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Soil Pollution with Heavy Metals in the Turkestan Region

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ABSTRACT
Toxic pollutants of industrial origin can be dangerous for professionals who come into contact with them at work, and also for the people who live near the sources of environmental hazards. There is a known relationship between the soil pollution with heavy metals and the morbidity of the population. This paper reports a study of the soil pollution with ions of heavy metals in the Turkestan region, Kazakhstan. The study found technogenic geochemical anomalies of various size, intensity and origin in the soils of the Turkestan region. The distribution of lead, copper, barium, zinc, molybdenum, phosphorus and arsenic was mapped based on the ecological and geochemical survey of the upper soil layer. The most polluted city is Kentau, where concentrations of Pb, Mo, Cu, Zn, As, Cd, Mn, Cr, Ni in the soil exceed the allowable level. The cause of pollution is erosion that occurs in the areas of technogenic waste storage. In some communities, the concentration of only one metal exceeded its MAC or the Clarke number, for example, only scandium exceeded its Clarke number by 1.1 in Lenger and only exceeded its Clarke number by 2.75 in Sholakkorgan.

Keywords: soil, heavy metal, distribution map, maximum allowable concentration, Clarke value, industrial pollutant, Turkestan region.

INTRODUCTION

Understanding how metals are distributed in the environment and why their concentration increases in some locations is an urgent environmental issue. The anthropogenic input of heavy metals into the environment has sharply increased over the past century. It comes not only from the continuously growing volumes of metal production, but also from the erosion processes that occur at the mineral and technogenic waste storage sites (Barbiery, 2016; Moiseenko, 2017). Many factors determine the distribution of chemical elements in natural environments. In the absence of anthropogenic load, the content of chemical elements and their compounds in natural substrates depend on the composition of such substrates and the natural conditions that cause the accumulation and the migration of matter (Väänänena et al., 2018; Moiseenko, 2019). Such conditions include meteorological situation, landscape, geochemical background, water migration in the hypergene conditions and others. The element distribution in the environment can also be steered by such physicochemical processes as diffusion, infiltration, mechanical transfer, biochemical and chemical reactions (Wang et al., 2015; Moiseenko et al., 2019). The rate of change in the element concentration is hardly noticeable under natural conditions when the relative equilibrium of occurring processes prevails in nature.

In industrial areas, the natural balance is disturbed in all geospheres under intense anthropogenic load. Pollution occurs in production activities of all types. The disturbance of the soil cover is predominantly mechanical: by changing the natural landscape during the construction of utility infrastructure, structures, tailing dumps, ash dumps and otherfacilities. This shapes a technogenic landscape with different properties compared to the natural one.

Contamination of natural environments under technogenic conditions occurs in several ways. Air flows carry some of the pollutant away in the form of dust and gaseous emissions, and it settles on the ground, forming technogenic dispersion halos. They have much higher concentrations of the pollutant than the natural environment and can be rather large, depending on the intensity of emissions and atmospheric conditions of the area. Chemical substances, falling on the soil cover, accumulate or migrate according to the landscape-geochemical setting of the area (Pooladi & Bazargan-Lari, 2020).

Contamination of the soil cover from the hydrosphere is carried out by the transfer of chemicals by hydrodynamic phenomena. The under-ground and above-ground flows filter these substances into the surrounding rocks and soil (Kurwadkar et al., 2020; Liu et al., 2021). The hydrogeological, geological and landscape-geochemical conditions in the area determine the size and density of the resulting pollution halos, as K. A. Ghazaryan, H. S. Movsesyan and N. P. Ghazaryan (2017) showed in mining regions of Armenia.

Moreover, significant contributors to soil pollution are landfills of technogenic and household waste often found near production sites, fuel spills, industrial materials scattered around utility infrastructure and other contamination sources that make the formation of stable organometallic compounds possible (Smith et al., 2015; Dinu, 2015; Dinu,2017; Dolev et al. 2020, Yue et al. 2021).

Industrial genotoxic pollutants can be dangerous not only for professionals who come into contact with them because their jobs, but also for local residents who live near sources of environmental hazards. Although thousands of workers are exposed to the negative effects of mutagens and carcinogens at industrial sites, still in the latter case entire communities in industrial regions become vulnerable to a similar, albeit less intense, mutagenic load (Moiseenko et al., 2018).

The spectrum of pollutants specific for each community depends on the character of industrial production, the intensity of traffic, the use of agricultural pesticides and, probably, some other factors caused by climatic and geographical features (temperature regime, prevailing winds, atmospheric precipitation, contamination in deep and surface soils, background radiation). The vast majority of early works devoted to the analysis of spontaneous chromosomal mutagenesis, paid insufficient attention to environmental factors. The distribution of chemical elements in the soil cover reflects pollution processes in all geospheres, complemented by the accumulation of heavy metals in biological objects (Ediagbonya et al., 2015; Merrington et al., 2016; Perez & Hoang, 2017; Tekade et al., 2018, Agrelli et al., 2020). The role of plants and microorganisms in the accumulation of heavy metal ions is also important (Azab & Hegazy, 2020, Benidire et al., 2021; Palm et al., 2021; Simiele et al., 2021). Since the rate of matter migration in the soil is much lower than in other media, the soil composition can point to long-term pollution processes caused by the production activities of industrial enterprises.

A body of studies, Ugonna et al. (2020) and Nkwunonwo et al. (2020) papers among them, revealed the now known causal relationship between the level of soil pollution by various ecotoxicants and the indices of population morbidity. They urged the authors of this paper to study the level of soil pollution with heavy metal ions in the Turkestan region of Kazakhstan.

MATERIALS AND METHODS

The Turkestan region (until June 2018 South Kazakhstan region) is located in the southern part of the Republic of Kazakhstan. It occupies an area of 117,300 km^2 or 4.3% of the territory of Kazakhstan (Environmental Protection, 2018). The distance between the northernmost and the southernmost points in a straight line is 600 km (Figure 1).

In the Turkestan region, there are 13 districts: Baydibek, Keles, Kazygurt, Maktaaral, Ordabasy, Otyrar, Saryagash, Sayram, Sozak, Tole Bi, Tulkibas, Shardara and Zhetisay; and three cities: Turkestan, Kentau and Arys (Administration of Turkestan Regio, 2020). The population of the region amounted to 1,963,400 people as of 1st September 2018. The average population density is 23.8 people per sq km, which is one of the highest in the Republic of Kazakhstan (BNSASPRK, 2020).

The regional center is the city of Turkestan with an area of 19,627 hectares, of which 9800 are built-up. The population of Turkestan is

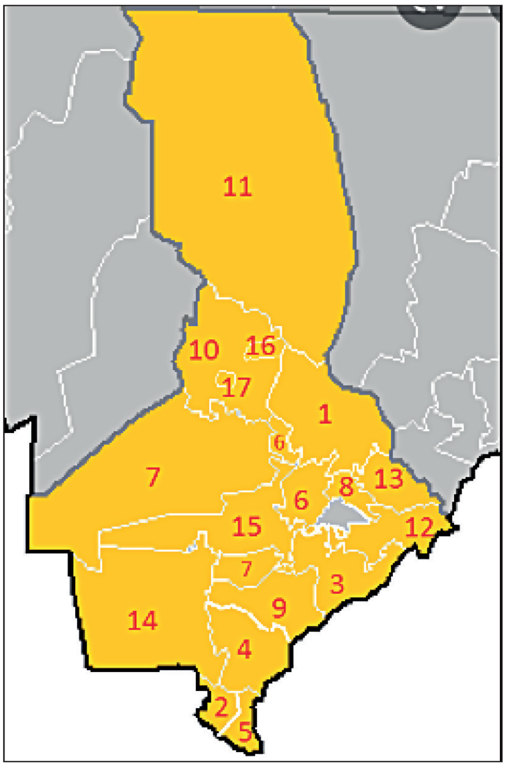

Figure 1. Map of the Turkestan region, Kazakhstan

163,696 people as of 1st September 2018 (Bureau of National Statistics 2018). The industry is concentrated in the western part of the city adjacent to the railway. The Western Europe – Western China International Transit Corridor and the railway main line pass through the city.

Turkestan region includes the following natural zones:

- flat steppes of Betpak-Dala;
- semi-deserts, a transitional zone from steppes to deserts;
- deserts of Moyun-Kum and Kyzyl-Kum;in Turkestan region, the Kyzyl-Kum desert is located between the Syrdarya and the border with Uzbekistan;
- floodplain forests along the Syrdarya and the Arys;
- oases of Kentau, Shymkent and Shardara;
- piedmont steppes, a transition zone from plains to mountains;
- light juniper forests in the Aksu-Zhabagly nature reserve and the Sairam-Ugam national park;
- subalpine and alpine meadows in the mountains of the Western Tien-Shan above the juniper forest belt;
- glaciers and snowfields in the high mountains of the Western Tien-Shan.

The landscapes of the Turkestan region are represented by piedmont, mountain-steppe and steppe zones. The soils in the piedmont and mountain-steppe zones are medium and heavy loamy sierozems and leached heavy loamy sierozems; the soils in the steppe zone are light calcareous medium loamy sierozems.

In total, 105 soil samples were taken in communities of the Turkestan region: 30 samples in Turkestan, 20 samples in Kentau, three samples in Aksukent, three samples in TurarRyskulov, three samples in Lenger, three samples in Kazygurt, three samples in Abay, three samples in Zhetisay, three samples in Myrzakent, three samples in Shardara, three samples in Temirlanovka, three samples in Shaulder, three samples in Shayan, three samples in Sholakkorgan, three samples in Saryagash, three samples in Kyzylsay, three samples in Sastobe, one sample in Baba-ata, one sample in Ybyrai, one sample in Tasty, one sample in Bayaldyr, one sample in Zhuinek, one sample in Orangay, one sample in Shornak, one sample in Yntymak, one sample in Ikhan and one sample in Ibata.

Since the upper soil layer is the main depositor of contaminants from atmospheric precipitation, the soil samples were taken directly from the surface, the vegetation layer removed. The sampling depth was no more than 10 cm. The sampling was performed in accordance with the requirements of standards GOST 17.4.3.01-83 (1983), GOST 28168-89 (1989) and GOST 17.4.4.02-84 (1984).

For chemical elements, which Maximum Allowable Concentrations (MAC) are undetermined, the concentrations were compared to their relative average content in Earth's crust, also called the Clarke number, expressed in weight percent (Kasimov &Vlasov, 2015). On the basis of the analysis of the soil and waste samples, the following works were carried out:

- quantitative characteristics of the chemical composition of the samples was determined;
- the main pollutants were determined and listed;
- a set of ecological and geochemical maps was created, including soil cover pollution maps and composite maps by groups of pollutants;
- the territory was divided into zones by sources and intensity of pollution.

The pollution maps of the survey area were constructed using the algorithms of multiple weighted averaging, and the optimality was assessed according to special criteria of rank approximation.

The office analysis of the soil sampling data was performed following the standard procedure adopted for processing geochemical information. To process the data, a computer technology was used in which special methods of optimization of calculations are applied to maximize the output of useful information. The estimation of statistical parameters (mean and standard deviations) took into account the law of their statistical distribution.

RESULTS AND DISCUSSION

The methodologically indivisible ecogeosystem of Turkestan region can be regarded as a set of functionally interconnected natural environments (soil cover, underground and surface waters, air basin, biosphere). Its current environmental state is subject to the general technogenic load and the impact on these environments of emissions from the lead plant (during its operation) and related industries (production waste, wastewater systems, etc.). Given the industrial development of Turkestan region, the main soil pollutants have been lead, zinc, copper, arsenic and cadmium (Ministry of Energy of Kazakhstan, 2018).

The city of Kentau is known for a high level of heavy metals content in the soil. Having stopped their production in 2008–2009, PK Yuzhpolymetal Joint-Stock Company and Shalkiya Zinc Ltd. Limited Liability Partnership suspended irrigation of the tailing dump—a storage site for processed polymetallic ores that, due to wind erosion, poses a serious threat to the environment and the health of population of Kentau and villages around it (Ecology Department of the South Kazakhstan Region, 2017). However, a more pressing issue is the penetration of mine waters from the Mirgalimsay mine into the underground and surface waters and the resulting pollution of soil resources. The problem lies in the high content of heavy metal ions in these waters, which at one time were used to flood mine voids after ore extraction. Despite the positive findings of long-term monitoring of waters, it is possible that over time the preserved reagents will dissolve in aqueous solutions that can become sources of additional toxic impact on public health.

To make the comparative assessment of pollution of the soil layer with heavy metal ions, the authors referred to their MAC values for arable soils (Table 1). If MACs are complied with, there should be neither direct, nor indirect negative impact on water and air in contact with the soil and, consequently, on human health. The self-cleaning capacity of the soil should also remain unaffected.

Table 1. Maximum allowable concentrations for heavy metals polluting the soil

Metal	MAC in the soil (mg/kg)
Lead (total form)	32.0
Copper (active form)	3.0
Chromium (active form)	6.0
Chromium $^{6+}$	0.05
Manganese (total form)	1500
Vanadium (total form)	150
Nickel (active form)	4.0
Zinc (active form)	23.0
Cadmium (active form)	0.5

It was planned to establish the content of the following elements in the soil samples: Al, Ag, Be, Yb, Mo, Sn, Sc, Ga, Co, Cu, Bi, Ge, Ni, Pb, V, Nb, Au, In, Cd, Y, Pt, Tl, Cr, Zr, W, Li, Mn, Sb, Th, Zn, Hf, Ti, Ta, Sr, Ba, As, Ce, U, B, Te, P, Fe, and La. The laboratory tests showed that the samples did not contain Au, Hf, In, Pt, Ta, Te, Tl, U, Bi, W, Nb, or Sb.

Having studied the distribution of pollutants in the upper soil layer, it was found that almost all chemical elements, which were subject to the analytical determinations in this work, participate in environmental pollution and form technogenic geochemical anomalies of various sizes, intensity and origin in the soils of the Turkestan region.

Anthropogenic pollution of the natural environment in the zone of industrial influence in the region has a very complex and multifaceted character due to the presence of multipleemitters. The main depositor of gas-and-dust emissions is the upper soil layer with a thickness of 1–2 cm that divides the two different natural media and also plays an important role in determining further migration routes in the accumulation of anthropogenic emissions. The deposition layer of atmospheric precipitation is an indicator that captures the general picture of pollution in the region. At the modern instrumental and analytical level, it allows outlining the main trends and patterns of distribution of a number ofelements that are not inherent to the soils in natural landscapes in observed concentrations but come from industrial and economic activities.

On the basis of the ideas of the indicative role of the soil layer, depositing atmospheric gas-and-dust sediments, and the leading part of these

Figure 2. Distribution maps of heavy metal concentration in the soils of the Turkestan region: (a) lead, (b) copper, (c) zinc, (d) barium, (e) molybdenum, (f) phosphorus, (g) arsenic

sediments in environmental pollution, this study made emphasis on the ecological and geochemical survey of the upper soil layer. The constructions were made for the entire region and for the cities of Turkestan and Kentau. The survey results were presented on the distribution maps (Figure 2), where the numerator shows the concentration in mg/kg; the denominator, in MAC or Clarke fractions. The concentration values in the communities where more than one sample were taken, were averaged.

The maps were constructed for those chemical elements whose concentrations exceeded the MAC or Clarke value in more than one community. These elements happened to be lead, zinc, phosphorus, molybdenum, copper, arsenic and barium. In addition, a map reflecting the values of the total pollution index (Zc) was made. The Zc values were calculated for all elements with concentrations above the MAC or Clarke value. The level of pollution is considered allowable if Zc < 16; moderately dangerous if Zc = 16 – 32; dangerous if Zc = 32 – 128; and extremely dangerous if Zc > 128.

The distribution patterns of the main elements were as follows:

Lead. The Clarke number of lead in Earth's crust is 16 ppm (mg/kg); in sedimentary rocks, 20 mg/kg; MAC is 32 mg/kg. The minimum concentration in the studiedregion was 10.91 mg/kg in Sholakkorgan; maximum 398.8 mg/kg in Kentau (exceeding MAC by 12.5). Similar concentrations of 397.5 mg/kg were found in the village of Bayaldyr (exceeding MAC by 12.4) that is located near the city of Kentau. The lead concentrations, exceeding MAC by 1.1 in Turkestan to 3.7 in Ibata, show the degree of soil pollution in communities around the city of Kentau. Obviously, it is a consequence of industrial activities in the city in previous years. A lower degree of soil pollution was found in the villages located in the eastern part of the Turkestan region: Sastobe (exceeding MAC by 1.4), Turar Ryskulov (by 1.4), Aksukent (by 1.3) and Kyzylsay (by 1.5).

Copper. The Clarke number of copper in Earth's crust is 47 mg/kg; in sedimentary rocks, 57 mg/kg. The minimum concentration in the studied region was 15.7 mg/kg in Tasty; maximum 144.33 mg/kg in Bayaldyr (exceeding MAC by 2.57). In Kentau, the average concentration was 53.4 mg/kg (0.94 of Clarke); in Turkestan, 35.3 mg/kg (0.62 of Clarke). In other cities and towns, the average concentrations did not exceed the Clarke number.

Zinc. The Clarke number of zinc in Earth's crust is 83 mg/kg; the average concentration in soil in usually taken as 80 mg/kg. The minimum concentration in the studied region was 34.74 mg/

kg in Tasty; maximum 1,015.55 mg/kg in Bayaldyr (exceeding Clarke by 12.69). In Kentau, the average concentration was 490.5 mg/kg (6.1 of Clarke); in Turkestan, 84.2 mg/kg (exceeding Clarke by 1.1). The zinc concentrations, exceeding the Clarke number by 1.1 in Turkestan to 3.3 in Ibata, show the degree of soil pollution in communities around the city of Kentau. Obviously, it is a consequence of industrial activities in the city in previous years. The soil pollution with zinc was found in the villages located in the eastern part of the Turkestan region: Sastobe (exceeding clarke by 1.8), TurarRyskulov (by 3.2), Aksukent (by 1.4) and Kyzylsay (by 1.3); and also in the southern part in Myrzakent (by 1.54).

Barium. The Clarke number of barium in Earth's crust is 650 mg/kg; in sedimentary rocks, 800 mg/kg. The minimum concentration in the studied region was 469.8 mg/kg in Shaulder; maximum 4,984.3 mg/kg in Bayaldyr (exceeding Clarke by 6.2). In Kentau, the average concentration was 4,550 mg/kg (exceeding Clarke by 5.7); in Turkestan, 999 mg/kg (exceeding clarke by 1.25). The barium concentrations, exceeding the Clarke number by 1.02 in Ybyrai to 1.79 in Orangay, show the degree of soil pollution in communities around the city of Kentau. Obviously, it is a consequence of industrial activities in the city in previous years. The soil pollution with barium was also found in the villages of TurarRyskulov and Kazygurt.

Molybdenum. The Clarke number of molybdenum in Earth's crust is 1.6 mg/kg; in sedimentary rocks, 2 mg/kg. The map shows that the molybdenum concentrations were undetectable in nine communities. The minimum concentration in the studied region was 1.25 mg/kg in Sastobe; maximum 2.94 mg/kg in Myrzakent (exceeding Clarke by 1.5). In Kentau, the average concentration was 2.1 mg/kg (exceeding Clarke by 1.05); in Turkestan, 2.13 mg/kg (exceeding clarke by 1.06). The molybdenum concentrations, exceeding the Clarke number by up to 1.42 in Bayaldyr, show the degree of soil pollution in communities around the city of Kentau. Obviously, it is a consequence of industrial activities in the city in previous years. The soil pollution with molybdenum was also found in the villages of Sholakkorgan, Zhetisay, Temirlanovka, Shayan and Yntymak.

Phosphorus. The Clarke number of phosphorus in Earth's crust is 1,000 mg/kg; in sedimentary rocks, 770 mg/kg. The minimum concentration in the studied region was 408.7 mg/kg in Tasty; maximum 1,704.1 mg/kg in Bayaldyr (exceeding Clarke by 2.21). In Kentau, the average concentration was 949.5 mg/kg (exceeding Clarke by 1.23); in Turkestan, 747.4 mg/kg (0.97 of Clarke). The phosphorus concentrations, exceeding its Clarke number, were observed in 22 of 27 communities. It is likely that this may be due to the naturally increased content of phosphorus in the soil due to high phosphorus content in the underlying rocks (Tleukeyeva et al., 2022).

Arsenic. The Clarke number of arsenic in Earth's crust is 0.4 mg/kg; MAC is 2 mg/kg. The arsenic concentrations were undetectable in 13 communities. The minimum concentration in the studied region was 1.44 mg/kg in Turkestan; maximum 13.42 mg/kg in Bayaldyr (exceeding MAC by 6.71). Similar concentrations were noted in Kentau: 10.72 mg/kg (exceeding Clarke by 5.36). Obviously, it is a consequence of industrial activities in the city in previous years. In other communities, where arsenic was detected, MAC was exceeded by 1.2 to 4.3.

As for the other 22 chemical elements, six of them had unallowable concentrations in one community each:

- cadmium, its MAC exceeded by 5.3 in Kentau;
- silver, its Clarke number exceeded by 1.03 in Sastobe;
- scandium, its Clarke number exceeded by 1.1 in Lenger;
- strontium, its Clarke number exceeded by 2.75 in Sholakkorgan;
- cerium, its Clarke number exceeded by 1.2 in Kazygurt;
- zirconium, its Clarke number exceeded by 1.15 in Kazygurt.

Thus, it was found that in Turkestan the maximum Zc value was 16; the minimum value being zero. The most intense anomalous zone, reaching a maximum of Zc = 16, was noted in the southwestern part of the city. Its epicenter can be categorized as moderately dangerous. In Kentau, the maximum Zc value was 85, the minimum value being five. The most intense anomalous zone, reaching a maximum of Zc = 85, was noted on the western side of the tailing dump outside the city. This anomaly is caused by high concentrations exceeding MAC or the Clarke number of the following chemical elements: Pb, Mo, Cu, Zn, As, Cd, Mn. The second most intense anomalous zone with Zc = 85 was located in the northeastern part of the city behind the railway tracks. This anomaly is caused by high concentrations exceeding MAC or the Clarke number of the following chemical elements: Pb, Mo, Cu, Zn, As, Cd, Mn, Cr, and Ni. These two areas were polluted by the activities of PK Yuzhpolymetal Joint-Stock Company and Shalkiya Zinc Ltd. Limited Liability Partnership. Other parts of the city can be categorized as moderately dangerous with 16 < Zc < 32.

CONCLUSIONS

The study revealed technogenic geochemical anomalies of various size, intensity and origin in the soils of the Turkestan region. The main soil pollutants are Pb, Mo, Cu, Zn, As, Cd, Mn, Cr, and Ni. The highest degree of pollution was found in Kentau, which is due to erosion processes in the waste dumpsleft behind by mining and metallurgical enterprises. In some communities, the concentration of only one metal exceeded its MAC or the Clarke number, for example, only silver exceeded its Clarke number by 1.03 in Sastobe.

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