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Dynamics of concentrations of heavy metals in industrial soils

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Dynamics of concentrations of heavy metals in industrial soils

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Abstract. The paper presents the results of a study of pollution by heavy metals of 1 and 2 hazard classes of the soil cover of the territory adjacent to the industrial zone of the Aktobe ferroalloy plant. The article evaluates changes in the concentration of heavy metals of various hazard classes in terms of the ecotoxicological indicator in comparison of two periods. In the selected soil samples, the pH value was determined, the gross concentrations of cadmium, copper, zinc, nickel, chromium were determined. An excess of concentrations in the soil has been established: an excess of zinc is on average 1.19 times higher than the MAC, nickel is 5.4 times higher than the MAC, cadmium is 4.2 times higher than the MAC, and chromium is 62.13 times higher than the MAC.

1. Introduction

In many studies of the soils of large industrial cities, the content of heavy metals is studied, since they are a mandatory component of assessing the impact on the environment. Their contribution to soil toxicity is up to 34.8%.

A characteristic feature of heavy metals is their rapid accumulation in the soil and very slow removal. In the first period of removal of half of the initial concentration of heavy metals for various elements varies considerably and takes a very long period of time: for zinc - 70-510 years; cadmium - 13-110 years.

Our research consisted in the analysis of soil monitoring data in the territory adjacent to the sanitary protection zone of the Aktobe Ferroalloy Plant in the city of Aktobe, Republic of Kazakhstan. The proximity of an industrial facility determines a high susceptibility to toxic soil pollution. Early studies of the contamination of soils in Aktobe with heavy metals at the border of the SPZ of the plant and at a distance from it revealed a critical ecological situation. It was found that chromium and nickel were fixed most strongly in the soil.

The relevance of the study is due to the need for a modern assessment of the ecological state of soils adjacent to the industrial area of the plant.

The aim of this work is to study the dynamics of the content of gross forms of heavy metals in the industrial soils of Aktobe and assess the level of their pollution.

2. Materials and methods

In the eroded area, to determine heavy metals in the surface layer of the soil at 4 points, soil samples were taken to a depth of 0-10 cm, where heavy metals are mainly deposited and accumulated [1].

The first sampling period is October 2020; the next period is April 2021. Observation points were selected in the residential area, taking into account the dominant wind directions, in order to study the distribution of the alleged traces of pollutants. (500 m and 1000 m to the west and south-west) (figure 1).

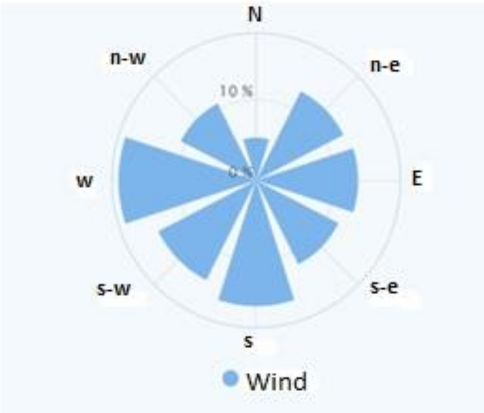

Figure 1. The wind rose of Aktobe.

Sampling was carried out in accordance with GOST 17.4.3.01-83 "General requirements for sampling" (figure 2). Determination of the total content of heavy metals was determined by atomic absorption spectrometry [2].

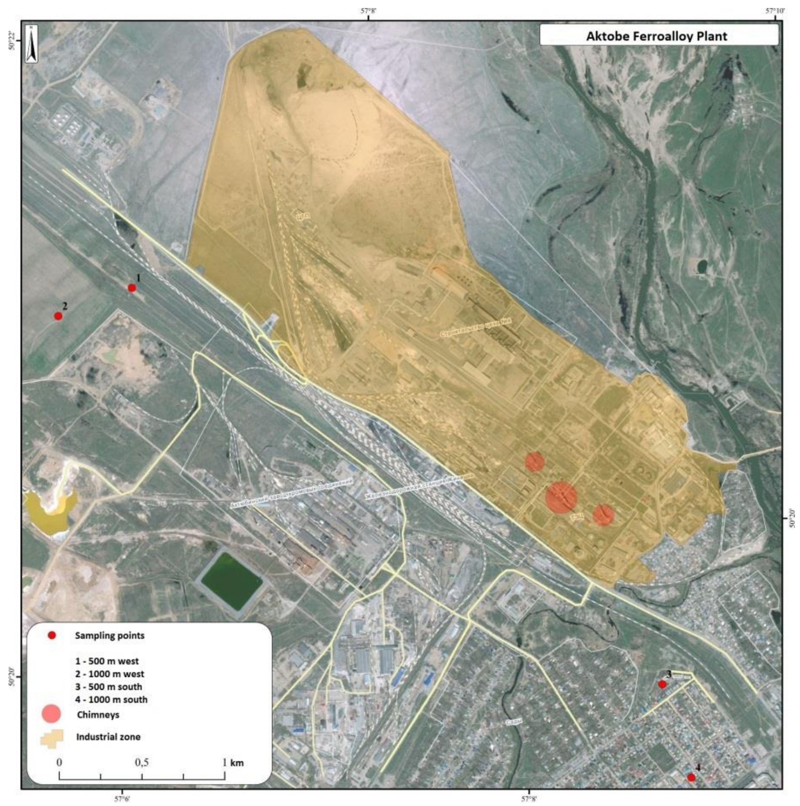

Figure 2. Sampling scheme.

In the first period, soil samples were analyzed for the content - Pb^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Cr^{6+}, Mn^{2+}, Cd^{2+} according to GOST 26423-85 “Soils. Methods for determining the specific electrical conductivity, pH and dense residue of the aqueous extract ”[3]. In the second period of sampling, the samples were analyzed for the content of elements exceeding the maximum permissible concentration (MAC): Zn^{2+}, Ni^{2+}, Cd^{2+}, Cr^{6+}.

3. Results

The results of the analysis of soil samples for the concentration of heavy metals exceeding the MAC level are shown in table 1. The data obtained helped to calculate the multiplicity of the MAC excess. Particular attention is paid to heavy metals 1 and 2 hazard classes - hexavalent chromium, cadmium, nickel, zinc. A critical excess of concentrations in the autumn period (October 2020) of Cr was revealed in the southern direction by 32.8 times, and in the western one - 160.6 times higher than the MAC. The results obtained in the spring period are similar to those in the autumn period (33.3 - 163.2 times). The total pollution is maximal in the western part of the SPZ. This factor can be associated with the location of the dumps on the western border of the SPZ. Dust particles are removed from the surface of the dump as a result of wind erosion and are deposited on the soil. This leads to additional pollution of atmospheric air, soil and vegetation, and an increase in the concentration of heavy metals.

The Cd content, depending on the direction of sampling, varied from 2.32 to 6.8 times higher than the MAC. In the samples of spring sampling at a distance of 1000 m to the south, the Cd content exceeds by 31.8% in comparison with the analogous sample of autumn sampling. This is due to precipitation and leaching by precipitation of the autumn-winter period.

Table 1 shows that the Zn content ranged from 19.04 to 49.7 mg / kg. The maximum value was noted at a distance of 1000 m to the west (49.7 mg / kg), which exceeds the MAC level by 26.7 mg / kg. It should be noted that the increased gross zinc concentration is observed in the western direction, regardless of the sampling period. A similar picture developed in terms of the Ni content, that is, the maximum concentration was noted in the western direction at a distance of 1000 m (31.57 mg / kg).

Table 1. Gross content of heavy metals (Zn^{2+}, Ni^{2+}, Cr^{6+}, Cd^{2+}), mg / kg.

Selection time	Sampling points	Cr	MAC	Zn	MAC	Cd	MAC	Ni	MAC
October 2020	500 m to the West	553.6	6.0	27.55	23.0	2.59	0.5	28.73	4.0
	1000 m to the West	963.68		40.67		2.04		28.95	
	500 m to the South	197.07		21.16		1.61		14.92	
	1000 m to the South	260.18		21.05		2.05		21.55	
April 2021	500 m to the West	572.3		30.5		3.4		31.04	
	1000 m to the West	979.4		49.7		2.8		31.57	
	500 m to the South	200.07		19.04		1.16		12.15	
	1000 m to the South	281.4		23.1		3.01		22.4	

4. Discussion

The comparative analysis of the two periods shows that the concentration in the second period increases in comparison with the first period. In our opinion, the increased content of pollutants as a result of increased emissions of heavy metals into the environment may be associated with an increase in production by 7.4%. The results obtained show that the excess of the maximum permissible concentration of chemicals corresponds to an extremely dangerous degree.

Strong compounds of heavy metals can be due to a high pH (pH = 7.79-8.11) [4]. In an alkaline environment, heavy metals are strongly sorbed and interact with soil humus, forming poorly soluble compounds in the upper layer. A high concentration of cadmium has a toxic effect on beneficial microbes, disrupts their metabolic process and inhibits their growth. Cadmium has a long biological half in humans (10–35 years) [5].

Based on the results of measurements of the content of gross concentrations of heavy metals, the concentration coefficients K_c of an individual element and the total indicator of chemical contamination Z_c at each point were calculated using formula 1. The data obtained are presented in table 2.

$$Z_c = \sum (K_{ci} +_{\dots} + R_{cn}) - (n - 1) \quad (1)$$

Table 2. The total indicator of chemical soil contamination,%.

Selection time	Sampling points	Concentration factor				Z_c - total pollution indicator
		K_c (Cr)	K_c (Zn)	K_c (Cd)	K_c (Ni)	
October 2020	500 m to the West	92.27	1.2	5.18	7.1	101.75
	1000 m to the West	160.6	1.7	4.08	7.2	173.58
	500 m to the South	32.8	0.92	3.22	3.73	36.67
	1000 m to the South	43.3	0.91	4.1	5.3	49.61
April 2021	500 m to the West	95.38	1.32	6.8	7.68	107.18
	1000 m to the West	163.2	2.16	5.6	7.81	174.7
	500 m to the South	33.3	0.82	2.32	3	35.44
	1000 m to the South	46.9	1.004	6.02	5.54	55.4

According to the results of calculations, the maximum contribution to soil pollution is made by chromium, the coefficient of which in some points varies from 32.8 to 160.6. Zinc has the minimum values, not exceeding 1% in the samples taken in the southern direction, the maximum value (2.16) at the point 1000 m west of the SPZ. The concentration coefficients of cadmium and nickel are minimal, their average values do not exceed the limits.

Within the study area, the maximum values of the total indicator of chemical pollution reach 173.58 (2020) and 174.7 (2021) at a point 1000 m west of the SPZ, at a point 500 m in the same direction the values are slightly lower (101.75 and 107, eighteen). The total indicator at the southern sampling points classifies this area as a hazardous category according to the standard limits of the hazard of chemical pollution according to Z_c. At the observation point 1000 m westward, an extremely dangerous situation was detected, exceeding the threshold of 128% (173.58; 174.7). Based on the above, we can talk about the uneven distribution of heavy metals within the area of the study area.

To assess the nature of pollution and determine the potential risk associated with the impact of environmental sensitivity, concentration and toxicity of HMs in soil, we also used the international contamination factor (Cf_i) and potential ecological risk index (PERI) indices.

Cf_i is the ratio of the concentration of each metal in the soil to the baseline or background value. According to our data, the Cf_i index for Zn (0.3) characterizes low soil contamination with this metal; in turn, pollution with Cd (1.3) according to the classification refers to soils of moderate pollution. The most critical indicator is for Cr (6.7), the value of which is greatly exceeded. (Cf_i <1 (low pollution), $1 \leq Cf_i < 3$ (moderate pollution), $3 \leq Cf_i < 6$ (significant pollution) and $Cf_i \geq 6$ (very high pollution)) [6].

The potential environmental risk of an individual metal element (formula 2) is determined by the product between the coefficient of the toxic reaction for each metal and the quotient of the concentration of the element in the soil sample to the geochemical background value of the unaffected soil [7]:

$$E_r^i = C_r^i * T_r^i = \left(\frac{C_r^i}{C_n^i}\right) * T_r^i \quad (2)$$

Where T_r^i for Zn = 1, for Cd = 30, for Cr = 2, for Ni = 3 [8].

Our E_r data for each studied element (Cr = 13.4; Zn = 0.3; Cd = 39) showed a low environmental risk, despite high concentrations [9-10].

The regularity of the concentrations with the highest values of metals in soils at a distance of 1000 m from the sanitary protection zone has been noticed. On the contrary, low values were noted in observation samples at a distance of 500 m from the SPZ. One of the possible factors is an increase in the temperature difference between the emission temperature and the ambient air temperature, which contributes to a decrease in the maximum concentration and an increase in the distance to it due to a lighter hot mixture that rises to a greater height and dissipates further from the pipe over a large area. With an increase in the amount of air entering the pipe inlet at a constant intensity of emissions of harmful substances, they are diluted in the pipe itself and the concentration decreases, the total consumption of the mixture increases. Due to the increase in flow rate, there is an increase in the rate of exit of the mixture from the source. Due to the increase in speed, the mixture is thrown out to a great height, and, falling from a greater height in the presence of wind, harmful substances diluted in the pipe beforehand are dispersed over large areas and distances from the pipe, the maximum concentration naturally shifts further from the pipe (figure 3). If the temperature of the emissions rises, then the temperature difference between the temperature of the emissions and the atmospheric air increases, the maximum concentration under the same conditions decreases due to the fact that hot emissions, as lighter ones, rise to a greater height, and, falling from a greater height, are scattered over a large area and further from the pipe [11].

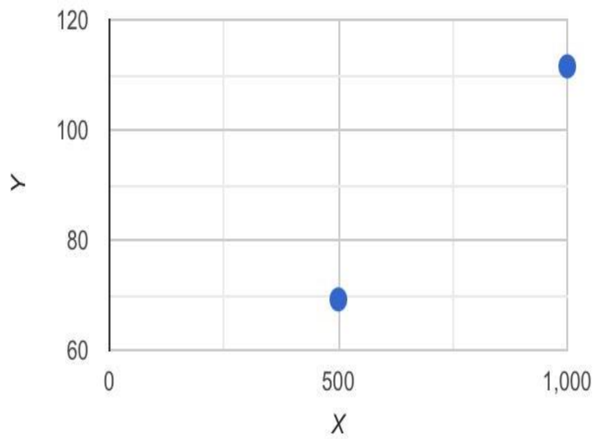

Figure 3. Correlation between the concentration of HM and the distance of sampling points.

A direct correlation was found between the content of gross forms of heavy metals in the soil profile and the distance of sampling points assigned to the experimental plots. The concentration of accumulated pollutants in the soil increases in direct proportion with the distance from the chimney. A very high and direct linear relationship is visually determined between the factorial attribute distance (X) and the effective attribute (Y).

It should also be noted that combinative combinations and concentrations of different metals in the environment lead to changes in the properties of individual elements as a result of their synergistic or antagonistic effects on living organisms. That is, a mixture of zinc and nickel is five times more toxic than the arithmetically obtained sum of their toxicity, which is due to the synergy with the combined effect of these elements. However, zinc and cadmium show mutual physiological antagonism.

5. Conclusion

The concentration of toxic and heavy metals in the soil decreased in the following sequence Cr^{6+}> Cd^{2+}> Ni^{2}> Zn^{2}. Chromium, cadmium and nickel make a real contribution to the total pollution index. The main pollutant is chromium, its average concentration exceeds the permissible standards by 82.2 times. A difference in the nature of the distribution of Cd, Ni, Zn is noticed, their concentrations are increased at the western points of observation. In total, the most HM-polluted zone is within 1000 m to the west of the SPZ. The soil of the investigated area is classified as "extremely hazardous" according to the normative limits for the hazard of chemical pollution according to Z_c.

At the same time, the universally used international indicator - the indicator of potential risk characterizes the studied soils as soils of a low level of ecological risk.

The maximum concentration of harmful substances, previously diluted in the pipe, is naturally dispersed over large distances and areas from the pipe, moving further from the pipe.

The formed correlation can be used in assessing the level of soil pollution and monitoring studies.

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