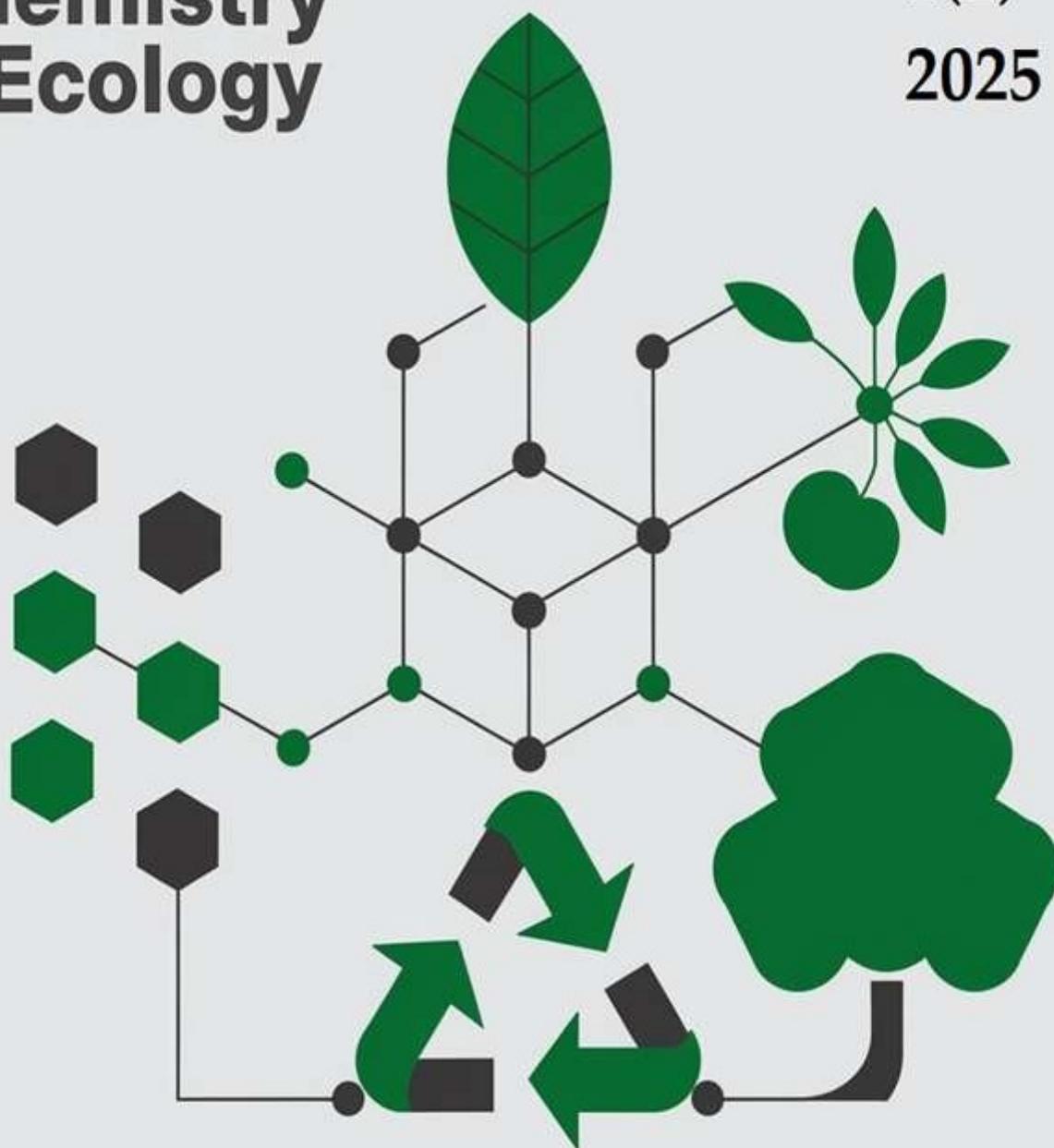


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**ENVIRONMENTAL AND GEOCHEMICAL ASSESSMENT OF TECHNOGENIC
LANDSCAPES IN THE AREA OF LLP PRODUCTION COMPANY «SEMEY CEMENT
PLANT»**

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ANNOTATION

The article presents the results of a comprehensive study of a long-term local geochemical anomaly identified in the influence zone of Site No. 1 “Cement Production” of the enterprise LLP “Production Company Cement Plant Semey.” The research was conducted to assess the degree of pollution in the upper soil horizon by chemical elements, particularly heavy metals, which may accumulate in the soil and pose a potential environmental threat. Modern high-precision methods of mass spectrometry and atomic emission spectrometry were applied to analyze the concentrations and spatial distribution of the elements. The obtained data were compared with published sources and previous studies, which confirmed the existence of a stable anomaly and made it possible to evaluate the possible causes of its formation.

DUST, ENVIRONMENT, SOIL, SPECTROMETRY, CHEMICAL ELEMENTS

1 Introduction

Modern industrial production exerts a global impact on the environment. Pollution from industrial emissions negatively affects both public health and the state of ecosystems. Cement manufacturing enterprises, in particular, are characterized by substantial emissions containing both solid and gaseous pollutants. These facilities are significant sources of cement dust, which influences all components of the environment, including the atmosphere, lithosphere, hydrosphere, and biota.

The global significance of the cement industry is determined by Portland cement, as it comprises the major elements of the Earth’s lithosphere—O, Si, Al, Fe, and Ca—which together account for 92.6% of its mass [1].

Portland cement consists of ground clinker, gypsum, and, when required, mineral additives, which ensure its rapid setting both in water and in air. Clinker is produced in specialized kilns, where all components undergo processes of calcination and fusion [2].

The volumes of pollutants containing heavy metals (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Sn, Hg, Pb, Bi, and others) are increasing annually, causing damage to the environment and disrupting the established ecological balance [3].

During fuel combustion, its components are released into the air with the flue gases. A portion of the suspended and volatilized metals, in the form of fine particles and vapor, is carried away by heated air streams through chimneys, subsequently depositing onto soils at varying distances from the emission source, depending on particle size. In addition, under the influence of cement dust, a technogenic surface layer enriched with heavy metals forms in the emission zone of the cement plant. More than 95% of heavy metals enter the soil in the form of anthropogenic dust. Among the harmful substances released into the atmosphere from industrial emissions, heavy metals are particularly hazardous to living organisms due to their high toxicity, mobility, and bioaccumulative properties. Analysis of cement plant dust has revealed elevated concentrations of lead (1800 mg/kg), zinc (410 mg/kg), cadmium (93 mg/kg), and copper (62 mg/kg) [4].

The results of studies on the dispersed composition of dust generated during the production of Portland cement clinker demonstrate that the dust released into the atmosphere after gas cleaning contains higher concentrations of Cd, Pb, and Zn compared to the dust present in the gas stream prior to cleaning. The high concentration of dust in emissions causes significant damage to the environment [5].

At present, monitoring of land conditions in areas exposed to industrial impacts is scarcely conducted, which underscores the relevance of research aimed at assessing soil contamination levels.

The operating cement plants in Kazakhstan include AlaCem, CaspiyCement, Bukhtarma Cement Company, ShymkentCement, KazakhCement, among others. The total cement production capacity within the republic exceeds 15 million tons per year [6].

At the same time, the largest enterprise in the industry remains the Semey Cement Plant, located in the Abai Region. Built in 1958, it operates four rotary kilns for clinker firing using the wet process, with a production capacity of 1.15 million tons per year. The Semey Cement Plant manufactures various types of Portland cement, including general-purpose cement (PC 400-D20) and high-grade cements (PC 400-D0, PC 500-D0, PC ACI 400), which are widely used in engineering and construction works.

Research Objective: to investigate the content of chemical elements in the upper soil horizon as an indicator of technogenic impact in the vicinity of LLP Production Company Semey Cement Plant.

Research Tasks:

1. To review available data on the composition of emissions from the industrial facility;
2. To collect soil samples and develop a sampling map of the study area;

To analyze the samples using mass spectrometry and atomic emission spectrometry, followed by comparison with available literature data.

2 Materials and Methods of the Study

The study was conducted at the Institute of Radiation Safety and Ecology of the National Nuclear Center of the Republic of Kazakhstan (Kurchatov, Kazakhstan). Analytical investigations were carried out in the certified and accredited laboratory of Environmental Sample Elemental Analysis, employing standard reference materials for comparison.

2.1 Materials

In accordance with the aims and objectives of the study, the research objects were soil samples collected under favorable weather conditions.

Soil sampling was conducted in compliance with GOST 17.4.3.01-2017 «Environmental Protection. Soils. General Requirements for Sampling» [7, 8].

Based on the «Wind rose» (Figure 1), eight soil samples were collected as follows:

- Four samples along the cardinal directions at a distance of 1000 m from the emission source;
- Two samples at distances of 1500 m and 1950 m from the emission source along the predominant wind direction toward the west;
- One sample from the residential area «Cement Settlement» located 1990 m from the emission source;
- One background sample from the «Kontrolny Settlement» located 6700 m from the emission source.

Sampling maps were generated using Yandex Maps [9].

Point samples were obtained using the “envelope” method from a depth of 0–5 cm by averaging material from five individual subsamples.

Subsequently, the soil samples were air-dried in accordance with GOST 5180-2015 «Soils. Laboratory Methods for Determining Physical Characteristics» and subjected to chemical analysis [10].

As a background site, territories with an identical soil-forming genesis located in the opposite direction from the predominant wind directions indicated by the «Wind rose» were used (Fig. 1).

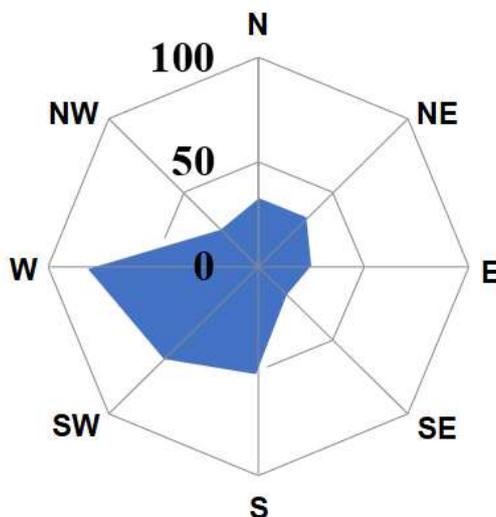


Figure 1 – Wind Rose

2.2 Methods

At present, modern methods for multielement analysis of environmental samples include inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES), which make it possible to determine a wide range of elements within a single sample in one analysis.

The combined application of ICP-MS and ICP-AES is particularly effective: ICP-MS is highly sensitive to trace and ultra-trace elements, while ICP-AES is better suited for elements present at higher concentrations, such as major components (Mg, Ca, Fe, and others). Therefore, the use of these two complementary methods provides the most promising results for studying the chemical composition of environmental samples.

Accordingly, the concentrations of chemical elements in the soil samples were determined using ICP-MS and ICP-AES.

The elemental analysis of soil samples included the following stages:

- Preparation of laboratory glassware;
- Preparation of auxiliary calibration solutions;
- Acid digestion of samples using an autoclave decomposition method;
- Preparation of the Agilent 7700x mass spectrometer and the iCap 63 Duo atomic emission spectrometer for operation;
- Adjustment of main systems and setting of instrumental parameters for the Agilent 7700x mass spectrometer and the iCap 63 Duo atomic emission spectrometer;
- Development of the analytical program and configuration of instrumental parameters for both spectrometers;
- Data analysis and real-time quality control;

- Generation of the measurement protocol.

Soil sample preparation was carried out by autoclave digestion to determine the total content of chemical elements:

- a weighed portion of the air-dried soil sample (0.2000 ± 0.0001 g) was placed into a reaction vessel (insert). To prevent excessive foaming, 5 cm³ of 7 M nitric acid was added in small portions. After gas evolution ceased, an additional 5 cm³ of 7 M nitric acid was added, bringing the total volume to 10 cm³.

- the reaction vessel was sealed with a lid, inserted into the outer autoclave body, and placed in a steel clamping device. The lid of the outer body was secured with a screw to ensure tight sealing.

- the autoclaves were then placed in a drying oven preheated to 160 ± 5 °C and maintained for 2.5 hours from the moment the target temperature was reached. After completion of digestion, the autoclaves were cooled to room temperature.

- subsequently, the autoclaves were depressurized, the reaction vessels were removed, their outer surfaces wiped with water-moistened cotton followed by ethanol, and the lids were opened. The solutions were quantitatively transferred into centrifuge tubes and centrifuged for 10 minutes at a rotation speed of 4000–6000 rpm.

- the supernatant was transferred into a volumetric tube. The residue was treated with 4–5 cm³ of 7 M nitric acid, mixed with a Teflon rod, and centrifuged again.

- the supernatant and wash solution were combined, and the volume was adjusted to 15 cm³ with 7 M nitric acid, mixed thoroughly, and transferred into tubes.

- immediately before analysis, all solutions obtained after autoclave digestion were diluted 100-fold with deionized water. Dilution was performed using a dispenser with disposable tips or by means of volumetric pipettes and a burette.

3 Results and Discussion

Soil samples were analyzed for a wide range of chemical elements, from which the priority pollutants characteristic of typical cement plants were identified, and the mean concentrations of the chemical elements were determined (Table 1). Based on the mean concentrations across all studied sampling sites, the elements in soil are arranged in the following descending order (mg/kg):

Ca ($50,000 \pm 10,000$) > Fe ($22,000 \pm 4,400$) > Al ($11,000 \pm 2,200$) > Mg ($2,900 \pm 600$) > Mn (420 ± 84) > Ba (280 ± 57) > Zn (84 ± 17) > Cu (23 ± 4.7) > Pb (17 ± 3.5) > Ni (11 ± 2.3) > As (8.5 ± 1.7) > Co (5 ± 1) > Cd (0.4 ± 0.6).

The assessment of the ecological–geochemical specialization of the study area [11] was carried out by calculating the concentration factor (Clarke ratio), that is, by determining the ratio of

the content of a chemical element in the soil to its Clarke value in the upper continental crust (Table 2), according to the following formula:

$$K_c = C/K$$

where K_c is the Clarke concentration factor of the element,

C is the content of the chemical element in a given type of rock (mg/kg).

Based on the calculated Clarke concentration factors, the chemical elements are arranged in the following descending order:

$K_c(\text{As}) = 1.518 > K_c(\text{Ca}) = 1.285 > K_c(\text{Zn}) = 1.12 > K_c(\text{Pb}) = 1.00 > K_c(\text{Cd}) = 0.625 > K_c(\text{Cu}) = 0.59 > K_c(\text{Ba}) = 0.549 > K_c(\text{Mn}) = 0.545 > K_c(\text{Fe}) = 0.542 > K_c(\text{Co}) = 0.294 > K_c(\text{Ni}) = 0.22 > K_c(\text{Mg}) = 0.164 > K_c(\text{Al}) = 0.145$.

Table 1 – Total Concentrations of Chemical Elements in the Collected Soil Samples, mg/kg

Sampling Point	Elements												
	Cd	Co	As	Ni	Pb	Cu	Zn	Ba	Mn	Mg	Al	Fe	Ca
North – 1000 m	1,2±0,2	8,8±1,8	24,0±4,8	18,0±3,6	57,0±11,0	68,0±14,0	270,0±53,0	470,0±94,0	440,0±87,0	4500,0±900,0	16000,0±3200,0	27000,0±5400,0	100000,0±20000,0
West – 1000 m	0,4±0,1	4,3±0,9	11,0±2,2	8,8±1,8	29,0±5,9	29,0±5,9	100,0±20,0	740,0±150,0	720,0±150,0	2000,0±390,0	7200,0±1400,0	41000,0±8300,0	100000,0±21000,0
West – 1500 m	0,10±0,02	3,7±0,7	3,3±0,7	11,0±2,1	4,8,0±1,0	6,9±1,4	22,0±4,4	91,0±18,0	310,0±61,0	3000,0±600,0	10000,0±2100,0	16000,0±3200,0	9600,0±1900,0
West – 1950 m	0,10±0,01	2,6±0,5	2,5±0,5	8,0±1,6	3,5±0,7	5,2±1,0	17,0±3,5	64,0±13,0	220,0±44,0	2100,0±420,0	6900,0±1400,0	13000,0±2700,0	8100,0±1600,0
East – 960 m	0,20±0,04	6,1±1,2	7,2±1,4	12,0±2,4	12,0±2,5	19,0±3,9	78,0±16,0	250,0±50,0	620,0±120,0	3100,0±620,0	11000,0±2200,0	26000,0±5100,0	75000,0±15000,0
South – 1000 m	0,4±0,1	6,3±1,3	11,0±2,1	14,0±2,8	20,0±4,1	39,0±7,8	110,0±21,0	350,0±71,0	280,0±56,0	2500,0±500,0	12000,0±2400,0	17000,0±3400,0	64000,0±13000,0
Cement Settlement – 2000 m	0,20±0,04	4,4±0,9	6,2±1,3	12,0±2,4	9,3±1,9	13,0±2,6	49,0±9,8	210,0±41,0	440,0±87,0	3700,0±740,0	12000,0±2500,0	21000,0±4200,0	34000,0±6800,0
Background Site (Mirmy Settlement) – 6700 m	0,2±0,1	3,6±0,7	2,7±0,6	10,0±2,0	3,2±0,6	6,5±1,3	23,0±4,7	75,0±15,0	310,0±63,0	2900,0±590,0	10000,0±2100,0	13000,0±2500,0	6200,0±1200,0
Average Concentrations	0,4±0,6	5,0±1,0	8,5±1,7	11,0±2,3	17,0±3,5	23,0±4,7	84,0±17,0	280,0±57,0	420,0±84,0	2900,0±600,0	11000,0±2200,0	22000,0±4400,0	50000,0±10000,0

The average contents of elements such as As, Ca, Zn, and Pb exceed the Clarke values for soils worldwide, which may indicate that the rocks composing the area near the plant are enriched in these chemical elements. The results of the study suggest that the geochemical specialization in the vicinity of the plant is primarily associated with arsenic.

To assess the sanitary and hygienic condition of the soil cover in the study area, the total pollution index (**Zc**) was applied. This index represents the sum of the concentration coefficients (**Kc**) of toxicants (pollutants) belonging to hazard classes I, II, and III, calculated relative to their background values.

The total pollution index (**Zc**) was calculated according to the following formula:

$$Z_c = \left(\sum_{i=1}^n K_c \right) - (n - 1)$$

where **Kc** is the concentration coefficient of the *i*-th chemical element, and **n** is the number of elements included in the geochemical association.

The concentration coefficient (**Kc**) was calculated using the formula:

$$K_c = C_i / C_{\text{background}}$$

where C_i is the actual content of the element (mg/kg), and $C_{\text{background}}$ is the geochemical background value (Table 2), mg/kg.

By conducting a comparative analysis of the average concentrations of chemical elements in soils at the sampling sites (Table 1) with the geochemical background concentrations for the soils of Semey (Table 2), the concentration coefficients for a number of chemical elements were calculated (Table 2).

Based on the calculated concentration coefficients, the total pollution index (**Zc**) was determined relative to the geochemical background:

$Z_c = (1,026 + 0.641 + 0,863 + 1,090 + 1,870 + 0,543) - (6 - 1) = 5,392 - 5 = 0,392$, which makes it possible to conclude that the level of contamination falls within the permissible range [12, 13].

However, the average concentrations of certain chemical elements exceed their geochemical background levels (Cd by a factor of 1.02, Cu by a factor of 1.09, and Zn by a factor of 1.87), which confirms soil contamination in the study area by these elements.

A comparative analysis was carried out between the average concentrations of chemical elements in soils at the sampling sites and the maximum permissible concentrations (MPC) of chemical substances in soils [14]. The analysis (Table 2) clearly shows that the average concentrations of the studied chemical elements are below the MPC values, with the exception of arsenic, which exceeds the permissible level by a factor of 4.25.

Table 2 – Summary of Data

Elements	Clarke Values of the Upper Continental Crust, mg/kg	Geochemical Background of Semey Soils, mg/kg [15]	Concentration Coefficient (Kc)	MPC in Soils, mg/kg [14]
Cd	0,64	0,39	1,026	3
Co	17,0	7,8	0,641	100
As	5,6	-		2
Ni	50,0	-		100
Pb	17,0	19,7	0,863	32
Cu	39,0	21,1	1,090	100
Zn	75,0	44,9	1,870	300
Ba	510,0	-		-
Mn	770,0	773,0	0,543	1500
Mg	17700,0	-		-
Al	76100,0	-		-
Fe	40600,0	-		-
Ca	38900,0	-		-

Note: «-» indicates absence of literature data.

4 Conclusion

The analysis of the results of soil sample studies in the vicinity of Site No. 1 “Cement Production” of LLP *Production Company Semey Cement Plant* has shown the following:

1 The chemical elements in the soil across all studied sampling sites, based on their average concentrations, are arranged in the following descending order (mg/kg):

Ca(50000±10000)>Fe(22000±4400)>Al(11000±2200)>Mg(2900±600)>Mn(420±84)>Ba(280±57)>Zn(84±17)>Cu(23±4,7)>Pb(17±3,5)>Ni(11±2,3)>As(8,5±1,7)>Co(5±1)>Cd(0,4±0,6).

2 The high accumulation of Ca in the soils of the studied areas is a result of CaO emissions from the cement plant.

3 The average contents of elements such as As, Ca, Zn, and Pb are several times higher than their Clarke values in global soils, which may indicate that the parent rocks composing the study area are naturally enriched with these chemical elements.

4 The geochemical specialization in the vicinity of the plant is primarily associated with arsenic, which belongs to the group of refractory, non-volatile metals. During clinker firing, these metals are almost entirely absorbed into the clinker and removed from the kiln along with it. In flue gases, they may be present only in the form of dust, and their emissions into the atmosphere depend exclusively on the efficiency of dust-collecting devices.

5 The average concentrations of chemical elements are several times lower than the maximum permissible concentrations (MPC), with the exception of arsenic, which exceeds the MPC by a factor of 4.25.

6 The lead concentration at a distance of 1000 m was found to be 1.78 times higher than the MPC in the northern direction, while in the western direction it was close to the MPC threshold.

7 Out of the eight sampling sites, the most contaminated was the soil sampling point located 1000 m north of the emission source, where elevated concentrations of Cd, Co, As, Ni, Pb, Cu, Zn, Mg, and Al were detected. This sampling point is not prioritized according to the wind rose; however, its proximity to a heavily trafficked highway may have influenced the results, given that the soil was sampled at a depth of up to 5 cm.

8 The sampling point located 1000 m west of the emission source was found to be most contaminated with Ba, Mn, and Fe, while the Ca content was at the same level as that observed at the sampling point 1000 m north of the emission source.

9 The concentrations of chemical elements decreased significantly along the predominant western direction of the wind rose at distances of 1500 m and 1950 m. The presence of a Class I sanitary protection zone (1000 m) is therefore considered optimal for this enterprise.

10 The level of soil contamination, as indicated by the total pollution index, falls within the permissible range. The impact level on the residential area "Cement Settlement," located 2000 m from the emission source, is satisfactory for all studied chemical elements, with the exception of arsenic, which exceeds the MPC by a factor of 3.1.

Thus, the study of the chemical composition of soils in the vicinity of Industrial Site No. 1 of Semey Cement Plant Production Company revealed elevated concentrations of several chemical elements (As, Zn, Pb, Ca, Cu, Cd). This is attributable not only to the production technology but also to the geochemical background of natural origin. These findings highlight the necessity for continuous ecological and geochemical monitoring of the input and distribution of chemical elements within the study area.

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"СЕМЕЙ ЦЕМЕНТ ЗАУЫТЫ ӨНДІРІСТІК КОМПАНИЯСЫ" ЖШС АУДАНЫНДАҒЫ ТЕХНОГЕНДІК ЛАНДШАФТТАРДЫ ЭКОЛОГИЯЛЫҚ- ГЕОХИМИЯЛЫҚ БАҒАЛАУ

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АНДАТПА

Мақалада «Семей цемент зауыты» ӨК ЖШС-ның №1 «Цемент өндіру» алаңының ықпал ету аймағында анықталған ұзақ мерзімді жергілікті геохимиялық аномалияны кешенді зерттеудің нәтижелері ұсынылған. Зерттеу жоғарғы топырақ горизонтының химиялық элементтермен, әсіресе топырақта жиналып, экологиялық қауіп төндіруі мүмкін ауыр металдармен ластану деңгейін бағалау мақсатында жүргізілді. Элементтердің концентрациясын және олардың кеңістіктік таралуын анықтау үшін масс-спектрометрия мен атом-эмиссиялық спектрометрияның заманауи жоғары дәлдікті әдістері қолданылды. Алынған деректер ғылыми әдебиеттердегі мәліметтермен және бұрын жүргізілген зерттеулермен салыстырылып,