Heliyon 7 (2021) e05844

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Research article

Heavy metal deposition through precipitation in Kazakhstan

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ARTICLE INFO ABSTRACT Keywords: The active development of industry, primarily mining and metallurgical, as well as energy, is accompanied by Heavy metals significant emissions of pollutants into the atmosphere. We collected data and analyzed the intake of heavy metals Wet and dry deposition (HM) of lead (Pb), copper (Cu) and arsenic (As), cadmium (Cd) in precipitation (wet deposition) on typical natural Precipitation and snow cover Kazakhstan ecosystems. The average Pb, Cu, As and Cd wet deposition was 3.80 \pm 1.52, 16.11 \pm 1.48, 0.96 \pm Ecological regions and ecosystems 0.84 and 0.88 \pm 0.44 µg/L, respectively, with a large variation among the different sites of Kazakhstan. In addition, we identified the most significant industrial areas in the republic and determined the concentrations of the listed metals in the precipitation for each of them. The relationship between these concentrations and industrial activity in the regions, and the presence of a mutual correlation between them were also investigated. We obtained that the atmospheric deposition of Pb, Cu and As were higher in the central industrial areas (Dzhezkazgan, Balkhash), as well as in the south (Chimkent) and in the east (Ust-Kamenogorsk), where large mining and metallurgical enterprises are located. In these cities, there are high concentrations of pollutants (PS) in the atmosphere, exceeding the maximum permissible concentrations (MPC) by several times. Significant sedimentation of pollutants, primarily HM, is noted, adversely affecting soils and surface runoff. The total deposition of heavy metals on snow cover was determined. We obtained that the average total deposition for Pb, Cu, As and Cd was $4.4\pm1.28,\,20.6\pm1.43,\,3.23\pm0.81$ and 1.03 ± 0.47 µg/L. Calculations performed for comparable time intervals showed that dry deposition is two to five times greater than wet deposition and the smaller the precipitation in the

region, the greater the dry deposition, ceteris paribus. At the level of climate assessments, it is shown that there is a transboundary transfer of heavy metals from both the territory of Kazakhstan from the territory of Russia.

1. Introduction

Various pollutants deposited with precipitation, primarily heavy metals, significantly affect natural terrestrial ecosystems. Despite the measures taken to reduce emissions of pollutants, their release into the atmosphere and then loss on the terrestrial ecosystems remains significant. The main sources of heavy metals entering the atmosphere are industrial enterprises (Al-Khashman et al., 2013; Bacardit and Camarero, 2009), although they may be released as a result of volcanic activity or soil erosion and subsequent transport of particles by the wind. However, these are irregular sources of heavy metals. The HM, especially their soluble phase, are poisonous for plants, animals and humans, by altering their metabolism, inhibiting growth, and decreasing the production (Das et al., 1997; Nagajyoti et al., 2010; Singh et al., 2013; Grosbois et al., 2006; Le Cloarec et al., 2011; Le Pape et al., 2012). In regions with high concentrations of HM, natural ecosystems have a significant negative impact (Shanker et al., 2005; Bacardit and Camarero, 2009; Luo et al., 2013; Bian et al., 2015; Gunawardena et al., 2012; Kara et al., 2014; Meybeck et al., 2007; Madibekov and Kogutenko, 2018).

Despite the fact that the meteorological service of Kazakhstan inherited from the former Soviet Union a fairly good network of observations of precipitation chemistry (about 48 cities), there is practically no research in this area, even local ones (Figure 1). Perhaps this is due to the fact that the main research on the quality of surface water in rivers and reservoirs, on the quality of atmospheric air in cities, etc., has been widely developed. However, the successful implementation of such studies is impossible without information on wet and dry deposition of pollutants onto the soil surface. Our study is the first attempt to estimate the values of heavy metal fallout with precipitation and snow, the fluctuations of these values and their impact on the terrestrial ecosystems of Kazakhstan. The main goals of our study were: 1) to quantify the atmospheric heavy metal deposition through precipitation and snow cover in

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https://doi.org/10.1016/j.heliyon.2020.e05844

Received 1 March 2020; Received in revised form 21 August 2020; Accepted 22 December 2020

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our natural ecosystems; 2) to assess the role of own industrial enterprises in the pollution of the territory with heavy metals; 3) to show the presence of the problem of the transboundary transfer of heavy metals from the territories of neighboring countries, as well as to the territories of neighboring countries.

2. Methods

2.1. Site description

Our studies were carried out on the basis of observations of a regular meteorological network of stations that select precipitation for chemical analysis (Figure 1). About forty-eight meteorological stations were selected to monitor the atmospheric heavy metal deposition through precipitation. We did not use the data from the three stations, as not causing full confidence. The stations are located in different typical natural ecoregions, including steppe, forests, grasslands, deserts, mountains, industrial territories. First, we divided the entire territory of the republic into 4 large typical natural regions (provinces): the region of mountains (A), the forest-steppe and steppe region (B), which is the territory of active agriculture in the republic, the semi-desert and desert region (C), which is mainly a pasture territory. We also identified a region where the concentration of heavy metals in the soil exceeds 5-50 maximal allowable concentration (MAC), region D. The maximum permissible concentration of HM for water is 30, 1, 1000, and 50 µg/L for Pb, Cd, Cu, and As, respectively. We imposed eight industrial territories (ecosystems) with active industrial activity on these four large natural regions (Figure 2). Since we used two different principles of typification, it turned out that strict demarcation between the regions and ecosystems we have selected is impossible, but this was not required to solve the set tasks. Thus, the central region D is a semi-desert region, i.e. part of region C. At the same time, there are provinces where geochemical anomalies in the soil reach 50 MAC, and therefore there are two large industrial ecosystems 2c and 2e for the extraction and processing of ore and the smelting of non-ferrous metals. In the northern part is the industrial ecosystem 2d, where coalmines and ferrous metallurgy are located. In the north-west, north and east, we identified small regions D1, D2 and D3, where the concentrations of heavy metals in the soil also exceed 50 MPC. There are also other combinations (Figure 2). The characteristics of all regions and ecosystems are given in the legend to Figure 2.

2.2. Sampling and analysis

According to the long-term monitoring guide RD (1991) and others, which are in compliance with international precipitation sampling regulations INAA and ICP-MC and China's guide Cheng (2003). Precipitation water (snow) was picked up at 1.5 m above the ground during the year. All our samples were only collected over the duration of precipitation, and included soluble and insoluble particulates. In detail, the samples were collected from one to five precipitation events per month in 2002–2018 by manual collection. After each precipitation event, the samples were stored in a standard polyethylene plastic bottle, and at the end of the month, these subsamples were transported to the central chemical laboratory for analyses. All polyethylene plastic buckets and polyethylene plastic bottles were cleaned with distilled water three times and finally dried prior to use.

In general, there are three types of pretreatments for heavy metals in precipitation (Sakata et al., 2008; Kim et al., 2012). We used the acid digested method for the unfiltered precipitation and then determine the total heavy metal in precipitation (Cizmecioglu and Muezzinoglu, 2008; Pan and Wang, 2015). An important factor determining the ratio of dissolved and insoluble heavy metal fractions is pH, although pH had different effects on the solubility of elements. However, Cizmecioglu and Muezzinoglu (2008) reported that Cr, Cd, and Pb in precipitation samples



Figure 1. Location of the observation sites in Kazakhstan.



Figure 2. Ecological regions (provinces) and ecosystems (industrial ecosystems).

were 80%, 87%, and 93%, respectively. Pan and Wang (2015) estimated that the concentrations of acid-soluble fraction for some elements, such as Cd and As, were comparable to that of the water-soluble fraction. Therefore, we found it possible in this work to consider only the total metal content in the sediments, without highlighting the soluble component. Since up to 80% of the territory of Kazakhstan belongs to the zone of deserts and semi-deserts, during some months, especially summer ones, there may be no precipitation in this territory at all, or their amount was insufficient for reliable chemical analysis. Therefore, the calculation results for these areas of wet fallout per unit area by Eq. (1) were obviously presented as a smaller part of the total fall out. The same time the total fallout is most important in terms of their impact on vegetation, surface runoff and soil (Bian et al., 2015; Cong et al., 2015; Das et al., 1997; Meybeck et al., 2007; Shanker et al., 2005 and others).

The problem of estimating dry deposition is very important because we are able to estimate the magnitude of the deposition of particles, which have passed, as a rule, a long way in the atmosphere. At the same time, the very process of sampling dry particles is difficult (Connan et al., 2013; Pan and Wang, 2015 and others), for this one has to choose areas from which dusting is excluded, there are no enterprises emitting significant amounts of solid particles, etc (Connan et al., 2013). To assess dry deposition, we used deposition on snow cover with simultaneous measurements of wet deposition. Samples of snow cover were taken at the end of winter. Sampling was carried out in accordance with the same RD (1991) for a three-month period. These samples contained not only heavy metals dropped with precipitation, but also the result of dry deposition of these heavy metals between precipitations for about three months. It made possible to determine the value of dry deposition of heavy metals as the difference in their concentration in snow minus concentration in precipitation over the same period. Unfortunately, south of 50 N.L. snow cover is rarely set for all three months. Therefore, for stations located along and southern of 50N. L. we selected the years when the snow cover was kept for three (or two) months. For the southernmost stations (Chimkent and others), we supplemented the samples up to two months from other nearest years of observations, simultaneously taking precipitations for the same periods necessary for calculating the ratio of dry to wet deposition.

2.3. Calculation and analysis

Much of our data on heavy metals in precipitation was analyzed and presented in μ g/L. In cases where we considered the values of heavy metal deposition through rainfall (or snow) per unit area, they were calculated as:

$$D = \sum_{i=1}^{n} C_i \times P_i \tag{1}$$

where D (µg/m⁻²) is the annual deposition flux of a specific heavy metal (i.e. Pb, Cu, As, or Cd); C_i is the monthly rainfall concentration of a specific heavy metal (µg/L), Pi is the monthly precipitation (mm), and n is the number of months.

Then, the atmospheric wet deposition fluxes of the heavy metals for the provinces and regions were averaged for the observation sites in the specific regions and ecosystems. The values of dry deposition were defined as the difference between the content of heavy metals in the snow cover, which is constantly open for dry deposition, and their content only in precipitation (snow).

The some way we obtained the atmospheric heavy metal wet and dry deposition for the all regions and ecosystems. Linear and curvilinear regressions were used to evaluate the relationships between the atmospheric heavy metal deposition and the mean annual precipitation, number of vehicles, oil consumption, and coal consumption. A significance level of P < 0.1 was used for all tests.

The datasets for the number of vehicles, oil consumption, coal consumption and were obtained from the National Agency for Statistics of Kazakhstan (Statistical Digest, 2015). Data of heavy metal concentration in soil for different provinces of Kazakhstan were obtained from Panin (2011).

3. Results

3.1. Wet deposition of heavy metals on the territory of Kazakhstan

3.1.1. Heavy metals in precipitation

We calculated the average annual values of wet deposition of heavy metals Pb, Cu, As and Cd for all ecological and industrial ecosystems over a five-year period (Table 1).

The average long-term atmospheric wet deposition is estimated to be 3.8 ± 1.52 , 16.11 ± 1.48 , 0.96 ± 0.84 , and $0.88 \pm 0.44 \mu g/L$ for Pb, Cu, As, Cd, respectively. Meanwhile, the fluxes of mean multi-month wet deposition of heavy metals are quite wide (Table 1). The wet deposition was lowest in the mountain regions as well as in the regions B and C, in places where industrial ecosystems are absent. Analysis Table 1 shows that zero-monthly concentrations of heavy metals can be observed not only far from emission sources, but even in the area of the sources themselves. Thus, zero or close to them concentrations of lead and copper also occur in the areas of Balkhash and Dzheskazgan — the main sources of these emissions metals (Statistical Digest, 2015).

Several studies (Zhu et al., 2015; Connan et al., 2013; Bacardit and Camarero, 2009; Colomb et al., 2007; Sakata et al., 2008; Kim et al., 2012; Kara et al., 2014 and others) provide data on the amount of deposition of TM per unit area per year. The obtained values are compared with data from other authors. We also performed this work by calculating the average fallout. For characteristic ecological regions: A-(mountain ecological region, one station), B- (rural region of Northern Kazakhstan, 3 stations), D- (region of high concentrations of HM in soil, 3 stations) The results are shown in Table 2.

It can be seen that the values of the wet depositions contained in (Colomb et al., 2007) obtained for the industrial Massachusetts area are close to ours; the data for rural areas (they are not included into Table 2) are also close. Significant precipitation of HM, exceeding that obtained by us for Kazakhstan, was obtained for the west of Turkey (Kara et al., 2014). All authors note large fluctuations in the concentration values from sample to sample, which is consistent with our data (Table 1).

Local studies carried out for Jordan (Al-Momani, 2008), India (Sharma and Agrawal, 2008), Japan (Sakata et al., 2008), China (Bian et al., 2015; Cheng, 2003; Pan and Wang, 2015) and other countries also note a large temporal and spatial variability of HM concentrations in wet and dry deposition. From Table 2, important conclusions can be drawn. First of all, the data on the concentrations of HM in wet and dry deposits obtained by different methods of sampling and analysis will vary. Therefore, it is only advisable to compare the data obtained by the same or similar sampling and analysis methods.

The next important conclusion is the fact that the values of the wet deposition of HM are not comparable at all. As follows from Eq. (1), they are a function of the amount of precipitation falling in a particular place. The greater the amount of precipitation, the greater the amount of wet deposition. For Kazakhstan, in industrial areas where the concentration of HM in precipitation (μ g/L) is high, the annual deposition is lower than in the relatively clean mountain region of Mynzhilki, because in the mountains the amount of precipitation is two to three times more. The ratio between wet and dry deposition also depends on the amount of precipitation. So, in Connan et al. (2013) for the north-west of France and in (Bacardit and Camarero, 2009), where the precipitation is 750-800 mm/year, it was found that the values of the dry and wet deposition of HM are approximately the same. For the west of Turkey, where the amount of precipitation is about 500 mm, according to (Kara et al., 2014), dry deposition noticeably exceeds wet. The presence of the above features arising in the assessment of wet deposition per unit area makes it preferable to analyze the concentration of HM in the precipitation.

Consider maps of the spatial distribution of HM concentrations across Kazakhstan. Extremely high concentrations of heavy metals can be observed far from emission sources. The highest concentrations of copper in precipitation are recorded in Karaganda, and also quite high in Kostanay and Atyrau, where there are no non-ferrous metallurgy enterprises. The peculiarities of such a distribution of concentrations are explained by meteorological factors (Bugayev et al., 1997).

The spatial distribution of mean annual concentrations of heavy metals in precipitation is shown in Figure 3.

Comparing the distribution of concentrations of heavy metals by region, it can be seen that the distribution of Pb, Cu, As by coincidence of extremes is quite similar, the maximum concentration is located in the central regions of Kazakhstan, in ecosystems 2b, 2c and 2g, where the main mining and metallurgical industries non-ferrous metals. As for Cd, its distribution is quite peculiar. A number of stations note high Cd concentrations, where no high concentrations of other elements were observed.

3.1.2. Wet deposition on the territory of Kazakhstan with precipitation per unit area

We next consider the spatial distribution of heavy metals that fall out with precipitation per unit area (Figure 4), and compare the results with the spatial distribution of their concentrations per liter of precipitation (Figure 3).

It can be seen that the spatial distribution of depositions TM per unit area differs significantly from the spatial distribution of their concentrations per liter of precipitation. This is a consequence of the fact that according to Eq. (1) the amount of deposition depends not only on their concentration in precipitation, but also on the amount of precipitation. Thus, for Pb in the region of ecoregions 2c and 2e, where its high concentrations is noted, there is no place of high deposition (compare Figures 4a and 3a), while regions of 2h and 2f have become more pronounced. Increased values of depositions occur along the foothills and in the mountains in the south and southeast, as well as in the north and

Table 1. Variability of heavy metals in precipitation in some industrial ecosystems of Kazakhstan (monthly averages), μ g/L.

Natural ecoregions, ecosystems, stations (numbers)	Heavy metals				
	РЪ	Cu	As	Cd	
C, 2h, Almaty (23)	0–30.2	1.7–32.5	0–1.3	0 - 2.1	
A, Mynzhilky (27)	0–18.4	0.0–30.0	0–2.9	0–1.9	
C 2h, Kapchagai (25)	0–11.6	0.7–29.1	0–0.7	0-0.7	
C (D), 2c, Zhezkazgan (31)	0–49.8	3.5–89.5	0–29.2	0–24.6	
C (D), 2e, Balchash (28)	0.18–38.1	0.43–33.7	0.4–44.6	0.6–3.6	
C (D), 2d, Karaganda (33)	0–7.5	0–101.0	0–1.7	0–2.8	
C, 1 Atyrau (6)	0–13.8	2.7–56.0	0–1.13	0.6–5.3	
B Kostanai (32)	0–16.3	0.8–51.4	0–2.7	0-5.2	

Table 2. The average precipitation per unit area in some regions of the world and in Kazakhstan (µg/L/year).

Country	Years	Locations	Kind of sample	Heavy metals	Heavy metals			Reference	
				Pb	Cd	Cu	As		
China	2013-2014	Rural	Wet soluble	0.06–0.50	0.03–0.98			Zhu et al. (2015)	
France	2010-2012	Rural, northwest	Wet + dry	142	9			Connan et al. (2013)	
Spain	2004–2006	Pyrenees	Wet + dry	1.50	1.32	1.19	0.07	Bacardit and Camarero (2009)	
USA	1992–1993	Massachusetts	Wet + dry	2700	405	3500	132	Colomb et al. (2007)	
Japan	2008	West coast	Dry	3.7–5.2	0.14-0.17	0.71-2.4	0.49–0.71	Sakata et al. (2008)	
South Korea	2006-2009	Rural	Wet + dry	1.06	0.05			Kim et al. (2012)	
Turkey	2009-2010	Industrial	Wet + dry	189000	4200	44800	2000	Kara et al. (2014)	
Kazakhstan	2013-2018	Rural, north Kazakhstan	Wet	570	57.1	3800	114	Present study	
Kazakhstan		Mountains Mynzhilki	Wet	1520	206.9	7720	275.9	Present study	
Kazakhstan		Industrial Dzheskazgan	Wet	1130	414.1	2970	828.2	Present study	



Figure 3. Distribution of mean annual concentrations of heavy metals in precipitation on the territory of Kazakhstan, µg/L: a) Pb; b) Cu; c) As; d) Cd.

north-west of the territory of Kazakhstan, where there is a significant amount of precipitation.

A similar situation occurs in the distribution of wet Cu deposition (Figures 4b and 3b). The highest Cu depositions occur in ecoregion 2h, slightly lower in 2g, then 2f. Further, increased depositions in the north and north-west of the republic. In the central regions of the republic, where the main sources of Cu emissions are located, deposition per unit area is minimal.

As is the only element for which the maximum concentrations in precipitation and maximum sedimentation values per unit area are coincide (Figures 4c and 3c). The reason for this is unusually high concentrations of arsenic in ecoregions 2c and 2e compared with others. Thus, in the 2e region, As concentrations are 11.3 μ g/L with an average precipitation of 60.9 mm. For comparison, in Almaty (ecoregion 2h), As concentrations were only 0.5 μ g/L, i.e., 22 times less, but with precipitations of 649.2 mm, the deposition values per unit area turned out to be only 2 times lower than in the region 2e. The rest of the spatial distribution of wet deposition per unit area and per liter of precipitation of As is similar to other heavy metals. The spatial distribution of Cd deposition per unit area of elevated deposition in central regions remains (ecoregions 2c and 2e), but maximum depositions per unit area occur in ecoregion 2h, as well as in 2f and 2g (Figure 4d).

3.2. Distribution of heavy metals in snow cover

3.2.1. Distribution of heavy metals in snow cover (μ g/L)

In Figure 5 is a map of the distribution of heavy metals in snow cover. The region of high concentrations of Pb, more than 35 μ g/L, occupies the central regions of Kazakhstan, region C (D), which captures the east of the republic, including the ecosystem 2f and the south of ecosystem 2h (Figure 5a). Areas of elevated concentrations were also noted in the north and north-west of region B. Minimum lead concentrations, less than 2 μ g/L, occurred in the west of region C, as well as in region B and in region A.

In the spatial distribution of Cu, there are several non-extensive areas of elevated concentrations (Figure 5b). Maximum concentrations of Cu, more than 20 μ g/L, occurred in region D, concentrations of 3–5 μ g/L were also observed in ecosystems 2a, 2b, 2c, and 2g. Minimum concentrations of Cu, about 3–10 μ g/L, occurred in the western part of region C and in the central part of region B.

The highest concentrations of Cd, more than 5 μ g/L, occurred in region D, ecosystems 2c and 2e, as well as in region B, ecosystems 2d, 3.3 μ g/L. The lowest concentrations of Cd, less than 0.5 μ g/L, occurred in the western part of region C, as well as in most parts of region B and in region A (Figure 5d).



Figure 4. Distribution of wet deposition on the territory of Kazakhstan, $\mu g/m^{-2} yr^{-1}$: a) Pb; b) Cu; c) As; d) Cd.



Figure 5. Average concentrations of heavy metals in snow cover on the territory of Kazakhstan, µg/L: a) Pb; b) Cu; c) As; d) Cd.

3.2.2. Spatial distribution of heavy metal deposition values per unit area

Consider further the spatial distribution of deposition values per unit area (Figures 6a, b, c, d).

The spatial distribution of Pb deposition is very similar to the spatial distribution of concentrations per unit volume of precipitation (Figures 5a and 6a). Almost all extremes are preserved, but spatial contrasts have somewhat decreased. All extremes are also preserved in the spatial distribution of Cu deposition (Figures 5b and 6b). Similar proximity occurs in the concentration distribution in precipitation in As precipitation (Figures 5c and 6c) and Cd (Figures 5d and 6d). Comparing the concentrations of heavy metals in snow cover (a period of three months) and in liquid sediments (a period of 12 months) we can conclude the following: 1) at the same stations where there were high concentrations of heavy metals in precipitation, there are also high

concentrations in snow cover; 2) concentrations of heavy metals in snow cover are close to or higher than in liquid precipitation. The second feature is because the snow cover also contains dry sedimentation deposited between the precipitation.

3.3. Factors influencing atmospheric wet and dry heavy metal deposition

3.3.1. Connection of heavy metal concentrations with industrial activity

The main sources of heavy metal emissions are mining and metallurgical enterprises for the processing of non-ferrous metal ores, energy companies and motor vehicles. Distant and transboundary transport to the territory of the republic is also possible. Selecting the contribution of a particular source of emissions outside the specific industrial ecosystem, and often within it, is rather difficult. This is similar to the task of



Figure 6. Average concentrations of heavy metals in snow cover on the territory of Kazakhstan: a) lead ($\mu g/m^2$); b) copper (mg/m^2); c) arsenic ($\mu g/m^2$); d) cadmium ($\mu g/m^2$).

estimating the contribution of a single enterprise that is the source of an emission of a substance to the average concentrations of this substance in the city's air basin in the presence of other emission sources. In Cherednichenko et al. (1996) we have shown that such a problem is solvable, if: 1) there is complete information about the mode of operation of the enterprise; 2) there is complete data on the dynamics of pollutant concentrations in the air basin of the city; 3) if the contribution of the source enterprise to the concentration of the pollutant in the air is significant, it exceeds the calculation error. For our task, the third condition is important. The presence of large sources of emissions of heavy metals in the form of metallurgical enterprises in industrial ecoregions 2c, 2e, 2d, 2g, and 2f did not allow us to estimate the amount of heavy metals from the underlying surface, despite the fact that in all these areas soil contains up to 50 MPC our heavy metals (Figure 2). However, the establishment of some links is still possible.

We tried to identify ecosystems in which the influence of any one factor is decisive, and we also used data on wet deposition values for the period from 2002 to 2017 inclusive, during which production, fuel consumption changed significantly with a minimum around 2008. During this time, the number of passenger cars in the country doubled from 1.5 million in 2003 to 3.45 million in 2017 (Statistical Digest, 2015).

We investigated the dependence of heavy metal deposition on 1) the number of vehicles; 2) the amount of liquid fuel burned, 3) the amount of coal mined; 4) the amount of ore mined; 5) the amount of precipitation. For all industrial ecoregions from 2a to 2h, we tried to find a relationship in the form of a conventional linear regression between the products they produce and the concentrations of heavy metals in wet sediments.

Table 3 presents the dependences of heavy metal fallout on the number of vehicles at stations located in different natural regions, as well as in industrial ecosystems.

From Table 3 it can be seen that the desired connections, in general, take place. However, in two industrial ecosystems 2a and 2b, where industrial activity is minimal (Statistical Digest, 2015), R2 <0.25 for all four TM. In the remaining six industrial ecosystems, R2> 0.25 for one to four HM.

For stations located far from industrial ecosystems in areas with low concentrations of heavy metals, there is a link between the number of vehicles and the concentrations of most heavy metals. There is also a link to the amount of liquid fuel burned in industrial ecosystems, on the background of emissions from large industrial enterprises; such a link is weak in essence for all heavy metals.

3.3.2. On the impact of motor transport

In ecosystem 2h, where industrial mining and processing production is located in the extreme north-northeast of the ecosystem about 250 km from Almaty (23) and 200 km from Kapchagai (25), its influence in these cities turned out to be weak. Near Almaty (about 30 km to the north), there are two large coal-fired thermal power plants, and another station is located directly in the city, which runs on natural gas and provides heat to the city during the cold season, its load is minimal in the summer. At the same time, Almaty is the largest city of the republic, with more than 1.5 million inhabitants, 740-1200 m above sea level. Therefore, out of 4 million cars available in the country, more than 750 thousand (20%) are in Almaty. At the same time, about 500 thousand cars belong to private owners and are intensively exploited only in the warm part of the year, although this is typical for most of the vehicles. Therefore, it was possible to estimate the emissions of heavy metals, at least Pb from motor vehicles. Figure 7 presents a graph of the annual variation of Pb concentrations at the stations of Almaty (23), Kapchagai (25) and Mynzhilky (27). Kapchagai is located 60 km north of Almaty and 25-30 km from thermal stations serving Almaty, 452 m above sea level. Mynzhilky (27) are located 35-40 km south of Almaty in the mountains, 3014 m above sea level.

In the same time, the nearest metallurgical plant, whose emissions contain Pb, is located 300 km north-northeast of Almaty, i.e. in the direction of Kapchagai. It is natural to expect that in Kapchagai such emissions would also be recorded in greater quantities than in Almaty. We, however, see that the highest lead concentrations occur in Almaty. In Kapchagai, the annual lead concentration repeats its annual variation in Almaty, but the quantities themselves are smaller. This fact suggests that the main source of emissions is in Almaty. The annual course of Pb concentrations in Mynzhilky in the wintertime repeats its course in Almaty, but the summer maximum concentrations are absent. We explain this by the fact that in summer the main source of Pb is motor vehicles, emissions of which occur in the lowest layer of the atmosphere. Receipt of these emissions in the high atmosphere, where Mynzhilky are located, is difficult. In winter, when the main source of emissions are energy enterprises, emissions of which occur at altitudes of 100m or more, their

Ecosystems	The main types of economic activity	Heavy metals	Heavy metals		
		Pb	Cu	As	Cd
2a	energy, coal mining	0.22	0.17	0.16	0.22
2b	mining	0.21	0.19	0.22	0.24
2c	mining, non-ferrous metallurgy	0.39	0.51	0.30	0.23
2d	ferrous metallurgy, coal mining	0.22	0.28	0.25	0.28
2e	mining, non-ferrous metallurgy	0.35	0.50	0.43	0.34
2f	non-ferrous metallurgy, mining	0.47	0.22	0.24	0.21
2g	non-ferrous metallurgy, mining	0.49	0.28	0.28	0.32
2h	Energy, mining, motor transport	0.44	0.40	0.19	0.17

Table 3. R² values between mining and processing facilities and heavy metal concentrations.



Figure 7. The annual variation of lead concentrations at the stations of Almaty (23), Kapchagai (25) and Mynzhilky (27).

transfer to the Mynzhilky altitude is facilitated. Thus, if it is assumed that the impact of emissions from thermal power plants on Almaty and Kapchagai districts is about the same, and then the impact of Almaty's vehicle emissions can be estimated as the average difference in concentrations of Almaty and Kapchagai over the year, it is about 17 µg/L. In summer, it increases to 22 µg/L (difference in Almaty and Mynzhilky concentrations). The total impact of vehicles on Pb concentrations can be estimated as the average difference between Pb concentrations in the Almaty and Mynzhilky wet depositions for the year (where there are no vehicles), it is 20 µg/L. Therefore, in this region 100 thousand cars account for five µg/L of Pb emissions recorded in liquid sediments.

3.3.3. Estimation of the value of dry deposition

In accordance with Eq. (1), the amount of depositions on the soil is determined not only by the concentrations of HM per unit volume, but also by the amount of precipitation. It is in these regions that elevated precipitation occurs, and the central and western regions of the republic belong to desert and semi-desert zones, where precipitation can be less than 100 mm per year. From Table 4 it can be seen that at Dzhezkazgan and Balkhash stations, where Pb and Cu concentrations in precipitation are highest in Kazakhstan, the fallout on the soil is small, they are several times less than in Almaty and even less than in Mynzhilky.

To assess real dry fallout, we collected data and performed a comparative analysis of heavy metals in snow cover and in the precipitation that formed this snow cover. The difference represents dry deposition on snow cover.

Table 5 presents the results of calculations of dry deposition of heavy metals, as the ratio of their content in snow cover and precipitation over the period of existence of snow cover for the main industrial ecosystems and ecological regions.

From Table 5 it follows that the values of dry deposition are significant for all metals. They are most significant in those industrial

ecosystems where the main release of a particular metal occurs, and minimal for places remote from industrial ecosystems.

For the desert and semi-desert zones of Kazakhstan, this is up to 80% of its territory, the usual situation is when one, two consecutive months (sometimes three) precipitation is missing, or it is below a qualification limit. Such cases occur even for Almaty, where the annual precipitation is more than 620 mm/year. This leads to an underestimation of wet deposition over the year; incl. wet deposition per unit area (Connan et al., 2013; Bacardit and Camarero, 2009; Kara et al., 2014)several times (Table 5).

3.3.4. Dependence of concentrations of heavy metals on the amount of precipitation

Figure 8 shows the dependence of the amount of deposited Pb and Cu per unit area, depending on the amount of precipitation.

For each of the metals, two regression lines were built, one for the Mynzhilky station alone, where the greatest amount of precipitation falls, and the second for all four stations, thus covering almost the entire range of precipitation, which means a place in Kazakhstan. It can be seen that with a smaller range of changes precipitation for in Mynzhilky (less than 300mm compared to 800 mm for four stations), the range of precipitation values is essentially the same. The less precipitation falls on the station, the smaller the sedimentation range (Figure 8a, and b). Consequently, wet precipitation in a particular region is determined by the amount of precipitation. It can be seen that a certain dependence takes place and it is of interest to clarify the physical essence of this fact. The processes of suspended matter in the atmosphere, dry deposition and removal of substances outside the region tend to a certain dynamic balance, equilibrium. The precipitation disturbs this balance by washing away some of the suspensions. The more often precipitations take place and the more intense they are, the more suspended solids are washed out and the further from the dynamic equilibrium the mentioned processes will be.

Table 4. Pb and Cu concentrations in precipitation at some stations.

Stations	Precipitation, mm	Pb		Cu	
		µg/L	mg/m ⁻²	µg/L	mg/m ⁻²
Mynzhilky	689.7	2.2	1.52	11.2	7.72
Almaty	649.2	6.8	4.14	18.2	11.82
Ridder	503.5	5.8	2.92	18.1	9.11
Ust-Kamenogorsk	360.8	7.0	2.52	18.7	6.75
Taraz	263.7	3.5	0.92	13.3	3.51
Atyrau	158.5	3.0	0.48	15.5	2.46
Dzhezkazgan	121.8	9.3	1.13	24.4	2.97
Balchash	60.9	8.7	0.53	24.9	1.52
Aul-4	60.9	4.6	0.28	17.9	1.09

Table 5. The ratio of the content of heav	y metals in the snow cov	over to the c	content in precipit	ation.
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Ecological systems and regions	Heavy metals				
	РЬ	Cu	As	Cd	
2a	1.8	2.3	1.6	2.2	
2в	1.9	3.6	3.2	2.2	
2c	3.1	3.9	2.8	3.5	
2d	2.1	3.9	1.2	1.3	
2e	3.2	4.7	2.7	3.3	
2f	2.5	4.4	3.0	3.2	
2g	2.1	4.2	2.3	2.3	
2h	1.8	1.6	2.2	1.2	
B (north)	1.5	2.9	1.2	1.5	
B (northwest)	1.7	2.6	1.3	1.6	
C (west)	1.4	1.6	1.2	1.3	
C (south east)	1.4	1.5	1.3	1.2	

Therefore, from a certain moment, the relationship between the amount of precipitation and the amount of sedimentation of suspended matter per unit area should decrease. The moment of transition from linear to parabolic dependence will be determined by the rate of intake of deposited substances and meteorological conditions, i.e. in each particular region, it is your own. In a particular region, precipitation fluctuates around the climate norm. Consequently, the amount of wet sediments should also fluctuate around some norm, ceteris paribus. These fluctuations are due to the meteorological conditions of accumulation and depositing of pollutants in a particular region.

4. Discussion

4.1. Atmospheric heavy metal deposition in precipitation

The magnitude of wet deposition of heavy metals in Kazakhstan is large. They are comparable to the most polluted areas for which data are available. In comparison with the literature data, the range of concentrations measured in the Marais Vernier (Connan et al., 2013) are in the lower range to what has been measured by other authors. With regard to the measured contents, it may be concluded that the Marais Vernier site is protected from the influence of nearby industrial or urban pollution and that, given the regular measurement of the precipitation; the concentrations of metals in the rain remain throughout the year at low concentrations without many variations. We received the average concentrations are respectively 5.4 \pm 5.4 μ g L⁻¹ for Zn, 0.6 \pm 0.3 μ g L⁻¹ for Ni, $0.2 \pm 0.2 \ \mu g \ L^{-1}$ for Pb, $0.02 \pm 0.01 \ \mu g \ L^{-1}$ for Cd. The values we obtained for Pb and Cd are many times greater than the data Connan et al. (2013), which is natural. Al-Khashman et al. (2013); Bacardit and Camarero (2009) show that the average values of wet depositions on the soil for Jordan are given: 0.5mg/m^{-2} for Pb, and 0.092mg/m^{-2} for Cd.

Similar results were obtained in Sharma and Agrawal (2008) for India. Our results on average values of lead deposition are close to these data, but in places of maximum deposition, they exceed the data for Jordan by 8–10 times. Pan and Wang (2015) reported that atmospheric wet deposition of Pb, Cd, and Cr were 4.0–10.0, 0.16–0.32, and 0.26–0.75 mg m⁻²/yr. at 10 sites (only including 1 rural sites) in Northern China. These data are close to those obtained by us, but the concentration of cadmium at the maximum points is about two times higher than the concentration of Pb and Cu obtained in Bacardit and Camarero (2009); Cong et al. (2015) for the north of Spain, Lake Redon, 2240 m above sea level. The sea level is 2 times lower than at the high-mountain station Mynzhilki. At the same time, the concentrations of Cd and As are close. A common fact is that the concentration of HM in wet deposition in Kazakhstan is equal to or higher than the concentrations given in the cited sources.

From 35 million tons copper ore about 28 million tons is mined and processed in Dzhezkazgan and Balkhash (ecosystems 2c and 2d). From 55 million tons about half of the iron ore is mined and processed here (Temirtau) in the Karaganda region (ecosystem 2d), i.e. within the natural region D, which is part of the semi-desert region C (Statistical Digest, 2015). The emissions of enterprises for the extraction and processing of non-ferrous metal ores, primarily copper, explain the constant existence of areas of high concentrations of heavy metals in precipitation in the central part of the country (natural regions C and D).

4.2. Distribution of heavy metals in snow cover

Concentrations of heavy metals in the snow cover is a similar to their distribution in precipitation, but there are also differences. Above, we have shown that dry deposition on snow cover in winter significantly exceeds wet deposition during all year. At the same time, it should be noted that the location of the maxima of HM concentrations in the



Figure 8. The dependence of the amount of Pd (a) and Cu (b) on the amount of precipitation.

precipitation and in the snow cover also do not coincide somewhat. Indeed, the region of high concentrations of Pb in precipitation is located there, but it is shifted compared to the wet deposition region to the west and south-west (Figures 3 and 5). Areas of high concentrations of As and Cd have a similar distribution (Figures 3 and 5). The displacement to the west in relation to wet deposition also has an area of high Cu concentrations. There are other less noticeable, but important features. According to Bugayev et al. (1997), Terechov et al. (2019) and others, in winter, a latitude-oriented high-pressure ridge, due to the Siberian anticyclone, is located above the central regions of Kazakhstan. Its axis is located on average about 48-50 N. L., i.e. somewhat north of ecosystems 2c and 2e, passes through ecosystems 2b and 2d, and divides the territory almost in half into north and south. As a result, if wet deposition, including snow falls during the passage of atmospheric fronts from the western component, then dry precipitation on the snow cover of the southern part of the territory occurs with weak winds from the eastern and north-eastern component. North of the axis of the ridge, this is dominated by the winds of the south-west direction. We also note that the Siberian anticyclone is a stable baric formation. Accordingly, this explains why areas of high concentrations of all heavy metals in snow cover are shifted to the east in relation to wet deposition, as well as their elongation from industrial ecosystems to the south-west in the southern part and to the northeast - in the northern part of the territory under consideration.

Comparing the content of heavy metals in precipitation and snow cover, we found that the values of dry (solid) deposition on snow cover in Kazakhstan are significant for all metals. They are 2–5 times higher than in precipitation. Dry depositions are most significant in those industrial ecosystems where the main release of a particular metal occurs, and minimal for places remote from industrial ecosystems.

Connan et al. (2013) constantly measured wet and dry components of depositions. At the same time, the value of dry fallouts was measured during the rain. The authors have received that during the rainy periods (>60 mm), the wet deposition percentage is often of the order of 90% or more. Cd and Pb are the only elements where dry deposition was, for a moment, greater than wet deposition. As noted above, Marais Vernier is located in a rural environment, benefiting from the oceanic climate. . Let us to note that the site is subjected to very weak winds most of the time, which reduces the dry deposition contribution. Similar results are obtained in Galloway (1982) and others. At the same time, in Selezneva and Drozdova (1974) on the basis of studies of the results of chemical analysis of precipitation samples collected in 1968–1970 at 15 stations of the Soviet Union received that the contribution of dry deposition on average for all stations is about 40%. However, it can vary from month to month

and depending on the location of the stations and on meteorological conditions. Later they also received that the contribution of dry fallout for various elements varies greatly in different geographic areas and can sometimes reach 70–80%. For desert and semi-desert regions, they assumed that dry deposition might exceed wet once (Selezneva and Drozdova, 1974). For Jordan (Al-Khashman et al., 2013) are obtained that dry fallouts exceed wet. For the territory of Kazakhstan, we received that dry deposition may exceed the wet once several times.

4.3. Factors influencing atmospheric wet and dry heavy metal deposition

For all industrial ecoregions from 2a to 2h, we tried to find a relationship between the products they produce and the concentrations of heavy metals in wet sediments. However, it was succeeded to find reliable communications only in separate of them and with separate elements.

Referring to the study of Zhu et al. (2015) let's look at their Figure 3, where the authors give a correlation between the heavy metal content (y-axis) on the one hand and the amount of fuel consumed by cars, as well as precipitation on the other (abscissa axis). Firstly, R2 is small and it is only visually clear that the angle of inclination of the regression line is close to zero, which indicates a weak dependence of the content of heavy metals on the amount of fuel consumed. Secondly, of particular interest is the third column, in which graphs are placed for the consumed liquid fuel. All points are located in the lower left corner for all three heavy metals Cr, Cd and Pb. Only one point (oil consumption> 500 tkm) provided the construction of lines regressions for all three metals. It is obvious that the authors also had problems with establishing the desired links.

To determine emissions of heavy metals by road, we chose the 2h ecosystem, in which the largest city of the country, Almaty, is located, in which almost 20% of the vehicles available in the country are concentrated. In recent years, humankind has taken serious steps to reduce emissions from motor vehicles. Thus, leaded gasoline has disappeared, gasoline quality has been increasing, diesel cars have become cleaner, etc. Where did such noticeable emissions, especially lead, come from? Well-known specialists from Ecological Center "West" Pacyna and Pacyna et al. (2001) answer this question: «Combustion of leaded, low-leaded, and unleaded gasoline continues to be the major source of atmospheric Pb emissions».

Recently, Pan and Wang (2015) pointed out that the atmospheric wet deposition of Pb was much higher in Xinglong in northern China (even higher than that in urban or industrial sites), reaching 8.4 mg/m²/yr. Even though there were no local emission sources near remote research

sites, the long-range transport of heavy metal pollutant from upwind areas and around metropolis might lead to the higher heavy metal deposition in those sites. Our data and data, (Cong et al., 2015; Gateuille et al., 2014; Kara et al., 2014; Sharma and Agrawal, 2008) conform this results.

It was clear that quantity of precipitation significantly affects wet heavy metal deposition, potentially leading to a higher deposition in the rainy season than in the dry season (Pan and Wang, 2015). Therefore, there were clear differences among the observation sites as the different anthropogenic disturbances, topographic and geomorphic conditions, and distance to important pollutant sources, which might partially explain the large variations in atmospheric heavy metal deposition observed among these sites.

The amount of wet deposition of HM increases with an increase for precipitation, which is natural, since only part of suspended solids in the air is washed out even during the heaviest rains (Connan et al., 2013). At the same time, suspended particles cannot endlessly accumulate in the air. They, having reached some limit level of concentration, fall out on the soil in the form of dry sediments. Consequently, regardless of the time between depositions, there is no excess of suspended particles in the air. As a result, the amount of wet deposition is determined solely by the amount of precipitation falling in a given place. This conclusion is well confirmed by the results of our research. The scatter of HM deposition at a particular station with a small scatter of precipitation is also determined by the difference in weather conditions under which these precipitations fall.

4.4. On transboundary transport of heavy metals

The problem of transboundary transport of pollutants, including heavy metals, is very important and deserves independent research. However, according to our data, certain conclusions can be made at the level of climate assessments. As shown above, in the regimes of precipitation of wet precipitation with precipitation and dry deposition on snow cover, they are rather stable (Bugayev et al., 1997). As a result, on the basis of long-term data, we obtained maps of the spatial distribution of heavy metals in precipitation and snow cover, which reflect not only the average values of heavy metals, but also the features of their distribution under the influence of average meteorological (climatic) conditions (Figures 3 and 5). One can see that there is a lot in common in the distribution of concentrations of heavy metals in transboundary areas, since the transfer conditions are common. The central regions of high concentrations (wet deposition) of all elements are shifted eastward in the direction of the wind during precipitation. This provides the possibility of partial transfer of wet deposition of all metals into China. In the extreme south-west, where there is no industry, we observe an area of high concentrations of all metals, as the likely result of its removal from the southwest during precipitation, either from Turkmenistan or from Azerbaijan. Emissions of heavy metals (except cadmium) by enterprises of the industrial ecosystem 2g, located in the extreme south, enter the territory of neighboring Kyrgyzstan and Uzbekistan. However, there are fundamental differences. Therefore, for Pb in the west of the natural regions B and C, as well as in the far north of the territory, its elevated concentrations are observed - the result of its transfer from the territory of Russia. In the southwest of the natural region C, there is a very extensive region of Cu in comparison with other elements. The second area of high concentrations of Cu, due to its removal from the territory of Russia, is located in the north-west of the territory, region B; other elements do not have elevated concentrations in this area. This area is almost connected to a vast area above the central regions, but this is not the emissions of our enterprises of industrial ecosystems 2c and 2e, since atmospheric fronts and precipitation in the north-west direction do not move. Cd is characterized by high concentration areas exceeding three maximum permissible concentrations (MACs) in the west of natural regions B and C, and two more concentration areas also exceeding or close to three MACs occur in the north of the region B. Cd to these places

probably comes from Russia. The region of high concentrations Cd, more than 3 MAC, is in the south-west of the region C. It can be seen that the removal of Pb in the form of dry deposition is very likely on the territory of Russia through the northeastern border of the republic in a fairly wide strip in the Ust-Kamenogorsk region, and also partially in the region of China. In the southwestern border on the section from the Aral Sea to Chimkent, dry deposition of Pb is also likely to be carried to the territory of Uzbekistan, more intense than in the northeast. Accordingly, the transfer of other substances, Cu, As and Cd, will take place along the same trajectories as Pb, and their concentration on the territory of Kazakhstan will be determined by the concentration values at the place of emissions, distance, as well as meteorological conditions.

. In this respect, the region of high concentrations of Cu in the snow cover in the northwest of the republic is interesting. According to the wind rose, the removal of Cu from the territory of Russia is possible. The vastness of this area in Kazakhstan, it stretches to the southeast almost to the Aral Sea, the presence of emission sources in our territory and the absence of those in the adjacent territories of Russia allows us to consider this area is a case of emissions by our own enterprises. This example shows the complexity of assessments without special studies, it is necessary to trace the directions of transport, to build trajectories, as was done in Pan and Wang (2015) and Kim (2019).

In Ihon (2006) the author provides a very detailed map of the distribution of precipitation in China over a two-week period of 2006. From the map it can be seen that air masses moving from Kazakhstan to China (northwest China), having crossed the frontier mountains, acquire a downward direction. This leads to the destruction of clouds and precipitation in the strip 200–300 km. Then clouds and precipitations are restored in the form of a strip parallel to the mountains. The China stations Aksu and Fukad are located just in the band where lowering of clouds and precipitation occurs. Naturally, in such a situation, wet deposition calculated by Eq. (1) cannot be significant, at least, only because of the small amount of precipitation.

It can be seen that the problem of the transboundary transfer of heavy metals, both on the territory of Kazakhstan and beyond, is highly relevant and requires independent in-depth research.

5. Conclusions

As a result of the study of the spatial-temporal distribution of the concentrations of heavy metals in precipitation over the territory of Kazakhstan, the values of depositions, and the identification of links with economic activity, we obtained the following:

- A distinctive feature of the spatial distribution of heavy metals over the territory is the presence of a region of high concentrations in the central part of Kazakhstan, region C (region D) for all heavy metals. This feature is characteristic of wet, dry and total (bulk) depositions with some differences in details;
- The mean annual wet deposition concentrations of Pb, Cu, As and Cd in Kazakhstan natural ecosystems was estimated to be 3.8 \pm 1.52, 16.11 \pm 1.48, 0.96 \pm 0.84, and 0.88 \pm 0.44 µg/L respectively. The fluxes of medium perennial atmospheric wet deposition of heavy metals ware quite wide. The wet deposition was lowest in the mountain regions as well as in the regions B and C, in places where industrial ecosystems are absent. The highest concentrations of Pb (>5 µg/L) occurred in the central part of Kazakhstan (region C, (D), ecosystems 2c and 2e), as well as in ecosystems 2g, 2h and 2f (Figure 3a). Cu concentrations (>20 µg/L) took place in the same place; they were somewhat lower in region C around the Aral Sea and also in ecoregions 2d, 2f (Figure 3b). As and Cd have a similar spatial distribution;
- We showed that the concentration of HM in precipitation is determined by the amount of precipitation which is natural, since only part of suspended solids in the air is washed out even during the heaviest rains;

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- Spatial distribution of depositions of HM per unit area differs significantly from the spatial distribution of their concentrations in precipitation. The reason for the observed differences in the distribution of concentrations and wet deposition per unit area is that the values of precipitation are proportional to the amount of precipitation, which differ by a factor of three or more times;
- The location of the maxima of HM concentrations in the precipitation and in the snow cover also do not coincide somewhat. This is due to the fact that precipitation and dry snowfall occur under different weather conditions. Precipitation occurs during cyclone weather and winds with a western component. Dry precipitation occurs during anticyclone weather in the ridge system of the Siberian anticyclone. At the same time, winds north of 48 N.L. have a south-western or western component, and south of- a north-eastern or eastern component.
- In snow cover, an area of high concentrations of Pb, more than $35 \mu g/l$, occupies in the central regions of Kazakhstan, region C (D), which also captures the east of the republic. Minimum Pb concentrations, less than $2 \mu g/L$, occurred in the west of region C, as well as in region B and in region A. Other HM have a similar distribution. In the snow cover in three months, the same or more HM accumulate than in the whole year in the precipitation, which indicates a significant proportion of the dry component falling directly on the snow cover and also on the soil between precipitation in the warm period;
- In industrial ecosystems, there is a link between the activities of large industrial enterprises and the concentrations of heavy metals emitted by these enterprises. Connection is satisfactory in essence for all heavy metals;
- For region 2h, where the number of vehicles is large, it was possible to establish its contribution to wet deposition. In this region, 100 thousand cars account for five μ g/L of lead emissions recorded in liquid precipitation;
- The presence of metallurgical enterprises as sources of HM emissions did not allow us to distinguish the influence of these HMs coming from the soil, even in those regions where there content exceeded 50 MAC;
- Analysis of the spatial distribution of wet and dry deposition of heavy metals showed that the enterprises of Kazakhstan can be sources of receipt of these metals in the territory of the countries of Russia, China, Uzbekistan, Kyrgyzstan. In turn, heavy metals from emission sources in Russia and other countries may enter the territory of Kazakhstan. The problem of the transboundary transfer of heavy metals, both on the territory of Kazakhstan and beyond, is highly relevant and requires independent in-depth research.

Declarations

Author contribution statement

Cherednichencko Vladimir: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Cherednichencko Alexandr: Analyzed and interpreted the data; Wrote the paper.

Cherednichencko Alexey: Analyzed and interpreted the data.

Zheksenbaeva Aliy: Performed the experiments; Contributed reagents, materials, analysis tools or data.

Madibekov Azamat: Performed the experiments.

Funding statement

This work was supported by the Ministry of science and education of Kazakhstan (APO5131867).

Data availability statement

The data that has been used is confidential.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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