металдар, өндірістік аймақ, қар жамылғысы, жалпы ластану, шашырау, тұндыру.

А.А. Фаурат, Г.С. Ажаев, Ш.К. Какежанова, М.Т. Досова

Загрязнение снежного покрова тяжелыми металлами в г. Павлодаре

Исследование содержания тяжелых металлов в снежном покрове проводилось в г. Павлодаре на территории влияния Павлодарского нефтехимического завода (ПНХЗ) и других промышленных объектов. Были выявлены значительные превышения фоновых концентраций марганца, хрома, ванадия и других металлов. Распределение металлов в снежном покрове показало, что элементы имеют высокие значения вблизи нефтеперерабатывающего завода и снижаются на расстоянии от 700 м. Возможное влияние других промышленных предприятий и направление ветров от ТЭЦ–3 также отмечены. Марганец и барий демонстрируют более стабильные значения, а хром, цинк, свинец и кадмий имеют повышенное содержание вблизи АО «Каустик». Общее содержание марганца, стронция, кобальта и мышьяка варьирует незначительно на всех участках, указывая на равномерное загрязнение этими веществами. Свинец имеет наибольшее содержание на промышленных участках и в населенных пунктах с автострадами. Алюминий и железо распространены повсеместно, с наименьшими значениями в поселке Жанаул на расстоянии 3 км от ПНХЗ. Результаты исследования подчеркивают важность контроля и мониторинга загрязнения окружающей среды тяжелыми металлами и необходимость принятия мер по сокращению антропогенного воздействия на окружающую природную среду.

Ключевые слова: тяжелые металлы, промышленная зона, снежный покров, суммарное загрязнение, рассеивание, осаждение.

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