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HEAVY METAL ACCUMULATION IN PLANTS OF ATYRAU REGION

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Abstract

This article represents data on determination of heavy metals (Pb, Cd, Zn, Cu, Mn, Co, Ni) in the samples of dominant plants and soils of Atyrau region in Kazakhstan. High population density and enhanced agriculture and industrial activity are main reasons for pollution and degradation of vegetation in these areas. Accumulation of heavy metals in forage plants and subsequent transfer of metals along the food chain might have a negative impact on the health of the population. The areas for sample collection were as follows: Point 1 (Atyrau, farm, Ulan), Point 2 (Kulsary, v. Turgysba) and Point 3 (v. Inder, farm, Isayev). The ability for heavy metal accumulation was different in various plant species. It was revealed that *Artemisia terrae-albae* was able to accumulate the highest concentration of the heavy metals namely lead, zinc, nickel and manganese compared with the other species. *Tamarix ramosissima* and *Ceratocarpus arenarius* were distinctive as having the least amount of heavy metals compared with the other species growing in similar environmental conditions. In all the studied areas the content of heavy metals was within the maximum permissible level. However, it was observed that the insignificant evaluation of zinc and cobalt up to 1.09-1.72 MPC might be related to physiographic and geologic factors of the studied area.

Key words: Atyrau region, Heavy metals, Atomic absorptive spectroscopy, Dominant plant species, Potential for accumulation.

Introduction

Atyrau region is located in the Caspian lowlands below sea level. Transgressions and regressions of the Caspian Sea in ancient and modern times, the activity of rivers, the vast influence of the sea on the coastal landscape, the rise of the sea level and the associated environmental problems and the rich flora and fauna of the Caspian Sea have made this region a unique location. Its uniqueness necessitates the sustainable conservation of the region's biological diversity, genetic resources and ecosystems. The common features of the northeast coast relief are reflected in the main geotectonic element of the territory: the Caspian tectonic depression and the corresponding accumulative lowland plains.

The climate here is continental, obviously dry, with hot summers and moderately cold winters. The absence of high natural barriers promotes the free penetration and movement of Atlantic moisture mass and cold Arctic air as well as the dry air of the subtropical deserts of Kazakhstan and Central Asia. Being the main area for oil production in the Republic of Kazakhstan, the Atyrau region is considered to be under great anthropogenic impact. Insufficient ecological management and oilfield accidents in the refinery plants have resulted in continuous oil leaks and heavy-metal pollution leading to soil degradation and the subsequent decrease of plant biodiversity. It is well known that oil pollution is accompanied by the releasing of concomitant heavy metals. Metals are naturally found in soils but usually in concentrations below those posing significant health risks. Problems arise when metals are highly concentrated and bioavailable. In this case forage plants may be considered accumulators of heavy metals, providing metal transduction along the food chain to cattle and further consumers (Prasad & Shih, 2016; Aksoy, Leblebici, & Prasad, 2015; Prasad & Shih, 2016). Recently, investigation of plant biodiversity in the Atyrau region of the Caspian Sea shore and determination of oil products has been the focus of numerous field and indoor research (Askarova & Mussagaliyeva, 2014; Konuspayeva, Faye, De Pauw & Focant, 2011).

In the period 1986-2001, the biodiversity of terrestrial plants of the Caspian Sea in Atyrau region was investigated by researchers from the Botany and Phytointroduction Institute of the Ministry of Education and Science of the Republic of Kazakhstan. It was argued that the sequence of families dominant in the Caspian region corresponds to that of the Turan flora. The dominance of *Chenopodiaceae* (49 species) is observable on the vegetation of Atyrau region (Baibulov & Ogar, 2002).

In the period 1989-1991, researchers investigated the flora and its species distribution by environmental type in the southwestern part of the Caspian lowland on the east coast of the Caspian Sea, in the mid-desert subzone. Species analysis revealed 30 life forms of plants. The prevalent species were grasses (75%). The flora was divided according to ectomorphs as xerophytes (43%) and mesophytes (49%). A large number of xerophytes there demonstrate the desert character of the area, while the significant number of mesophytes is evidence of the abundance of water and coastal species spread along the Caspian coast. Salt-tolerance is the main limiting factor of species distribution. The flora was rich with psammophytes (22%). The largest number of the ammophile species belongs to the Asteraceae family as well as the Fabaceae family (Baibulov & Ogar, 2002; Baibulov *et al.*, 2003). The complex communities dominated by *Artemisia terrae-albae*, *Artemisia lercheana* and *Anabasis salsa species* are highly distributed in the investigated area. These communities grow mainly on desert solonetz soils and include eutherophytes (*Eremopyrum orientale, Eremopyrum triticeum, Ceratocephala falcata, Ceratocephala testiculata, Lepidim perfoliatum, Alyssum desertorum)* and perennials (*Tanacetum achilleifolium, Prangos odontalgica, Ferula caspica, F. tatarica, Rh. Tataricum).*

Materials and Methods

The route over which the samples of vegetation and soil were collected for determination of the heavy metals content and oil products was first designed and is shown in Fig. 1. The plant samples were collected at three points:

1	Point (Atyrau, farm, Ulan)	N 47° 15.29’ E 051° 57.31’
2	Point (Kulsary, v. Turgysba)	N 47° 00 887’ E 053° 51. 129’
3	Point (v. Inder, farm, Isayev)	N 48° 31. 268’ E 051°42. 831’

High population density, enhanced agriculture and industrial activity are the main reasons for pollution and degradation of vegetation in these areas. Accumulation of heavy metals in forage plants and subsequent transfer of metals along the food chain might have a negative impact on the health of the population. At Point 1 (Atyrau, farm, Ulan) plants and soil collection were performed in two communities, camel-thorn and wormwood motley grasses. The protective cover in these communities had been decreased due to overgrazing, constituting 65% and 70%, correspondingly. Dominant and fodder plants were collected as test objects.

In the camel-thorn community the dominants collected that were also forage plants included *Alhagi pseudoalhagi* (M.B.) Desv. (*Fabaceae*) and *Agropyron repens* (L.) P.V. Agrost. – (*Poaceae*) and associated forage plants *Eremopyrum orientale* (L.) Jaub. et Spach, *Aeluropus littoralis* (L.) Jaub. et Spach. (Poaceae), *Lactuca tatarica* (L.) C.A. Mey. (*Asteraceae*), *Carex physodes* MV Mem - (*Cyperaceae*). In the wormwood community the dominant forage collected was *Artemisia terrae-albae* Krasch (*Asteraceae*).

At Point 2 (Kulsary, v. Turgysba) collection of plants and soil samples was carried out in two communities, wormwood motley grass and tamarisk and oleaster motley grass. Protective cover was decreased due to overgrazing and remained at only 60% and 70% in the two communities, respectively. Grass change was observed and forage species (grasses, wormwood) in some places were replaced by weeds of little value (*Xanthium strumaruim*) and toxic species (*Peganum harmala, Sophóra alopecuroídes*).

In the wormwood community *Artemisia terrae-albae* was the dominant species and subdominants were *Aeluropus littoralis, Eremopyrum orientale* and those with forage value, *Alhagi pseudoalhagi* and *Carex physodes*. In the second community *Tamarix ramosissima* Ldb (Tamaricaceae) dominated, while the subdominant species was *Agropyron repens*. Samples of both were collected. Around many settlements (e.g.v. Turgysba), natural vegetation cover had degraded and replaced by the weeds *Xanthium strumaruim, Peganum harmala* and *Sophóra alopecuroídes.* These overtaken sites were local and did not cover large areas.

Fig. 1. Sampling points location.

At Point 3 (v. Inder, farm, Isayev) plants and soil samples were collected from among the wormwood motley grasses. For further analysis, the dominant *Artemisia terrae-albae*, subdominans *Eremopyrum orientale*, fodder plants *Alhagi pseudoalhagi, Agropyron repens, Lactuca tatarica* and *Tamarix ramosissima* were collected.

Thus from Points 1 and 2 seven plant species and from Point 3, six species were analysed respectively. Plant identification was preceded by geobotanical description of the communities in the three points (Fig.1) in tenfold replication. The dominant and the forage species viz., *Agropyron repens, Alhagi pseudoalhagi, Artemisia terrae-albae, Carex physodes, Lactuca tatarica, Eremopyron orientale* and *Tamarix ramosissima* were further used as objects of research. The determination of heavy-metal content in the plant samples was conducted using the atomic absorption spectrometer AAS-1N (Slavin, 1993; Li, N.Y., Guo, Li H., Fu, Feng & Ding, 2016). The following heavy metals Pb, Cd, Zn, Cu, Mn, Co and Ni were determined in the samples of soil and dominant plants:. The analysis was conducted using a calibration chart based on reference solutions of the metals mentioned earlier.

Results and Discussion

In the course of the investigation the plant communities and flora of Atyrau region were analysed for their composition and geomorphological conditions. Species analysis revealed that the Atyrau region had 132 plant species belonging 24 families and 87 genera. The dominant species were of *Chenopodiaceae*, *Poaceae*, *Asteraceae* and *Fabaceae*. Representatives of dominant families were collected for further analysis of oil products and the content of concomitant heavy metals. The results of the soil sample analysis are shown in (Table 1).

It may be concluded from (Table 1) that most heavy metals were present within the pollution standards: lead – 0.36 MPC, cadmium – 0.72 MPC, zinc – 0.79 MPC, copper – 0.95 MPC, nickel – 0.97 MPC, cobalt – 0.97 MPC and manganese – 0.38 MPC (Ilyin & Syso, 2001; Informational…, 2014; MPC: Maximum…, 2006).

In Points 2 and 3 the content of lead (0.21 and 0.24 MPC, respectively), cadmium (0.58 and 0.54 MPC), zinc (0.60 and 0.63 MPC), copper (0.50 and 0.48 MPC), nickel (0.50 and 0.81 MPC), cobalt (0.77 and 0.78 MPC) and Mn (0.33 and 0.34 MPC) was also within the pollution standards. However, heavy-metal content, with the exception of cadmium and copper was less in Kulsary (v. Turgyzba).

According to Kazhydromet (Informational…, 2014) in 2014 in all of the soil samples taken from different areas of Atyrau, the cadmium content ranged from 0.18 to 0.68 MPC, lead, 0.012 to 0.054, copper, 0.42 to 0.73, chromium, 0.02 to 0.20 and manganese, 0.40 to 0.88 MPC i.e. their content did not exceed the MPC and was less than in the samples we collected in 2015 in Atyrau (Point 1). Thus, the highest amount of heavy metals in the soil was found in the Ulan farm near the city of Atyrau, while the lowest was found in the soil from Kulsary (v. Turgysba).

Plants may be considered as one of the indicators of the environment. The results of heavy-metal content in plant samples from the three points 1-3 are shown in (Table 2). According to the data shown in (Table 2) the content of Pb, Cd, Zn, Cu, Ni, Co and Mn in dominant terrestrial plants collected from Point 1 (Atyrau, farm, Ulan) was within the MPC (Ilyin & Syso, 2001).

The studied plants possessed differing ability for accumulating heavy metals in their tissue. Thus, *Artemisia terrae-albae* accumulated the highest amount of Pb, Cu, Cd and Mn compared with the other plants, while *Eremopyrum orientale* accumulated more Ni and *Tamarix ramosissima accumulated more* Co. Thus, these species might be considered as test objects for ecological monitoring in areas with similar pollution. Based on the results, it is recommended that these plant communities be avoided.

The results of heavy-metal content in plant samples from the Bereke farm are shown in (Table 2). According to the data the content of Cd, Cu, Ni, Co and Mn in the dominant terrestrial plants was within the MPC, with the exception of *Eremopyrum orientale* and *Artemisia terrae-albae.*

In all the samples of dominant terrestrial plants, the content of lead was within 0.27-0.98 MPC, cadmium, 0.50-0.96 MPC, zinc, 0.59-0.97 MPC, copper, 0.51-0.97 MPC, nickel, 0.54-0.98 MPC, cobalt, 0.08-0.28 MPC and manganese, 0.15-0.78 MPC. The studied plants had differing ability for accumulating heavy metals in their tissue. So, *Artemisia terrae-albae* accumulated the highest amount of Pb and Mn, compared with the other plants, *Lactuca tatarica* accumulated the highest amount of Cd, Cu, Ni and Co and *Alhagi pseudoalhagi*, accumulated the highest amount of Zn. *Carex physodes* accumulated the least amount of Pb, Cu, Ni and Mn, *Agropyron repens*, the least amount of Cd, *Alhagi pseudoalhagi*, the least amount of Co and *Eremopyrum orientale,* accumulated the least amount of Znas compared with the other plants (Table 2).

The results of heavy-metal content investigation in samples of dominant plants collected from Point 2 (Kulsary, v. Turgysba) are shown in (Table 2). According to data, the content of Pb, Cd, Zn, Cu, Ni, Co and Mn in all the dominant plants examined was within the MPC. In all the samples of dominant terrestrial plants the content of lead was within 0.55-0.94 MPC, cadmium, 0.28-0.76 MPC, zinc, 0.63-0.89 MPC, copper, 0.39-0.76 MPC, nickel, 0.80-0.96 MPC, cobalt, 0.08-0.26 MPC and manganese, 0.23-0.73 MPC. It was noted that under the present ecological conditions, *Tamarix ramosissima* accumulated the greatest amount of Pb and Co in comparison with the other dominant plants. *Alhagi pseudoalhagi* accumulated the most of Cd, *Artemisia terrae-albae*, Zn, Cu and Mn and *Eremopyrum orientale*, Ni. The lowest amount of Pb and Cu, compared with the other plants was accumulated in *Eremopyrum orientale*, Cd, Zn and Mn was lowest in *Tamarix ramosissima* and Ni in *Agropyron repens* and Co in *Alhagi pseudoalhagi*.

According to the data shown in (Table 2) the content of all the studied heavy metals in the dominant plant samples collected from Point 3 (v. Inder, Isayev farm) was within the MPC. In all the samples of the studied dominant terrestrial plants collected from Point 3 the content of lead was within 0.55-0.96 MPC, cadmium, 0.50-0.94 MPC, zinc, 0.54-0.86 MPC, copper, 0.34 0.78 MPC, nickel, 0.81-0.97 MPC, cobalt, 0.16-0.27 MPC and manganese, 0.26-0.59 MPC. It was revealed that under the present environmental conditions, *Tamarix ramosissima* accumulated the highest amount of Pb in comparison with the other dominant species, *Lactuca tatarica* accumulated the most Cd, Ni, Co and Mn and *Alhagi pseudoalhagi*, Zn and Cu (Table 2). The least amount of Pb and Ni was found in *Artemisia terrae-albae* samples, Cd and Co in *Agropyron repens* and Zn, Cu and Mn in *Eremopyrum orientale*.

Table 1. Content of heavy metals in soil samples from the three studied points.

Point	Compound content, mg/kg						
	Pb	Cd	Zn	Cu	Ni	Co	Mn
Point 1 Atyrau, farm, Ulan	11.52 ± 3.24	0.36 ± 0.11	18.11 ± 4.03	2.87 ± 0.20	3.88 ± 0.12	4.85 ± 0.19	570.30 ± 189.10
Point 2 Kulsary, v. Turgysba	6.72 ± 2.01	0.29 ± 0.09	13.82 ± 3.60	1.51 ± 0.48	2.00 ± 0.56	3.85 ± 0.88	502.40 ± 167.72
Point 3 v. Inder, farm Isayev	7.69 ± 2.26	0.27 ± 0.08	14.41 ± 4.50	1.44 ± 0.37	3.23 ± 0.67	3.90 ± 0.92	505.20 ± 167.30

Table 2. Average content of heavy metals in plant samples from the three studied areas.

Plant species	Content (mg/kg)						
	Pb	Cd	Zn	Cu	Ni	Co	Mn
	The content of heavy metals in plant samples from Point 1, Atyrau, farm. Ulan						
Eremopyrum orientale	1.6 5± 0.44	0.28 ± 0.07	13.64 ± 4.34	2.37 ± 0.61	3.81 ± 0.27	0.59 ± 0.18	89.46 ± 27.86
Agropyron repens,	1.64 ± 0.51	0.25 ± 0.05	14.96 ± 4.78	2.23 ± 0.64	2.99 ± 0.19	0.99 ± 0.31	74.12 ± 22.70
Aeluropus littoralis	1.65 ± 0.38	0.33 ± 0.09	18.92 ± 4.02	1.90 ± 0.62	2.48 ± 0.51	0.79 ± 0.24	77.96 ± 23.98
Lactuca tatarica	1.10 ± 0.39	0.48 ± 0.03	17.60 ± 5.30	2.91 ± 0.12	3.92 ± 0.11	1.39 ± 0.45	85.62 ± 26.54
Carex physodes	1.09 ± 0.25	0.47 ± 0.04	16.28 ± 5.12	1.53 ± 0.49	2.19 ± 0.63	0.58 ± 0.18	38.34 ± 11.78
Alhagi pseudoalhagi	2.20 ± 0.63	0.30 ± 0.12	22.23 ± 1.41	2.46 ± 0.52	3.80 ± 0.17	0.40 ± 0.12	94.57 ± 29.52
Artemisia terrae-albae	3.90 ± 0.23	0.40 ± 0.07	15.62 ± 5.10	2.79 ± 0.29	3.75 ± 0.23	0.98 ± 0.33	194.25 ± 62.75
	The content of heavy metals in plant samples from Point 2, Kulsary, v. Turgysba						
Aeluropus littoralis	3.27 ± 0.81	0.32 ± 0.11	15.88 ± 4.29	1.78 ± 0.57	3.70 ± 0.35	0.57 ± 0.18	83.07 ± 25.69
Alhagi pseudoalhagi	3.30 ± 0.69	0.38 ± 0.10	16.16 ± 5.18	1.23 ± 0.39	3.50 ± 0.61	0.39 ± 0.13	66.45 ± 21.15
Agropyron repens	2.74 ± 0.85	0.35 ± 0.13	17.32 ± 4.77	1.92 ± 0.66	3.21 ± 0.87	0.40 ± 0.12	142.25 ± 45.20
Tamarix ramosissima	3.77 ± 0.37	0.14 ± 0.05	14.52 ± 4.94	1.24 ± 0.43	3.26 ± 0.81	1.33 ± 0.42	56.87 ± 15.96
Artemisia terrae-albae	3.45 ± 0.56	0.32 ± 0.09	20.52 ± 2.33	2.27 ± 0.65	3.42 ± 0.64	1.18 ± 0.35	181.47 ± 57.47
Carex physodes	3.65 ± 0.44	0.37 ± 0.13	18.68 ± 4.88	1.75 ± 0.59	3.23 ± 0.71	0.78 ± 0.24	85.62 ± 26.23
Eremopyrum orientale	2.20 ± 0,76	0.21 ± 0.06	15.28 ± 5.07	1.16 ± 0.28	3.85 ± 0.32	0.79 ± 0.25	102.24 ± 32.07
	The content of heavy metals in plant samples from Point 3, v. Inder, farm, Isayev						
Aeluropus littoralis	3.27 ± 0.81	0.32 ± 0.11	15.88 ± 4.29	1.78 ± 0.57	3.70 ± 0.35	0.57 ± 0.18	83.07 ± 25.69
Alhagi pseudoalhagi	3.30 ± 0.69	0.38 ± 0.10	16.16 ± 5.18	1.23 ± 0.39	3.50 ± 0.61	0.39 ± 0.13	66.45 ± 21.15
Agropyron repens	2.74 ± 0.85	0.35 ± 0.13	17.32 ± 4.77	1.92 ± 0.66	3.21 ± 0.87	0.40 ± 0.12	142.25 ± 45.20
Tamarix ramosissima	3.77 ± 0.37	0.14 ± 0.05	14.52 ± 4.94	1.24 ± 0.43	3.26 ± 0.81	1.33 ± 0.42	56.87 ± 15.96
Artemisia terrae-albae	3.45 ± 0.56	0.32 ± 0.09	20.52 ± 2.33	2.27 ± 0.65	3.42 ± 0.64	1.18 ± 0.35	181.47 ± 57.47
Carex physodes	3.65 ± 0.44	0.37 ± 0.13	18.68 ± 4.88	1.75 ± 0.59	3.23 ± 0.71	0.78 ± 0.24	85.62 ± 26.23
Eremopyrum orientale	2.20 ± 0.76	0.21 ± 0.06	15.28 ± 5.07	1.16 ± 0.28	3.85 ± 0.32	0.79 ± 0.25	102.24 ± 32.07

Conclusion

Based on the results of the dominant and forage plant analysis it was determined that the content of Pb, Cd, Zn, Cu, Ni, Co and Mn in plants in the investigated territory of Atyrau region was within permissible concentration levels (MPC).

The highest amount of lead and manganese was found in *Artemisia terrae-albae*, (3.90 mg/kg and 194.25 mg/kg,), while the highest amount of cadmium, copper, nickel, cobalt was detected in *Lactuca tatarica* (0.48 mg/kg, 2.91 mg/kg, 3.92 mg/kg, 1.39 mg/kg). The maximum amount of zinc content was found in *Alhagi pseudoalhagi* (22.23 mg/kg) compared with the other species.

Eremopyrum orientale and *Agropyron repens* are remarkable for showing the least accumulation of heavy metals compared with the other plants growing in the same environmental conditions.

To improve the ecological conditions the environment forecast should include regular monitoring of heavy-metal content in soil and vegetation samples. This study highlights that the methods of bioindication applied in environmental assessment may be a useful tool for decreasing the risk on health from environmental pollution.

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