



Pollution, Ecological and Health Risk Assessment of Heavy Metals in Urban Soils of Industrial City in the North-East of Kazakhstan

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ABSTRACT

The contamination of urban soils with heavy metals poses a threat to both the ecosystem and human health. Despite its relatively small population, Pavlodar serves as the industrial center of Kazakhstan, yet its soil pollution is comparable to that of major industrial cities worldwide. This study examines the problem of soil contamination in the city of Pavlodar with heavy metals and its potential impact on the environment and human health. The study used a variety of indices, including pollution indices, ecological risk assessments and potential health risk assessments. This study considered the territorial patterns of the distribution of microelements in the soil. The results revealed that the highest concentrations of most metals were found in the central part of the city, whereas the northern industrial zone was the least polluted. The pollution indices generally indicate low levels of soil pollution, but increased level was observed in the city center. A high carcinogenic risk for children associated with the chromium content in soils has been observed. In general, this article emphasizes the need to control and monitor the level of soil pollution in the city of Pavlodar to protect the environment and ensure public health.

Keywords: Heavy metals; Urban soil; Pollution indices; Risk assessment

Article History

Article # 24-748

Received: 07-Aug-24

Revised: 09-Oct-24

Accepted: 16-Oct-24

Online First: 01-Nov-24

INTRODUCTION

Urban soil pollution is a serious environmental problem due to the accumulation of various pollutants from industrial activities, transport emissions and other sources. Urban soil pollution is exacerbated by various factors, including low water and nutrient contents, inadequate soil structure, and the accumulation of industrial and household waste (Ma et al., 2020). Research findings indicate a rising trend in urban soil contamination by trace elements, toxic metals, and polycyclic aromatic hydrocarbons (PAHs) (Ma et al., 2020; She et al., 2022; Sidikjan et al., 2022). Heavy metal pollution is also a common problem in urban soils, with pollutants such as lead (Pb), cadmium (Cd), and nickel (Ni) (Luo & Lu, 2020; Wang et al., 2022) and lead being remains a significant problem. Urbanization increases the spread of pollutants such as black carbon (BC) in urban soils, which contain

heavy metals. At the same time, there is a significant correlation between BC and heavy metal pollution indices (Li et al., 2018).

Pollution indices serve as valuable tools in assessing soil contamination levels. Single indices such as the pollution factor (PI), enrichment factor (EF), geoaccumulation index (Igeo), and contamination factor (CF) offer comprehensive assessments of the extent of soil contamination (Kowalska et al., 2018, 2022). They help identify sources of pollution, especially from anthropogenic activities in urban and industrial areas. In addition, pollution indices have been found to be effective in assessing heavy metal contamination in soils compared to simply analyzing total metal concentrations (Weissmannová et al., 2019). The complex pollution indices such as pollution load (PLI), Nemerov pollution index and others are used to assess multi-element pollution in urban soils (Weissmannová et al., 2019). The use of pollution

Cite this Article as: Faurat A, Azhayev G, Satybaldiyeva G, Kaliyeva A, Utarbayeva A, Akhmetov K and Bekpergenova Z, 2024. Pollution, ecological and health risk assessment of heavy metals in urban soils of industrial city in the North-East of Kazakhstan. International Journal of Agriculture and Biosciences 13(4): 820-835. <https://doi.org/10.47278/journal.ijab/2024.183>



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indices is considered a comprehensive method for assessing soil pollution, providing insight into the accumulation and origin of potentially toxic elements under different environmental conditions (Mazurek et al., 2019). These indices play an important role in assessing soil quality and determining the characteristics of heavy metals in various land uses (Liu et al., 2021).

The Potential Environmental Risk Index (PERI) is widely used to assess the impact of heavy metal pollution on soil quality and ecosystem health (Liu et al., 2019; Zhao et al., 2022a). Researches have shown that ERI considers toxic and cumulative heavy metal exposure, offering a comprehensive assessment of soil contamination (Liu et al., 2019; Zhao et al., 2022b). This index is applied in various regions, including agricultural, industrial, and urban environments (Miao et al., 2021; Zhang et al., 2020), aiding in quantifying environmental risks and informing remediation strategies (Miao et al., 2021; Zhang et al., 2020). Moreover, PERI is often combined with other pollution indices for a comprehensive assessment of soil pollution levels and potential risks (Miao et al., 2021).

Urban soil pollution poses a threat to human health. Health risk indices are important tools for assessing potential risks associated with soil contamination with heavy metals and other pollutants. These indices provide valuable information about the impact of soil pollution on human health and the environment. Various studies have used health risk indices to assess the health risks associated with soil pollution (Adediji et al., 2019; Rinklebe et al., 2019; Tong et al., 2020). Despite extensive research conducted on soil contamination in Pavlodar (Azhayev et al., 2020; Faurat et al., 2023), comprehensive soil pollution indices, environmental and health risk assessments have not been previously undertaken in this major industrial northeastern Kazakhstan city, with a population of 533.4 thousand people (Kismelyeva et al., 2021; Kakabayev et al., 2023). Since the city has two large industrial zones with a petrochemical plant, aluminum production, chemical, metallurgical, and energy production, it is of interest to identify patterns of heavy metal pollution in various areas of the city. Thus, within the framework of our study, the following objectives were established: determining the general concentrations and statistics of heavy metal pollution in the city's soils, as well as in various zones (1); the use of single and complex indices to assess soil pollution, as well as determine potential environmental risk (2); calculation of carcinogenic and non-carcinogenic health risk indices to assess the potential impact of heavy metals on human health. The goal of this study was to examine soil contamination of the city of Pavlodar with heavy metals and its potential impact on the environment and human health.

MATERIALS & METHODS

Study Area and Sample Collection

As one of the major industrial hubs in the country, Pavlodar plays a crucial role in Kazakhstan's economy, with a strong emphasis on heavy industries such as metallurgy, energy production, and machinery manufacturing (Kassenova et al., 2024; Sergeeva et al., 2024). The total

area is 326,882 hectares (0.3 thousand km²). The largest industrial enterprises include aluminum, chemical, petrochemical, metallurgical plants and others. In addition, in the city there are 3 thermal power plants, more than 20 boiler houses and 5,751 private housing construction units, collectively consuming over 3.5 million tons of coal annually. The city is home to over 60,300 garden plots and numerous vegetable gardens managed by private households. These gardens play an important role in the local food economy and community life, offering residents access to fresh produce and a connection to traditional agricultural practices.

Geographically, Pavlodar is situated on the first accumulative floodplain terrace of the Irtysh River (Akhazhanov et al., 2023). This terrace gradually transitions into a lacustrine-eluvial denudation plain towards the eastern part of the city. The soils in this area are predominantly classified as chestnut soils, which are typical of the dry steppe zone. These soils are characterized by a light loamy mechanical composition, with a humus layer (comprising the A+B horizon) that typically measures 40-50cm in thickness. The humus content of these soils' ranges from 3.5 to 4.0%, indicating moderate fertility. However, these chestnut soils are often associated with solonchaks, indicating the presence of saline properties, which can affect soil productivity and crop yields.

In 2023, a comprehensive soil sampling program was conducted across various areas of Pavlodar, including its industrial zones, to assess soil quality and potential contamination. The sampling was carried out according to standard methodological recommendations, ensuring the collection of representative data. Within the city, soil samples were collected from areas influenced by large industrial enterprises and heat supply facilities, which are known to impact local soil conditions. Additionally, samples were taken from gardens located within the city, as well as from dachas (city gardens) situated on the outskirts of Pavlodar.

The soil sampling process involved collecting samples from a depth of 0-15cm, which is the typical rooting depth for most garden crops and an important zone for assessing soil health. In total, 32 soil samples were collected and subsequently analyzed to determine the levels of various pollutants and to assess the overall soil quality. For comparison, background soil samples were also taken from locations more than 50km away from the city, in a direction opposite to the prevailing wind patterns, to establish baseline soil conditions unaffected by urban and industrial activities.

These soil studies are crucial for understanding the impact of industrial activities on local agriculture and for guiding future land use and environmental protection efforts in Pavlodar. The data collected provides valuable insights into the extent of soil contamination and helps in formulating strategies to mitigate any adverse effects on the city's gardening and agricultural practices.

Laboratory Analysis

Laboratory analyses were conducted at the laboratory of the Institute of Radiation Safety and Ecology, a branch

of the National Nuclear Center of the Republic of Kazakhstan, which operates under the Ministry of Energy of the Republic of Kazakhstan. The soil samples were analyzed for chemical element content using mass spectrometry with inductively coupled plasma (ICP-MS) on an Agilent 7700 X ICP-MS system. The procedure followed the guidelines outlined in 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 and Mass Spectral Methods with Inductively Coupled Plasma," KZ.07.00.03351-2016, as established by the Kazakhstan Institute of Standardization and Metrology. The analysis covered 27 elements, including Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Sr, Mo, Cd, Cs, Ba, La, Ce, Nd, Eu, Gd, Dy, Lu, Ho, Pb, and U. 12 metals and metalloids, known for their high toxicity and significant contribution to soil contamination in the city, were selected for analysis in our study: Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Pb.

Pollution Assessment

The assessment of soil contamination by heavy metals involves the use of various indices, which can be broadly categorized into individual and complex indices. Individual indices are essential tools that provide a focused evaluation of soil contamination by specific heavy metals. These indices enable researchers to assess the level of pollution associated with each metal independently, offering a detailed understanding of how individual contaminants impact soil quality. Among the commonly used individual indices are the Pollution Index (PI), CF, Igeo, EF, and the Potential Impact Index (PImpc). Each of these indices offers a unique perspective on the presence and concentration of heavy metals in the soil, allowing for a more granular analysis of environmental risks associated with specific contaminants.

In contrast, complex indices provide a more holistic approach to assessing soil contamination by heavy metals. These indices are designed to evaluate the cumulative impact of multiple heavy metals present in the soil, thereby offering a comprehensive picture of overall soil pollution. The calculation of complex indices often involves the aggregation of total concentrations of all analyzed heavy metals, which allows for a broader understanding of the contamination level. In some cases, complex indices also incorporate individual values from calculated indicators, thereby blending the detailed insights from individual indices into a more integrated assessment. Key complex indices include the Sum of Pollution Indices (P_{sum}), Pollution Load Index (PLI), Nemerow Pollution Index (P_{Nemerov}), and the Risk Index (RI), as discussed in studies like Kowalska et al., (2018).

These indices, whether individual or complex, are crucial for determining the extent of heavy metal pollution in soils. They help in identifying areas at risk, guiding remediation efforts, and informing environmental policies aimed at reducing soil contamination and protecting public health. Health risk assessment: HI, CR (Weissmannová et al., 2019).

The Single Pollution Index

The single PI is frequently employed to determine which heavy metal poses the greatest threat to the soil environment. This index is also essential for calculating certain complex indices, including the PI Nemerow and the PLI.

PI

$$PI = C_n / B_g \quad (1)$$

where C_n is the content of heavy metals in the soil, B_g is the content of heavy metals in background samples.

The CF

In our study, we calculated the CF, a key metric that expresses the ratio of the average concentration of a specific metal in the soil (denoted as C_n) to its pre-industrial concentration (referred to as B_g). This calculation is crucial for understanding the extent of metal pollution in soils, and we used the concentration of elements in the earth's crust as a baseline reference value, following a methodology similar to that outlined by Loska et al. (2004). This approach allows for a clear comparison between current metal levels and their natural, pre-industrial baselines, providing insight into the degree of contamination.

Additionally, we employed the Igeo, which is a widely used tool for assessing the degree of heavy metal contamination in soils. The Igeo index evaluates soil contamination based on the concentration of heavy metals in the A or O soil horizons, which are layers closely associated with a specific geochemical background. The index is calculated using the formula:

$$I_{geo} = \log_2 C_n * 1.5 B_g \quad (2)$$

where C_n represents the concentration of a particular heavy metal in the soil, B_g is the geochemical background value, and 1.5 is a constant introduced to account for natural variations in metal concentrations due to processes such as weathering or soil formation. This index provides a logarithmic scale to assess the contamination level, with higher Igeo values indicating more significant pollution.

Another important index used in our study is the EF. The EF is designed to measure the potential impact of human activities on the concentration of heavy metals in soils. This factor compares the concentration of a heavy metal in the soil sample to its natural background level, while also normalizing for variations using iron (Fe) as a reference element. The EF is calculated as:

$$EF = (C_{n_{sample}} / Fe_{sample}) / (C_{n_{background}} / Fe_{background}) \quad (3)$$

where C_{n sample} is the concentration of the metal under study, C_{n background}-B_g from Table 1, Fe is the concentration of iron used in this study as a reference

Complex Pollution Indexes

The Pollution Sum (P_{sum}) is an aggregate measure that accounts for the presence of multiple heavy metals

in the soil. It is calculated by summing the individual PI values for each selected heavy metal. This index provides a straightforward way to assess the overall level of contamination by combining the contributions of various pollutants into a single value. The formula for PI_{sum} is:

$$PI_{sum} = \sum PI \quad (4)$$

Here, PI represents the calculated values of the single pollution index for each heavy metal, and n denotes the total number of heavy metals analyzed in the study. Another important tool used for evaluating soil contamination is the Soil Pollution Index (PLI). This index offers a comprehensive assessment of soil pollution by considering the cumulative impact of all analyzed heavy metals. PLI is particularly useful because it provides a simple method to confirm the extent of soil degradation due to heavy metal accumulation. The PLI is calculated as the geometric mean of the PI values for all heavy metals, using the formula:

$$PLI = \sqrt[n]{PI_1 * PI_2 * PI_3 * \dots * PI_n} \quad (5)$$

In this formula, n is the number of heavy metals analyzed, and PI represents the calculated values of the single pollution index for each metal. The PLI provides a more balanced view by considering the collective influence of all pollutants, rather than just focusing on the most or least contaminated.

The PI Nemerow is another comprehensive tool that assesses overall soil contamination. This index integrates the content of all analyzed heavy metals and is designed to provide a more nuanced understanding of the contamination level by combining both the average and the maximum pollution index values. The formula for PI Nemerow is:

$$PI_{nemerov} = \sqrt{\left(\frac{1}{n} \sum PI\right)^2 + PI_{max}^2} / n \quad (6)$$

In this equation, PI represents the calculated single pollution index for each heavy metal, measuring contamination relative to a baseline level. PI_{max} is the highest value of this index among all metals analyzed, indicating the most severely polluted metal. The variable n denotes the total number of heavy metals studied, ensuring a comprehensive assessment and normalizing the overall pollution index to evaluate the combined contamination from all metals. This index helps identify the overall pollution severity by considering both the general contamination level and the presence of any particularly hazardous metals.

Lastly, the Potential Ecological RI is used to evaluate the potential environmental risk posed by heavy metal concentrations in the soil. This index assesses the risk level by considering both the toxicity of the metals and their pollution levels. RI is calculated using the formula:

$$RI = \sum E_i^r \quad (7)$$

where n is the number of heavy metals and E_i^r is a single index of environmental risk factor, calculated according to the equation:

$$E_i^r = T_i^r * PI \quad (8)$$

where T_i^r is the toxic response factor of a particular metal, reflecting its toxicity, and PI is the calculated value of the single pollution index. The RI provides an integrated measure of both the level of contamination and the potential ecological impact, helping to prioritize areas for remediation based on their environmental risk.

Human Health Risk Assessment

Health risk assessment indices are widely used to quantify human exposure to chemical elements, including both carcinogenic and non-carcinogenic risks through three exposure routes: inhalation, dermal absorption, and ingestion.

In this study, we employ an exposure model grounded in the methodology developed by the US Environmental Protection Agency, as outlined in Weissmannová et al. (2019). The model is used to calculate the average daily doses (ADD) of potentially toxic metals in both adults and children through three different exposure pathways: ingestion, inhalation, and dermal contact. The formulas for these calculations are as follows:

$$ADD_{ing} = C * R * CF * EF * ED / BW * AT \quad (9)$$

$$ADD_{inh} = C * EF * ED * ET / PEF * BW * AT \quad (10)$$

$$ADD_{derm} = C * SA * CF * SL * ABS * EF * ED / BW * AT \quad (11)$$

where C is the concentration in soil (mg/kg), R — rate of entry into the body (100 mg/day (adults), 200mg/day (children)), CF — 10^{-6} , EF — frequency of exposure (350 days/year), ED — duration of exposure (24 years (adults), 6 years (children)), AT — duration of exposure (24 hours/day), BW — body weight of the exposed individual (70kg (adult), 15kg (children)), AT - averaging time (days), $365 \times ED$ adult/children, ET is the exposure duration (24h/d), SA — open skin area (5700cm²); SL — adhesion coefficient: 0.07mg/cm², ABS - skin absorption fraction: 0.03 (As), 0.001 (other metals), PEF - particle emission coefficient: 1.36×10^9 m³/kg⁻¹.

The Hazard Index (HI) is a key metric used to assess the overall potential non-carcinogenic risk from exposure to multiple toxic metals. By aggregating the risks from various heavy metals, the HI provides a comprehensive evaluation of their combined health effects. This index is particularly valuable in environmental studies where individuals are exposed to multiple contaminants simultaneously.

In this study, nine heavy metals—chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd), and lead (Pb)—were analyzed for their potential non-carcinogenic effects. The HI is calculated by comparing the average daily dose

(ADD) of each metal to its reference dose (RfD). The HI is calculated using the following equations:

$$HI = \sum HQ_i \quad (12)$$

$$HQ_i = \sum ADD_i / RfD_i \quad (13)$$

where RfD (mg /kg⁻¹ /day⁻¹) is the reference dose for each heavy metal.

If the HI value is less than 1, it suggests that non-carcinogenic effects are unlikely. However, if the HI exceeds 1, there is a potential risk for adverse health effects, with the likelihood increasing as the HI value rises.

For metals such as arsenic (As), nickel (Ni), and chromium (Cr), which are classified as carcinogenic, the carcinogenic risk (CR) is calculated as:

$$CR = \sum ADD_i * SF_i \quad (14)$$

SF (mg/kg⁻¹ / day⁻¹) -1 - probability of carcinogenic risk for toxic metals. If CR < 10⁻⁶, the carcinogenic risk is considered negligible; if CR > 10⁻⁴, there is a high risk of developing cancer in a person; and when 10⁻⁶ < CR < 10⁻⁴, there is an acceptable risk to humans (Lu et al., 2014).

Statistical Analysis

A statistical analysis of heavy metal concentrations in soil samples was conducted using Microsoft Excel. Key measures such as mean, minimum, maximum values, standard deviations, and coefficients of variation were calculated for each metal. These metrics provided insights into the data's central tendency, spread, and variability, helping to identify patterns and anomalies in heavy metal distribution across the city. (Microsoft Inc., Redmond, Washington, USA).

Cartographic Representation

The cartographic material presented herein was generated through interpolation using the Arc Toolbox tools of the ArcGIS 10.1 software. Interpolation tools utilize values measured at control sites to create a continuous (or predicted) surface of values for all locations in the output raster dataset, regardless of whether a measurement was taken at that site or not. For this study, the Spline tool was selected, which interpolates the raster surface based on site values using a 2D curvature-minimizing spline method. The resulting smooth surface directly passes through the input sites.

RESULTS

Heavy Metal Concentrations in Urban Soils of Pavlodar

Statistical characteristics of the content of heavy metals in the soils of Pavlodar are presented in Table 1. The series for the average content of elements in the city total has the following values: Al (41531.3) > Mn (21837.5) > Fe (19875) > Zn (202.6) > Cr (130.6) > V (55.3) > Cu (26.1) > Ni (22.8) > Pb (20.3) > As (8.5) > Co (7.3) > Cd (0.2). The metals with the highest concentrations in the city are aluminum, manganese and iron, their content is very high and exceeds 20,000mg/kg. Next comes zinc, the content range of which is very large from 72 to 1150mg/kg. Chromium ranks as the 5th most prevalent contaminant, with concentrations in the city's overall soils and northern industrial zone measuring 130.6mg/kg. In the eastern industrial zone, levels are slightly lower at 125mg/kg, while the city center reveals the highest concentration, reaching 140mg/kg. The series for the average content of elements in the northern industrial zone has the form: Al (41428.6) > Mn (21607.1) > Fe (19285.7) > Zn (140.21) > Cr (130.6) > V (55.2) > Ni (22.6)

Table 1: Statistical data of the content of chemical elements in the soil of Pavlodar, mg/kg

Total	Statistics	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
	Min	31000.00	45.00	85.00	19000.00	17000.00	3.00	13.00	14.00	72.00	0.40	0.09	6.00
	Max	51000.00	73.00	210.00	26000.00	24000.00	14.00	35.00	130.00	1150.00	19.00	0.50	72.00
	Mean	41531.25	55.31	130.63	21837.50	19875.00	7.25	22.84	26.13	202.63	8.47	0.22	20.25
	SD	4142.50	5.98	29.04	1978.07	2028.03	1.76	4.36	22.23	200.87	5.13	0.11	14.25
	Variation (%)	10	11	22	9	10	24	19	85	99	61	50	70
North	Min	38000.00	49.00	85.00	19000.00	17000.00	3.00	13.00	15.00	72.00	0.40	0.09	7.00
	Max	51000.00	60.00	195.00	25000.00	22000.00	14.00	33.00	61.00	300.00	19.00	0.28	22.00
	Mean	41428.57	55.21	130.57	21607.14	19285.71	7.50	22.57	20.93	140.21	8.01	0.16	13.79
	SD	3344.67	4.53	28.20	1820.59	1683.79	2.47	5.08	11.83	69.67	5.37	0.06	4.00
	Variation (%)	8	8	22	8	9	33	23	57	50	67	37	29
East	Min	36000.00	45.00	85.00	20000.00	17000.00	3.00	13.00	14.00	74.00	0.50	0.09	6.00
	Max	50000.00	73.00	170.00	26000.00	24000.00	9.00	35.00	65.00	1150.00	17.00	0.50	39.00
	Mean	43083.33	57.00	125.00	22166.67	20666.67	7.00	22.50	23.67	233.00	8.54	0.24	19.42
	SD	4231.02	7.27	24.68	2037.53	2015.09	1.48	5.35	13.49	293.51	4.96	0.12	9.76
	Variation (%)	9.8	12.8	19.7	9.2	9.8	21.1	23.8	57.0	126.0	58.0	51.0	50.2
City center	Min	31000.00	45.00	85.00	20000.00	17000.00	3.00	13.00	16.00	140.00	3.40	0.11	19.00
	Max	43000.00	61.00	210.00	25000.00	23000.00	8.00	25.00	130.00	560.00	17.00	0.46	72.00
	Mean	38571.43	51.00	140.00	22328.57	20000.00	6.14	21.00	38.86	261.43	10.30	0.29	37.14
	SD	3952.09	5.80	45.55	2165.42	2581.99	1.68	4.16	40.92	157.74	5.58	0.13	19.57
	Variation (%)	10	11	33	10	13	27	20	105	60	54	45	53
	Background (Bg)	42000	53.5	36.9	20000	18500	6.5	22.5	19	42.4	12	0.19	13
	BG	80500.00	90.00	83.00	1000.00	46500.00	18.00	58.00	47.00	83.00	1.70	13.00	16.00
	MPC	-	150.00	100.00	700.00	-	5.00	20.00	33.00	55.00	2.00	0.50	32.00

*-: no relevant data; Min: minimum; Max: maximum; SD: standard deviation; Bg: concentration of heavy metal (n); BG: geochemical background; BG -Clark in the earth's crust; MPC: maximum permissible concentration (in Kazakhstan (Ministry of Health of the Republic of Kazakhstan, 2021), Russian GOST (Chief State Sanitary Doctor of the Russian Federation, 2006).

> Cu (20.9) > Pb (13.8) > As (8) > Co (7.5) > Cd (0.2). Vanadium values did not differ much depending on the city zones and ranged from 45 to 73mg/kg. An increased copper content is observed in the city center with a value of 38.9mg/kg, but in the northern industrial zone Cu (20.9mg/kg) is inferior to nickel (22.6mg/kg). A series of average contents of elements in the city center, in the residential area: Al (38571.4) > Mn (22328.6) > Fe (20000) > Zn (261.4) > Cr (140) > V (51) > Cu (38.9) > Pb (37.1) > Ni (21) > As (10.3) > Co (6.1) > Cd (0.3). The highest lead content is observed in the soils of the city center and amounts to 37.1mg/kg, which is 2.7 times higher than its content in the north and almost 2 times in the east in industrial zones. Series by average content of elements in the eastern industrial zone: Al (43083.3) > Mn (22166.7) > Fe (20666.7) > Zn (233) > Cr (125) > V (57) > Cu (23.7) > Ni (22.5) > Pb (19.4) > As (8.5) > Co (7) > Cd (0.2). A slight difference in metal concentrations, depending on the zone, is noted for arsenic, cobalt and cadmium; in the city their values are 8.5; 7.3; 0.2mg/kg, respectively.

Analyzing the concentrations of heavy metals in soils across different areas of the city reveals several key insights. The central part of the city exhibits the highest levels of several metals, including zinc, chromium, copper, lead, and arsenic. This elevated concentration is largely attributed to pollution from vehicle exhaust emissions and the use of stove heating in these areas. These sources contribute significantly to the accumulation of heavy metals in the soil, highlighting the impact of urban activities on environmental quality. In the eastern industrial zone, aluminum predominates in the soil, primarily due to the presence of the aluminum smelter, while a high concentration of vanadium (57mg/kg) is also detected in this area. Based on the average content of the studied elements in the soil, the northern industrial zone is the most unpolluted, with the lowest concentrations of heavy metals.

Spatial Distributions of Trace Elements in Pavlodar

Based on the average concentrations of heavy metals in the soils of the city of Pavlodar, the following maps were obtained, based on data extrapolation (Fig. 1, 2). Some studies note that interpolation methods are associated with inaccuracy, and results obtained from specific data should be regarded as probable approximations rather than absolute values.

As a result of the analysis carried out to calculate the excess of maximum permissible concentrations, it was revealed that heavy metals that have high values include manganese, strontium, arsenic and chromium (Fig. 3). Manganese has concentric areoles around industrial enterprises in the north and east of the city and has high concentrations in areas with stove heating (up to 26,000mg/kg in the area of the aluminum plant – sampling site 23). In the city center, as well as in the territory of dachas (city gardens), a slight decrease in manganese content is observed (less than 20,000mg/kg – sites 27, 28 and others).

The highest concentrations of manganese were recorded on the main streets of the city center (maximum

– 210mg/kg), as well as in the northern (site 5-195mg/kg) and eastern (site 26-160mg/kg) ash dumps of thermal power plants. Chromium contents of less than 100mg/kg were noted for urban gardens (minimum on site 9-91mg/kg) and areas remote from urban industrial enterprises (site 16-75mg/kg). In general, chlorine pollution can be traced to the city center.

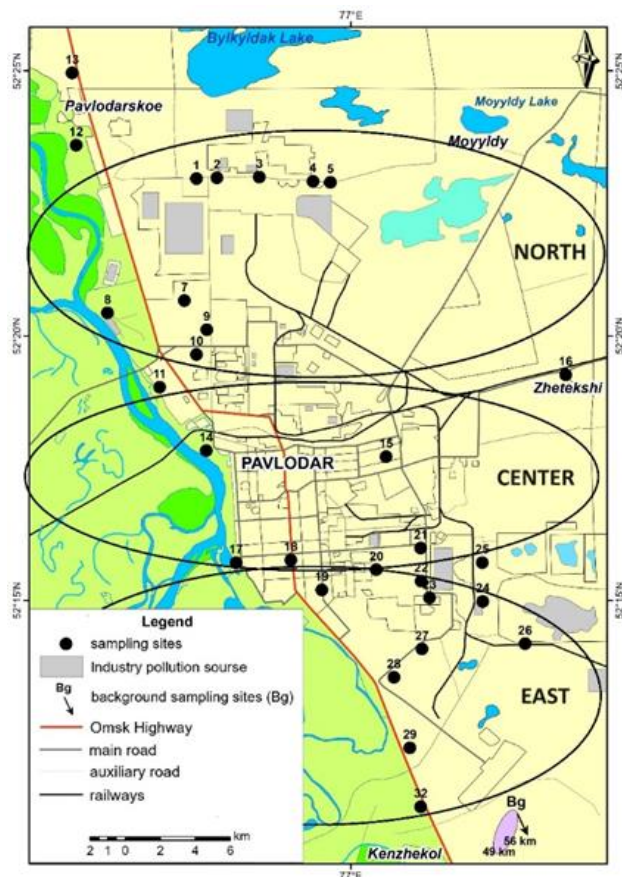


Fig. 1: Location of the study area and sampling sites in the city of Pavlodar

Areas of high arsenic concentrations do not present obvious patterns. The highest concentrations of arsenic in soils are presented everywhere with maximum values at site – 7 on the territory of the city garden with a value of 19mg/kg, at sites 18, 20 – in the city center with a value of 17mg/kg, as well as in the area of the aluminum plant – site 25 – 15mg/kg. Minimum values not exceeding 0.1mg/kg were recorded at site 19, on the territory of a private urban garden, as well as in the northern industrial zone at site 2 – not far from a chemical plant - 0.4mg/kg.

In general, the city has a high geochemical background of strontium in the soils. High concentrations of strontium are observed everywhere, with maximum values in areas in the southeastern and northwestern directions. The minimum value of 67mg/kg was noted at site 16 at the maximum distance from the city. It is known that the maximum content of various elements in the soil is not associated with one center, but is concentrated in several centers that differ in the composition of the elements and their level of accumulation (Tong et al., 2020; Li et al., 2022).

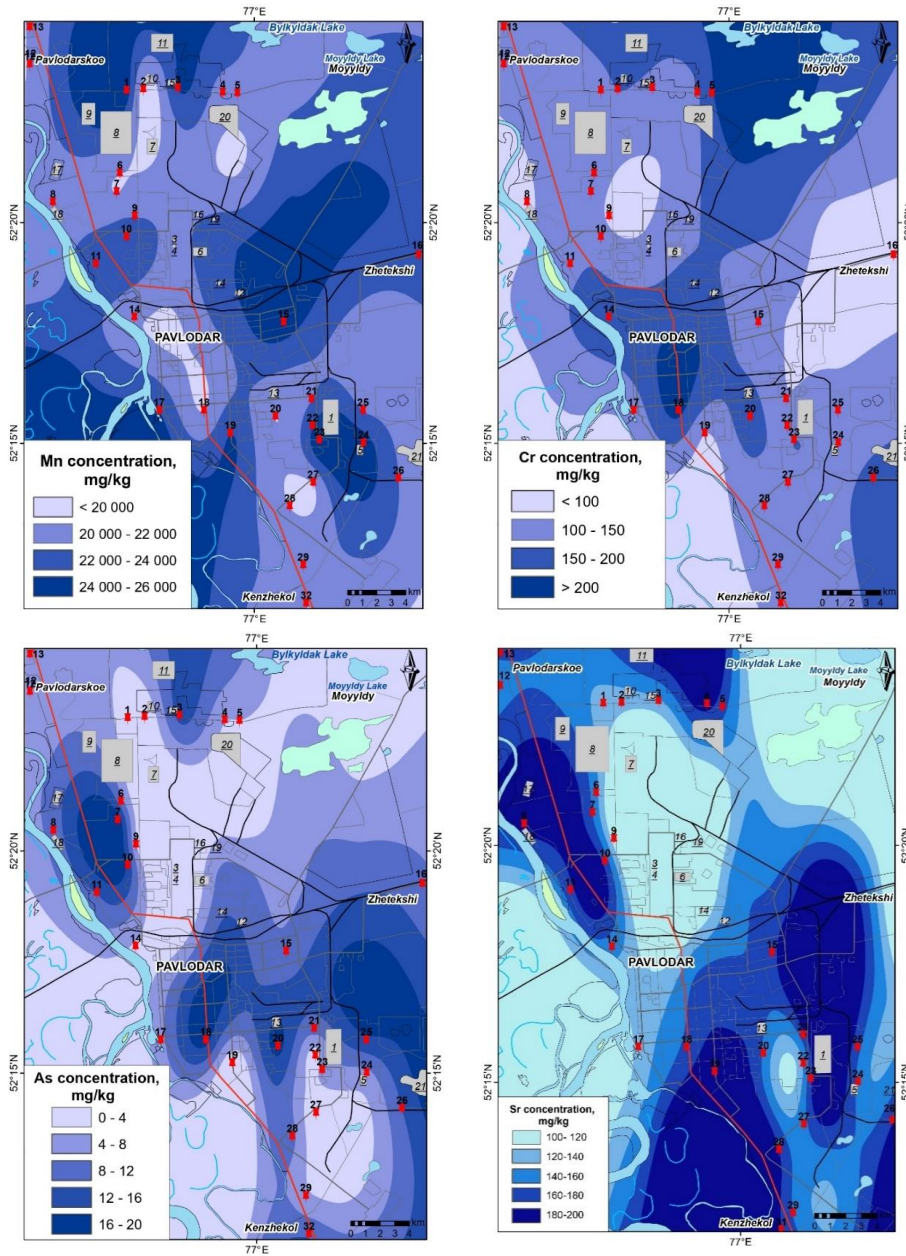


Fig. 2: Spatial distribution of heavy metal content in urban soils of Pavlodar

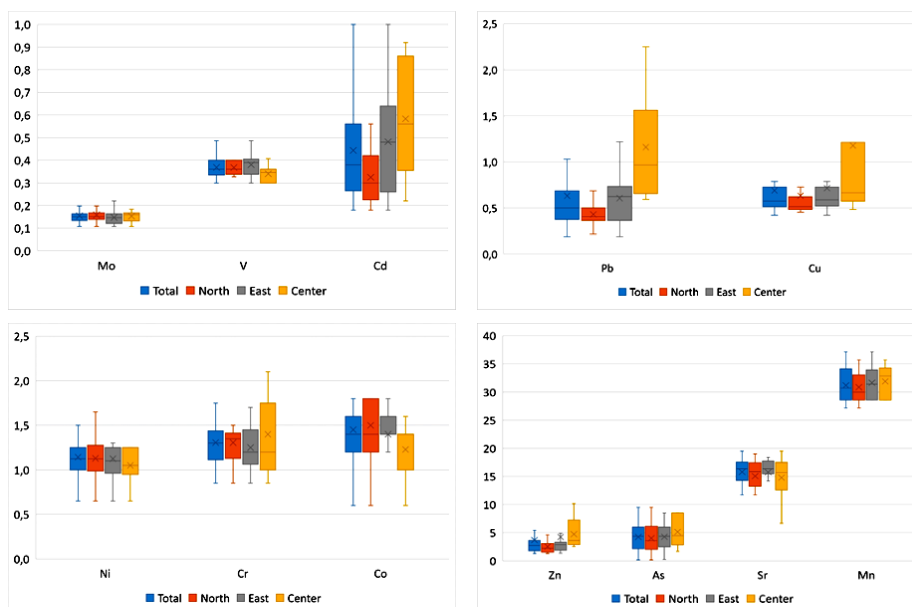


Fig. 3: Exceeding the MPC values of soils with heavy metals

Assessment of Heavy Metals Pollution Using Single and Complex Geochemical Indices

Based on the concentrations of heavy metals in Pavlodar's urban soils, both single and complex indices were calculated to assess pollution levels. Single indices, including the PI, Igeo, EF, CF, and maximum permissible concentration exceedance (Plmpc), provide insights into individual metal contamination. Complex indices like the Plsum, PLI, and PI Nemerow evaluate the cumulative impact of multiple metals. The PI is calculated by comparing metal concentrations in the soil to their background levels, highlighting human impact on soil quality.

The pollution index is based on the ratio of the element concentration in the soil to the background metal concentration (Bg) determined in this study (Table 1). As indicated in the research materials, the background sites were located at a considerable distance from the city (more than 50 km) in the opposite direction of the winds, with no industrial impact. However, despite this, the background values were not slightly lower than the control values. Thus, the areas represent areas with anthropogenic impact, including vehicles and stove heating of nearby villages. In this regard, most of the trace elements considered have low or no contamination (Fig. 4).

The descending series of average values of the pollution index for the city total is as follows: $Zn > Cr > Pb > Cu > Cd > Co > Mn > V > Ni > Al > As$. Index values below 0 mean the absence of contamination compared to the background for such metals as aluminum (0.99) and arsenic (0.71). Low pollution with an index below 2 applies to most metals copper (1.4), cadmium (1.2), cobalt (1.1), manganese (1.1), vanadium (1.03), nickel (1.02) and lead (1.6). The metals zinc and chromium have medium to severe contamination levels. The majority of soil samples containing chromium are highly contaminated, with an average value of 3.5. Despite the fact that zinc has a higher coefficient of 4.8, the degree of soil contamination has a wide range from low to very heavy contamination.

The northern industrial zone has the lowest pollution

index values. Unlike other zones, chromium has the highest value here (3.5), and cadmium here also has the lowest value of all zones - 0.86mg/kg. The coefficient of heavy metal pollution in the soils of the eastern industrial zone is higher than that of the northern one but is in many respects inferior to the indicators of the city center. In the city center, the pollution coefficient for zinc (6.2) is considered very severe, chromium (3.8) for severe pollution, and lead (2.9) and copper (2.1) for moderate pollution. The difference between the PI indicators in the city center is that here a larger number of heavy metals belong to the level - absence of pollution (V, Co, Ni, Al, As).

For example, in Shenyang, China, the lead (Pb) pollution index ranged from 0.00 to 24.08, with an average of 3.04, indicating severe Pb pollution in urban soils. Our studies found lead and chromium contamination levels higher than those recorded in Chinese urban gardens. For example, the chromium pollution index in our studies exceeds similar indicators in Chinese studies by 3.2 times. It is also worth noting that the level of arsenic contamination measured in the Chinese studies (2.8) is significantly higher than our results (0.71) (Gao et al., 2021).

To calculate the geo-accumulation index, the Clarke (geochemical background) values of heavy metals obtained from literary sources were used. This index indicates the degree to which soils are enriched with a particular metal compared to the natural geochemical background of the area. During the calculations, a correction factor was taken into account, which considers natural background fluctuations influenced by natural factors. Across the city, the accumulation index values varied for V from -0.83 to -0.14, Cr from 0.62 to 1.92, Mn from -0.66 to -0.21, Fe from -0.71 to -0.21, Co from -1.7 to 0.52, Ni from -1.38 to 0.05, Cu from -1.03 to 2.19, Zn from 0.18-4.18, As from -5.49 to 0.08, Cd from -1.66 to 0.81, Pb from -1.7 to 1.88, Al from -1.02 to -0.3. According to calculations, most heavy metals, with the exception of zinc, chromium and lead in some areas, do not affect soil pollution compared to the accepted geochemical background (Clarke) (Fig. 5).

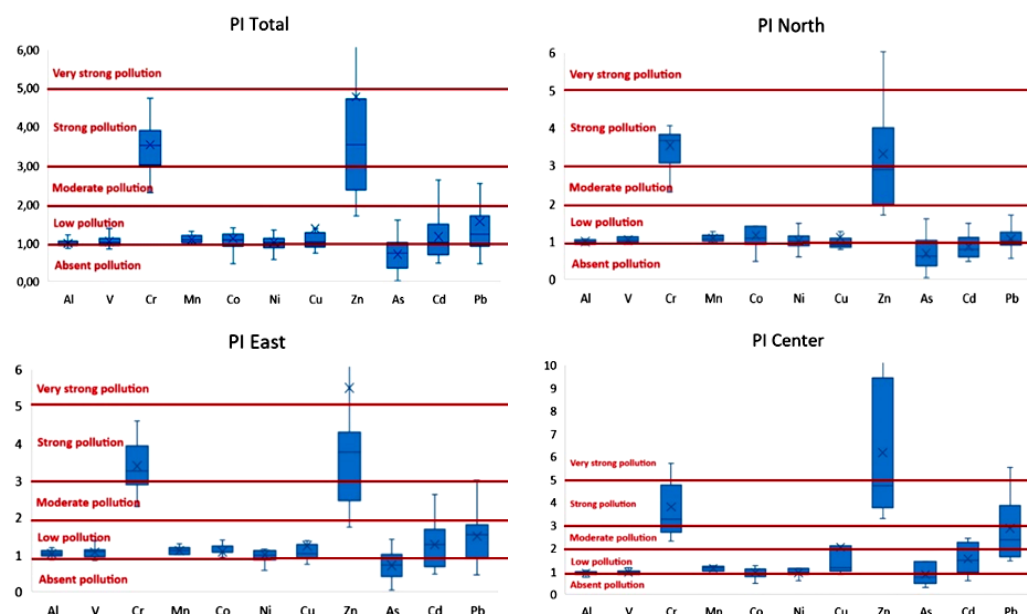


Fig. 4: Box-plots of the pollution index

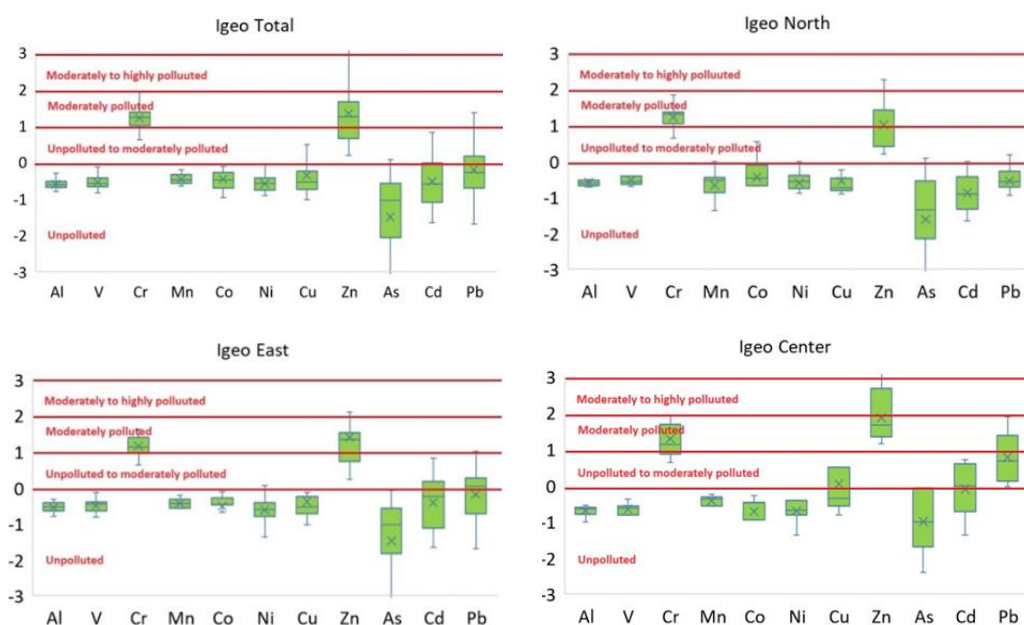


Fig. 5: Box-plots of the geoaccumulation index

Zinc and chromium have a high accumulation index in all zones. In general, chromium and zinc pollution levels in the city are moderate. However, zinc also has moderate to high levels of contamination in some areas. High zinc contamination includes sites 26 - the southern part of the ash dump of the thermal power plant of the eastern industrial zone ($I_{geo} = 4.18$), as well as in areas with stove heating and vehicle exhausts, sites 11, 15, 19 with a geoaccumulation index of 2.24; 2.65 and 3.14, respectively. The northern industrial zone is contaminated only with chromium and zinc in relation to the geochemical background, while the values of the remaining metals are below 0. In the eastern zone, in addition to chromium and zinc, I_{geo} values increase for cadmium and lead in some areas. In the center, residential zone of the city, such metals as copper (maximum value at site 15 $I_{geo} = 2.19$), cadmium (site 19 $I_{geo} = 0.46$) and lead (site 15 $I_{geo} = 1.88$) are soil pollutants in the areas with stove heating and vehicle exhausts.

Comparison of heavy metal geoaccumulation index data is quite unreliable because different studies use different background data or background Clarke concentrations of metals in the Earth's crust. When evaluating various sources, it was revealed that Clarke concentrations are generally similar, but differ for some metals and areas. Thus, the comparative assessment of indices will be approximate.

Geoaccumulation index values of various heavy metals such as Cd from 0.25 to 3.85 mg/kg, Cu from 4.30 to 183 mg/kg and Pb from 1.50 to 139 mg/kg have been recorded in agricultural top-soils in urban areas. Additionally, in the area of coal-fired power plants in South Africa, geoaccumulation index values indicate moderate levels of contamination by various metals, with lead showing moderate to severe contamination. In urban gardens in China, the accumulation coefficient of cadmium and arsenic exceeds our data, and the indices of chromium and lead in our studies are higher (Gao et al., 2021). In studies conducted in China, a comparative analysis of the geoaccumulation index in roadside dust, urban soils and

agricultural soils was performed. In contrast to our studies, urban soils in China showed a significant excess of the geoaccumulation index for most metals, with the exception of zinc (0.57) and chromium (minus 0.15). Our studies showed that the excess of zinc content was 2.3 times, and chromium - 8 times. Beijing soils, which are statistically average in our data, also showed low or no contamination, especially zinc and chromium. Regarding the analysis of geoaccumulation indices of roadside dust, the coefficient of zinc pollution in our study was consistent with the I_{geo} of zinc (1.48) in this dust. In agricultural soils of Chinese cities, including Beijing, the level of geoaccumulation indices of the metals in question was significantly lower, and the soils were qualified as uncontaminated, with the exception of cadmium (1.08 for agricultural soils in China, 0.21 for Beijing), the content of which in our studies was significantly lower and amounted to -0.33.

The EF allows us to estimate the intensity of anthropogenic activities. In our study, iron (Fe) concentration was used as the reference background concentration. As a result of calculations, data on soil enrichment in various zones of the city of Pavlodar was obtained (Fig. 6). In general, in the city the enrichment of soils with heavy metals is presented in the following series: $Mn > As > Zn > Cr > Pb > Al > V > Cu > Co > Ni > Cd$. The same row with minor differences is represented by microelements in other zones of the city. Thus, in all areas of the city, aluminum, vanadium, nickel and cadmium have a low enrichment (100% of sites) of less than 2. While manganese has an extremely high enrichment in all areas of the city, with a value from 46.5 to 54.7. The enrichment of zinc, arsenic and lead ranges from moderate to very high enrichment.

Enrichment ratios of copper (1.2), nickel (1), and cobalt (1.1) in the Aidi Lake basin region of northwest China (Zhang et al., 2022), as noted in their studies using iron as a reference concentration, are almost identical to those of our study. While other values of the soil enrichment coefficient in our studies turned out to be higher, with an extreme excess noted for manganese (16 times).

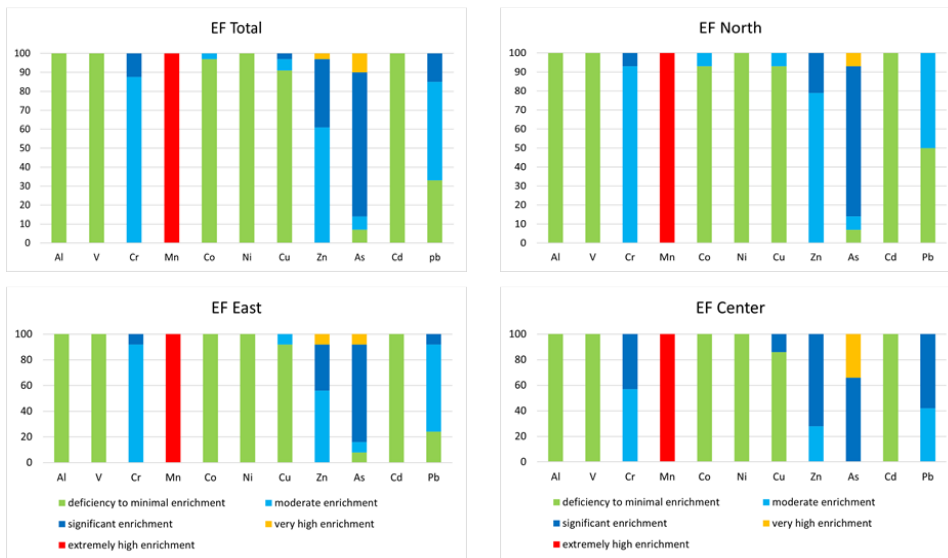


Fig. 6: The proportion of the Enrichment factor of heavy metals in urban soils in Pavlodar

The excess enrichment factor for zinc, lead, chromium and arsenic varies from 1.3 to 2.7 times. In a large urban agglomeration in southern Poland (Wieczorek & Baran, 2021) enrichment of metals is less than in Pavlodar for such metals as copper, zinc, lead from 1.7 to 3.2 times, and for chromium - 8.7 times less than in our study. The main difference is the EF of cadmium (2.95), which exceeds our values by 73 times.

The pollution factor (CF) is used to estimate soil pollution as a function of heavy metal concentrations in soils and pre-industrial reference levels. In our study, clarks of heavy metal concentrations (geochemical background) were used as pre-industrial levels. This coefficient has something in common with the pollution index, in which the background concentrations of our study were used as a geochemical background. Thus, it is possible to compare anthropogenic pollution of city soils by industrial enterprises. Lead, chromium, and zinc have moderate contamination by pollution factor in all zones except the city center, where zinc has significant contamination (Fig. 7). Arsenic is also a significant contamination at all study sites. Manganese has a very high contaminant factor with values of 21.6–22.3. The remaining metals vanadium, copper, aluminum, cobalt, nickel and cadmium have a low pollution factor.

The descending series of average values of the pollution factor for the city total is as follows: $Mn > As > Zn > Cr > Pb > V > Cu > Al > Co > Ni > Cd$. The series of decreasing values of the pollution index differs from the series of the pollution factor, primarily due to the high values of manganese and arsenic in the latter. Thus, it can be assumed that on the territory of the city of Pavlodar the natural geochemical background of manganese and arsenic quite high compared to other territories. In the small port city of Volos (Golia et al., 2021), where studies were conducted on the anthropogenic impact on soils in the city center, a pollution factor was identified and it is many times higher than the CF in the city of Pavlodar for most metals, only zinc slightly predominates in Pavlodar, and manganese has a critical excess of 16 times. Rahman et al. (2012) in their study reported CF values in agricultural soils around the Dhaka export processing zone with

coefficient values for cadmium (0.02), lead (1.38), chromium (1.42) and zinc (2.95) in the dry season are close to the pollution factor of the city of Pavlodar. While for copper (4.68), nickel (2.4) and arsenic (2715.36) the CF in Dhaka is much higher than our data.

Assessment of Soil Pollution Relative to the Maximum Permissible Concentrations of Heavy Metals

Maximum permissible concentrations of heavy metals in the soil determine hygienic standards for a safe living environment. Among the metals studied, the least contamination is observed in molybdenum, vanadium, and cadmium (Fig. 3). According to soil assessment based on sanitary and chemical indicators, these metals belong to clean soil. Severely contaminated soil includes all metals exceeding the MPC from 1 to 10. All metals, except those listed above, have values exceeding 1 at some sites, while the average content may be below this value. The highest values of exceeding the MPC relate to manganese, strontium, arsenic and zinc. In the city total, the excess of Mn is 31.2 times, strontium – 15.8, and arsenic – 4.2. According to the Kazakhstan standard of hygienic regulations, pollution with metals of hazard class 1, the excess of MPCs of which is above 3, as well as heavy metals of hazard class 3, with a value above 25, are considered an environmental disaster. These metals include arsenic and manganese (Hygienic standards, 2004).

As for the spatial distribution of heavy metal pollution in urbanized soils, the following picture emerges. The greatest differences in the direction of increasing the excess of the MPC are cadmium, lead, copper and chromium. In the city center and residential zones, cadmium exceeds from 0.22 to 0.9, lead also has high values in this zone, reaching 2.3 times in some sites, which classifies these territories as soils with an environmental emergency, according to the Hygienic standards (Ministry of Health of the Republic of Kazakhstan, 2021), because lead belongs to hazard class 1. The excess of copper in the city center also reaches 3.9, and chromium – 2.1 values of the maximum permissible concentration. In the eastern industrial zone, zinc and cadmium predominate, the maximum excess of which is 20.9 and 1.0, respectively.

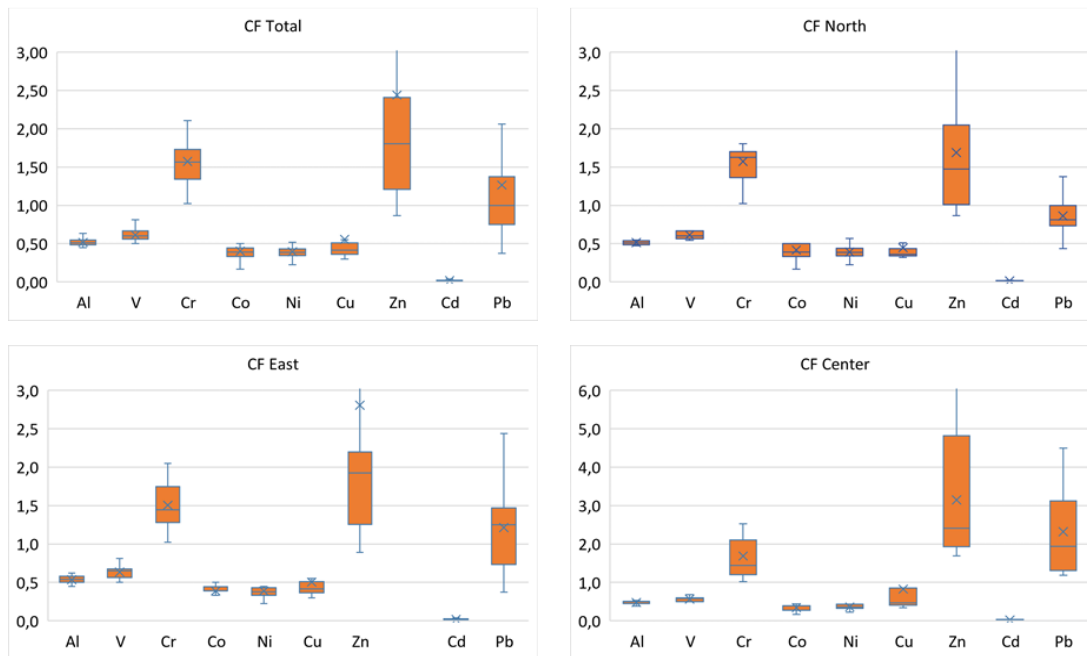


Fig. 7: Box-plots of the contamination factor

Complex pollution indices, which include the sum of pollution, the PIL, and the Nemerov pollution index, in general, characterize soil pollution in Pavlodar as low, with a slight increase in the city center and the smallest in the northern industrial zone (Table 2).

According to the evaluation criteria presented in studies of Tomlinson et al. (1980), the PIL of the north, east and the city total belongs to the moderately polluted to unpolluted zone, while the city center belongs to the moderately polluted zone. The widely used PIL is presented in many studies (Table 3).

Table 2: Comprehensive indices of soil pollution in the city of Pavlodar

Indexes/zone	City	North	East	Center
Sum of pollution (PI sum)	19.44	16.83	20	23.2
Pollution Load Index PIL	1.62	1.17	1.67	2.24
Nemerov Pollution Index PI Nemerov	1.4	1.09	1.45	1.67

Ecological and Health Risk Assessment

In our study, despite high average concentrations of metals in the soil, exceeding MPC concentrations, and some high single coefficients, the index of potential environmental risk is low, except in the city center, where it slightly reaches the average level (Fig. 8). The low values of this coefficient may be due to the use of a limited number of heavy metals for which toxicity response coefficients have been calculated. These include cadmium, arsenic, copper, lead, chromium, zinc and nickel. Metals that were considered major pollutants in other coefficients in our study were not considered, such as manganese, strontium, and aluminum. The RI values of 14 Liaoning cities were below 150, indicating that these cities face less potential environmental risk of heavy metal accumulation. In general, the content of heavy metals in the topsoil of most Liaoning cities has low or medium potential environmental risk (Zhao et al., 2022a, 2022b).

The risk assessment for human health from exposure to heavy metals was calculated using the hazard index (HI) and lifetime carcinogenic risk (CR). Carcinogenic and non-carcinogenic risk assessment was conducted for both

adults and children. Three ways of exposure to the body were taken into account: ingestion (CD_{ing}), dermal absorption (CD_{derm}) and inhalation (CD_{inh}) (Table 4).

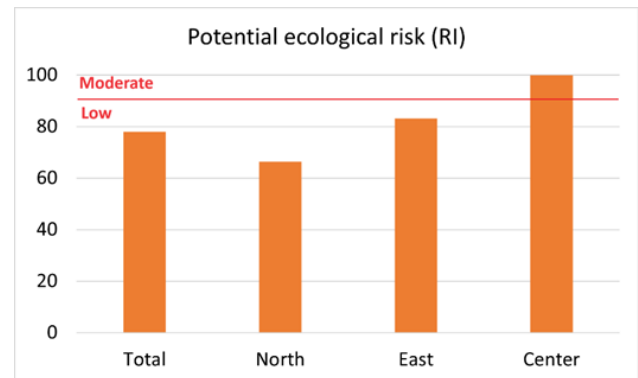


Fig. 8: Potential environmental risks

The greatest intake of heavy metals was found to occur through ingestion for both children and adults, a finding also supported by previous studies (Tong et al., 2020). The hazard quotient (HQ) for each element and the different exposure routes HQ_{ing} > HQ_{derm} > HQ_{inh} behave in the same way, in all cases the exposure in children exceeds that in adults (Table 5).

The Hazard index shows the cumulative non-carcinogenic risk of exposure to metals at different levels of exposure to the body. If HI is less than 1, adverse health effects are unlikely. Most metals in the city of Pavlodar do not pose a threat to the health of children and adults, except for chromium, manganese, iron and arsenic. Manganese and iron are of critical importance and the occurrence of negative consequences for the health of children and adults of a non-carcinogenic nature is very high. Chromium also has adverse health effects, with values of 1.57 and 7.62 for adults and children, respectively. In addition, arsenic is of moderate danger to children.

Table 3: Load index values in various studies

Hołtra & Zamorska-Wojdyła, Weissmannová et al., Gao et al., 2021 – Rinklebe et al., 2019 – Lu et al., 2014 – Lu et al., 2014 – Wieczorek & Baran, 2021 – 2020 – industrial soil	2019 – urban soil	urban garden	wetland soil	urban soil	road dust	agricultural soil
5.54	1.5	1.1	1.9	2.0	7	1.48

Table 4: Chronic daily intake (CDI) of metals

City total	CDI _{ing}		CDI _{derm}		CDI _{inh}	
	Adults	Children	Adults	Children	Adults	Children
Cr	1.79E-04	1.67E-03	7.14E-07	3.33E-06	4.29E-05	2.00E-04
Mn	2.99E-02	2.79E-01	1.19E-04	5.57E-04	7.18E-03	3.35E-02
Fe	2.72E-02	2.54E-01	1.09E-04	5.07E-04	6.53E-03	3.05E-02
Ni	3.13E-05	2.92E-04	1.25E-07	5.83E-07	7.51E-06	3.50E-05
Cu	3.58E-05	3.34E-04	1.43E-07	6.66E-07	8.59E-06	4.01E-05
Zn	2.78E-04	2.59E-03	1.11E-06	5.17E-06	6.66E-05	3.11E-04
As	1.16E-05	1.08E-04	4.63E-08	2.16E-07	2.79E-06	1.30E-05
Cd	3.04E-07	2.84E-06	1.21E-09	5.66E-09	7.29E-08	3.40E-07
Pb	2.77E-05	2.59E-04	1.11E-07	5.17E-07	6.66E-06	3.11E-05

E represents scientific notation, where '1E+03' means 1×10^3

Table 5: The mean values of the hazard quotient (HQ) and hazard index (HI) for Children and Adults posed by each element, according to exposure pathway

City total	HQ _{ing}		HQ _{derm}		HQ _{inh}		HI	
	Adults	Children	Adults	Children	Adults	Children	Adults	Children
Cr	5.96E-02	5.57E-01	1.19E-02	5.55E-02	1.50E+00	7.01E+00	1.57E+00	7.62E+00
Mn	6.50E-01	6.07E+00	6.49E-02	3.03E-01	5.02E+02	2.34E+03	5.03E+02	2.35E+03
Fe	9.08E+00	8.47E+01	2.41E-03	1.13E-02	2.18E+00	1.02E+01	1.13E+01	9.49E+01
Ni	1.56E-03	1.46E-02	2.27E-04	1.06E-03	3.65E-04	1.70E-03	2.16E-03	1.74E-02
Cu	8.95E-04	8.35E-03	1.19E-05	5.55E-05	2.15E-04	1.00E-03	1.12E-03	9.41E-03
Zn	9.25E-04	8.64E-03	1.85E-05	8.61E-05	2.22E-04	1.04E-03	1.17E-03	9.76E-03
As	3.87E-02	3.61E-01	3.86E-04	1.80E-03	8.99E-03	4.19E-02	4.81E-02	4.05E-01
Cd	3.04E-04	2.84E-03	1.21E-04	5.66E-04	1.28E-03	5.97E-03	1.70E-03	9.37E-03
Pb	7.93E-03	7.40E-02	2.11E-04	9.84E-04	1.93E-03	9.01E-03	1.01E-02	8.40E-02

E represents scientific notation, where '1E+03' means 1×10^3

Table 6: Cumulative hazard index (HI) for non-carcinogenic risk

	HI	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Adults	North	1.57E+00	4.97E+02	1.09E+01	2.13E-03	8.98E-04	8.07E-04	4.54E-02	1.25E-03	6.85E-03
	East	1.51E+00	5.10E+02	1.17E+01	2.12E-03	1.02E-03	1.34E-03	4.85E-02	1.85E-03	9.65E-03
	City center	1.69E+00	5.14E+02	1.13E+01	1.98E-03	1.67E-03	1.50E-03	5.84E-02	2.24E-03	1.85E-02
Children	North	7.62E+00	2.32E+03	9.21E+01	1.72E-02	7.54E-03	6.75E-03	3.83E-01	6.87E-03	5.72E-02
	East	7.29E+00	2.38E+03	9.87E+01	1.71E-02	8.52E-03	1.12E-02	4.08E-01	1.02E-02	8.05E-02
	City center	8.17E+00	2.40E+03	9.55E+01	1.60E-02	1.40E-02	1.26E-02	4.92E-01	1.23E-02	1.54E-01

E represents scientific notation, where '1E+03' means 1×10^3

Table 7: The mean values of the carcinogenic risk quotient and carcinogenic risk over lifetime (CR) for Children and Adults posed by each element, according to exposure pathway

City total	CR _{ing}		CR _{derm}		CR _{inh}		CR	
	Adults	Children	Adults	Children	Adults	Children	Adults	Children
Cr	8.95E-05	8.35E-04	1.43E-06	6.66E-06	1.80E-04	8.42E-04	2.71E-04	1.68E-03
Ni	5.32E-05	4.97E-04	5.31E-07	2.48E-06	6.76E-06	3.15E-05	6.05E-05	5.31E-04
As	1.74E-05	1.63E-04	1.70E-07	7.91E-07	4.21E-06	1.96E-05	2.18E-05	1.83E-04

E represents scientific notation, where '1E+03' means 1×10^3

When determining non-carcinogenic health risks in various zones of Pavlodar, the values presented in Table 6 were obtained. The study revealed that chromium, manganese, and iron have the most significant negative impact across all city zones. While arsenic levels in the city's soils are unlikely to harm adults, they could pose health risks to children. Additionally, cadmium (0.023) and lead (0.154) concentrations in the city center may negatively affect children's health.

Among the ten elements examined in Zhang et al. (2022), the HQ indicator for lead (Pb) in children was the highest, with a value of 2.11E-02, followed by the HQ_{inh} indicator for arsenic (As) in adults at 1.62E-02. In the research by Tong et al. (2020), the average HI values for the eight metals studied suggested that adverse health effects were unlikely. Next, the carcinogenic risk for chromium, nickel and arsenic was calculated at different intakes, as well as the overall lifetime cancer risk (LCR) for adults and children (Table 7).

Carcinogenic risk values of less than 10^{-6} , which

correspond to an insignificant risk in the territory of Pavlodar for the metal's chromium, nickel and arsenic, have not been identified, neither for children nor for adults. Chromium has a high carcinogenic risk (0.00168) for children. Acceptable threshold levels for children are nickel (0.000531) and arsenic (0.000183), as well as chromium for adults with a value of 0.000271.

When assessing the spatial distribution of the carcinogenic risk of exposure to heavy metals in soils, it was revealed that for children all the considered zones of the city are dangerous for chromium, and for nickel and arsenic they have a threshold permissible level (Table 8).

Table 8: Total carcinogenic risk over lifetime (CR) for adult and child

	CR	Cr	Ni	As
Adults	North	2.71E-04	5.98E-05	2.06E-05
	East	2.60E-04	5.96E-05	2.20E-05
	City center	2.91E-04	5.56E-05	2.65E-05
Children	North	1.68E-03	5.24E-04	1.73E-04
	East	1.61E-03	5.23E-04	1.84E-04
	City center	1.80E-03	4.88E-04	2.22E-04

E represents scientific notation, where '1E+03' means 1×10^3

DISCUSSION

For adults, nickel and arsenic have an acceptable health risk, while chromium values in all zones of the city are at threshold levels. In similar studies (Weissmannová et al., 2019) a carcinogenic health risk was identified for lead, a high risk for cadmium and a very high risk for chromium for children. In addition, as a result of assessing the overall carcinogenic risk at work of Rezapour et al. (2022), found that it ranged from $5.88\text{E-}05$ to $1.17\text{E-}04$ for children and from $1.17\text{E-}04$ to $2.30\text{E-}04$ for adults, indicating a greater associated health risk for children. Calculation of carcinogenic risks in research (Zhang et al., 2022) showed that the values of As, Cd, Co, Cr and Ni were $4.1299\text{E-}09$, $1.56155\text{E-}11$, $6.0499\text{E-}12$, $1.58151\text{E-}07$ and $8.40675\text{E-}10$, respectively. Also, these studies (Tong et al., 2020; Zhang et al., 2022) proved that the average carcinogenic risk values for As, Cr and Ni for children and adults suggested an acceptable carcinogenic risk for humans.

The results of this study of heavy metal soil pollution in urban cities like Pavlodar follow the current trend consistent with urban and industrial soil pollution. Our results partially agree with the works of (Long et al., 2021), who investigated the effects of different industrial activities (notably metallurgy and thermal energy) on soil heavy metal pollution, ecological risks, and health risks. From their results, we see a higher concentration of Vanadium than Chromium, which is quite different from our findings and may indicate the presence of different factors in determining heavy metal concentration. However, there is consistency in the minuscule concentration of Arsenic and Cadmium.

In the study (Ramazanov et al., 2021) in the soils of the cities of Kazakhstan most contaminated with heavy metals, Igeo was 3.81 for Pb and 3.45, which significantly exceeds our data for these metals. In studies conducted in central Greece (Golia et al., 2021), we found that accumulation indices for copper were consistent with our results. However, the accumulation of zinc and lead in our studies is significantly higher. In terms of other metals, soils in the city of Volos were the most contaminated.

The elevated concentrations of certain metals in various parts of the city, as shown in our results, agree with the works of (Faurat et al., 2024), who conducted an analysis of the Heavy Metals Contamination in the Snow Cover of Pavlodar and concluded that the increase in certain metal concentrations like copper and manganese can be credited to anthropogenic factors such as vehicle emission. Our study shows an average distribution of lead in the sample sites of Pavlodar. Although this is favorable, it contrasts with the works of (Faurat et al., 2024), who recorded high lead levels in petrochemical industries and manganese in metal smelting areas in Pavlodar. Our work also contradicts their claim that the distribution of aluminum is not dependent on a specific source of contamination. However, the presence of aluminum smelters may be responsible for the large concentration of aluminum in Pavlodar.

Our study agrees with the work of (Haidar et al., 2023), who confirmed ingestion as one of the common ways of

heavy metal intake. However, they also highlighted the prevalence of inhalation in industrial settings, which is a precursor for respiratory-related diseases. For adults, nickel and arsenic have been shown to have an acceptable health risk factor, while chromium values in all city zones are at threshold levels. Our findings agree with the work of (Ahmad et al., 2021) on toxic and heavy metals contamination assessment in soil and water to evaluate human health risk. They concluded that in places polluted with heavy or toxic metals, children stand a risk of developing cancer due to lifetime exposure to chromium.

The results of our research also correlate with the pollution index data published in Wieczorek (Wieczorek & Baran, 2021). The study was carried out in a large urban agglomeration in southern Poland, where a variety of anthropogenic impacts as well as mining activities are present. In our study, we found that the index values contamination slightly exceeds the values presented in the work of J. Wieczorek, for cadmium and lead, practically coincides for copper and nickel, but exceeds 1.3 times for chromium and 2.8 times for zinc compared to Polish studies (Wieczorek & Baran, 2021).

From a global perspective, our results indicate that the targeted remediation strategies should prioritize areas with high concentrations of chromium, manganese nickel, and arsenic, particularly in the city center where pollution levels are most severe and carcinogenic risk is imminent. The use of eco-friendly and sustainable techniques like phytoremediation, as suggested by Bhat et al. (2022), can be explored to mitigate the heavy metal contamination in these areas. The results of our study underline the need for both local and global interventions relevant to heavy metal soil pollution in Pavlodar; this would imply further development of monitoring and remediation systems within the most contaminated areas, with emphasis on the center of the city where concentration is high. Heavy metals can largely be controlled from accumulating in urban soils in Pavlodar and around the world by the actions of industrial-emission-restricting policies and sustainable urban planning.

In Polish studies of the impact of various sources of pollution on soils (Hołtra & Zamorska-Wojdyła, 2020), the values of heavy metal content in the area of the Oława metallurgical plant had closer values to our studies. In studies conducted in the Czech Republic, in a highly industrialized area, the impact of the metallurgical and mining industries (Weissmannová et al., 2019), the content of copper (21.11mg/kg), cadmium (0.21mg/kg), zinc (204.57mg/kg) has similar values to our data, but the concentration of metals such as chromium is 17.46mg/kg (our values are 7.4 times higher), lead (1.9 times higher) is lower than in our study. The same goes for iron (our values are 2450 times higher) and manganese (15 times higher), in studies in the city of Ostrava (Czech Republic), our values are extremely high compared to their data. Also of interest is the analysis of urbanized soils in Chinese cities of Tong et al. (2020), which was carried out on soils of 71 cities. Thus, the average values for the content of metals such as nickel (26.4mg/kg), copper (34.87mg/kg), arsenic (6.67mg/kg), cadmium (3.2mg/kg) and lead (37.35mg/kg)

in studies in China slightly exceed our data, and the average content of metals such as zinc (107mg/kg) and chromium (66.3mg/kg) in Chinese cities is less than our average value for zinc - 202.63mg/kg and for chromium - 130.6mg/kg. However, the content of heavy metals in the city of Pavlodar corresponds to those in the following Chinese cities: Harbin, Wuxi, Baise, Tengzhou, with excess zinc in our studies.

When compared with other studies conducted in Kazakhstan on agricultural lands (Zhyrgalova et al., 2024), it was found that the nickel content in our study slightly exceeds the concentration of this metal in agricultural soils (1.3 times), a significant excess is observed for arsenic, lead and zinc (2.4-2.6 times). However, the copper and cadmium contents in our study are lower (1.2-1.8 times). A study of the content of heavy metals in the cities of Kazakhstan (Ramazanova et al., 2021) revealed that the most contaminated soils are in 4 cities of the country (Balkhash, Ust-Kamenogorsk, Ridder, and Shymkent) with average concentrations of the studied metals varying between 251 and 442mg/kg for Pb, 5–9mg/kg for Cd, 8–138mg/kg for Cu, 87–178 mg /kg for Zn, and 2–5mg/kg for Cr. For chromium and zinc, the values in the city of Pavlodar exceed the values of the most polluted cities in the country.

Conclusion

During the study of soil contamination of the city of Pavlodar with heavy metals, various indices were used to characterize the degree of pollution, environmental risk and assess the potential impact on human health. The study also took into account the territorial patterns of distribution of microelements in the soil. In general, for the city, the descending series of heavy metal content following as: Al (41531.3) > Mn (21837.5) > Fe (19875) > Zn (202.6) > Cr (130.6) > V (55.3) > Cu (26.1) > Ni (22.8) > Pb (20.3) > As (8.5) > Co (7.3) > Cd (0.2). High concentrations of most metals such as zinc, chromium, copper, lead and arsenic are observed in the center of the city. The eastern industrial zone is characterized by a high aluminum content (43083.33mg/kg) in the soil, as well as a high concentration of vanadium (57mg/kg). The northern industrial zone, on the contrary, is the cleanest area with the lowest content of heavy metals.

A pollution index value of less than 2 characterizes most metals: copper (1.4), cadmium (1.2), cobalt (1.1), manganese (1.1), vanadium (1.03), nickel (1.02) and lead (1.6). For the metals zinc and chromium, contamination levels in the medium to severe range are observed. Most soil samples containing chromium are classified as highly contaminated, with an average value of 3.5. In the case of zinc, despite its higher coefficient (4.8), the degree of soil contamination varies from low to very high.

According to the values of the geoaccumulation index, it was revealed that in the city total, the soils for most of the studied heavy metals are uncontaminated or moderately polluted. Zinc and chromium have a high accumulation index in all zones of the city.

The EF of manganese has extremely high enrichment in all areas of the city, with values ranging from 46.5 to

54.7. Enrichment of zinc, arsenic and lead ranges from moderate to very high. The remaining metals have low enrichment. The highest values of exceeding the MPC relate to manganese (31.2), strontium (15.8), arsenic (4.2) and zinc (3.68).

Complex pollution indices such as pollution sum, PIL and Nemerov pollution index generally indicate low levels of soil pollution in Pavlodar, with a slight increase in the city center and the lowest levels in the northern industrial zone. The Potential Ecological Risk Index also exhibits a low level, except for the central part of the city, where it is slightly elevated and transitions to a moderate level.

Most metals in the city of Pavlodar do not pose a threat to the health of children and adults, with the exception of chromium, manganese, iron and arsenic. The chromium content is especially unfavorable for health, with values of 1.57 for adults and 7.62 for children. A high carcinogenic risk is associated with chromium content (0.00168) in soils for children. Acceptable threshold levels for children are 0.000531 for nickel and 0.000183 for arsenic, and for adults it is 0.000271 for chromium.

Supplementary Materials: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

Author's Contribution: Conceptualization: AF, GA; methodology: AK; validation: AU; formal analysis: AU; investigation: AF, KA; data curation: GS, ZB; writing—original draft preparation: AF; writing—review and editing: GS, AK; supervision: GA; project administration: AF. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan, IRN AP15473194 "Assessment of the accumulation and distribution of microelements in atmospheric precipitation (snow cover), soils and vegetable crops in urbanized areas of Pavlodar".

Conflict of Interest: The authors declare no conflicts of interest.

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