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Original Research

Assessment of Soil Contamination by Heavy Metals: A Case of Turkistan Region

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Abstract

The ecological situation continues to remain very tense in the Turkistan region, which is associated with the consequences of the extensive economic activity of the past decades with the use of outdated technologies, as well as the urbanization of the city of Shymkent. The aim: to determine the impact of industrial pollution on the state of soils in technogenic landscapes. Objectives: (1) to identify polluted industrial areas in the Turkistan region; (2) to distinguish the primary pollutants emitted from industries in the Turkistan region; and (3) to assess the state of soil in industrial areas of the Turkistan region. To obtain a qualitative analysis of the soil, the method of atomic absorption spectrometry was used, then the method of a scanning electron microscope was used to obtain enlarged images and morphology of the soil. The scanning electron microscope made it possible to obtain quantitative data on the elements contained in soils. The examined soil specimens were found to have very low concentrations of metals, such as aluminum (Al), silicon (Si), phosphorus (P), sulfur (S), and titanium (Ti). The primary pollutants (Pb, Zn, Cu, and Cd) were determined. These metals were present in concentrations that significantly exceeded the regional background values.

Keywords: heavy metal pollution, soil, soil contamination, urban

Introduction

Heavy metals are already the second most hazardous substances, yielding to pesticides and significantly ahead of such well-known pollutants as carbon dioxide and sulfur. Heavy metal contamination is associated with their widespread use in industrial production [1]. In connection with imperfect cleaning systems, heavy metals enter the environment, including the soil, polluting and poisoning it. Heavy metals are special pollutants that must be monitored in all environments because they can persist for a long time as a result of poor disposal in landfills and industrial waste, which is especially relevant for the republics of the former Soviet Union [2].

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Many heavy metals have high biological activity and are able to accumulate in natural environments, including the human body. This accumulation takes place and at concentrations much lower than the maximum permissible, especially in children. The greatest danger to humans and the environment is from mercury and lead [3]. They are alien to bio-organisms in any content and therefore are included in the list of the main pollutants (global eco-toxicants) by a number of international organizations [4, 5]. Essential elements such as Zn and C can also exhibit toxic effects at elevated concentrations.

Among the pollutants, the hazardous heavy metals such as arsenic (As), cadmium (Cd), lead (Pb), copper (Cu), chromium (Cr), nickel (Ni), zinc (Zn), aluminum (Al), and manganese (Mn) have known to be the major threats to the environment [6-8] and human health [8-10].

First of all, heavy metals change the biological activity of the soil. Microscopic fungi, ammonifiers, nitrogen-fixing bacteria, and enzymes that control the catalase, invertase, and cellulose activity of the soil were found the most sensitive. The general indicator of soil life or biological activity is soil respiration. When soil is mildly polluted (plants continue to grow), heavy metals, primarily Cr, stimulate the microbiological activity and enhance soil respiration (the production of carbon dioxide). Consequently, soil loses humus. In addition, chromium depreciates the catalase activity of the dark-colored soil, rich in humus [1, 11-16].

Today, the massive increase in industrial production is accompanied by the release of high loads of heavy metals into the environment. A substantial portion of these contaminants spread around the pollution source, resulting in the emergence of geochemical human-induced perturbations across a landscape. Other portion of chemical elements is carried away from the pollution source by natural forces, which leads to the contamination of new areas.

The major anthropogenic sources of soil pollution by heavy metals are thermal power stations, transport, and chemical controls used in agriculture. Plants grown in contaminated soils accumulate an excessive amount of heavy metals beyond the maximum permissible level (MPL). Metals such as zinc, lead, and cadmium are more readily taken up by plants when compared to other micronutrients; therefore, the risks of absorbing a hazardous concentration of these metals is higher [17].

Most studies determine the contents of heavy metals and other chemical elements in soil using physical methods and atomic absorption spectrometry [2, 18-20]. One of the indicators of soil environmental quality is the presence of essential micronutrients under the maximum permissible level (MPL). According to soil quality assessments [21-24], some metals (Cd, Pb, Cu, Zn, and Cr) found around large industrial enterprises and along highway corridors in urban areas exceed their MPLs.

The problem of intoxication with heavy metals is very relevant for the territory of the Turkistan region, where there are large sources of pollution: chemical plants and enterprises. Therefore, it is extremely important to control the content of Hg and other heavy metals in the environment. There are no comprehensive studies on the distribution of heavy metals in soils in this region, which determined the relevance of this study, the nearest region is Armenia [22]. The aim of the study was to investigate the peculiarities of heavy metals accumulation in soils of Turkestan on the example of Turkestan region and Shimkent city. To obtain the necessary information, a comprehensive approach was used - a combination of standard techniques for determining the concentration of heavy metals [25-32] and methods of atomic sorption spectrometry, as well as the method of obtaining images using a scanning electron microscope.

The objectives of the study were to: (1) determine the contents of heavy metals in soils from some parts of the Turkistan region and the city of Shymkent; (2) identify the natural or anthropogenic sources of heavy metal contaminants through principal component analysis; and (3) determine the levels of heavy metal contamination of topsoils through scanning electron microscopy (SEM) tests. The results of the study may be relevant to urban planners and environmental risk managers seeking to promote responsible, environmentally friendly strategies for economic development.

Material and Methods

Location and Object of Study

All studies were carried out on soil samples from the Turkistan region (latitude 43°00′N, longitude 68°30′E) and Shymkent 42°18′N w. 69°36′E d. The total land area of the region is 116.280 km², 4.3% of the country's territory. The straight-line distance between the most northern and southern points of the region is 600 km. Turkistan consists of 13 districts and 3 cities of regional subordination. Turkistan region was founded on March 10, 1932 as the South Kazak region, the name of which was changed to South Kazakhstan in 1936. From May 3, 1962 to July 6, 1992, the region was called Shymkent, and in 1992 the name of the region was returned to South Kazakhstan. On June 19, 2018, by the decree of the President of Kazakhstan, the South Kazakhstan region was renamed into Turkistan, and its administrative center was moved from Shymkent to Turkistan; Shymkent was removed from the South Kazakhstan region, having received the status of a city of republican significance (a separate administrative-territorial unit, equal to the region). The authors include 2 factories as research objects which are located in Shymkent - phosphorus factory and lead factory.

At present, the major source of soil contamination in the Turkistan region is the Shymkent lead factory, which annually emits 677.7 tons of lead, 1.660 tons of other heavy metals, 18.000 tons of sulfur dioxide, 21.000 tons of carbon dioxide, and 0.47 tons of chemical substances [33-35].

The landscape of southern Kazakhstan has some diversity: its plains are broken by lowlands and mountains of varying heights, and sandy areas are present. The diversity of landscape patterns not only affects the climate but also affects the soil environment. For instance, plain soils and mountain soils both can be found in the southern part of the country. At the same time, a substantial portion of the southern Kazakhstan is desert with very small air humidity (0.1 to 0.05) and 80-150 mm of rainfall per year [36, 37].

Soil Sampling and Analysis

Soil samples were taken at different locations in the city of Shymkent and Turkistan region: around industrial sites (phosphorus, cement, and lead factories), around polymetal factories on Achysai and Baizhansai, along Kentau transform factory. Sources of pollution as well as the presence of erosion were determined through reconnaissance survey, the preliminary examination of the region.

The soil sampling was performed according to ISO 10381 and GOST, the Russian state standard for soil sampling [27-32]. Samples were collected from different soil layers and the morphogenetic properties of soils were determined.

The soil tests were run by different procedures. The humus level was determined according to Tyurin [38]. The content of nitrogen was measured by the Kjeldahl method [39]. The content of phosphorus was assessed using the Ginsburg and Shcheglova methods [40]. The total potassium content of soil was evaluated using Smith method [41]. The hydrolyzable nitrogen content was determined with the help of the Tyurin-Kononova method [38]. The content of mobile phosphorus was assessed by the Machigin method [42]. The content of mobile potassium was assessed using modified Grabarov method [43]. For pH measurement, the potentiometric method was used [43]. The absorbed bases (Ca and Mg) were determined by the trilonometric method [43]. Granulometric composition was determined by pipette method using pyrophosphate method of probe preparation (modified by Grabarov) and micro aggregate analysis by Kachinskiy [43]. The specific gravity of soil was determined by using a pycnometer and the bulk density of the soil specimen was determined with the help of a cylindrical drill (50 m^3) by Kachinsky [43].

Samples were tested for qualitative content on atomic absorption spectrometry at IRLIP laboratory. According to the amount of absorption, the authors found a ratio between absorption and concentration of elements; thus, elements with high absorption were highlighted.

The contents of heavy metals were evaluated by scanning electron microscopy using a JSM-6460LV scanning electron microscope (Jeol, Japan).

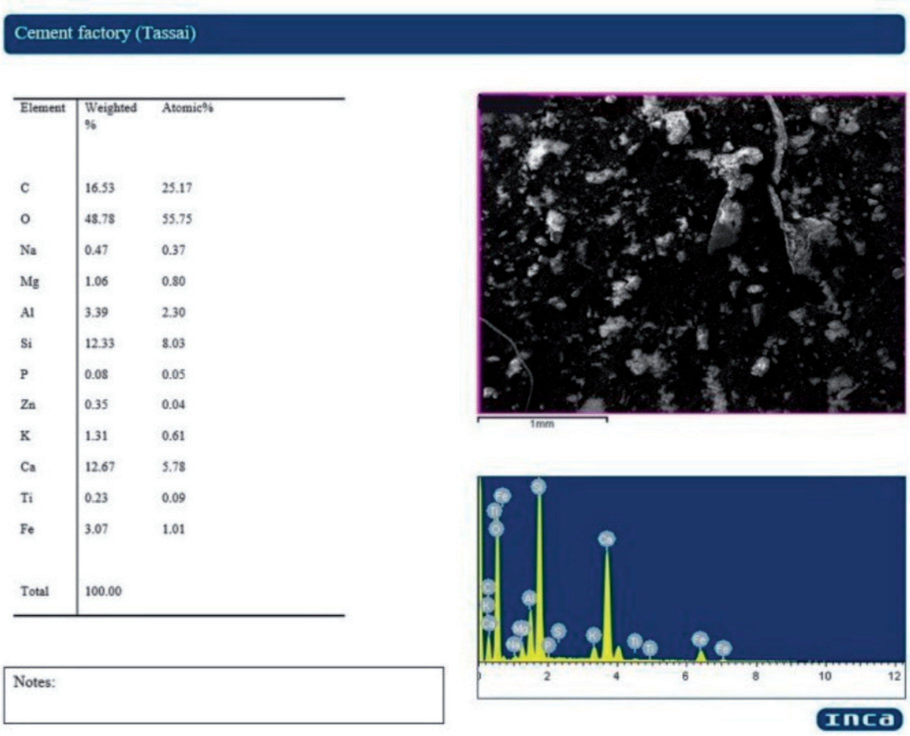
Results and Discussion

The results of heavy metal soil tests for different areas are depicted in Table 1 and Figs 1-6. As can be seen by the data below, the amounts of elements such as Na, Al, Si, P, S, Ti, C, O, Mg, Ca, and Fe were below the level of concern.

According to data in Table 1, some elements (Al, Si, P, S, and Ti) were found in concentrations lower than the permissible levels ($p \leq 0.05$, in all cases 10x repetition). The only exception is the sample of soil from the phosphorus factory where the content of phosphorus was found to be beyond the guideline value ($p \geq 0.05$). The low quantity of silicon in soil leads to the emergence of Si deficiency symptoms in cultivated plants, such as the weak root system, small leaf size, late blossoming, low resistance to adverse environmental factors, and poor yields. This deficiency of micronutrients (Table 1) suggests that areas under investigation have soils with decreased fertility and the elevated level of phosphorus around the phosphorus factory indicates the presence of soil contamination.

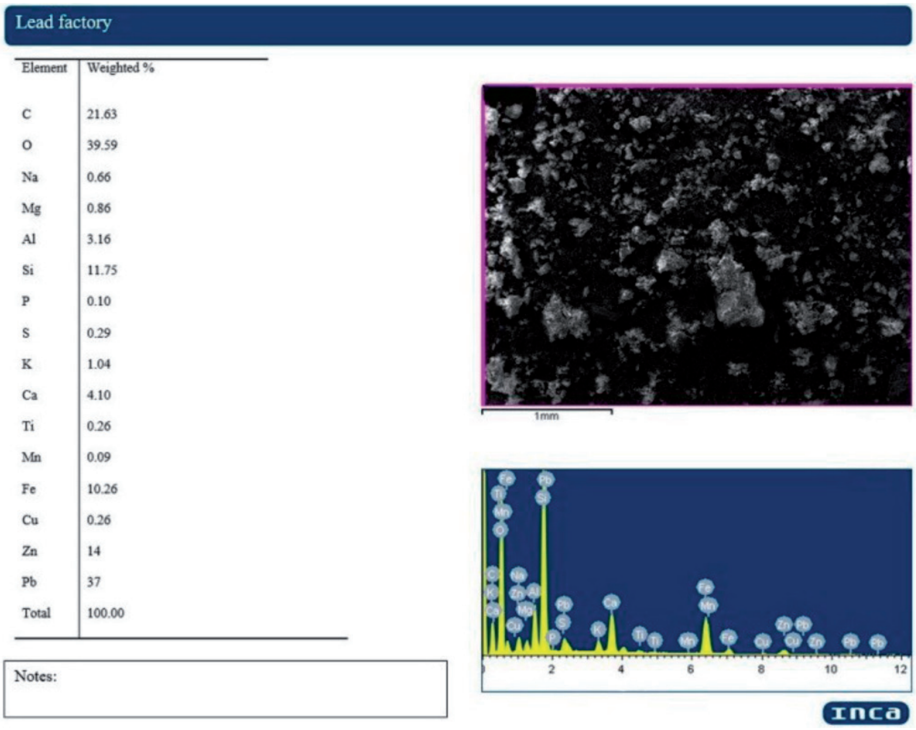
Table 1. The contents of heavy metals in the examined soil specimens.

Sampling site	Al	Si	P	Zn	Pb	Ti
Cement factory	3.39	12.33	0.08	0.35	0.14	0.23
Lead factory	3.16	11.75	0.10	14	37	0.26
Achisai Polymetallic Combine	4.94	18.39		24.01	0.74	0.33
Bayzhansayskoe deposits of ores	5.07	16.5	0.06	22.94	3.02	0.34
Kentau transformer factory	6.65	24.24		2.96	2.84	0.46
Phosphorus factory	5.06	16.28	1.25	1.41	0.41	0.31
Permissible concentration	-	-	-	23	32.0	-



Element	Weighted %	Atomic%
C	16.53	25.17
O	48.78	55.75
Na	0.47	0.37
Mg	1.06	0.80
Al	3.39	2.30
Si	12.33	8.03
P	0.08	0.05
Zn	0.35	0.04
K	1.31	0.61
Ca	12.67	5.78
Ti	0.23	0.09
Fe	3.07	1.01
Total	100.00	

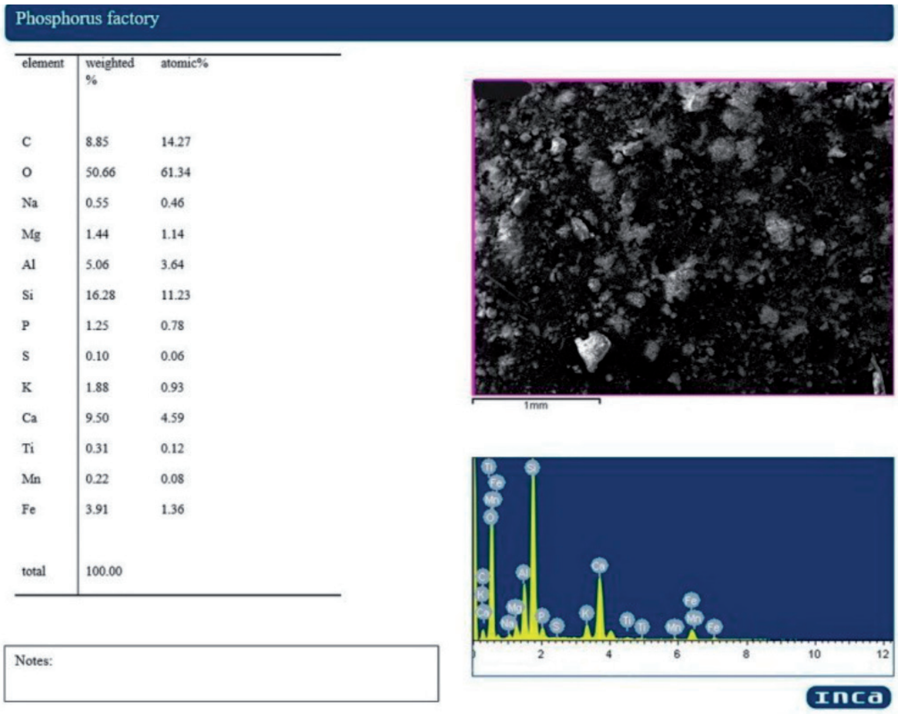
Fig. 1. SEM and EDAX images of the examined metals in soil samples from the area around the cement factory, Tassai.



Element	Weighted %
C	21.63
O	39.59
Na	0.66
Mg	0.86
Al	3.16
Si	11.75
P	0.10
S	0.29
K	1.04
Ca	4.10
Ti	0.26
Mn	0.09
Fe	10.26
Cu	0.26
Zn	14
Pb	37
Total	100.00

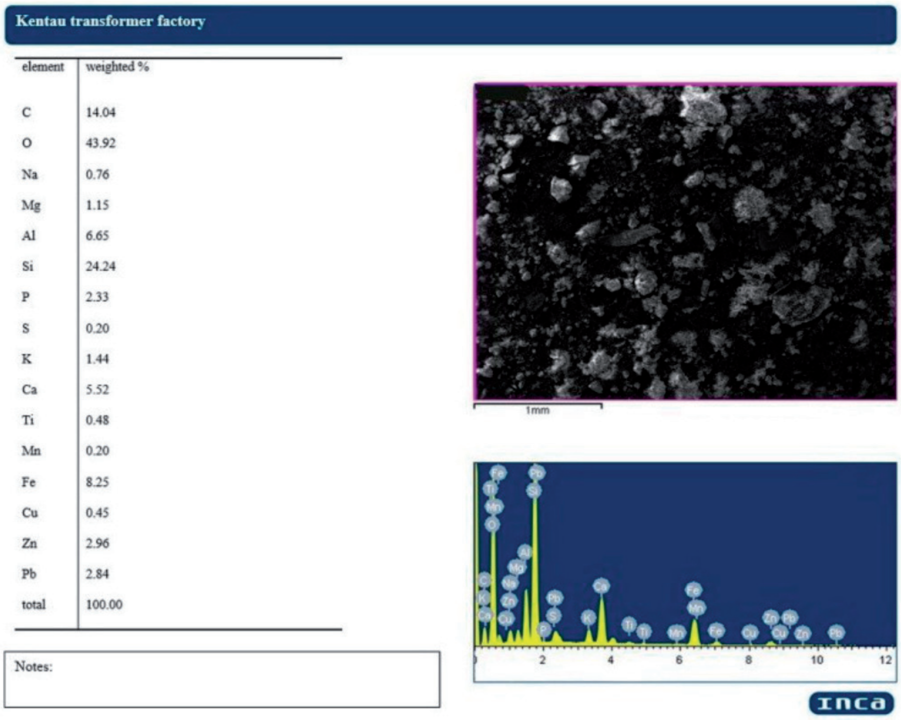
Fig. 2. SEM and EDAX images of the examined metals in soil samples from the area around the lead factory.

According to data in Figs 4-6, 4 out of 5 areas under investigation were contaminated with elevated amounts of metals such as Na, Mg, K, and Ca. In particular, the content of sodium (Na) around the lead and phosphorus factories, as well as along the highway corridor (lead factory) was higher than the permissible level ($p \leq 0.05$). The contents of Na in soils around the cement factory were found to be lower than the permissible level ($p \leq 0.05$). The elevated concentration of mobile sodium in soil can disrupt its physical and chemical composition.



element	weighted %	atomic%
C	8.85	14.27
O	50.66	61.34
Na	0.55	0.46
Mg	1.44	1.14
Al	5.06	3.64
Si	16.28	11.23
P	1.25	0.78
S	0.10	0.06
K	1.88	0.93
Ca	9.50	4.59
Ti	0.31	0.12
Mn	0.22	0.08
Fe	3.91	1.36
total	100.00	

Fig. 3. SEM and EDAX images of the examined metals in soil samples from the area around the phosphorus factory.



element	weighted %
C	14.04
O	43.92
Na	0.76
Mg	1.15
Al	6.65
Si	24.24
P	2.33
S	0.20
K	1.44
Ca	5.52
Ti	0.48
Mn	0.20
Fe	8.25
Cu	0.45
Zn	2.96
Pb	2.84
total	100.00

Fig. 4. SEM and EDAX images of the examined metals in soil samples from the area around the Kentau transformer factory.

Mg concentrations obtained from each soil sample collected exceeded the threshold of 0.63% ($p \leq 0.05$). A decline in magnesium along with the reduction of organic content in soil can enhance its negative properties. The highest Mg concentration was discovered in soil samples from areas around the lead factory ($p \leq 0.05$). This elevation in Mg may be associated with the practice of bismuth extraction, which is performed using magnesium and calcium. Ca concentrations were found to be higher than the 1.37% threshold in all the soil samples under study ($p \leq 0.05$). As expected, the highest Ca concentrations were found in soil samples from areas around the cement factory. Since calcium is commonly used in the manufacture of cement,

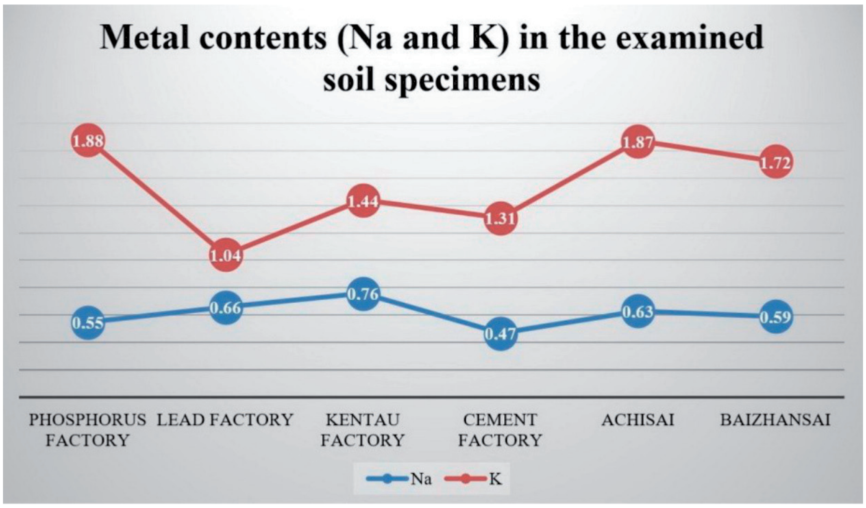


Fig. 5. Metal contents (Na and K) in the examined soil specimens.

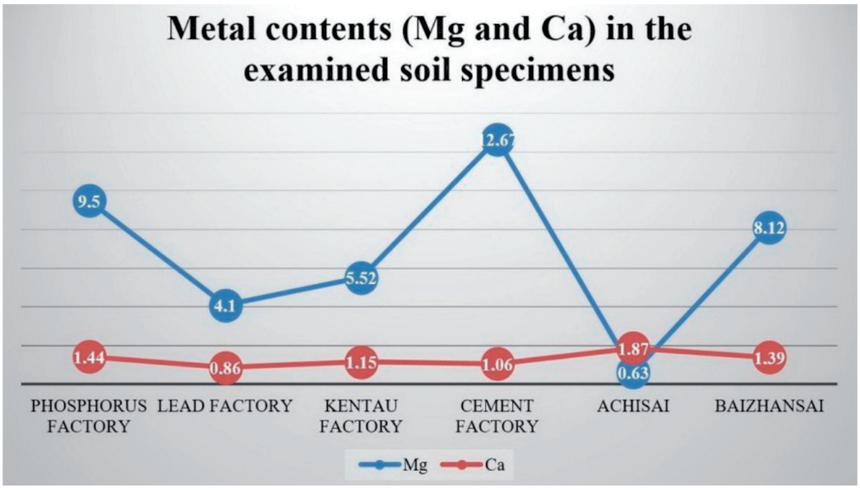


Fig. 6. Metal contents (Mg and Ca) in the examined soil specimens.

its concentrations around the cement-manufacturing units is often elevated. The high content of Ca also was found in soil samples from the lead factory ($p \leq 0.05$). Too much calcium in the soil may result in chlorosis and the depletion of boron. Excess calcium also inhibits the uptake of trace elements by plants. In general, the optimal ratio of calcium to magnesium should be 5:1 to enhance the growth of plants, yet it was found to be below this level.

The analysis of soil specimens from industrial sites and the highway roadside suggests that the said territories experience a decrease in soil fertility. Among all tested specimens, samples from the territory around the phosphorus factory had the highest contents of aluminum, silicon, phosphorus, sulfur, and potassium. At the same time, these samples contained the least amount of calcium. These findings may be useful in preventing and reducing the heavy metal soil pollution.

Although only topsoil from a depth of 0~20 cm was collected in this study, while samples were collected from 0 to 5 or 0 to 10 cm and from areas with different land uses in other studies, the relatively lower concentrations of heavy metals in the soils in Kentau could be the result of a shorter accumulation time and lower rate. Certainly, the deeper sampling depth of this study may also influence the concentration levels. Compared to average concentrations in urban soils, phosphorus concentrations in topsoil samples near phosphorus factories are slightly lower but are comparable to those measured in other parts of the world, except for Shenzhen. The concentrations of Ti in the analyzed samples are also generally lower than those reported in studies of metropolitan areas in some big cities, such as Chengdu, Central Jordan and Sicily, and are comparable to those measured in some other parts of the world.

In the past 5 years, there has been a great deal of interest in soil contamination by heavy metals caused by industrial operations. For example, Zhang et al. [44] assessed the impact of coal mining on the spatial distribution of potentially toxic metals in arable farmlands across the Shandong Province, China. The results showed that the concentration of the tested toxic metals declined to the following order: Cd, Ni, Cr, Zn, Cu, and Pb. Jiang et al. [45] looked at the concentrations of metals (Hg, As, Ni, Pb, Cd, Cr, Cu, and Zn) in soil, groundwater, air, and plants (wheat and maize) cultivated in a village located near a battery factory in Xinxiang (Henan Province, China). The authors found that some metals (Cd, Ni, and As) came from industrial sources, such as wastewater for irrigation and sludge generated from battery industry, whilst other metals (Pb and Cr) originated from agricultural sources. Chen et al. [46] collected 90 soil samples from varying depths (0-20, 20-40, 40-60 cm) and 120 gridded plant samples from coal waste reclamation areas in Huainan, China, to investigate the concentrations and distribution features of toxic elements in soils and plants.

Previous studies of soil revealed high concentrations of lead (1800 mg/kg), zinc (410 mg/kg), cadmium (93 mg/kg), and copper (62 mg/kg) [47, 48]. The studies conducted 1.5 km away from the Shymkent lead factory found out that soils exposed to industrial waste (oils, dyes, petroleum products, phosphates, lead, arsenic, etc.) discharged by the factory contained 40 times more cadmium than it was considered acceptable [3]. According to field measurements [49, 50], soil contaminants such as sulfur dioxide and other sulfur compounds are often accompanied by released gases and fine particles, such as ash, limestone dust, and heavy metal particles from industrial plants.

Among the many problems currently facing humanity, one of the first places is occupied by the problem of environmental pollution by various chemical substances - products of technogenesis, most of which accumulate in the soil. Heavy metals occupy a significant place among the pollutants. The main factor in the severity of this environmental situation remains the high concentration of nature-polluting and nature-destroying industries. Ferrous and non-ferrous metallurgy, chemical and mining industries, mechanical engineering and others are dominant environmentally hazardous industries. Anthropogenic soils differ from natural soils in chemical and water-physical properties. They are mixed with construction waste, household waste, which is why they have a higher alkalinity than their natural counterparts. The main part of pollutants enters urban soils with atmospheric precipitation, from places of industrial and domestic waste. Particularly dangerous is soil pollution with heavy metals. To assess the content of heavy metals (copper, nickel, zinc, lead) in natural and anthropogenic soils of the Turkistan region, the content was measured using a scanning electron microscope. This method can be described as follows. The electrons of the probe (beam) interact with the sample material and generate various types of signals: secondary electrons, back-reflected electrons, Auger electrons, X-rays, light radiation (cathodoluminescence), etc. These signals are carriers of information about the topography and material of the sample. From the measurement results, it can be seen that the highest content of heavy metals in the soil is observed directly near the source of pollution. The uneven distribution occurs due to the different intensity of the anthropogenic factor in the places of measurements. It is in the cities and the territories closest to them that industrial production and agricultural zones are concentrated. The most obvious pollution is found in the anthropogenic soils of Ashysai, Baizhansai and the Lead Plant in Shymkent, which is associated with the developed industry in these areas, intensive agriculture and an extensive developed network of roads.

Thus, according to the present research, there is a noticeably increased content of heavy metals in the soil in many areas of the Turkistan region. However, a significant excess of permissible standards is observed in close proximity to large industrial enterprises, based on which it can be concluded that the pollution is narrowly localized. Basically, on the territory of the Turkistan region, the content of heavy metals in the soil is within the normal range. However, according to forecasts, taking into account the constant growth of the industry and the increase in road congestion, the situation may change for the worse.

Conclusions

It was found that Mg concentrations in each collected soil sample exceeded the threshold value by 0.63% ($p \leq 0.05$). The maximum Mg concentration was found in soil samples from areas near the lead plant ($p \leq 0.05$). Ca concentrations above the threshold value of 1.37% were observed in all soil samples studied ($p \leq 0.05$) near the cement plant, as well as in soil samples from the lead plant ($p \leq 0.05$).

This study presents the results of soil contamination tests conducted in the Turkistan region and Shymkent. Some metals (Na, Mg, K, and Ca) were found to be elevated in samples taken at 6 sampling sites. Namely, the elevated concentrations of Na were detected in samples collected around the lead and phosphorus factories and along the highway corridor. The highest concentrations of Mg were found in the samples from the lead factory. The highest Ca concentrations were detected in samples taken near the cement factory. Some metals (Al, Si, P, S, and Ti) were found to be lower that the recommended thresholds. Among other things, this poses a risk of declining yields. Samples from the territory around the phosphorus factory were higher in Al, Si, P, S, and K when compared to samples from other sites.

The principle of operation of the SEM Jeol has been studied. An increased content of heavy metals (copper, zinc, lead) was revealed in the soil samples of Ashysai, Baizhansai and the former lead plant in the city of Shymkent, which is associated with the location of large industrial enterprises in these areas.

Based on the cartogram of soil contamination with heavy metals in the Turkistan region, Ashchysai, Kentau, Phosphorus plant belong to the zone of medium pollution, and the lead plant and Baizhansai belong to the zone of high pollution.

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Conflict of Interest

The authors declare no conflict of interest.

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