agronomy

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Spatial and In-Depth Distribution of Soil Salinity and Heavy Metals (Pb, Zn, Cd, Ni, Cu) in Arable Irrigated Soils in Southern Kazakhstan

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Abstract: Most irrigated lands in the Republic of Kazakhstan are in its southern part, in the large deltas and ancient alluvial plains in the basins of the rivers Syr Darya and Ili. The combination of climatic features and anthropogenic pressures leads to increased salinity and contamination of cultivated soils in this region, resulting in a qualitative and quantitative decline in crop production. The study's primary goal was to assess soil secondary salinity and selected heavy metals (Pb, Zn, Cd, Ni and Cu) contamination in irrigated arable soils. To identify the potential source of soil pollution, we compared the concentration of salt and heavy metals (both total and mobile forms) in different soil types in three depths of soil profiles obtained from irrigated cultivated and non-cultivated (abounded) territory in the Shauldara massif in the southern part of Kazakhstan. All studied soils are prone to secondary salinization with either a medium or high content of sum of salts with domination by Na^{+} among cations and by SO_4^{2-} among anions. The soil contamination with heavy metals was low, and, in most cases, except for cadmium, it was below the limits developed for arable soils in most countries. Soil contamination with cadmium results from contamination of the water used for irrigation of farmland.

Keywords: arid regions; Kazakhstan; irrigated soils; soil salinity; heavy metals

Citation: Suska-Malawska, M.; Vyrakhamanova, A.; Ibraeva, M.; Poshanov, M.; Sulwiński, M.; Toderich, K.; Mętrak, M. Spatial and In-Depth Distribution of Soil Salinity and Heavy Metals (Pb, Zn, Cd, Ni, Cu) in Arable Irrigated Soils in Southern Kazakhstan. *Agronomy* **2022**, *12*, 1207. https://doi.org/10.3390/agronomy12051207

Academic Editors: Lisa Lobry de Bruyn, Tiziano Gomiero and Ji Li

Received: 11 April 2022
Accepted: 15 May 2022
Published: 17 May 2022

1. Introduction

Saline soils occupy about 10% of the world and are distributed globally. In many arid and semi-arid regions, saline soils are natural and common, e.g., in steppe and desert landscapes of the world [1]. The formation of natural saline soils in arid and semi-arid regions is driven by several factors, including hydrogeological and geochemical features of landscape formation, geographic and climatic conditions, and vegetation cover. However, human-induced drivers mainly from industrial and agricultural sectors affect changes in soil chemistry by increasing soil salinity and soil contamination with a considerable amount of chemicals such as heavy metals and pesticides [2]. Concerning the agricultural sector, it is well known that irrigation is the principal cause of secondary salinization on a global scale [3]. The provision of irrigation water, particularly in arid and semi-arid areas, is an essential factor in expanding agricultural production and increasing the productivity of cultivated lands. However, according to FAO estimates, between 20% and 50% of irrigated soils are salt-affected, mostly due to secondary salinization processes [4]. Soil secondary salinization is a major global problem, affecting both surface and groundwater systems, and impacting crop production, water quality, biogeochemical cycling, as well as human and ecosystem health.

Due to the 'region's arid climate, most cultivated lands in Central Asia must be irrigated to increase agricultural production and stabilize crop yields. Therefore, large-scale irrigation systems were developed there in the 1960s and 1970s, and to date, irrigation is an integral part of the economies and politics of Central Asian states. However, even up to 80% of water transported via these irrigation systems can be lost, mostly due to infrastructure deterioration [5]. In many areas, such great water losses increased the water table and led to waterlogging and salinization of arable lands. It is estimated that irrigation-related secondary salinization adversely affects over 4 mln ha in Central Asia [6].

Most irrigated lands in the Republic of Kazakhstan are in its southern part, in the large deltas and ancient alluvial plains in the basins of the rivers Syr Darya, Ili, Talas, and others. These basins are endorheic and located in geochemically diversified hydromorphic regions. As there is no free outflow from the basins, they become the areas of final deposition of chemical elements, and as a result, they are susceptible to salinity [7]. Simultaneously, these areas are relatively densely populated and support industrial and agricultural infrastructure. The combination of climatic features and anthropogenic pressures leads to increased salinity and contamination of cultivated soils in this region, resulting in a qualitative and quantitative decline in crop production. The availability and good condition of land and water are natural preconditions for agriculture, the principal basis of food production. The situation of human society in Kazakhstan and managing the use of all resources define the framework for agricultural production and food security [6].

Crop production in the Syr Darya river basin is essential for the economy and almost entirely depends on irrigation [8–10]. Therefore, this area provides many examples of the adverse effects of irrigation, such as the formation of water-logged and saline soils along unlined canals or the formation of spotty saline fields, due to the lack of proper drainage installations for the evacuation of saline subsoil water. These types of soil degradation can be observed, e.g., in the irrigation zone of the Arys–Turkestan canal, which irrigates approximately 70,000 ha in southern Kazakhstan. Apart from irrigation-related factors, such as the quality of groundwaters and salt content in soils, a range of heavy metals is also affected by geochemistry and geology, relief, eolian dust, wetting of the soil profile, and rainfall infiltration [8,11–16].

Considering the importance of proper soil quality in the Syr Darya river basin and the fact that simultaneous assessment of soil secondary salinity and contamination with heavy metals at the regional scale allows specification of the 'metals' sources in different soil horizons, the primary goal of this study was to determine salinity and content of selected heavy metals (Pb, Zn, Cd, Ni, Cu) in irrigated arable soils. We compared the concentration of salts and heavy metals (both total and mobile forms) in different soil types in three available depths of soil profiles. To identify the potential source of soil pollution, we analyzed the relationships between physical and chemical properties and the content of heavy metals in the studied soils.

2. Study Sites, Materials and Methods

2.1. Description of the Study Area

The Shauldara massif is in the Turkestan region, southern Kazakhstan, on the Ortrar steppe, between the desert Turan Lowland and desert-steppe foothills of the western Thien Shan Mountains (Figure 1).

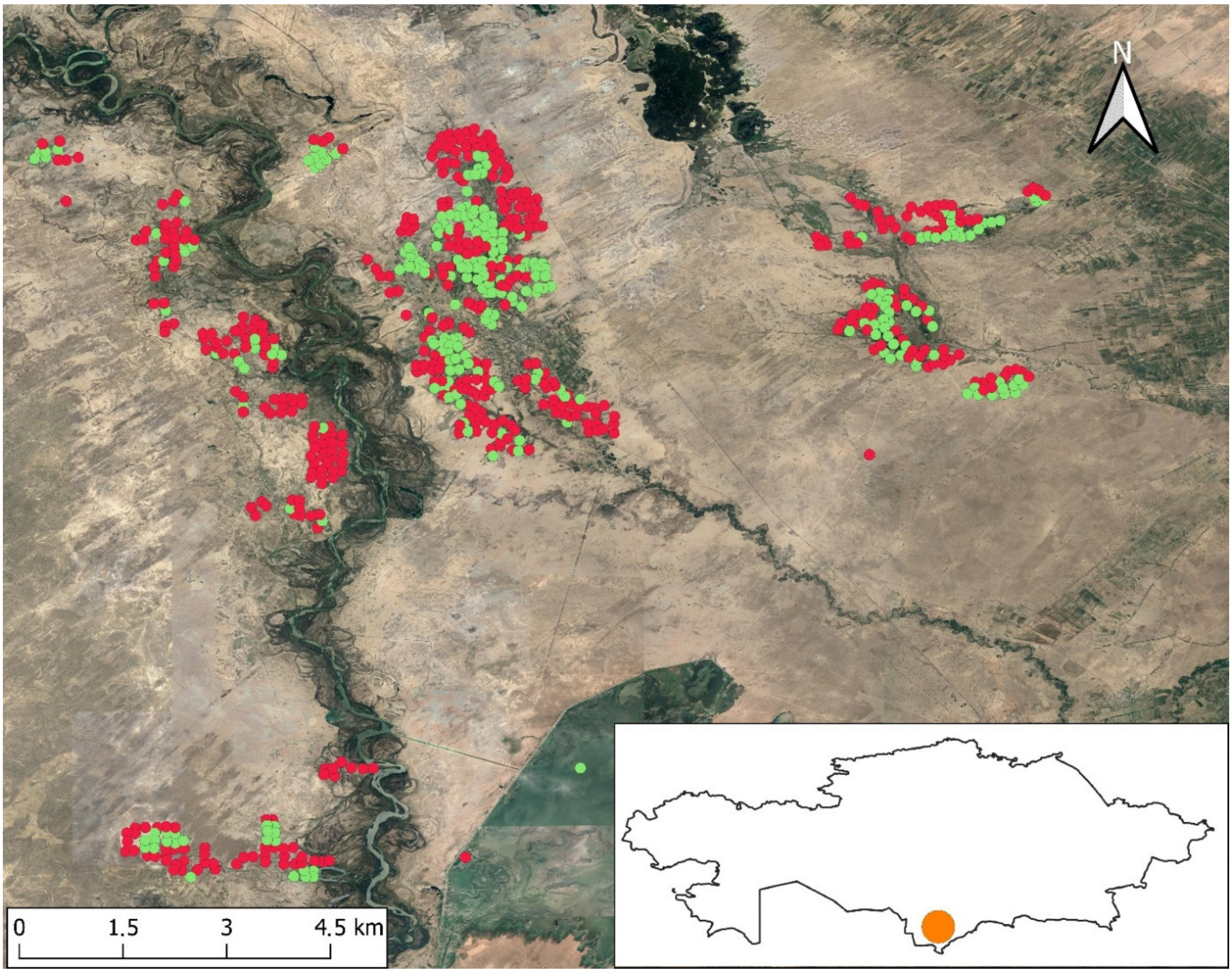


Figure 1. Map of the Syr Darya basin and localization of the study sites. Cultivated soils are marked with green dots, and uncultivated soils with red dots.

With over 300,000 ha of irrigated land, this region is one of the oldest agricultural areas in Kazakhstan [17]. The main irrigated area is located between the Arys and Bougun tributaries of the Syr Darya river and belongs to one of the six main irrigation districts created during the Soviet era, called the Arys–Turkestan irrigation system ("Artur" district). The primary irrigation water sources in this area are canals Arys–Turkestan and Shauldara, fed by the Syr Darya river. The water supply network comprises a main channel and various sprinklers distributed in soils. There are also additional sources of groundwater recharge. i.e., rainfall.

According to the long-term climatic data, the climate of the Turkestan region is continental, dry, and warm [18]. High continentality is manifested in high temperature contrasts between day and night and winter and summer. The warmest month is July, with the maximum temperature reaching 40 °C, and the coldest month is January, with a mean minimum temperature of −9.6 °C. Aridity is one of the main characteristics of the region's climate. Mean Annual Precipitation in the Turkestan region is between 150–250 mm, with relatively high precipitation during winter (up to 50 mm per month), and dry summers (less than 12 mm per month) [19].

For many geological epochs, the modern deserts of Kazakhstan have been areas of the earth's crust immersion. As a result, unconsolidated solid marine and continental sediments have accumulated there. The complexity of the geological structure of Kazakhstan is due to the participation of various rock complexes. The significant ore deposits were formed in the Middle and Late Paleozoic, whereas the Early Paleozoic deposits were few. Many ore deposits, especially those created in the later eras are associated with granitoid intrusion [20]. From the southwest of the Kazakhstan- Central Asian territory, a significant depression appeared, accumulating gypsiferous lagoon and purely continental red-carbonate sandy-clayey sediments [21].

The relief of the Shauldara massif was formed by the accumulative erosion activity of the Arys River, which created three main flooded terraces (Figure 2). On these terraces, hydromorphic soils (mainly Fluvisols) developed, whereas on upper non-flooded terraces various Calcisols developed. Fluvisols were represented by alluvial-meadow (AM), meadow, and meadow-serozem soils (M), often saline. To Calcisols belonged secondary solonchaks (SS) and various subtypes of serozems (S).

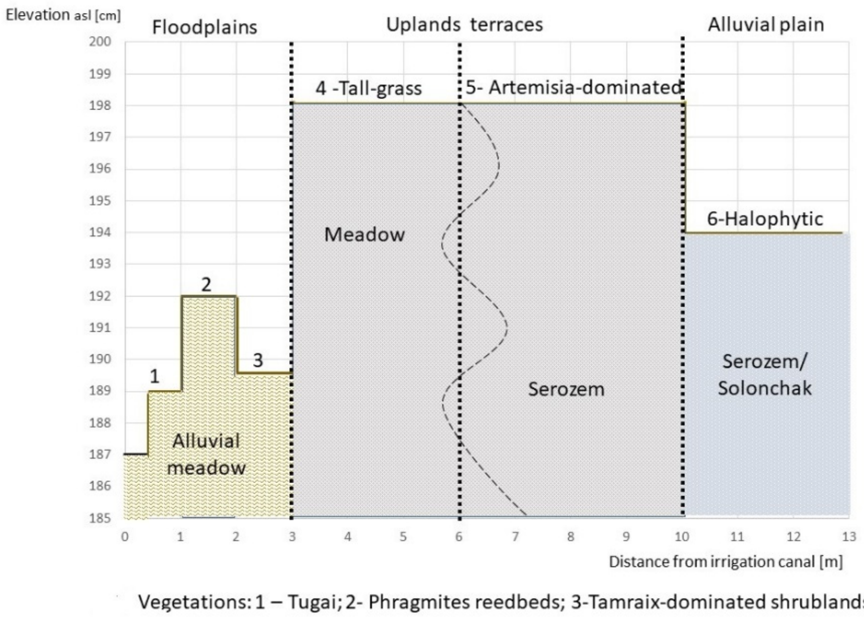


Figure 2. The scheme of the main floodplain terraces, soil types, and dominated vegetations on the Shauldara massif in the cross-section to the Syr Darya river, adopted after [19].

Vegetation occurring on alluvial-meadow soils developed on the flooded terraces of the Arys River, comprised of tugai vegetation distributed in discontinuous strips along the river and its tributaries, where highly mineralized groundwaters are close to the surface. These flooded forests harbour numerous species of trees and shrubs, such as *Populus ariana* Dode, *Populus pruinosa* Schrenk, *Elaeagnus angustifolia* L., *Salix songarica* Andersson, *Salix wilhelmsiana* M. Bieb., *Hippophae rhamnoides* L., *Caragana halodendron* (Pall.) Dum. Cours., and several herbaceous species occurring mainly on the edges of the forest e.g., *Alhagi pseudalhagi* subsp. *kirghisorum* (Schrenk) Yakovl., *Aeluropus littoralis* (Gouan) Parl., *Leymus multicaulis* (Kar. & Kir.) Tzvelev, *Suaeda salsa* (L.) Pall. Apart from tugai vegetation, the flooded terraces are covered with *Phragmites australis* L. reedbeds, with admixtures of *Typha angustifolia* L., *Bolboschoenus maritimus* (L.) Palla, *Juncus gerardi* Loisel., *Oxybasis rubra* (L.) S.Fuentes, and Uotila & Borsch, and with *Tamarix* shrublands with *Tamarix parviflora* var. parviflora, *T.laxa* Willd. and *T. ramossisima* Ledeb. On meadow soils developed on non-flooded terraces occurs herbaceous vegetation, mostly tall grasses such as *Calamagrostis pseudophragmites* (Haller f.) Koeler, *Typha laxmannii* Lepech., *Tripidium ravennae* (L.) H.Scholz, *Imperata cylindrica* (L.) P.Beauv., *Saccharum spontaneun* L. and *Elymus repens* (L.) Gould. Serozem soils on the non-flooded terraces, characterized by a high content of carbonates and gypsum, are covered with low grasslands and ephemeral Artemisia-dominated vegetation, with *Artemisia terrae-albae* Krasch., *A. diffusa* Krasch. ex Poljakov, *A. dracunculus* L., accompanied by *Carex pachystylis* J.Gay, *Poa bulbosa* L., annual chenopods, *Bromus tectorum* L., *Elymus repens* (L.) Gould, *Ceratocarpus arenarius* L., and *Alhagi pseudalhagi* subsp.

kirghisorum (Schrenk) Yakovl. On solonchaks developed in alluvial plain occurs halophytic vegetation with *Halocnemum cruciatum* Tod., *Halostachys caspica* (M.Bieb.) C.A.Mey., *Suaeda corniculata* (C.A.Mey.) Bunge, S. acuminata (C.A.Mey.) Moq., *S. salsa* (L.) Pall., *Salicornia europaea* L., *Halimocnemis villosa* Kar. & Kir., *Petrosimonia glauca* Bunge, *Atriplex verrucifera* M. Bieb., *Climacoptera turcomanica* (Litv.) Botsch., *C. turgaica* (Iljin) Botsch, *C. subcrassa* (Popov) Botsch., *Karelinia caspia* Less., *Ceratocarpus arenarius* L., *Caroxylon dendroides* (Pall.) Tzvelev, *C. orientale* (S.G.Gmel.) Tzvelev, *C. incanescens* (C.A.Mey.) Akhani & Roalson, and *C. scleranthum.*

In general, vegetation in the Arys river basin is significantly transformed by human-induced activities, which leads to a decrease in species diversity, the convergence of plant communities, and simplification of the spatial structure of vegetation cover.

2.2. Data Collection

2.2.1. Field Sampling

A robust collection of 715 soil samples from 348 soil profiles was gathered between 2015 and 2018 from irrigated pastures and arable fields in the Shauldara massif. In each profile, three layers (horizons) were distinguished—(1) 0–20 cm (plough layer), (2) 20–50 cm (eluvial-illuvial horizon for salts and heavy metals), and (3) 50–100 cm (parent material/rock horizon). Soil samples were taken from the middle part of each of the three determined levels of soil profiles. Profiles were located in each of the four major soil types identified in this area: alluvial meadow soil (AM) in the flooded terraces (floodplain), meadow soils (M), serozems (S) in non-flooded terraces, and secondary solonchaks (SS) in the alluvial plain.

The study area was in the past intensely cultivated mainly for alfalfa, cotton, or rice crop production, yet due to increasing soil salinization, some fields were either transformed into pastures or wholly abandoned. Most of the soil samples studied represent uncultivated land, either pasture or abandoned. Abandoned fields are characterized by a typical and recognizable vegetation succession, starting with the recovery of annual and multiyear herbaceous species, perennial woody species such as shrubs (e.g., *Tamarix* spp.), and some trees.

2.2.2. Laboratory Analyses

In the collected samples, basic soil features were analyzed, including pH and soil organic matter SOM [%], contents of Na^+, K^+, Mg^{2+}, and Ca^+ cations, and of Cl^-, $HCO_3{}^{2-}$, and $SO_4{}^{2-}$ anions expressed in cmol/g of soil (all of them measured in water/soil extract with a ratio of 1/5 *v/w*). SOM was determined by oxidizing it with potassium dichromate ($K_2Cr_2O_7$) according to the Tiurin'titrimetric method [22]. The Na^+, K^+, and Ca^+ content were determined on a flame spectrophotometer, and measuring of Mg^{2+} was performed with an atomic absorption spectrometer AA-6200 (Shimadzu, Kyoto, Japan). The anion content was measured using the colourimetric method.

Particle-size distribution of the studied soils was measured by gravimetric methods. The sum of salts % of the mass of dry soil was calculated using results obtained from the ions measured. Additionally, the total contents of the selected heavy metals (Pbtot, Zntot, Cdtot, Nitot, Cutot) were analyzed according to the ISO 11466 method [23] after mineralization in Aqua Regia (expressed in mg/kg of soil). The contents of mobile forms of Pbmob, Znmob, Cdmob, Nimob, and Cumob were extracted with an acetate-ammonium buffer solution at pH 4.8 (expressed in mg/kg of soil). Ultrapure reagents were used for all analyzes and deionized water for dilutions. Both forms of heavy metals were measured with an atomic absorption spectrometer AA-6200 (Shimadzu, Tokyo, Japan).

All analyses were performed at the Kazakh Research Institute of Soil Science and Agrochemistry laboratory, according to the standard analytical procedures recommended by the Ministry of Environment in Kazakhstan [2–26].

To assess the contamination status of the investigated soils, we used threshold values provided by the Ministry of Environmental Protection of Republik Kazakhstan (MEPRK) [27] for Kazakhstan and by Gawlik and Bidogiol [28] for the European Union.

2.2.3. Statistical Analyses

The number of samples used in the statistical analyses differed according to the soil layer sampled (the first layer was sampled in noticeably more locations than the second and the third layer) and to the parameter studied (due to lack of sampling and/or outlier exclusion). In the first soil layer, calculations of particle size distribution were performed on 300 samples in total; of pH and salinity parameters (sum of salts, the content of ions) on 325 samples; of SOM content on 465 samples in total; of total metal content on 309 samples in total; and the content of mobile metal fractions on 715 samples in total. No results of pH and SOM analyses were available for the second and the third layer. As in general, the studied parameters failed to meet the assumptions of parametric tests (normal distribution and/or equal variances), and non-parametric statistics were used. To compare values of the studied soil parameters in the distinguished soil layers and the distinguished soil types, Kruskal–Wallis tests were performed. To assess relations between physiochemical soil properties, including soil salinity, and contents of total and mobile fractions of heavy metals, Spearman rank correlations were calculated. All statistical analyses were performed with Statistica for Windows v. 13.

3. Results

3.1. Physical and Chemical Characteristics of the Studied Soils

Among the 715 studied soil samples, over 63% belonged to meadow soil type, 16% to solonchaks, and 11% and 10% to alluvial meadow soils and serozems, respectively. All the studied soils were silty loamy, with about 1% of soil organic matter in the surface layer and alkaline pH ranging from 8.2 to 9.7 (Table 1).

Table 1. The main characteristics of studied soils; background levels and regulatory standards for Kazakhstan and EU countries.

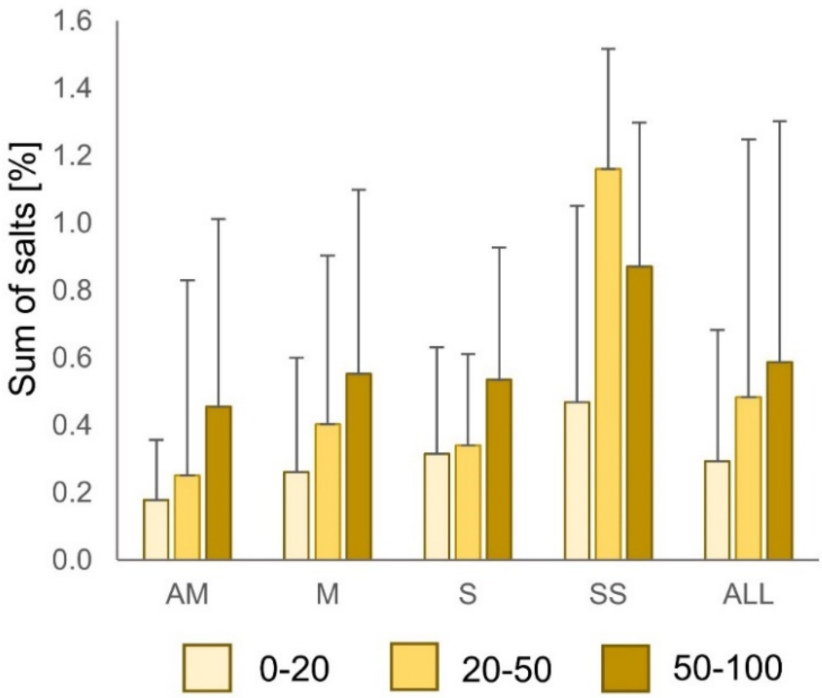
	Cdtot [mg/kg]	Cutot [mg/kg]	Nitot [mg/kg]	Pbtot [mg/kg]	Zntot [mg/kg]	pH	SOM [%]	Sand [%]	Silt [%]	Clay [%]
Data										
N	309	308	309	309	307	326	465	298	300	299
Median	2.4	24.0	43.6	12.8	66.0	8.2	1.0	18.9	63.5	16.3
Min	0.1	4.4	15.2	3.2	21.6	7.5	0.3	1.1	12.2	2.8
Max	4.8	48.8	70.4	24.8	107.2	9.7	2.8	78.5	80.8	34.9
Statistics										
Mean	2.5	24.4	43.6	12.8	66.9	8.3	1.1	21.3	61.4	17.1
SD	0.86	6.53	9.49	3.25	14.87	0.38	0.43	12.69	11.08	5.38
CV [%]	35	27	22	25	22	5	39	60	18	31
K-S (p)	<0.01	<0.01	>0.20	>0.20	>0.20	<0.01	<0.05	<0.01	<0.01	<0.10
References										
Background values *	≤20	≤35	≤40	≤35	≤100	x	x	x	x	x
Guidelines EU **	1.5	100	70	100	200	x	x	x	x	x
Exceeding EU	90.30%	0%	0.3%	0%	0%	x	x	x	x	x
Guidelines KAZ ***	0.5	33	4	32	23	x	x	x	x	x
Exceeding KAZ	98.40%	10.7%	100%	0.3%	100%	x	x	x	x	x

* Background: Natural background values (China) (after Guney et al. [29] ** Guidelines EU: Gawlik and Bidoglio, [28]; *** Guidelines KAZ: MEPRK [27] after Guney et al. [29].

Particle-size distribution of the studied soils was rather uniform in the profiles located on alluvial meadow soils, meadow soils, and serozems. In these soil types, sand comprised between 14.4% and 20.7%; silt between 61.2% and 68.8%, and clay between 16.5% and 21%. Solonchaks was characterized by slightly higher sand content (21.8–30.6%), and slightly lower both silt (54.6–64.8%) and clay content (14.4–16.2%). For alluvial meadow soils, meadow soils, and solonchaks, an increase in sand and silt can be observed with the depth. However, the observed differences showed no statistical significance in Kruskal–Wallis tests.

3.2. Soil Salinity

In the surface soil layer (0–20 cm) of all the studied profiles, the sum of salt values ranged between 0.05% and 3.28%, with a mean of 0.29% (SD = 0.39, as calculated jointly for all of them) (Figure 3). For the second (20–50 cm) and the third layer (50–100 cm), we observed an increase in the sum of salt values; a mean calculated for all samples from the second layer was 0.48% (SD = 0.58) and for all samples from the third layer it was 0.59% (SD = 0.56). These differences were of statistical importance, with a *p*-value in the Kruskal–Walli's test < 0.001. The same trends were recorded for alluvial meadow ($p < 0.01$), meadow ($p < 0.05$), and serozem soils, though for the latter soil type, the differences were not statistically significant ($p = 0.22$). In the case of secondary solonchaks, we observed an increase in the sum of salt values in the second layer, yet it was followed by a decrease in the third layer ($p < 0.05$). In comparison to other soil types, secondary solonchaks showed the highest values of the sum of salts, regardless of the sampling depth. However, the observed differences were statistically significant only in the first and the second layer (in both cases with $p < 0.001$).



SUM OF SALTS	AM	M	S	SS	p_{KW}
0-20 cm	a	a	ab	b	<0.0001
20-50 cm	a	a	a	b	<0.0001
50-100 cm	a	a	a	a	0.1174

Figure 3. Mean sum of salts [%] in three horizons (A-0–20 cm, B-20–50 cm, and C-50–100 cm) of the studied soil types, with statistically significant differences between the studied soil types and *p* values in Kruskal–Wallis tests provided in the table. Abbr.: alluvial meadow soil (AM), meadow soils (M), serozems (S), and secondary solonchaks (SS). The mean content of cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) and anions Cl^-, SO_4^{2-}, and HCO_3^{2-} are shown in Figure 4.

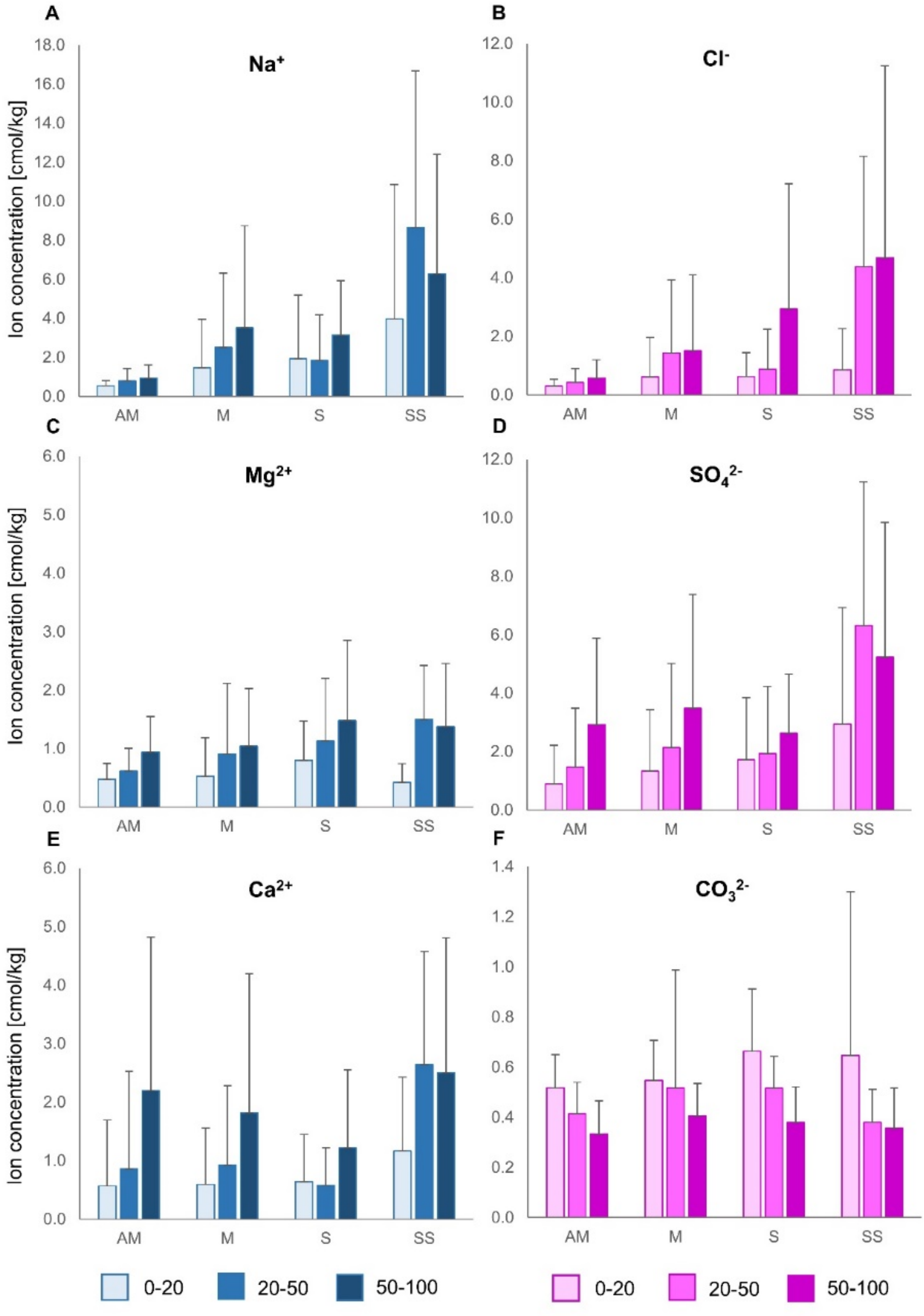


Figure 4. *Cont.*

Na^{+} [mmol/kg]	**AM**	**M**	**S**	**SS**	**p_{KW}**
0−20 cm	a	a	ab	b	<0.0001
20−50 cm	a	a	a	b	<0.0001
50−100 cm	a	a	ab	b	0.0034
Mg^{2+} [mmol/kg]	**AM**	**M**	**S**	**SS**	**p_{KW}**
0−20 cm	abc	ac	b	c	0.0003
20−50 cm	a	a	ab	b	0.0005
50−100 cm	a	a	a	a	0.0873
Ca^{2+} [mmol/kg]	**AM**	**M**	**S**	**SS**	**p_{KW}**
0−20 cm	a	a	ab	b	<0.0001
20−50 cm	a	a	a	b	<0.0001
50−100 cm	a	a	a	a	0.2423
Cl^{-} [mmol/kg]	**AM**	**M**	**S**	**SS**	**p_{KW}**
0−20 cm	a	a	a	b	0.0141
20−50 cm	a	a	a	b	<0.0001
50−100 cm	ab	a	ab	b	0.0015
SO_4^{2+} [mmol/kg]	**AM**	**M**	**S**	**SS**	**p_{KW}**
0−20 cm	ab	a	bc	c	0.0001
20−50 cm	a	a	ab	b	0.0001
50−100 cm	a	a	a	a	0.2051
CO_3^{2+} [mmol/kg]	**AM**	**M**	**S**	**SS**	**p_{KW}**
0−20 cm	a	a	b	ab	0.0074
20−50 cm	ab	a	a	b	0.0026
50−100 cm	a	a	a	a	0.1274

Figure 4. The mean content of cations and anions of soluble salts in 3 soil horizons of studied soils [cmol/100g soil] with statistically significant differences between the studied soil types and *p* values in Kruskal–Wallis tests provided in the table. Abbr.: alluvial meadow soil (AM), meadow soils (M), serozems (S), and secondary solonchaks (SS).

Samples of alluvial meadow soils, again regardless of the sampled layer, dominated Ca^{2+} ions. The mean concentrations of Na^{+} ions in all the three studied layers were the lowest in alluvial meadow soils (values below 1 cmol/kg) and the highest in secondary solonchaks (values above 4 cmol/kg). Mean Na^{+} concentrations recorded for meadow soils and serozems were similar and reached 2 cmol/kg in the first and second layers, and approximately 3 cmol/kg in the third layer. The recorded differences in mean Na^{+} concentrations among soil types were statistically significant (*p*-value always below 0.01). In the case of Ca^{2+} and Mg^{2+} ions, their mean concentrations were comparable in the corresponding layers of different soil types, with the exclusion of secondary solonchaks, in which mean Ca^{2+} concentrations were approximately two times higher than mean Mg^{2+} concentrations. Mean Ca^{2+} concentrations in all three studied layers were the highest in secondary solonchaks (around 1 cmol/kg in the first layer and around 2.5 cmol/kg in the second and the third layer) and the lowest in an alluvial meadow and meadow soils (around 0.6 cmol/kg in the first layer) or serozems (around 0.6 cmol/kg in the second layer and around 1.2 cmol/kg in the third layer). Differences in mean Ca^{2+} concentrations observed in the first and the second layer were statistically important (*p*-value below 0.0001). Considering mean Mg^{2+} concentrations, the highest was recorded in serozems in the first and the second layer (0.8 and 1.5 cmol/kg, respectively) and secondary solonchaks in the second layer (1.5 cmol/kg). In the first layer, the lowest mean Mg^{2+} concentrations were observed in secondary solonchaks (0.4 cmol/kg) and in the second and the third layer in alluvial meadow soils (0.6 and 0.9 cmol/kg, respectively). In alluvial meadow soils, meadow soils and serozems and all the studied cations showed a noticeable increase with the sampling depth. In the case of secondary solonchaks, the second layer was the richest in the studied cations.

Among anions, SO_4^{2-} ions dominated uniformly, regardless of the soil type and the studied layer. The mean anion contents in the soil surface layer (0–20 cm) are shown in descending order $SO_4^{2-} > HCO_3^{2-} > Cl^{-}$. The highest mean concentrations of SO_4^{2-} ions in all three studied layers were recorded in secondary solonchaks, in which they reached 2.9 cmol/kg, 6.3 cmol/kg, and 5.2 cmol/kg in the consecutive layers. The lowest mean concentrations of SO^{2-} were observed in alluvial meadow soils (0.9 cmol/kg in the first and 1.3 cmol/kg in the second layer) and serozems (2.62 cmol/kg in the third layer). The differences observed in the first two layers were statistically important ($p < 0.0001$). The mean concentrations of Cl^{-} ions showed trends like Na+ ions, namely, regardless of the layer studied. The lowest mean concentrations were recorded in alluvial meadow soils (always below 1 cmol/kg) and the highest mean concentrations in secondary solonchaks (around 1 cmol/kg in the first layer and around 4.5 cmol/kg in the second and the third layer). Mean Cl^{-} concentrations recorded for meadow soils and serozems were similar and reached around 0.6 cmol/kg in the first, one in the second, and two in the third layer). The recorded differences in mean Cl^{-} concentrations among soil types were statistically significant (*p*-value always below 0.05). The mean concentrations of HCO_3^{-} ions were the most uniform, around 0.5 cmol/kg, regardless of soil type and studied layer. Nevertheless, for the first and the second layer statistically important differences between the soil types were observed (*p*-value below 0.01). In the first and the third layer, the lowest mean concentration of HCO_3^{-} ions was observed in alluvial meadow soils (around 0.5 cmol/kg and 0.3 cmol/kg, respectively), and in the second layer in the secondary solonchaks (around 0.4 cmol/kg). The highest mean concentrations of HCO_3^{-} ions in the first layer were recorded in serozems (around 0.7 cmol/kg), in the second layer in both serozems and meadow soils (around 0.5 cmol/kg), and in the third layer in meadow soils (around 0.4 cmol/kg). All the studied anions, except HCO_3^{-}, showed a noticeable increase in the sampling depth, regardless of soil type.

3.3. The Total and Mobile Form Content of Selected Metals in the Studied Soils

The values for heavy metals in soil for a layer of 0–20 cm for all soil samples are summarized in Table 2. Abbr.: alluvial meadow soil (AM), meadow soils (M), serozems (S), and secondary solonchaks (SS).

The mean total contents of the studied metals were noticeably higher than the contents of their mobile forms; for Zn and Cu they were around 20 times higher, for Pb and Ni around 5 times higher, and for Cd around 2 times higher. If we compare the mean content of either the total or mobile form of a given metal, its absolute values are almost uniform, regardless of the studied layer or soil type. For Zntot and Nitot, distinguished soil types differed by a maximum of 10 cmol/kg, for Cutot by 5 cmol/kg, for Pbtot by 1.5 cmol/kg, and Cdtot by 0.9 cmol/kg. In the case of mean content of mobile metal fractions, distinguished soils differed by 0.9 cmol/kg maximum for each metal. Differences between mean metal content in soil layers were even smaller for Zntot, Nitot, and Cutot, where the maximum differences between layers were around 2 cmol/kg, for Pbtot around 0.8 cmol/kg, and Cdtot around 0.2 cmol/kg. The differences between the layers did not exceed 0.4 cmol/kg for mobile forms.

Table 2. Main statistics of heavy metals content in studied soils.

	AM	M	S	SS	*p* Values in Layers	
Zntot [mg/kg]	63.7 (12.1)	68.2 (15.6)	58.3 (13.4)	69.9 (12.2)	1st	<0.001
	63.5 (13.2)	66.8 (17.0)	62.9 (13.6)	70.5 (14.7)	2nd	<0.05
	61.7 (13.1)	67.3 (32.2)	64.6 (16.8)	71.1 (14.7)	3rd	ns
Pbtot [mg/kg]	12.5 (2.7)	12.8 (3.2)	12.3 (4.4)	13.9 (2.8)	1st	<0.05
	11.7 (3.4)	12.6 (3.4)	13.8 (3.6)	13.5 (4.2)	2nd	ns
	11.5 (3.1)	12.1 (3.6)	13.1 (3.9)	13.5 (3.7)	3rd	<0.01
Cutot [mg/g]	26.7 (7.8)	24.9 (6.4)	20.6 (6.7)	22.8 (4.2)	1st	<0.01
	25.9 (4.5)	24.8 (6.3)	22.2 (5.9)	23.9 (7.2)	2nd	ns
	28.0 (7.3)	25.2 (10.5)	22.4 (7.6)	24.5 (5.8)	3rd	<0.05
Cdtot [mg/kg]	2.91 (0.88)	2.47 (0.89)	2.36 (0.74)	2.32 (0.72)	1st	<0.01
	3.05 (0.81)	2.58 (0.92)	2.31 (0.84)	2.17 (0.72)	2nd	<0.001
	3.17 (1.07)	2.48 (0.92)	2.31 (0.87)	2.42 (0.93)	3rd	<0.01
Nitot [mg/kg]	44.3 (12.3)	44.8 (8.9)	34.3 (9.1)	43.9 (4.7)	1st	<0.0001
	44.3 (12.8)	44.9 (9.90)	36.3 (9.5)	42.5 (8.0)	2nd	<0.001
	43.1 (14.6)	45.1 (9.3)	36 (8.7)	45.6 (7.6)	3rd	<0.0001
Znmob [mg/kg]	2.94 (1.14)	3.04 (0.99)	2.95 (1.11)	3.02 (0.86)	1st	ns
	2.62 (0.58)	2.99 (3.45)	2.61 (0.83)	2.96 (0.76)	2nd	ns
	2.60 (0.81)	3.02 (3.22)	2.72 (0.67)	3.02 (0.67)	3rd	ns
Pbmob [mg/kg]	3.26 (0.96)	3.9 (1.85)	3.54 (1.58)	4.03 (1.25)	1st	<0.0001
	3.00 (0.81)	3.59 (1.78)	3.24 (1.22)	3.99 (1.10)	2nd	<0.01
	3.16 (0.79)	3.43 (1.46)	3.22 (1.29)	4.13 (1.46)	3rd	<0.05
Cumob [mg/kg]	1.9 (0.68)	1.73 (0.59)	1.95 (0.43)	1.64 (0.51)	1st	<0.0001
	1.93 (0.75)	1.83 (0.66)	2.03 (0.36)	4.65 (0.56)	2nd	<0.05
	2.11 (0.76)	1.83 (0.64)	2.14 (0.43)	1.78 (056)	3rd	<0.01
Cdmob m [mg/kg]	1.1 (0.26)	1.14 (0.30)	1.21 (0.28)	1.26 (0.29)	1st	<0.0001
	1.11 (0.27)	1.12 (0.32)	1.17 (0.22)	1.25 (0.30)	2nd	ns
	1.07 (0.24)	1.12 (0.33)	1.17 (0.27)	1.23 (0.29)	3rd	ns
Nimob [mg/kg]	7.03 (1.90)	7.39 (2.61)	8.05 (1.96)	8.47 (2.40)	1st	<0.0001
	7.34 (1.90)	7.48 (2.67)	8.15 (1.76)	8.41 (2.12)	2nd	ns
	7.15 (2.1)	7.51 (2.83)	8.28 (2.29)	8.66 (2.28)	3rd	<0.01

Nevertheless, some of these differences were statistically important, allowing us to observe some trends. A consistent increase in mean contents of both Cutot and Cumob with depth was observed in all soil types. It was statistically significant for Cu_{tot} in secondary solonchaks ($p < 0.01$) and for Cumob in meadow soils and serozems ($p < 0.001$ and $p < 0.05$, respectively). In the case of both Pbtot and Pbmob, we recorded a consistent decrease in depth, which was statistically significant for meadow soils (for Pbtot $p < 0.05$ and Pbmob $p < 0.01$). This tendency was disrupted by changes in mean Pbmob content in secondary solonchaks, in which the first two layers had similar Pbmob content, and the third layer showed a slight increase in these ions. For the mean content of Cdtot, we recorded both slight increases (AM, M, and S soils) and slight decreases (SS soils) in depth. For the mean Cdmob content, a uniform decrease in depth in all soil types was observed. Yet none of these trends was statistically important. In the case of mean contents of both Ni_{tot} and Ni_{mob}, slight increases with depth were recorded for serozems, secondary solonchaks, and meadow soils, for which these differences were of statistical significance (for Nimob $p < 0.05$). In alluvial meadow soils, a decrease in depth was noticed for Nitot and an increase in depth for Nimob. For mean contents of Zntot and Znmob, we recorded slight but statistically significant decreases with depth for alluvial meadow (for Znmob $p < 0.05$) and meadow soils (for Zntot $p < 0.001$ and Znmob $p < 0.01$). In serozems and secondary solonchaks, mean Zntot content increased with depth, whereas mean Znmob content decreased or remained stable; however, these changes were of no statistical significance.

Considering the differences in heavy metal content in the distinguished soil types, solonchaks were the richest in Zntot and Znmob. Differences in Zntot were statistically important for the first soil layer ($p < 0.001$), in which the mean Zntot content reached 69.9 cmol/kg, and for the second soil layer ($p < 0.05$), it tracked 70.5 cmol/kg. The mean Znmob content in solonchaks was slightly above 3 cmol/kg, yet these differences were of no statistical importance. We also recorded the highest contents of Pbtot and Pbmob in solonchaks. For Pbtot, the observed differences were of statistical importance for the first ($p < 0.05$) and the third layer ($p < 0.01$), in which the mean Pbtot content reached 13.9 cmol/kg and 13.5 cmol/kg, respectively. In the case of Pbmob, the differences were statistically significant in all the layers ($p < 0.0001$ in the first, $p < 0.01$ in the second, and $p < 0.05$ in the third layer), and the mean Pbmob content was slightly above 4 cmol/kg. Moreover, solonchaks had the highest content of Cdmob and Nimob in all the studied layers. In the case of Cdmob, the recorded differences were statistically important only in the first layer ($p < 0.0001$), in which the mean Cdmob content reached 1.3 cmol/kg. For Nimob, the observed differences were statistically important in the first ($p < 0.0001$) and the third layer ($p < 0.01$), with the mean values of 8.5 cmol/kg and 8.7 cmol/kg, respectively. Contrastingly, solonchaks were the poorest in Cdtot and Cutot and these trends were statistically significant in all the studied layers, with p values for Cdtot below 0.01 and Cumob below 0.05. The mean content of Cdtot recorded in solonchaks was around 2.3 cmol/kg, and the mean Cutot content was around 1.7 cmol/kg in all layers.

Serozems were the richest in Cumob, with the mean values slightly above 2 cmol/kg in all layers and p values always below 0.05. The content of Cdmob and Nimob was the second highest in serozems. For Cdmob, the observed differences were statistically significant in the first layer, with a mean content of 1.2 cmol/kg and $p < 0.0001$. For Nimob, the differences were significant in the first and the third layer, with a mean Nimob content of 8.1 and 8.2, respectively, and both p -values below 0.01. Simultaneously, in serozems, Cutot content was the lowest and Pbmob content the second lowest. The differences in the mean Cutot content were statistically significant in the first ($p < 0.01$) and the third ($p < 0.05$) layers, with values of 20.6 cmol/kg and 28.0 cmol/kg, respectively. In the case of the mean Pbmob content, the recorded trends were statistically significant in all layers, with the mean Pbmob values between 3.2 and 3.5 cmol/kg and p values always below 0.05.

The highest content of Cutot characterized alluvial meadow soils, with mean contents of 26.7 cmol/kg in the first layer, 25.9 cmol/kg in the second layer, and 28.0 cmol/kg in the third layer. In the first and the third layer, these tendencies were statistically significant, with p values below 0.01 and below 0.05, respectively. Concurrently, we reported the second-highest Cumob content in alluvial meadow soils, in all studied layers, with the mean values between 1.9 cmol/kg and 2.1 cmol/kg. These observations were statistically significant in all the studied layers with all p values below 0.05. Moreover, alluvial meadow soils were the richest in Cdtot, with the mean content reaching 2.9 cmol/kg in the first layer ($p < 0.01$), 3.1 cmol/kg in the second layer ($p < 0.001$), and 3.17 in the third layer ($p < 0.01$). Simultaneously, for alluvial soil meadows, we reported the lowest contents of Pbtot and mobile fractions for all metals except Cu. The mean Pbtot content in alluvial meadow soils was above 12 cmol/kg in the first layer ($p < 0.05$) and around 11.5 cmol/kg in the second and in the third layer ($p < 0.01$). In the case of mobile fractions, the observed differences were statistically significant in all studied layers for Pbmob (all p values below 0.05), in the first and the third layer for Nimob (both p values below 0.01), and the first layer for Cdmob ($p < 0.0001$).

For meadow soils, we usually observed intermediate values of metal contents, with this type of soil containing the second-highest amount of Zntot (statistically significant in the first and the second layer, with $p < 0.001$ and $p < 0.05$); Znmob; Cutot (statistically significant in the first and the third layer, with p values below 0.01 and below 0.05); Cdtot (statistically significant in all the studied layers, with p values always below 0.05); and Pbmob (statistically significant in all the studied layers, with p values always below 0.05). Concurrently, meadow soils showed the second-lowest content of Cdmob (statistically significant in the first layer with $p < 0.0001$), Cumob (statistically significant in all the studied layers, with p values always below 0.05), and Nimob (statistically significant in the first and the third layer, with $p < 0.0001$ and $p < 0.01$). For meadow soils, the highest metal contents were reported only for Nitot in the first and second layers, with a mean range of 44.8 cmol/kg and 44.9 cmol/kg, and the p values below 0.0001 0.001, respectively.

To sum it up, the analyzed sample contents of the studied metals, with the exception of cadmium, were relatively low and showed little variability between the soil layers and soil types.

Considering the EU thresholds for the total content of heavy metals in soils [28], 90.3% of the studied samples exceeded the threshold of 1.5 mg/kg given for Cdtot (Table 1). If we use the threshold of 0.5 mg/kg provided by the Ministry of Environment in Kazakhstan [27,29], 98.4% of the samples will exceed it. In the case of Cutot, Pbtot, and Zntot, all our results were below the EU thresholds. However, the Kazakhstan thresholds are noticeably lower, especially in the case of Zntot (100 mg/kg in the EU and 23 mg/kg in Kazakhstan). Therefore, if we compare our results to these thresholds, all the studied samples exceed limits for Zntot content, 10.7% of samples exceed Cutot content, and 0.3% of samples exceed Pbtot content. In the case of Nitot content, the EU limits were exceeded in 0.3% of the studied samples, yet the Kazakhstani limits are once again stricter and if compared to them, Nitot content in all the studied samples exceeds this threshold. Interestingly, the Kazakhstani thresholds for Cdtot, Zntot, and Nitot are noticeably higher, and in the case of Pbtot and Cutot, are equal to the natural backgrounds provided for Central Asia by Guney [29]. This observation will be further discussed in the following parts of the article.

3.4. Relationship between Physicochemical Soil Properties, including Soil Salinity and Content of Total and Mobile Forms of Heavy Metals

For most of the studied metals, statistically significant correlations with basic soil physiochemical properties and salinity parameters were scarce, with relatively low Spearman coefficient values (most of them between 0.1 and 0.3) (Table 3).

In the case of the total metal content, the most numerous and consistent correlations were recorded for Zntot in the second soil layer. The strongest positive correlations ($r^2 > 0.25$) for Zntot content were observed for clay content in the first layer ($r^2 = 0.28$), and content in the second layer ($r^2 = 0.32$), and salinity parameters in the second layer ($r^2 = 0.31$ for the sum of salts). These results were supported by positive correlations between Zntot content and concentrations of the ions measured in the second layer, with the highest r^2 values ($r^2 \geq 0.30$) recorded for Mg^{2+}, Ca^{2+}, and $SO_4{}^{2-}$ ions. Interestingly, we observed a weak negative correlation between Zntot and $HCO_3{}^{2-}$ ions in the second layer. While positive correlations of Zntot content with SAR, Mg^{2+}, Ca^{2+}, and $SO_4{}^{2-}$ were backed by the results for Znmob in the first soil layer, the negative correlation with HCO_3^{2-} was not reflected in the results for Znmob.

In the case of mobile fractions, relatively strong and consistent correlations were observed for Pbmob and included negative correlations with sand content for all soil layers, with r^2 of approximately 0.30, combined with positive correlations with clay content for the first two layers (r^2 = 0.31 and 0.46 respectively). Moreover, Pbmob has correlated with the concentration of Ca^{2+} ions (r^2 = 0.27). We observed several strong correlations as well between Cumob content and other soil parameters, including a positive correlation with sand content in the third layer (r^2 = 0.35) and positive correlations with SOM (r^2 = 0.31) and concentration of Mg^{2+} ions (r^2 = 0.25) in the first layer (Table 3). Moreover, we found several negative correlations with r^2 > 0.25, namely between Cdmob content and concentrations of Mg^{2+} ions in the third layer (r^2 = −0.26), between Nimob content and concentrations of K^+ ions in the third layer (−0.32), and between Znmob content and silt content in the third layer (r^2 = −0.28).

Table 3. Correlations between physicochemical soil properties, including soil salinity and content of total (**a**) and mobile forms (**b**) of heavy metals.

(a)

TOT	Sand [%]	Silt [%]	Clay [%]	pH	Salts [%]	SAR	SOM [%]	Na^+	Mg^{2+}	Ca^{2+}	K^+	Cl^-	CO_3^{2-}	SO_4^{2-}
Cd_A											−0.19			
Cd_B														
Cd_C												−0.20		
Cu_A							0.16						−0.22	
Cu_B													−0.22	
Cu_C														
Ni_A														
Ni_B											−0.26		−0.16	
Ni_C														
Pb_A	−0.19	0.17												
Pb_B					0.22	0.20		0.19		0.20				0.21
Pb_C														
Zn_A			0.28		0.13									
Zn_B	0.32				0.31	0.26		0.24	0.31	0.31	0.21	0.24	−0.19	0.30
Zn_C									0.17					

(b)

MOB.	Sand [%]	Silt [%]	Clay [%]	pH	Salts [%]	SAR	SOM [%]	Na	Mg	Ca	K	Cl	CO_3	SO_4
Cd_A			0.15				−0.17							
Cd_B														
Cd_C					−0.17	−0.20		−0.20	−0.26			−0.20		
Cu_A				−0.21	0.13		0.31		0.25			0.11	0.11	
Cu_B														
Cu_C	0.35													
Ni_A			0.13		0.16	0.19	0.11	0.19		0.14				0.13
Ni_B														
Ni_C											−0.32			
Pb_A	−0.27	0.13	0.31	−0.20						0.27				
Pb_B	−0.34		0.46											
Pb_C	−0.29													
Zn_A	−0.21			−0.11		0.12		0.13	0.17	0.17				0.13
Zn_B														
Zn_C		−0.28												

0	r2
	1–0.75
	0.74–0.50
	0.49–0.25
	0.24–0.0
	0
	(−0.25)–0.0
	(−0.49)–(−0.25)
	(−0.74)–(−0.50)
	(−1)–(−0.75)

4. Discussion

4.1. Soli Salinization

There are three major inland depressions in Kazakhstan. Each is a close catchment with a large lake, i.e., Caspian Lowland with the Caspian Sea, Turan Lowland with the Aral Balkhash, and Alakul Lowland with the Balkhash Lake. They cover 93.4 Mln ha, and with increased groundwater and soil salinity, comprise 70% of Kazakhstani salinated areas [6]. However, the lowlands mentioned above differ in geological structure and the presence of rocks rich in soluble salts; thus, they are characterized by different types of soil salinity. In the Caspian Lowland, SO_4-Cl dominates salinity; around the Aral Lake and in the Syr Darya floodplains Cl-SO_4 dominates salinity, and in the Balkhash-Alakul basin and along the Ili River CO_3-SO_4 dominates salinity. Lake terraces and alluvial plains in arid and semi-arid regions are sensitive to primary and secondary salinization, as they accumulate overland water flow due to their low relative elevation [30]. Moreover, in such areas, irrigated fields are usually located, which makes it difficult to provide drainage adequately, lowering groundwater levels and allowing water percolation, which sufficiently washes salts from soil profiles [11]. According to monitoring research performed by the U.U. Uspanov Kazakh Research Institute of Soil Science and Agrochemistry in Almaty between 1987 and 2010, secondary salinization is a major threat to the intensely irrigated depressions along the Syr Darya river. Over the last 30 years, the percentage share of lowly salinated areas in the Syr Darya river basin decreased by 32.1%. Simultaneously, the percentage share of highly salinated areas that had to be excluded from cultivation increased by 27.4% [13].

Therefore, we performed our soil monitoring activities in the Shauldara massif in the Syr Darya river basin. Among the soils occurring in the massif, meadow soils (meadow and meadow-serozem) can be distinguished, occurring on the medium terraces on saline, weakly loamy, and clayey sediments that predominate in this area. The average depth of mineralized groundwater is between 4 and 6 m. On the lower terraces, semi-hydromorphic solonchaks and solonetz occur, usually in slightly elevated areas (up to 50 cm), on calcareous or gypsum rocks under the strong influence of strongly influenced areas mineralized groundwater, at the depth of about 50 cm. Near rivers/canals, alluvial meadow soils are covered with reeds in the areas located in depressions. The predominant natural type of soil salinity in the Shauldara massif is chloride-sulfate and sulfate-chloride, sometimes with sodium chloride (NaCl). All developed soils are rich in non-soluble carbonates and are characterized by high alkalinity (pH 8–9). Depending on the degree of mineralization of the groundwater, the area of the massif belongs to the hydrogeological area with an intense inflow of shallow waters and difficult outflow of groundwater. Moreover, an increase in groundwater level can be caused by abandoned canals, collectors, and vertical drainage wells that currently function without any control. Considering the above-mentioned environmental issues, soils of the massif are prone to secondary salinization.

Most of the soils presented in this article were either of medium or high salinity. They were mostly highly alkaline, with a low amount of soil organic matter. Sulphates were the most abundant among the anions, especially in the deepest layer (50–100 cm). Contrastingly, carbonates were the least abundant, with the highest content in the surface layer (0–20 cm). These trends were the best visible in the studied solonchaks. The concentration of toxic chloride ions was slightly lower than that of sulphates, and it decreased with depth. The highest values were recorded for solonchaks. In the case of cations, sodium ions dominated over calcium and magnesium ions (concentrations on average two times lower than Na^+). Solonchaks were the richest in cations, and a strong increase in cation concentrations was observed for all the studied soil types. Soil salinity refers to water-soluble salts, usually including sodium, potassium, calcium, magnesium cations, chloride, sulphate, nitrate, and carbonate anions. As sodium and chloride ions are not considered plant nutrients and show noticeable toxicity to plants and soil fauna, soil salinity studies often focus on these two ions [30]. Moreover, an increase in the concentration of soluble salt, especially Mg, and accumulation of NaCl and Na_2SO_4, results in excess calcium carbonate $CaCO_3$, which in turn facilitates the formation of alkali. This situation was described by several studies in arable soils in Central Asia [31–33].

Funakawa et al. [34]], studying soil salinization in the irrigated areas in southern Kazakhstan, speculated whether an accumulation of gypsum and/or soluble salts near the soil surface suggests an upward movement of groundwater with a high concentration of salts, or whether salt accumulation in deeper horizons, in combination with a low soluble salt concentration, and an alkalized surface layer, would indicate that the soils were formed by leaching, with a positive reaction for residual sodium carbonate. According to Funakawa et al. [34], two mechanisms of soil salinization can be observed in the irrigated areas of S Kazakhstan: (1) through an upward movement of groundwater with a high concentration of salts, resulting in the accumulation of salts near the soil surface; or (2) through leaching and salt accumulation in deeper soil layers, resulting in a surface layer that is alkalized and has poor insoluble salts. The composition and distribution of salts in soil profiles are determined by the irrigation–drainage systems used and by the nature of irrigation water (Karimov et al., 2009). In irrigated paddy soils, it can wash the salts from the surface layer to a depth of 50 cm [35]. This observation is supported by long-term studies in the irrigated area along the Arys–Turkestan canal by Karimov et al. [36], who between 1967 and 1998 recorded a decrease of 50–80% in total soluble salts in the topsoil after 25 years of irrigation. A similar distribution of ions in the soil profiles, excluding carbonates, was observed in our studies. According to Karimov [36], the accumulation of Na^+, and to a large extent Mg^{2+}, in the lower horizon (20–40 cm) was caused by high mineralized groundwater, specifically rich in bicarbonates and Ca^{2+} [36]. Interestingly, concentrations of Na^+ in soils studied by Karimov were noticeably lower than in concentrations of Mg^{2+} [36], whereas our results showed apparent domination of Na+ in all soil types and all soil layers.

In the irrigated areas of southern Kazakhstan, increasing groundwater and mineralization is facilitated because the territory has not been washed in recent years. Moreover, a significant excess of evaporation over soil precipitation typical for continental climate contributes to a great accumulation of salts in waters and irrigated soils, especially in deeper horizons [35]. Under arid and semi-arid conditions, the less soluble salts, calcium carbonate ($CaCO_3$), gypsum ($CaSO_4$ $2H_2O$), and magnesite ($MgCO_3$), easily precipitate, causing a relative increase in the proportion of Na^+ ions in solution, and, consequently, a replacement of some exchangeable Ca^{2+} and Mg^{2+} by Na^+ in the exchange complex [36]. As a result, between 1940 and 2013, concentrations of major ions in the Syr Darya irrigation water used in S Kazakhstan (Kyzylorda region) increased significantly, including Na^+ and K^+ ions, up to 5 times, Mg^{2+} ions up to 3.5-times, and $SO_4{}^{2-}$ and Cl^- ions up to 4 and 4.5 times, respectively [37,38]. In the 1940s, the chemical composition of irrigation water was bicarbonate with the predominance of Ca^{2+} ions. In the 1970s, noticeable changes in irrigation and water composition were noticed, leading to the most intense salt accumulation in the mid-1980s, when the concentration of Na^+, K^+ and sulphates was several times higher than the baseline salt content in the waters of the Syr Darya river. Increased salinity of irrigation waters was reported in southern Kazakhstan until 2015. Interestingly, the Syr Darya waters are also prone to salinization due to anthropogenic factors, including industrial and agricultural production, and the inflow of urban domestic sewage [10]. Thus, soil secondary salinization in southern Kazakhstan/the Syr Darya river basin can be attributed either to waterlogging or to irrigation without proper leaching and drainage [16]. The latter is the most probable cause in the case of our studies. Due to intense leaching regimes imposed by improper irrigation management, soils in southern Kazakhstan were permanently altered through the leaching of primary cations and the most common anions (i.e., primary gypsum). This process caused a relative increase in the proportion of Na^+ ions in soil solution, and, consequently, the replacement of some exchangeable Ca^{2+} and Mg^{2+} by Na^+ in exchangeable complex [36]. In such transformed soils, apart from the changes in ion concentrations and distribution, soil organic matter is characterized by increased mobility and relatively rapid destruction, leading to losses of plant-available nutrients like N and P [14]. Thus, in the soils of S Kazakhstan (in the delta of the Ili river), a significant amount of soil organic matter (around 1%) can be found at a depth of 1 m, whereas negligible amounts of soil organic matter are reported in the topsoil layers. Moreover, heavy metals in soils are transformed into mobile forms and leached into deeper soil horizons [14]. Such problems may be more widespread and extensive than currently recognized in the irrigated areas of Central Asia.

4.2. Soil Contamination with Heavy Metals

Our research on the content of heavy metals in soils from the Shauldara massif revealed high variability and diversified distribution patterns of the studied metals (both in the landscape and in the profiles). Out of the five studied metals, only cadmium content (both total content and mobile fractions) exceeded the threshold values provided by the EU. Thus, apart from cadmium, there is no need to further assess ecological and/or health risks. Large metallic ore deposits formed during Central Asia's geological development/evolution [10]. Thus, natural background values of metal content in soils may be high and threshold values applied in monitoring studies should be adapted to them. Mean total concentrations of cadmium recorded during our research were relatively uniform, regardless of the layer and soil type (between 2.17 mg/kg and 3.17 mg/kg), yet they all exceeded the EU threshold value of 1.5 mg/kg. Considering all 715 studied soil samples, the EU threshold for Cdtot was exceeded in 90.3% of them. The high content of Cdtot in the soils of the Shauldara massif results mainly from anthropogenic input, including inflow with irrigation water, mineral fertilizers, pesticides, eolian deposits, and other industrial sources. These inputs add to the natural background values that are already relatively high in Central Asian soils [29]. In the case of agricultural soils in the Shauldara massif, the main source of heavy metal contamination is irrigation water provided by the contaminated Syr Darya River [34]. Chemical contaminants, including heavy metals, are present in the Shardara Reservoir, which collects waters from the lower part of the Syr Darya River and distributes them via irrigation canals into the arable fields. A study by Barinova et al. [39] showed that water in the Shardara Reservoir was permanently polluted with Cd between 2004 and 2015. Among the causes of heavy metal contamination of the Syr Darya River are industrial facilities, mainly from the mining and ore processing sectors that are located along the river [8,16]. Polluted river water, distributed over fields with irrigation canals, causes contamination of arable soils. Several authors report significant cadmium contamination of irrigated soils in the Turkestan region [9,10,16,29]. Thus, according to [2], who for the last 20 years have been studying 10 toxic trace metals in environmental matrices from the area of Kazakhstan, the Turkestan region is a hotspot of soil contamination with Cd.

5. Conclusions

Our research showed that most of the studied soils were moderately and highly saline, irrespective of soil type. Surprisingly, heavy metal contamination was low, and in most cases, except for cadmium, it was below the limits developed for arable soils in most countries. Soil contamination with cadmium results from contamination of the water used for irrigation of farmland. After we monitor arable soils that represent irrigated areas in the mid-stream of the Syr Darya river, we can expect these areas, used for agriculture due to secondary salinity, to be abandoned in the future. Therefore, farmers and agricultural producers need reliable soil and water monitoring results, enabling mitigation activities to reduce the risk of soil secondary salinization in question. Similar data are needed by the governmental bodies (local governments, agricultural administrations, environmental services, etc.) to make strategic decisions in terms of food security.

Author Contributions: Conceptualization, M.S.-M. and M.M.; Methodology, M.S.-M., A.V.; Investigation, A.V., M.I., M.P.; Resources, M.I., M.P., A.V.; Writing—Original Draft Preparation, M.S.-M., M.M.; Writing—Review & Editing, M.S.-M., M.M., M.S., K.T.; Visualization, M.S.-M., M.S., M.M.; Supervision, M.S.-M.; Project Administration, M.I., M.S.-M.; Funding Acquisition, M.I. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Monitoring. The concentration of heavy metals and organic pollutants in irrigated soils using GIS and developing methods to increase soil protective properties in relation to pollutants with the grant support of the Target Program Conservation and reproduction of soil fertility in Kazakhstan, grant number: O.0709.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Presented data in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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