

Article

Spatial Distribution of Cu, Zn, Pb, Cd, Co, Ni in the Soils of Ili River Delta and State Natural Reserve “Ili-Balkhash”

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Abstract: River delta soils are the final spatial units of the matter flow within the whole river catchment. Due to their spatial position in the catchment and due to their fine grain size composition, river delta soils are important matter sinks in general, especially for heavy metals. The article presents the results of spectrometric analysis of heavy metals in the soils of the Ili River Delta and State Natural Reserve “Ili-Balkhash” in 2021. This area is included in the list of wetlands of international importance under the Convention on Wetlands. Heavy metals in the samples were determined using the flame atomic absorption spectrometric method using the AA-7000 atomic absorption spectrophotometer. The spatial distribution of the metals was visualized in the ArcGIS 10.5 environment. Copper concentrations were measured in the soils of the dry steppe, semi-desert and desert zones with average values up to 28.5 mg kg^{−1} and a maximum level of 75.1 mg kg^{−1}. The concentrations of lead are 8.0–15.9 mg kg^{−1}. The cadmium content exceeds the standards from 2.1 to 6.5 mg kg^{−1} on the whole territory at MPC 2.0 mg kg^{−1}, reaching up to 3.3 MPC (Maximum Permissible Concentration). The cobalt concentration ranges from 6.7 to 20.6 mg kg^{−1}, and nickel ranges from 11.3 to 22.2 mg kg^{−1}. Soil contamination due to cobalt and nickel is observed in the northern and eastern parts of the study area. The received data about pollution of the soil cover by heavy metals makes it possible to assess the degree of anthropogenic load of the unique natural environment in the Ili River Delta and natural reserve.

Keywords: delta; natural reserve; anthropogenic load; soil; heavy metals; contamination; maximum permissible concentration



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1. Introduction

Increased anthropogenic load and the active use of natural resources have led to increased degradation of the environment. The intensive development of human economic activity inevitably leads to negative consequences and environmental side effects [1]. The level of load also differs due to the influence of pollutants on the environmental conditions, water, flora and fauna in different natural zones [2]. As a result of dangerous toxic ecological situations, specific and local environmental disturbances may occur.

In recent decades, the danger of the chemical contamination of soils has sharply increased. Thus, the central link of the ecosystem is experiencing technogenic loads. The environmental and economic damage due to the chemical contamination of soils and agricultural products is enormous [3,4]. The chemical contamination of soils should be understood as the man-made accumulation of chemicals in soils in quantities that pose a danger to living organisms. An especially dangerous situation is created when chemicals

in soils become accumulated and mobile. In this case, they can be directly absorbed by plants at the location of pollution or enter the atmosphere, hydrosphere or food chain. At the final stage, they may reach living organisms and poison them. Moreover, they are transported by water flows to accumulation zones, having direct or indirect harmful effects on organisms [5,6]. Heavy metals belong to the most dangerous chemical substances because they tend to accumulate in soils and sediments, and they cannot be mined or removed. The main anthropogenic sources of heavy metals are predominately industrial wastes, which are represented by the following branches of industry: ferrous and non-ferrous metallurgy, chemical, pulp and paper, construction, mechanical engineering, light and food, energy, petrochemical and oil refining [7,8].

The technogenic intake of heavy metals by industrial waste (aluminum, copper-zinc, lead, nickel, mercury and other plants) in the study area is especially dangerous, for instance, because of waste from the industrial enterprises LLP Balkhash Tuz, Balkhash CHPP, Kazakhmys Corporation, etc.), landfills for disposal of hazardous waste and warehouses for the incineration of hazardous industrial waste, which all are enriched by metals. Scattering areas of heavy metals appear around industrial and manufacturing enterprises also due to emissions into the atmosphere [9]. The maximum soil contamination was observed in the zone up to 5 km from the enterprise, and 10–30% of the total amount of metal in the emission is spread over distances of more than 10 km [10]. Long-range transport occurs as a result of aerosol emissions entering the atmosphere from technogenic sources, which are distributed in the landscape due to the influence of natural factors [11–15]. Pollutants such as heavy metals do have a different distribution tendency in dependence on their chemical and soil properties. In most cases, they tend to accumulate in soils because of their own positive charge and the negative charge of humus and clay minerals.

The degree of the mobility of heavy metals in soils is determined by their granulometric composition, pH, the humus content of the soil and the metal itself and its concentration. A high metal content is characteristic of silty and fine sand fractions of the upper layers of the soil profile. For almost all types of soils, the maximum concentration of metals is observed in layers with heavier granulometric composition, respectively, fine texture. The increased content of toxic elements is observed in silty and sandy fractions, which is associated with the presence of metals in primary minerals in the form of isomorphic impurities as well as industrial dust near enterprises [16]. Two-layered clay minerals can also have a high absorption capacity [17]. Thus, fine textured soils can bind heavy metals as well as contain clay minerals with a large inner surface. The sorption capacity of organic soil matter is very high for Cu and Pb, high for Cd, medium for Co and Ni and low for Zn [18,19]. Most heavy metals can get mobile under acid pH conditions. If the pH is lower than 6 Cd, lower than 5.5 Ni, Co and Zn, lower than 4.5 Cu, and lower than 4 Pb lose their sorption and may get mobile. The element-specific sorption and self-accumulation tendency is very high for Pb, high for Cu and medium for Zn, Co, Ni and Cd [20,21].

According to the World Overview of Conservation Approaches and Technologies in Natural Resources, soil pollution is one of the most dangerous types of land degradation associated with the properties of pollutants capable of long-range transport from local sources of pollution to global dispersion [20]. That is why the purpose of the study is to assess heavy metal soil contamination in the study area and to explore their spatial distribution.

2. Materials and Methods

2.1. Study Area

The study area of the Ili River Delta is the largest natural inland delta in Central Asia. The total area reaches 20 thousand km², of which the modern delta occupies about 8 thousand km², and the rest is an ancient delta with a net of channels—so-called Bakanases (Figure 1). The delta area was included in the Ramsar list of wetlands of international importance under the Convention on Wetlands [21]. The State Natural Reserve, “Ili-Balkhash”, within the area of the Ili River Delta, was created in 2018 in accordance with the decree of the Government of the Republic of Kazakhstan. This area is a unique object, with

a high level of protection, that has no analogs in the world in terms of environmental restoration [22–24].

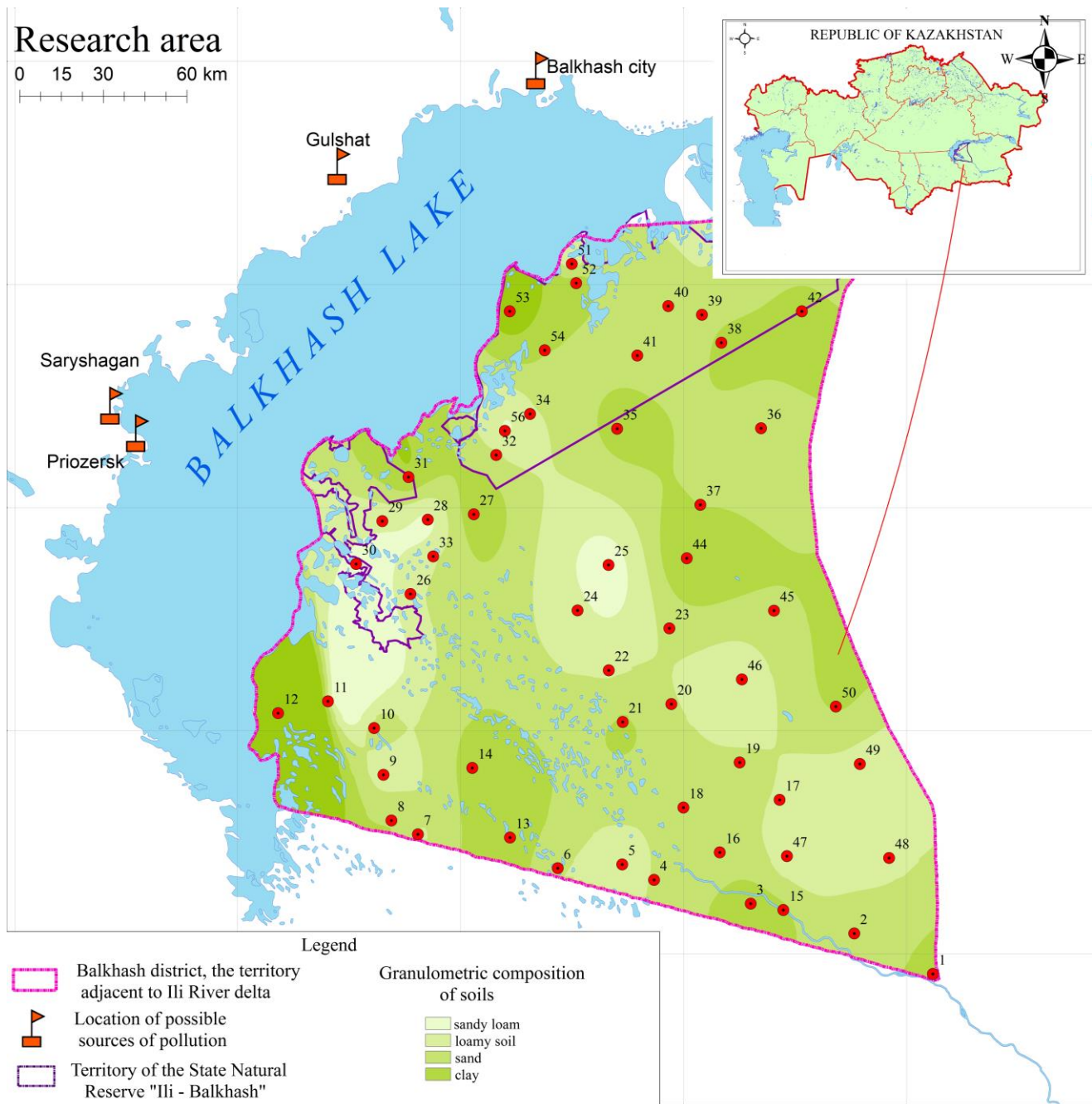


Figure 1. Study area with the indication of the key points for soil sampling. (authors Madibekov A.S., Zhadi A.O., Ismukhanova L.T.).

With its unique wealth and potential, this region experiences many social, economic and environmental problems, which is why it is under intensive environmental stress and highly vulnerable to anthropogenic impacts [23]. According to the results of studies, the pollution and destruction of the ecosystem due to heavy metals occurred in the considered study area over several years due to the impacts related to large metallurgical complexes [24–27]. The hazardous emissions released from the Balkhash Metallurgical Plant are of specific concern in terms of environmental pollution [28]. Thus, connected to the increasing levels of emissions being released into the atmosphere, the pollution in the

delta has also increased since pollutants entering the atmosphere from the above-mentioned enterprises spread over long distances [11,29–33].

The activity of this enterprise has social-economic importance for Kazakhstan. However, at the same time, it also introduces anthropogenic loads into the ecosystems of the region. It is obvious that despite the preventive measures to reduce the harmful effects of industrial emissions and the ongoing work to capture SO₂ from the atmosphere, the tailing dump of this plant (west of Balkhash town, on the lake shore) remains an acute environmental problem. Research indicates that the tailing dump stores solid waste (from the processing plant of the combine), which is transported there via the pulp feed line [34,35]. When copper ore is smelted, from 70 to 90% of the primary raw materials are transported to waste dumps. The tailing dump has accumulated up to 1200 million tons of waste containing a significant quantity of heavy metals. Most of the waste produced from copper smelting is exposed to weathering and is carried away from the tailings, reaching the regions of the southern Balkhash region.

2.2. Sediment and Soil Sampling Methods

The samples were collected from March 19 to April 17 in 2021. Preliminarily, the study area adjacent to the Ili River Delta, including the territory of the Ili-Balkhash State Natural Reserve, was divided into squares of equal area ($\approx 120 \text{ km}^2$) and numbered (54 points, Figure 1). The sampling points cover the territory of the reserve, in particular the enclosures for *Equus hemionus* and *Gazella subgutturosa* and, according to the recommendation of the program, for the reintroduction of the Turanian tiger to its former habitats. This reserve aims to save biological diversity and restore balance to nature, as supported by the World Wildlife Fund (WWF). The number of samples taken was 54 and, in total, 324 analyses were made. The investigations included an analysis of the following heavy metals: Cu, Zn, Pb, Cd, Co and Ni. Each sample was a part of the soil typical for genetic horizons or layers of the soil type. The number of spot samples corresponds to the State Standard valid in Kazakhstan [36]. The required conditions for taking soil samples protect them from secondary contamination at all stages of preparation. Soil samples intended for the determination of heavy metals were taken through the use of a metal-free instrument.

The combined samples were realized by mixing the spot samples from the same sample site. For chemical analysis, the combined samples were made from at least five-point samples taken from one sample site. The mass of the combined sample was at least 1 kg. To control the contamination due to surface-distributed pollutants (heavy metals), point samples were taken layer by layer from a depth of 5–20 cm, weighing no more than 200 g each. A necessary condition for soil sampling is protection from secondary pollution. The tool for soil sampling was a blade made of durable plastic (GD 52.18.289-90). The soil samples were recorded in a field journal. Paper envelopes with appropriate labels were used as packaging material for the transport and storage of the samples.

2.3. Grain Sizes and Soil Description

The texture of the soils of the southern Balkhash area was determined through the use of the visual method using the data provided in the table, “Signs for determining the granulometric type of soils” in 2001 [37–40]. According to this table, we could distinguish the following soil textures: loam, sandy loam, sand and others. Despite the fact that this method does not provide any quantitative assessment of certain fraction percentages in the rock, the correct assignment of clay rocks to clays, loamy soils or sandy clays should be considered already sufficient for a preliminary classification of Quaternary sediments and for a better understanding of their composition. According to [41,42], the majority of the study area is occupied by brown desert–steppe soils (Kastanozems and Regosols) on ridges, dunes and hilly sands in the northern part [41,42]. There are brown desert–steppe soils on fixed sands in the south. It is possible to distinguish the ancient delta of the Ili River in initially developed Takyr-like gray soils (Stagnosols and Solonchaks) on alluvial deposits in combination with ridge sands, which occupies up to 20–25% of the area, as

well as silty-sandy and sandy clay soils (Gleysols). Rice is grown on gray-brown sandy clay soils (Gleysols) and mainly on meadow-gray and floodplain-meadow soils (Fluvisols) along the Ili River near the village of Akzhar. The territory of the southern Balkhash region belongs to an area of deserted steppes with developed brown desert-steppe soils and low-carbonate gray soils (Kastanozems and Arenosols), which are mostly non-saline [41,42]. On the floodplain terraces of the rivers and in the deltas, there are areas of loamy and clay alluvium. Complexes of Takyr-like gray soils (Stagnosols), Takyr (Stagnosols) and alkaline soils (Solonchaks) are developed here. The surface of Takyr-like soils along the ancient valley of the Ili River is 60–70% bare and cracked. On vast inter-ridge depressions, the soils of sandy deserts are characterized by the presence of a low carbonate content and a weakly alkaline reaction (pH=7.5) of the soil solution [41–43].

2.4. Chemical Analyses

As an important driver of metal sorption on and desorption from soils and sediments, the pH values of the analysed samples were determined with the help of GOST 26423-85.

Soil samples weighing 30 g, weighed with an error of not more than 0.1 g, will be placed in conical flasks. Then, 150 mL of distilled water will be added to the samples with a dispenser. The soil and water will be mixed for 3 min with a stirrer and left for 5 min to settle. A 20 mL portion of the soil suspension will then be poured into a 50 mL beaker and used to measure the pH. The instrument readings will be taken no earlier than 1.5 min after the electrodes are immersed in the measured solution to measure the soil pH using a HANNA HI83141 pH meter (Hanna, Woonsocket, RI, USA).

During operation, the instrument is periodically calibrated against a pH 6.86 buffer solution [43].

The first stage of the laboratory method for heavy metals determinations is as follows: (1) scattering each sample on paper, (2) drying under air-dry conditions, (3) kneading large lumps using a pestle, pre-cleaning the inclusions (stones, branches and other foreign particles) and (4) using the quartering method, the soil weighing 0.2 kg is ground with a mortar and pestle and sifted through a sieve with a hole diameter of 1 mm. A sample with a mass of about 5.0 g was taken from the obtained air-dried soil sample.

The extraction of mobile forms of metal compounds from the soil samples was carried out according to this method [44], with a soil pretreatment using acetate-ammonia buffer solution with a pH of 4.8.

In total, 50 mL of acetate-ammonium buffer solution with a pH of 4.8 (ratio soil:solution = 1:10) was added to a 50 mL cylinder, and the soil sample was gently moistened through stirring. The soil sample in the acetate-ammonium buffer solution was incubated for 24 h at room temperature with a brief agitation of the soil sample.

After 24 h, the soil sample containing the solution was stirred and transferred for filtration through a funnel with a folded paper “white tape” filter into a clean measuring flask, washing the soil residue through the filter with buffer solution (about 50 mL). Then, the volume of the filtrate in the volumetric flask was supplemented with a buffer solution of 100 mL to conduct the further determination of the mobile forms of metals through the use of the atomic absorption spectrometric method [44,45].

The heavy metals present in the samples were determined using the flame atomic absorption spectrometric method using an AA-7000 atomic absorption spectrophotometer (Shimadzu, Kyoto, Japan) (Figure 2).

The assessment of the results of the content of metals in the soil was carried out in accordance with the regulatory documents [43,44] established in the Republic of Kazakhstan, which are updated annually by the JSC “National Center for Expertise and Certification” of the Republic of Kazakhstan.

These guidelines describe the assurance and quality control of metal content results.

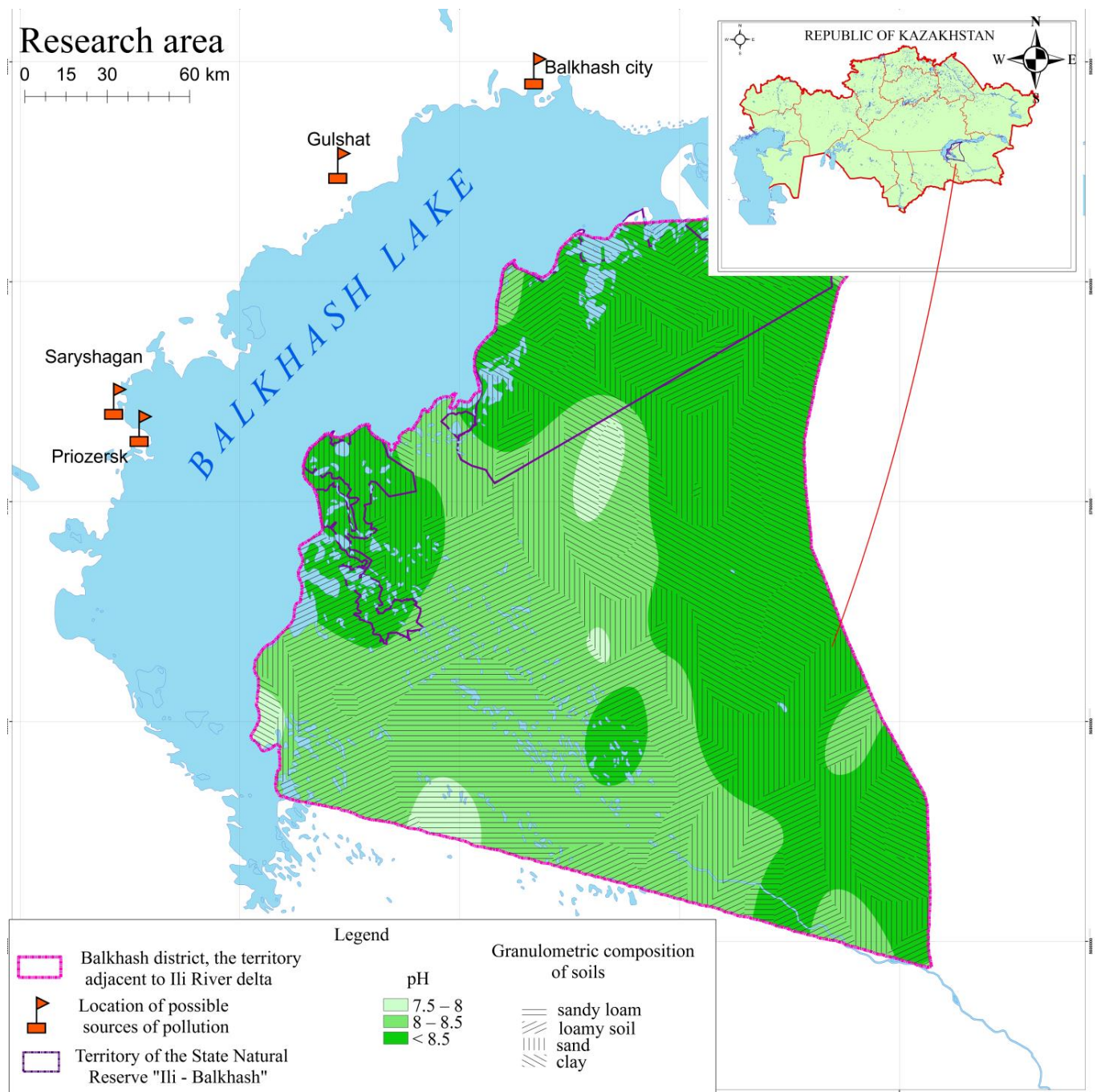


Figure 2. Granulometric composition and pH values of soils (authors Madibekov A.S., Zhadi A.O., Ismukhanova L.T.).

2.5. Use of the ArcGIS 10.5 Software Product

A map of the heavy metal distribution over the study area was built in ArcGIS 10.5 using the interpolation tool “spline with barriers” of spatial analysis (Spatial Analyst).

When mapping the distribution of heavy metals, the results taken from the samples of 56 points were used. The interpolation was performed on 51 points. The remaining 5 points were test points, and the interpolation and actual values were comparable to each other. In this regard, the accuracy of this method was higher than that of the others.

ArcGIS software is produced by ESRI, an American company that produces geographic information software products.

The coordinates were determined using Google Earth Pro. The sampling points are established taking into account the determination of the volume of pollutants per unit area, which will make it possible to identify the zonal features of their distribution and identify possible sources of pollution.

3. Research Results

3.1. Textures and Spatial Variation of Soil pH

According to the granulometric composition, the main part of the study area is characterized by the following textures: loamy soil and sand clay, and only a small part of it is clay, sand and alkaline soil (Figure 2). The changes in soil salinity, indicated by alkaline-expressing soil, have been identified in the area adjacent to Balkhash Lake, incl. the territory of the Ili-Balkhash State Natural Reserve. Such changes can lead to the complete degradation of the soil cover in the near future, which, in turn, will negatively affect the development of flora and fauna in the study area. The huge area, laying from the southeastern to the northwestern part, which belongs to the ancient delta, is characterized by loamy and clayey soils. Along the Ili River, from the southeastern to the southwestern part of the study area, sandy clays and sands occur.

The results of the pH measurements of the soil cover show changes in values from 7.5 to 9.5, averaging a pH of 8.5. The alkalinity of the soils throughout the study area varies, producing slightly alkaline to strongly alkaline reactions [41,42].

Soil salinization or alkalization occurs due to the excessive presence of alkali metals in the soil solution (calcium, magnesium and sodium). The pH of the soil cover, determined through the water extraction, ranges between 7.8 (alkaline) and 9.5 (highly alkaline) (Figure 2). The maximum accumulation of salts is characteristic of loamy soils and clays with a dense soil structure. High alkalinity, as a rule, will lead to the weakening of the biological cycle of substances and, as a consequence, many types of plant organisms will disappear. The gene pool of terrestrial populations will decrease due to the deterioration of the living conditions required by living organisms.

The results show that the carbonate content of soils is responsible for the averaged pH values of 7.5 in 2001; these values have increased up to a pH of 8.5 in 2021, which indicates the gradual salinization of the soils in the southern Balkhash region, as observed over a twenty-year period. It confirms the trend of soil salinization in the study area [43,44].

Thus, the high alkalinity of the soils, in addition to salinity, can lead to other negative consequences, such as the destruction of the soil structure, as a result of which leaching, waterlogging and alkalization will occur, leading up to complete degradation.

3.2. The Content of Heavy Metals in Soils and Their Spatial Distribution

The data analysis reflects local soil contaminations due to mobile forms of heavy metals exceeding the MPC, according to the Hygienic Standards [45]. MPC values (in mg kg^{-1}) for the mobile forms of metals are 3.0 for copper, 32.0 for lead, 4.0 for nickel, 23.0 for zinc, 5.0 for cobalt and 2.0 for cadmium.

The analysis of the existing standards of the Republic of Kazakhstan for MPC for heavy metals in soils was applied in this assessment to the level of accumulation in the soil, considering their physical properties [46–48].

The content and the behavior of heavy metals in soils are controlled through various parameters. In an acidic environment, microelements such as lead, cadmium, copper, zinc, manganese, nickel, cobalt, iron and chromium are the most mobile; in alkaline environments, these are arsenic, selenium, uranium and molybdenum. Lithium, rubidium, cesium, fluorine, bromine and boron are mobile in a wide range. The mobility of these elements also depends on granulometric and mineralogical composition and on the degree of humus content. Light and slightly humus soils are usually depleted by heavy metals in comparison with silt and organic matter, while two-layered clay minerals and humus have a high absorption capacity [49].

An amount of copper from 7.1 MPC to 8.6 MPC has been recorded throughout the whole coastal zone of Balkhash Lake. In the rest of the study area, the copper content ranges from 6.1 to 19.4 mg kg⁻¹. Local soil contamination due to mobile forms of copper, which is clearly expressed in the central and eastern parts of the study area, is up to 12.9 and 16.1 mg kg⁻¹, respectively (Figure 3a). The copper content in the soils on the left bank of the Ili River is, on average, 8.3 mg kg⁻¹, which corresponds to 2.8 MPC. Copper values exceed the standards by up to 6.5 MPC in the soil cover of Bakanas village. The same observation of high copper contents was found within the limits of the southwestern Balkhash region in the soils of the dry steppe, the semi-desert zones, by up to 28.5 mg kg⁻¹ [50]. This fact indicates the anthropogenic impact on soil pollution.

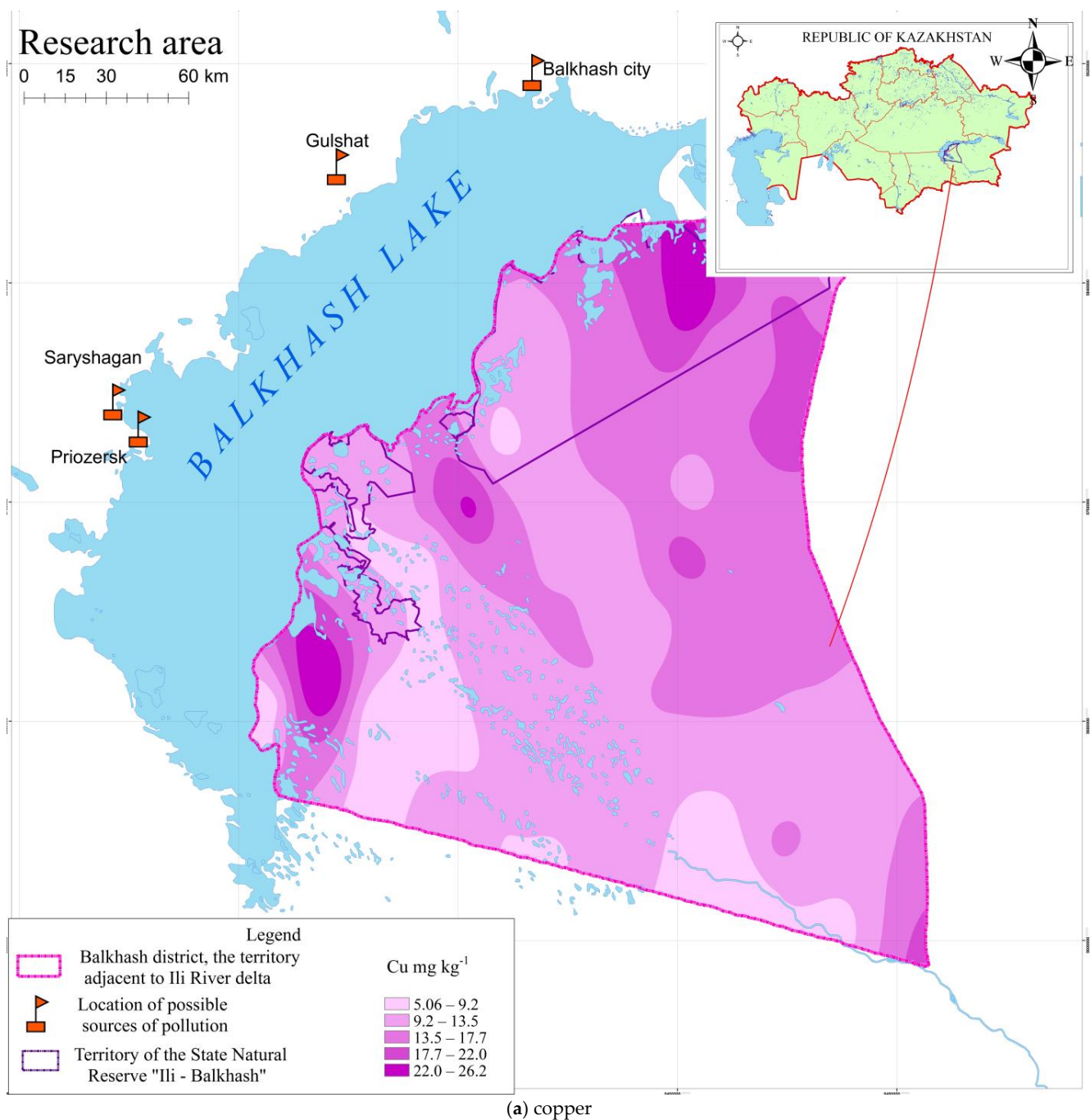


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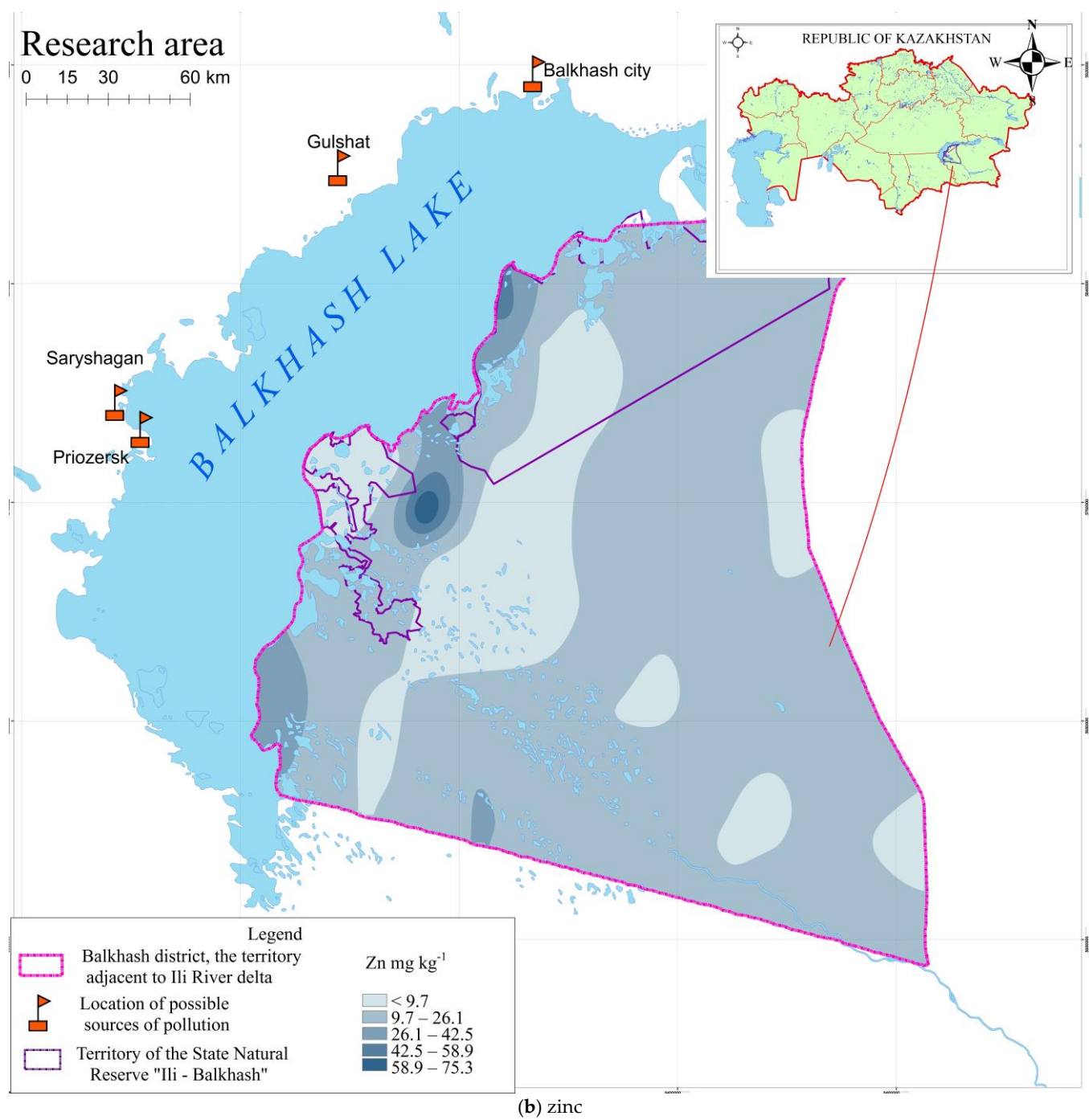


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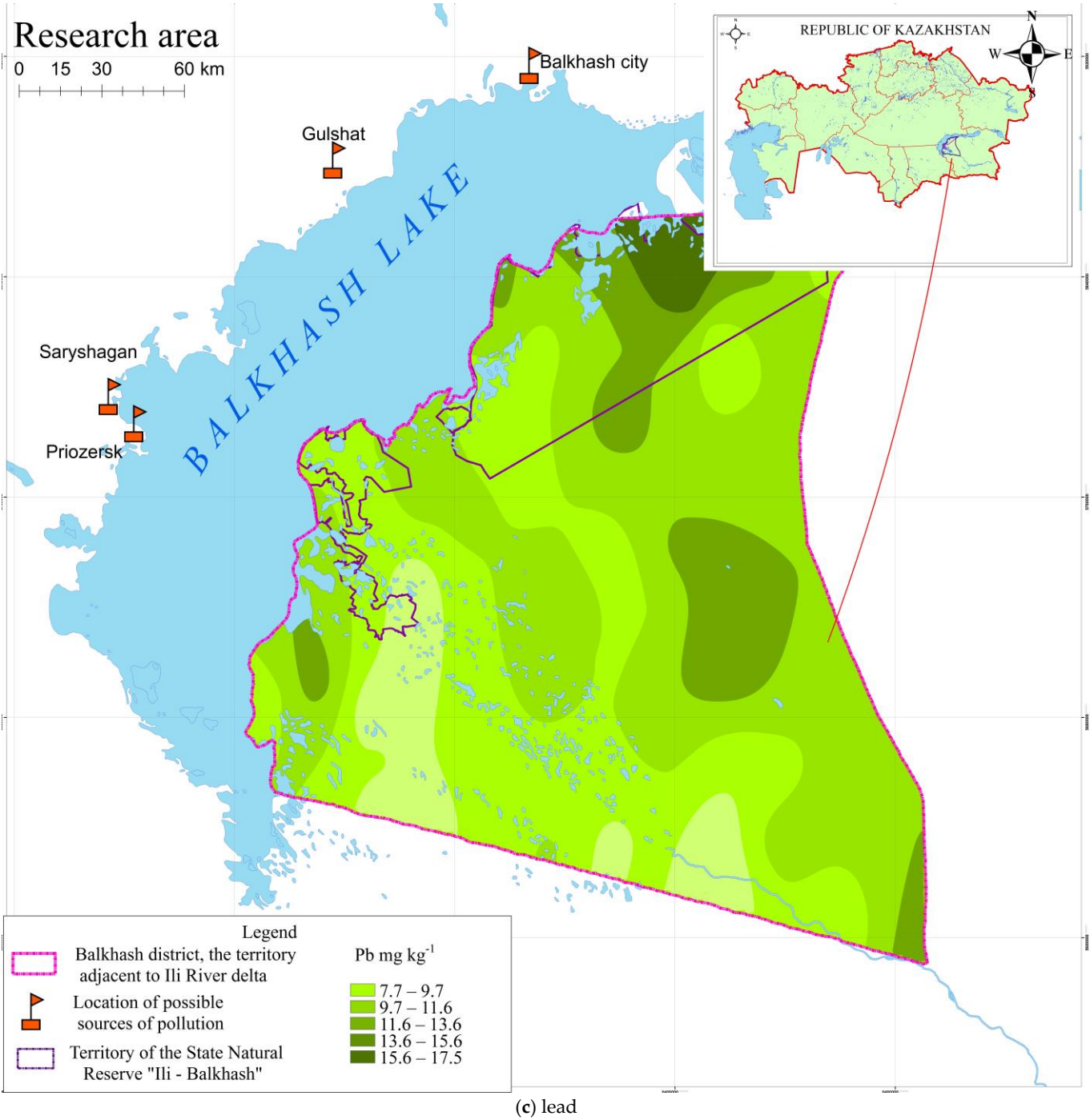


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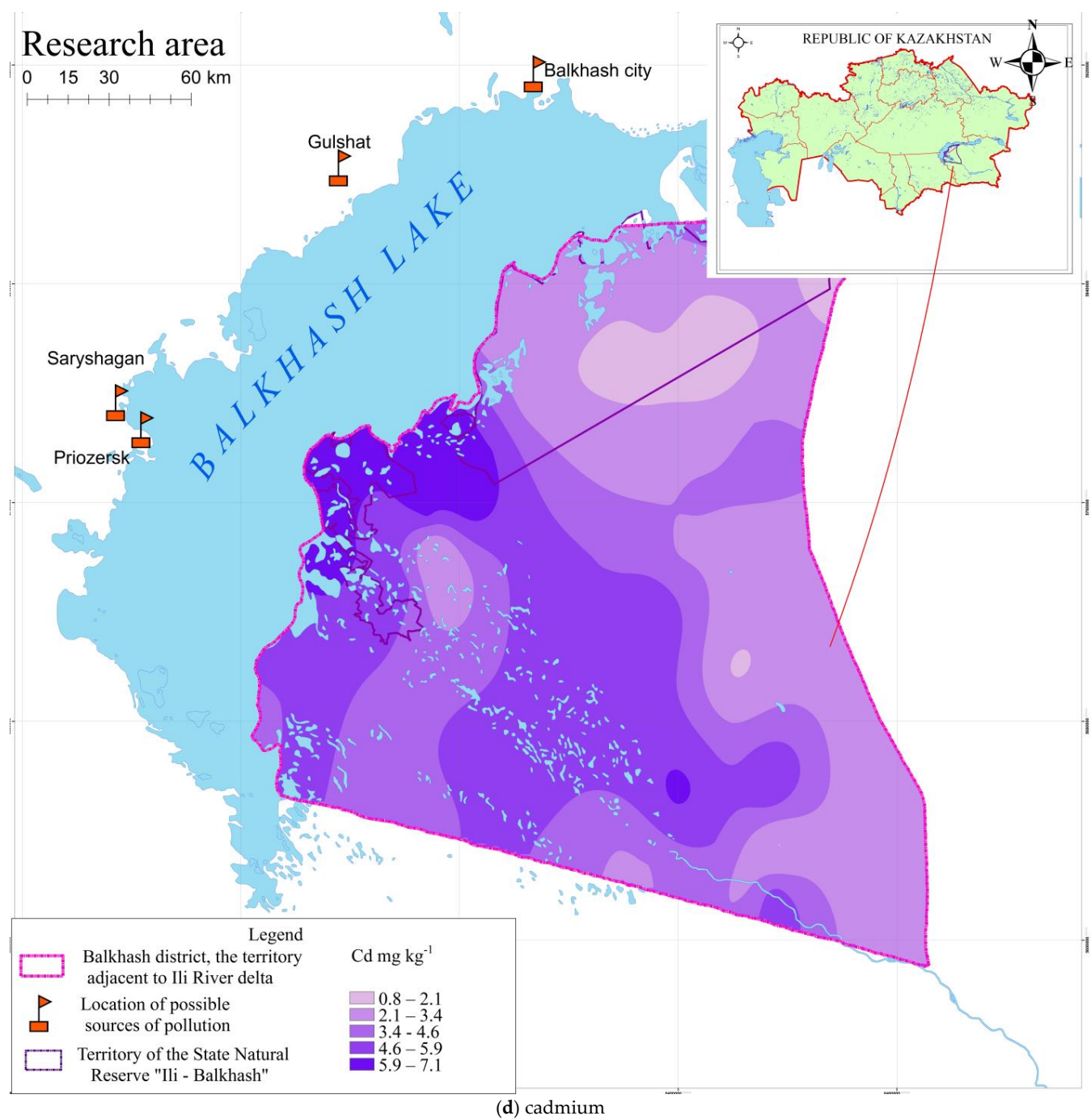


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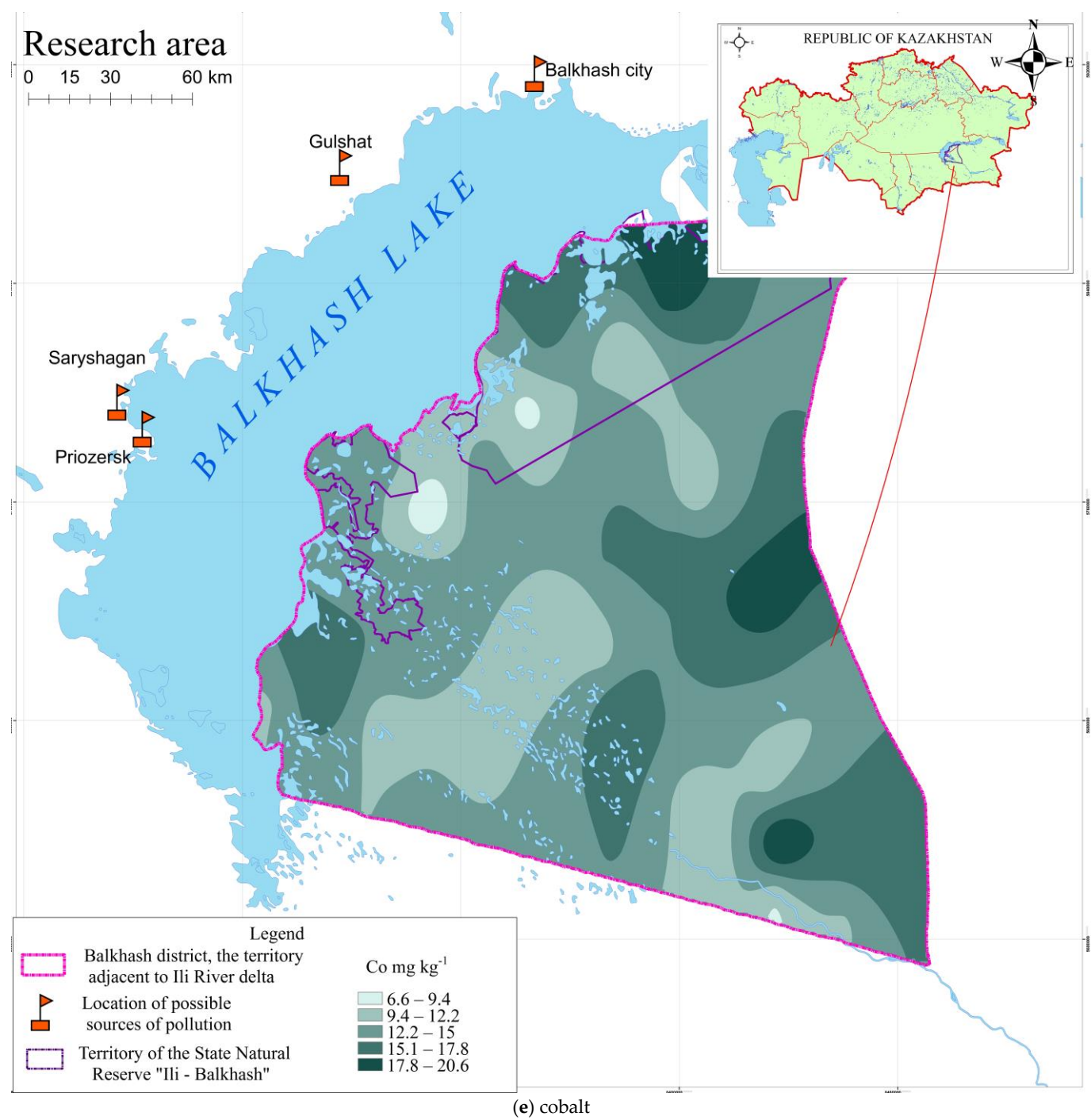


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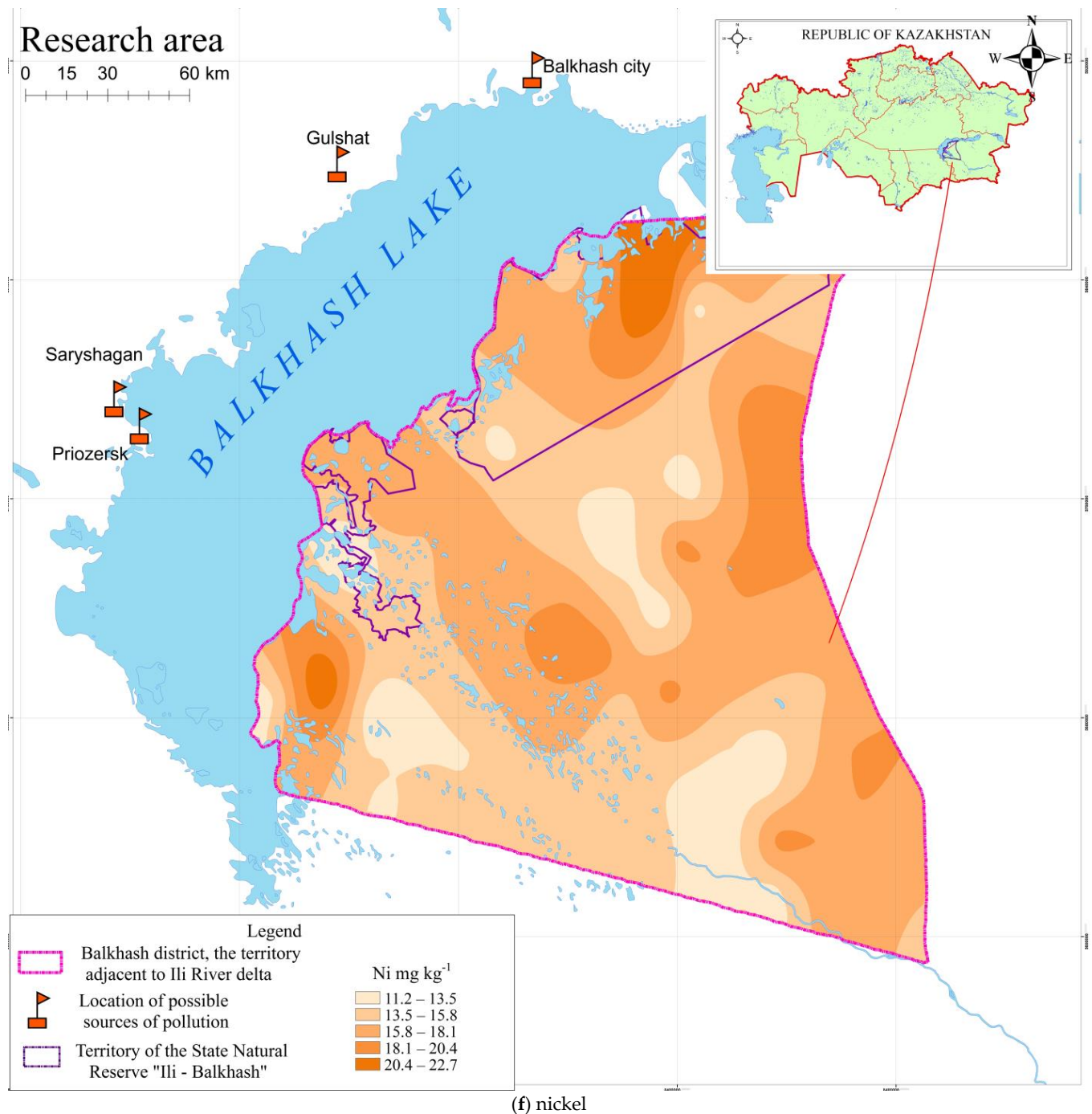


Figure 3. Metal concentrations of (a) copper, (b) zinc, (c) lead, (d) cadmium, (e) cobalt and (f) nickel in the soil cover in mg kg⁻¹ (authors Madibekov A.S., Zhadi A.O., Ismukhanova L.T.).

Zinc values in various directions range from 7.8 to 75.1 mg kg⁻¹ (Figure 3b). High levels of zinc were founded on the left bank of the Ili River at point No. 5 (Zheltorangy village), up to 25.9 mg kg⁻¹ (1.1 MPC), and No. 12 (Kuigan village), up to 37.2 mg kg⁻¹ (1.6 MPC). The maximum level was recorded at point No. 28 (10 km W of the village of Karoi), with up to 75.1 mg kg⁻¹, and at Kogaly cordon, with up to 46.0 mg kg⁻¹, reaching 3.3 MPC and 2.0 MPC, respectively. The average zinc level is 13.7 mg kg⁻¹. An excess quantity of zinc, up to 1.35 MPC, was observed only under the rice fields of Bakbaky village [40].

The concentration of lead was lower than the MPC, with a range from 8.0 to 15.9 mg kg⁻¹. The maximum values were recorded up to 14.0–15.9 mg kg⁻¹ in the central and eastern parts and also in the coastal zone of Balkhash Lake. The highest lead concentrations in the soil samples could be localized to the rice fields (Bereke village), but they have low average values (Figure 3c) [41].

Cadmium concentrations higher than the standard were recorded throughout the study area, with values from 2.1 to 6.5 mg kg⁻¹ for locations distributed across the village of Karaoi to the coast of the Balkhash Lake (up to 3.3 MPC), from the central to the southwestern part (up to 3.1 MPC) (Figure 3d). The soils of the northeastern part are less contaminated with cadmium, with a concentration of 0.9 to 2.0 mg kg⁻¹. According to some authors, an increase in cadmium concentration is directly related to soil pH, which affects the active migration ability of the metal [51,52].

The concentration of cobalt (Figure 3e) throughout the study area ranged from 6.7 to 20.6 mg kg⁻¹, and nickel ranged from 11.3 to 22.2 mg kg⁻¹ (Figure 3f). Exceeding the standards, cobalt contamination is up to 4.1 MPC, and nickel is up to 5.6 MPC. The spatial distribution of cobalt and nickel contents shows the same pattern of soil pollution (Figure 3e,f), with high values in the northern and eastern parts of the study area.

As can be seen from Figure 3a–f, the high contents of heavy metals are typical for loamy soils, clays and alkaline soils, which have high absorption capacities. Together with the absorptive capacity of soils, it is also necessary to take into account the migration activity of metals.

An important criterion in the assessment of soil contamination is the comparison of the obtained results with background indicators, i.e., the Clarke values of the elements in the lithosphere and soil cover of the region [53]. To assess the migration ability of heavy metals in the soil, the comparison of the average content of metals, according to field research data with their contents in the lithosphere and the soils of the study area, is provided [54,55].

4. Discussion

Previous research results have revealed the following: in the surface soil layer (0–20 cm), the concentration of cadmium is up to 0.031 mg kg⁻¹, while lead is below the MPC (maximum permissible concentration) [56] for most of the soil samples. The average zinc content slightly exceeds the MPC, with 1.35 under the rice fields of Bakbakty, but exceeds the MPC for all of the soil samples [34]. The largest amount of lead and copper was registered in the soils adjacent to the tailings dumps of the Balkhash Mining and Metallurgical Combine (BMMC): lead values ranged from 3.5 to 6.0 MPC, and copper values ranged from 3.5 to 9.4 MPC.

In general, the content of heavy metals in soils is relatively low compared to other investigations [9,19]. A significant exception is cadmium, wherein cadmium exceeds the MPC standard by 29 times. This indicates that different amounts of heavy metals may accumulate in soils under the same site conditions in terms of pollution. As a rule, cadmium pollution is polymetallic in nature. The distribution over the study area is mosaic-like, and centers of contamination form.

The measured soil pH averages 8.5, indicating an alkaline environment where the sedimentation of cadmium compounds has been taking place [46,52,57,58]. The concentration of other elements is significantly lower than their Clarke values, which may indicate their low migration activity [54]. However, considering the Clarke values for comparison is problematic because our metal analyses are the first investigations carried out in this area. All of the heavy metals were arranged in decreasing order of their concentration as follows: Zn > Ni > Co > Cu > Pb > Cd. According to this, the total content of heavy metals and chemical elements in the soils of the Balkhash region in terms of the average concentration of the studied elements in descending order are as follows: Mn > Cr > As > Ni > Pb > Cu > Cd [31]. The average concentration of metals in all of the studied soil samples exceeds the background by 1.6–22.5 times. The maximum excess of the background was typical for cadmium (5.4 times).

The soils of the Ili River Delta and the Ili-Balkhash State Nature Reserve are being studied for the first time. The measured metal concentrations are cumulative enrichments over a period of time [19]. Land degradation, as a consequence of long-term and/or intensive metal accumulation in the delta soils of this vast territory (about 8 thousand km²), cannot be excluded in the future.

Heavy metal soil contamination is common on a global scale [51,59]. The metals contained in soils can migrate into plant tissues, which, in turn, migrate along the food chain, leading to an increased concentration of heavy metals in grazing plants, which can be dangerous for wild animals, grazing animals and people who consume the meat of grazing animals [60–63].

5. Conclusions

Data analysis registers local soil contamination in terms of mobile forms of copper, zinc, cadmium, cobalt and nickel.

The amount of copper reached 28.5 mg kg^{−1}, which is clearly expressed in dry-steppe, semi-desert and desert soils within the southwestern Balkhash region. Zinc values in various directions range from 7.8 to 75.1 mg kg^{−1}.

High levels of zinc were found in the territory of the reserve (Kogaly cordon), up to 46.0 mg kg^{−1}. The presence of lead in the soils was found throughout the study area at significant concentrations up to 14.0–15.9 mg/kg. It is localized to rice fields (Bereke village).

The cadmium concentrations in the soils are higher than the standards that were recorded throughout the study area by up to 6.5 mg kg^{−1}, from the central to the southwestern parts. The behavior and the concentrations of cadmium are associated with soil pH, which affects the active migration ability of this metal.

The concentrations of cobalt throughout the study area range from 6.7 to 20.6 mg kg^{−1}, and the nickel concentrations range from 11.3 to 22.2 mg kg^{−1}, respectively. The spatial distribution of the cobalt and nickel concentrations shows the same pattern of soil pollution, with high values in the northern and eastern parts of the study area.

All of the heavy metals found in the soils were arranged in decreasing order of their concentration as follows: Zn > Ni > Co > Cu > Pb > Cd.

The visualization of the spatial distribution of the metal content of the soil cover reflects the influence of the Balkhash metallurgical plant and other sources of pollution located on the northern shore of Lake Balkhash. Although some of the metal concentrations are lower than in other polluted areas of the world, currently, the study area is experiencing a technogenic load, which in the future may lead to an ecological crisis and the disruption of the natural balance. This crisis can negatively affect plans for the reintroduction of the Turanian tiger to the natural reserve of “Ili-Balkhash”. That is why continuous monitoring of the metal load in the soils of the study area is recommended. Political and technological decisions and innovations must be realized to prevent further pollution. Specifically, in terms of heavy metals, it is always better to prevent their distribution in the environment and impact due to the fact that their withdrawal or transformation is nearly impossible.

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References

1. Motuzova, G.V.; Karpova, Y.A. *Chemical Pollution of the Biosphere and Its Ecological Consequences: Textbook*; Publishing House of Moscow University: Moscow, Russia, 2013; p. 304.
2. Durowoju, O.S.; Odiyo, J.O.; Ekosse, G.E. Horizontal variation in trace elements and soil characteristics at Siloam and Tshipise geothermal springs, Limpopo Province, South Africa. *Water SA* **2016**, *42*, 694–702. [CrossRef]
3. Seredina, V.P. *Soil Pollution*; Tomsk State University Publishing House: Tomsk, Russia, 2015; p. 346.
4. Ismukhanova, L.; Choduraev, T.; Opp, C.; Madibekov, A. Accumulation of Heavy Metals in Bottom Sediment and Their Migration in the Water Ecosystem of Kapshagay Reservoir in Kazakhstan. *Appl. Sci.* **2022**, *12*, 11474. [CrossRef]
5. Amirgaliyev, N.A.; Ismukhanova, L.T. The Level of Anthropogenic Pollution of the Kapshagay Water Reservoir, Republic of Kazakhstan. In *Water Resources Management in Central Asia*; Springer: Cham, Switzerland, 2020; Volume 105, pp. 143–162. [CrossRef]
6. Panin, M.S. *Ecology of Soils*; Rarite: Almaty, Kazakhstan, 2008; p. 528.
7. FAO and UNEP. *Global Assessment of Soil Pollution. Summary for policy makers*; Food and Agriculture Organization of the United Nations: Rome, Italy; United Nations Environment Programme: Rome, Italy, 2021; p. 84, ISBN 978-92-5-134448-4. [CrossRef]
8. Izydorczyk, G.; Mikula, K.; Skrzypczak, D.; Moustakas, K.; Witek-Krowiak, A.; Katarzyna Chojnacka, K. Potential environmental pollution from copper metallurgy and methods of management. *Environ. Res.* **2021**, *197*, 111050. [CrossRef]
9. Beier, T.; Opp, C.; Hahn, J. Sink and source functions for metal(loid)s in sediments and soils of two water reservoirs of the Ore Mountains, Saxony, Germany. *Appl. Sci.* **2022**, *12*, 635. [CrossRef]
10. Opp, C.; Stach, J.; Hanschmann, G. Load on differently used soils by heavy metals within the highly contaminated area of Bitterfeld (FRG). *Sci. Total Environ.* **1993**, *134*, 141–150. [CrossRef]
11. Madibekov, A.; Kogutenko, L. The Issue of transporting pollutants with atmospheric precipitation. *IOP Conf. Ser. Earth Environ. Sci.* **2018**, *107*, 0120643. [CrossRef]
12. Madibekov, A.S.; Nysanbaeva, A.S.; Kurmanova, M.S. Role of the chemical composition of an atmospheric precipitation in pollution of a surface water. *News Natl. Acad. Sci. Repub. Kazakhstan Ser. Geol. Tech. Sci.* **2018**, *5*, 120–127. [CrossRef]
13. Chichaeva, M.A.; Lychagin, M.Y.; Syroeshkin, A.V.; Chernitsova, O.V. Heavy Metals in Marine Aerosols of the Azov Sea. *Geogr. Environ. Sustain.* **2020**, *13*, 127–134. [CrossRef]
14. Marina-Montes, C.; Pérez-Arribas, L.V.; Escudero, M.; Anzano, J.; Cáceres, J.O. Heavy metal transport and evolution of atmospheric aerosols in the Antarctic region. *Sci. Total Environ.* **2020**, *721*, 137702. [CrossRef] [PubMed]
15. Kulshrestha, U.; Mishra, M. Chapter 3—Atmospheric chemistry in Asia: Need of integrated approach. In *Asian Atmospheric Pollution Sources, Characteristics and Impacts*; Elsevier: Amsterdam, The Netherlands, 2022; pp. 55–74. [CrossRef]
16. Li, Y.; Padoan, E.; Ajmone Marsan, F. Soil particle size fraction and potentially toxic elements bioaccessibility: A review. *Ecotoxicol. Environ. Saf.* **2021**, *209*, 111806. [CrossRef]
17. Ugwu, I.; Anthony Igbokwe, O. Sorption of Heavy Metals on Clay Minerals and Oxides: A Review. In *Advanced Sorption Process Applications*; IntechOpen: London, UK, 2019. [CrossRef]
18. *Methodical Recommendations for the Hygienic Substantiation of MPC for Chemicals in Soil*; Ministry of Health of the USSR: Moscow, Russia, 1982; p. 58.
19. Blume, H.-P.; Brümmer, G.W.; Fleige, H.; Horn, R.; Kandeler, E.; Kögel-Knabner, I.; Kretschmar, R.; Stahr, K.; Wilke, B.-M. *Scheffer/Schachtschabel Soil Science*; Springer: Berlin/Heidelberg, Germany, 2016; 618p.
20. WOCAT. Undated. WOCAT-Categorisation System. Available online: https://www.wocat.net/fileadmin/user_upload/documents/QT_and_QA/CategorisationSystem.pdf (accessed on 10 October 2021).
21. Convention on Wetlands of International Importance Principally as Habitat for Waterfowl. Adopted February 2, 1971. Available online: <https://www.wetlands.org/wetlands/ramsar-convention> (accessed on 23 October 2021).
22. State Natural Reserve “Ile-Balkhash” of the Forestry and Wildlife Committee of the Ministry of Agriculture of the Republic of Kazakhstan: Resolution of the Government of the Republic of Kazakhstan dated June 27, 2018. No. 381. Available online: <https://adilet.zan.kz/rus/docs/P1800000381/info> (accessed on 7 February 2021).
23. Koroleva, Y.G.; Dikareva, T.V.; Dikarev, V.A. Assessment of natural hazards in the Ile-Balkhash nature reserve (Kazakhstan). *Arid Ecosyst.* **2019**, *9*, 264–272. [CrossRef]
24. Available online: <https://wwf.ru/resources/news/tsentralnaya-aziya/ile-balkhash-tigr-vse-blizhe/> (accessed on 21 January 2021).

25. Madibekov, A.; Ismukhanova, L.; Mussakulkyzy, A.; Kulbekova, R.; Zhadi, A. Results of AAS-measurements of atmospheric deposition of copper and lead in the snow cover of Almaty agglomeration. *Pure Appl. Chem.* **2021**, *94*, 275–280. [\[CrossRef\]](#)
26. Ismukhanova, R.L.; Kulbekova, R.; Amirgaliyev, N.; Madibekov, A.; Zhadi, A. The research results of physical and chemical parameters of snow cover in the almaty agglomeration (Southeast of Kazakhstan). In Proceedings of the 20th International Multidisciplinary Scientific GeoConference SGEM 2020, Albena, Bulgaria, 18–24 August 2020; pp. 671–680. [\[CrossRef\]](#)
27. Cherednichenko, V.S.; Cherednichenko, A.V.; Nyssanbaeva, A.S.; Zhumalipov, A.R.; Madibekov, A.S. Heavy metal content in the snow cover in the republic of Kazakhstan. *Adv. Environ. Biol.* **2014**, *8*, 1393–1398.
28. Ramazanova, E.; Lee, S.H.; Lee, W. Stochastic risk assessment of urban soils contaminated by heavy metals in Kazakhstan. *Sci. Total Environ.* **2020**, *750*, 141535. [\[CrossRef\]](#) [\[PubMed\]](#)
29. Lin, M.; Chan, I.-N.; Chan, C.-Y.; Wang, X.-M.; Dong, H.-Y. Emerging Air Pollution Issues in Changing Pearl River Delta of South China. In *The Impact of Air Pollution on Health, Economy, Environment and Agricultural Sources*; IntechOpen: London, UK, 2011. [\[CrossRef\]](#)
30. Hu, B.; Li, G.; Li, J.; Bi, J.; Zhao, J.; Bu, R. Spatial distribution and ecotoxicological risk assessment of heavy metals in surface sediments of the southern Bohai Bay, China. *Environ. Sci. Pollut. Res.* **2013**, *20*, 4099–4110. [\[CrossRef\]](#)
31. Tilekova, Z.T. Environmental Assessment of Anthropogenic Impact to the Natural Environment of the Balkash Region. Ph.D. Thesis, Abai Kazakh National Pedagogical University, Almaty, Kazakhstan, 2015; p. 128.
32. Slukovskii, Z.; Belkina, N.; Potakhin, M. Assessment of contamination of recent sediments of a large reservoir in the catchment area of Arctic Ocean, Northern Europe. *Pol. Polar Res.* **2021**, *42*, 25–43. [\[CrossRef\]](#)
33. Cherednichenko, V.S.; Cherednichenko, A.V.; Zheksenbaeva, A.K.; Madibekov, A.S. Heavy metal deposition through precipitation in Kazakhstan. *Heliyon* **2021**, *7*, e05844. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Baimenova, Y.V. Assessment of the environmental impact of the tailing dump of the Balkhash concentrating mill. *Bull. KazNU. Geogr. Ser.* **2002**, *2*, 44–53.
35. Nurkeyev, S.S.; Kazova, R.A.; Musina, U.S. The problem of technogenic pollution of the north-western coast of lake Balkhash. International ecological forum “Balkhash-2000”. *Almaty* **2000**, *1*, 428–432.
36. State Standard 17.4.3.01-83; Nature Protection. Soils. General Requirements for Sampling. Standartinform: Moscow, Russia, 2018; p. 8.
37. Lomtadze, V.D. *Methods of Laboratory Studies of Physical and Mechanical Properties of Rocks (Guide to Laboratory Studies Prior to Engineering Geology)*; Nedra: Leningrad, Russia, 1972; p. 312.
38. Lomtadze, V.D. Physical and mechanical properties of rocks. In *Laboratory Research Methods*; Nedra: Leningrad, Russia, 1990; p. 328.
39. Chen, Y.; Wang, W.; Shi, H.; Wang, M.; Xu, C. Comparative Case Study on the Influence of Spatial Distribution of Heavy Metals in Regional Area. *Res. Environ. Sci.* **2019**, *32*, 1213–1223. [\[CrossRef\]](#)
40. IUSS Working Group WRB. World Reference Base for Soil Resources. In *International Soil Classification System for Naming Soils and Creating Legends for Soil Maps*, 4th ed.; International Union of Soil Sciences (IUSS): Vienna, Austria, 2022; 236p.
41. *The Current Ecological Condition of the Balkhash Lake Basin*; Kudekova, T.K. (Ed.) Kaganat: Almaty, Kazakhstan, 2002; p. 388.
42. *Problems of Hydroecological Sustainability in the Balkhash Lake Basin*; Samakova, A.B. (Ed.) Publiushing house “Kaganat”: Almaty, Kazakhstan, 2003; p. 584.
43. GOST 26423-85; Soils. Methods for Determination of Specific Electric Conductivity, pH and Solid Residue of Water Extract. Standartinform: Moscow, Russia, 2011; 4p.
44. GD 52.18.289-90; Technique for Measuring the Mass Fraction of Mobile Forms of Metals (Copper, Lead, Zinc, Nickel, Cadmium, Cobalt, Chromium, Manganese) in Soil Samples by Atomic Absorption Analysis. USSR State Committee on Hydrometeorology: Moscow, Russia, 1990; p. 36.
45. HS 2.1.7.2041-06; Maximum Permissible Concentration (MPC) of Chemicals in Soi. Federal Center for Hygiene and Epidemiology of Rospotrebnadzor: Moscow, Russia, 2006; p. 15.
46. Gadde, R.R.; Laitinen, H.A. Studies of heavy metal adsorption by hydrous iron and manganese oxides. *Anal. Chem.* **1974**, *46*, 2022. [\[CrossRef\]](#)
47. Vorobieva, L.A.; Ladonin, D.V.; Lopukhina, O.V.; Rudakova, T.A.; Kiryushin, A.V. *Chemical Analysis of Soils*; Moscow State University Press: Moscow, Russia, 2011; p. 186.
48. Tepikina, L.A.; Pinigin, M.A. Condition and ways of harmonizing hygienic standards for substances polluting the atmospheric air. *Hyg. Sanit.* **2006**, *5*, 102–104.
49. Opp, C. Schwermetalle. In *Analyse und Ökologische Bewertung der Landschaft*, 2nd ed.; Bastian, O., Schreiber, K.F., Eds.; Aufl. Spektrum Akademischer Verlag: Heidelberg, Germany; Berlin, Germany, 1999; pp. 239–246.
50. Kovalskiy, V.V.; Andrianova, G.A. *Microelements in the Soils of the USSR*; Nauka: Moscow, Russia, 1970; p. 180.
51. Alloway, B.J. *Heavy Metals in Soils*; John Wiley and Sons: New York, NY, USA, 1990; p. 339, ISBN 978-047021598-2.
52. Yang, Q.; Yang, Z.; Zhang, Q.; Liu, X.; Zhuo, X.; Wu, T.; Wang, L.; Wei, X.; Ji, J. Ecological risk assessment of Cd and other heavy metals in soil-rice system in the karst areas with high geochemical background of Guangxi, China. *Sci. China Earth Sci.* **2021**, *64*, 1126–1139. [\[CrossRef\]](#)
53. Vinogradov, A.P. *Introduction to Ocean Geochemistry*; Nauka: Moscow, Russia, 1967; p. 216.
54. Perelman, A.I. *Landscape Geochemistry*; High School: Moscow, Russia, 1975; p. 341.
55. Perelman, A.I.; Batulin, S.G. Migration rows of elements in the weathering crust. In *Weathering Crust*; Publishing House of the Academy of Sciences of the USSR: Moscow, Russia, 1962; Volume 4, p. 288.

56. Forbes, E.A.; Posner, A.M.; Quirk, J.P. The specific adsorption of divalent Cd, Co, Cu, Pb and Zn on goethite. *J. Soil Sci.* **1976**, *27*, 154. [[CrossRef](#)]
57. Bryan, G.W.; Langston, W.J. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: A review. *Environ. Pollut.* **1992**, *76*, 89–131. [[CrossRef](#)] [[PubMed](#)]
58. Enya, O.; Lin, C.; Qin, J. Heavy metal contamination status in soil-plant system in the Upper Mersey Estuarine Floodplain, Northwest England. *Mar. Pollut. Bull.* **2019**, *146*, 292–304. [[CrossRef](#)]
59. Canadian Soil Quality Guidelines. *Carcinogenic and Other Polycyclic Aromatic Hydrocarbons (PAHs) (Environmental and Human Health Effects)*; Scientific Criteria Document (rev.), No. PN 1445; Canadian Council of Ministers of the Environment (CCME): Winnipeg, MB, Canada, 2022; ISBN 978-1-896997-94-0. Available online: <http://ceqg-rcqe.ccme.ca/> (accessed on 15 October 2022).
60. Korfali, S.I.; Karaki, H. Speciation of metals in soils and water: Risk assessment. *Environ. Process.* **2018**, *5*, 101–125. [[CrossRef](#)]
61. Ali, H.; Khan, E.; Ilahi, I. Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation. *J. Chem.* **2019**, *2019*, 6730305. [[CrossRef](#)]
62. Chen, F.; Muhammad, F.G.; Khan, Z.I.; Ahmad, K.; Malik, I.S.; Ashfaq, A.; Naeem, M.; Nadeem, M.; Ma, J.; Awan, M.U.F.; et al. Bioaccumulation and transfer of zinc in soil plant and animal system: A health risk assessment for the grazing animals. *Environ. Sci. Pollut. Res.* **2022**, *29*, 2718–2727. [[CrossRef](#)]
63. Chen, H.; Teng, Y.; Lu, S.; Wang, Y.; Wang, J. Contamination features and health risk of soil heavy metals in China. *Sci. Total Environ.* **2015**, *512–513*, 143–153. [[CrossRef](#)]

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