DEPENDENCE OF MICROELEMENTS AND HEAVY METALS CONTENT IN SOILS OF SOME REGIONS OF KAZAKHSTAN ON THE ORGANIC STRUCTURE AND SOIL TYPE

Kamalidin Sharipov[1], Aray Kirgizbayeva[1], Kulshat Omirzakova[1],
Aygul Batyrbayeva[2], Assel Toktabayeva[2]

[1] *Asfendiyarov Kazakh National Medical University*
Biochemistry department
Tolebe 94, 050050, Almaty, Republic of Kazakhstan
E-mail: Skamalidin@mail.ru
[2] *Al-Farabi Kazakh National University*
Department of Chemistry and Chemical Technology
71 al-Farabi Ave., 050040, Almaty,
Republic of Kazakhstan

Received 27 February 2017
Accepted 02 May 2017

ABSTRACT

The content of microelements and organic compounds in the soils of the former Semipalatinsk test nuclear polygon is investigated (STNP). It is found that the latter is characterized by a low content of copper, zinc, cobalt and an increased content of manganese. A minimum content of trace elements is observed in salt marshes and dark chestnut soils, while a maximum one is found in light-chestnut, meadow-chestnut and dark chestnut soils. The values of the heavy metals (Pb, Zn, Co, Cu, Ni) content in the soils of the polygon region suggest that STNP is a relatively dangerous area from a contamination point of view. The soil type does not affect the heavy metals content under normal and increased radionuclides background. This is also valid for the micronutrients present. It is concluded that STNP soils can be used for agricultural purposes.

Keywords: *microelements, heavy metals, types of soils.*

INTRODUCTION

Microelements are a negligible fraction of the soil, but they are very important for plant nutrition. Manganese, copper, zinc and molybdenum are required for most biochemical processes in plants and animals. Microcells positive physiological effects manifest at low concentrations. Their excess or deficiency affects negatively many enzymological processes and human health [1 - 4].

The content of microelements in soils is closely related to the parent rocks present. A noticeable increase in heavy metals (Cu, Ni, Co, Pb, Zn) content, sometimes exceeding the background by more than 10 - 100 times, is noted in the upper horizons of the soil near large industrial facilities (up to 20 km from the source of pollution). Each region and soil type has its own level of background concentration. Therefore, it is not possible to reveal general patterns in case of higher background concentrations based on numerous soils sampling in different regions of the territory under consideration [5 - 9].

Zinc is a natural component of the earth's crust, but in many places it accumulates in quantities close to or exceeding the safe levels. Nowadays this metal is widely used. Therefore it is necessary to pay attention to the possible consequences associated with its increased content in the environment [10 - 13].

Systematic knowledge of heavy metals presence provides to develope strategies and follow-up actions aimed at achieving homeostasis in the environment contamination. Elevated levels of zinc can adversely affect the microbiological and biochemical processes occurring in the soil, the development of plants, which in turn affects the quantity and quality of crops. Therefore, the low bioavailability of heavy metals, including zinc, to the agricultural land is the key to ecosystem stability and food security [3, 14].

According to refs. [12, 13, 15 - 17], the content of gross forms of heavy metals (Cu, Ni, Co, Pb, Zn) is dynamic both in space and time, with spatial changes more significant than the temporary one. This leads to the conclusion that the gross content of heavy metals in soils is characterized by large fluctuations. Besides, a great amount of heavy metals accumulates in the upper soil layer. As soil is contaminated with heavy metals, its biochemical, physicochemical, chemical and physical functions are disturbed. The extent of exposure depends on the nature of the pollutant and its concentration in the soil. The purpose of the study reported is to establish the degree of soil contamination with heavy metals in different parts of the Semipalatinsk nuclear test site in view of transferring these territories to land use. The results obtained will provide to conclude whether the regional standards referring to the content of Cu, Ni, Co, Pb, Zn in soils [16 - 19] are observed.

EXPERIMENTAL

The following tasks were set to achieve the goal pointed above:

1. To determine the heavy metals (Pb, Zn, Co, Cu, Ni) content in different types of soils in the SISP region (i.e. soils from the Degelen Mountains, the Test Field and the Atomic Lake in the Abralynsky region).

2. To estimate the degree of heavy metals accumulation in soils depending on the distance from the pollution sources.

3. To identify the relationship between the microelement composition of soils and their type.

The microelements and organic compounds content of soil samples taken from the former Semipalatinsk test nuclear polygon (STNP, Kazakhstan) were studied. In fact samples of the soils from the Degelen Mountains, the Test Field and the Atomic Lake were taken. Degelen is a low mountain range located in the eastern part of the Kazakh hills. The slopes are covered with steppe vegetation. Shrubs are found in the river valleys. The test area “Degelen” of STNP has been housed in the Degelen Mountains until 1991. It is worth noting that 215 underground nuclear explosions were carried out there between 1961 and 1989. The Test Field was the first test area of STNP, which was used for atmospheric (air and ground) nuclear tests in the period from 1949 to 1962. The area is a plain, 20 miles in diameter, surrounded on three sides by low mountains. This is a large-scale complex of civil engineering buildings designed for testing and recording the parameters of the nuclear explosions under field experimental conditions. The Atomic Lake was formed by a thermonuclear explosion of 140 kt capacity. It resulted in a crater of 100 m depth and 400 m diameter at the confluence of the waterways of Shagan and Ashchisu rivers.

47 sampling points were selected. 4-5 samples were taken at each point. Thus, 225 soil samples were studied. The sampling was carried out taking into account the vertical structure and heterogeneity of the soil cover, the terrain, the nature and extent of radionuclide contamination. The selected area was treated prior to the sampling, i.e. the vegetation and the rocks were removed. A pit was dug at the sampling point and a sample block of ground from a predetermined depth (15 cm) was taken using a special blade with a sod. It was then packed in a plastic bag. The soil microelements content was determined by an emission quantitative method providing the identification of 28 elements in rocks, ores, minerals, soils, plants. DFS-8 spectrograph was used. The analysis was performed on the ground of a regular calibration curve obtained using standard samples (Research Council on Analytical Methods (RCAM), 1987).

The organic carbon in soil humus was determined by the wet combustion method of I. V. Tyurin. It is based on the oxidation of soil humus carbon in excess of dichromate according to the equation:

$$3C^0+K_2Cr_2O_7+H_2SO_4=2Cr(SO_4)_3+2K_2SO_4+8H_2O+3CO_2$$

Oxidation takes place in a strongly acidic medium and is followed by hexavalent chromium reduction. The dichromate excess in the solution after humus oxidation is titrated by Mohr’s salt:

$$K_2Cr_2O_7 +7\,H_2SO_4+6\,FeSO_4 = Cr(SO_4)_3+ K_2SO_4 +7\,H_2O$$

The calculated values of organic carbon are multiplied by 1,724 and converted into humus, the concentration of which is expressed in percentage.

RESULTS AND DISCUSSION

Some authors have noted that different types of soils contain different amounts of microcells. Their higher total content is typical for meadow and saline soils. We find no such pattern in the samples collected in the saline areas of Abralinskiy district (Table 1). The meadow soils of the Atomic Lake and Degelen contain the greatest amounts of microcells. The soils of the Atomic Lake are substantially free of an organic matter as a result from the thermonuclear explosion carried out in the area of the Atomic Lake.

The results summarized in Tables 1, 2 and 3 show that a minimum content of microcells is found in the saline and dark chestnut soils. In fact, the light chestnut, meadow chestnut and dark chestnut soils are characterized by a maximum content of microcells.

The dark- and light-chestnut soils of Degelen and the light chestnut soils of the Test Field are characterized by the highest concentration of lead (32.6 mg/kg - 39.1 mg/kg). The light chestnut soils of the Atomic Lake show the highest content of nickel and chromium (38 mg/kg and 120 mg/kg, respectively). The meadow chestnut soils of the Atomic Lake contain the largest amounts of barium (660 mg/kg) and manganese (2285.7 mg/kg).

The average content of humus ranges from 1.42 % to 1.58 % in the light-chestnut and saline soils, while it amounts to 13.6 % in the dark-chestnut one. Rich in humus are the soils of the Abralinskiy district and Degelen. The soils of the Test Field contain significantly less humus than the other soils studied. Virtually no humus is found in the soil samples taken in the area of the Atomic Lake. This is due to the open excavation explosions, which ashed the soil.

A relation between the heavy metals content and that of humus content is found in case of the soils of Degelen (Fig. 1). It can be seen that lead content increases with humus decrease. The inverse relationship is observed in case of nickel.

The influence of soil texture on the total content of metals and microcells can be outlined examining the data referring to samples of dark-chestnut soils (Table 4).

Table 4 shows that the total content of each metal sharply increases with heaving the soil texture. In the

Table 1. Microcells content in dark chestnut soils of STNP.

No.	Microcells, mg/kg	Abralinskiy district	Degelen
		M±m	M±m
1.	Pb	21.0±5.3	36.8±10.21
2.	Cu	12.5±2.1	16.6±3.69
3.	Zn	50.0±17.79	66.6±17.06
4.	Sc	26.25±16.3	7.0±1.21
5.	Mo	1.75±0.75	6.83±3.32
6.	Nb	7.0±1.68	10.3±4.74
7.	Be	2.75±0.63	9.0±3.75
8.	Ba	137.5±23.9	250.0±23.94
9.	Ni	25.0±7.9	9.3±2.14
10.	Cr	42.5±12.9	13.5±2.79
11.	V	76.5±21.3	38.8±6.26
12.	Y	21.0±4.3	32.6±7.38
13.	Yb	6.5±4.52	3.3±0.80
14.	Mn	512.5±173.6	621.6±165.8
15.	Ga	18.25±6.62	24.3±3.85
Total content		∑64.3	∑76.0

Table 2. Microcells content in light-chestnut soils of STNP.

No	Microcells, mg/kg	Abralinskiy district	Degelen	The Atomic lake	Test field
		M±m	M±m	M±m	M±m
1.	Pb	23.5±1.55	32.6±7.24	10.0±1.58	39.1±7.5
2.	Cu	11.0±1.68	27.4±5.91	38.0±4.98	29.4±5.4
3.	Zn	102.5±27.8	53.9±3(56	58.0+2.46	52.7±10.2
4.	Sc	26.75±3.61	9.14±0.73	18.0±0.89	10.1±2.0
5.	Mo	4.0±0.91	2.64±1.36	2.0±0.45	2.5±1.36
6.	Nb	10.5±0.5	7.14±1.24	5.0±0.12	7.14±1.24
7.	Be	4.0±1.47	2.17±0.64	3.0±0.21	2.17±0.64
8.	Ba	275±62.9	261.4±12.26	760.0±150.6	250±50
9.	Ni	24.75±4.4	15.71±2.45	38.0±3.65	19±3.5
10.	Cr	41.7±13.4	18.9±2.34	120.0±24.8	20±3.8
11.	V	145.0±20.2	54.35±5.79	64.0±6.45	63.3±12.0
12.	Y	23.5±2.53	18.64±2.98	19.0±2.4	12.5±2.5
13.	Yb	2.5±0.28	1.78±0.28	2.0±0.21	1.36±0.02
14.	Mn	937.5±37.5	1809.2±274.3	1600.0±230.0	2100±428
15.	Ga	22.5±1.44	30.07±1.14	12.0±3.41	30.0±6.0
Total content		∑110.0	∑156.0	∑183.0	∑193.0

transition from sandy-loam to medium-loam soils the lead content increases by 1.6 times, copper - 2.4 times, chromium, beryllium, manganese - 3 times, scandium - 7.5 times, titanium and vanadium - 4 times, ytterbium - 20 times, yttrium - 2.5 times, gallium - 11times.

The high organic content affects microcells presence in soils. Thus, the strong fixation of copper in soils rich in humus leads to copper increase in the feed, which becomes toxic to cattle. In comparison with literature data, soils of the Semipalatinsk region are characterized by a low total content of copper, zinc, cobalt and an increased total content of manganese (Table 5).

The results obtained in the course of this study (Table 6) show very high values of copper, zinc and manganese.

The Abralinskiy district soils contain slightly less copper, zinc and manganese than those of other regions studied. The copper content of the Degelen mountains soils is approximately 10 times higher than that of the soils of the other regions and 8.5 times higher than that of MAC, while the content of zinc and manganese differs slightly. The soils of the Atomic Lake and the Test Field are characterized by a very high content of manganese, which is 2.5 - 5.5 times higher than that of the soils of the other regions. The zinc content in the soils of the Atomic Lake and the Test Field is 1.5 times higher than that of the other regions soils. The copper content in the soils of the Atomic Lake and the Test Field exceeds by

Table 3. Microcells content in the meadow saline soils and meadow chestnut soils* of STNP.

No	Microcells, mg/kg	Abralinskiy district	Degelen	The Atomic lake
		M±m	M±m	M±m
1.	Pb	27.5±2.5	13.0±1.15	15.7±1.45
2.	Cu	12.5±0.5	14.0±1.56	33.5±3.85
3.	Zn	55.5±5.0	40.0±2.65	61.0±2.63
4.	Sc	22.5±12.5	9.0±2.5	15.4±0.99
5.	Mo	3.0±2.0	1.0±0.08	15.7±0.25
6.	Nb	10.0±0.0	5.0±1.89	9.35±2.58
7.	Be	2.5±0.5	1.0±0.07	1.85±0.34
8.	Ba	250.0±50.0	350.0±48.6	660.7±44.40
9.	Ni	87.5±62.5	17.0±2.56	33.7±1.63
10.	Cr	27.5±2.5	13.0±2.31	94.0±10.03
11.	V	135.0±35.0	64.0±1.45	62.7±2.95
12.	Y	23.5±3.5	10.0±2.97	22.8±1.69
13.	Yb	2.5±0.5	1.0±0.05	2.21±0.18
14.	Mn	900.0±0.0	2100.0±58.9	2285.7±131.3
15.	Ga	21.0±4.0	33.0±4.32	18.28±0.95
Total content		∑98.0	∑179.0	∑222.0

* meadow chestnut soils are primarily found in the area of the Atomic Lake.

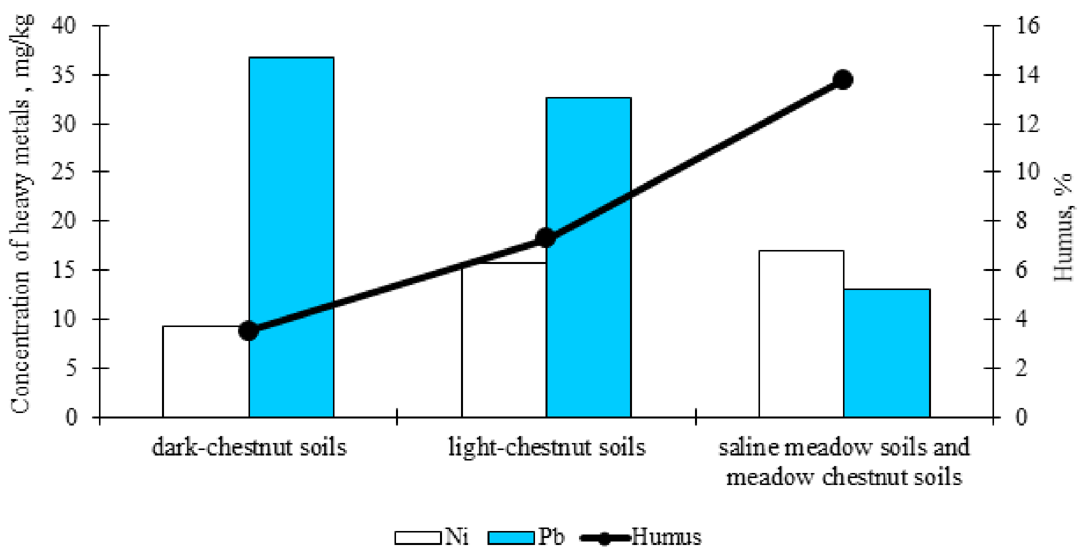

Fig. 1. Dependence of some heavy metals content on humus presence in the soils of Degelen.

1.7 - 1.8 times and 2 - 2.6 times, respectively, that of the soils of the other regions. The lead content at the explosion epicentre in the Test Field and Degelen is higher than that of the same soils of the Abralinskiy district. This can be attributed to the consequences of the nuclear explosions carried out in these areas.

CONCLUSIONS

The soil of the Semipalatinsk region is characterized by a low content of copper, zinc, cobalt and increased content of manganese in view of the ecological standards accepted. A minimum content of trace elements is observed in salt marshes and dark chestnut soils, while

Table 4. Total content (mg/kg) of metals in the dark-chestnut soil of Abralinskiy district as a function of the soil texture.

Metals	Soil texture	
	medium-loam with silt-like lumpy structure	sandy-loam with loosely-lumpy structure
Pb	15.0±3.0*	9.0±1.4
Cu	17.0±2.5*	7.0±1.4
Mn	900.0±135.0*	300.0±45.0
Sc	75.0±11.2*	10.0±2.0
Be	3.0±0.6*	1.0±0.15
Ti	8000.0±1440*	2000.0±400.0
Cr	50±7.5*	15.0±3.0
V	80.0±15.0*	26.0±3.5
Yb	20.0±3.0*	1.0±0.15
Y	25.0±3.7*	10.0±2.0
Ga	35.0±7.0*	3.0±0.5
Ba	100.0±18.0	100.0±20.0
* Authentically discernible results.		

Table 5. Heavy metals content (mg/kg) in soils of different regions.

Region	Cu	Zn	Mn	Co
Clark in soil	20	50	850	8
Midland of Eastern Kazakhstan	18.5	38.2	626.6	7.5
Kazakhstan in total	18.9	39.5	450.0	7.1
Altai Territory	18.0	32.0	890.0	13.5
South of Western Siberia	33.8	72.3	720.0	
Soils of dry steppe, semi desert zones	24.4	53.0	700.0	6.9
Territory of former Semipalatinsk polygon	14.3	20.8	768.0	6.4

Table 6. Heavy metals content (mg/kg) in the soils of the former Semipalatinsk polygon.

Region	Cu	Zn	Mn	Pb
Abralinskiy District	12±2	12.7±2.5	890±170	24±4.6
Mountain range Degelen	170±34	55±11	1100±200	27.4±5.4
Test field	48.4±9.6	60±12	2500±500	39.1±7.8
The Atomic Lake	34±7	61±12	2200±440	12.8±2.5
Maximum acceptable concentration	20	50	850	8

the maximum one is found in light-chestnut, meadow-chestnut and dark-chestnut soils. The slightly exceeding levels of heavy metals (Pb, Zn, Co, Cu, Ni) presence in the soils of the polygon region suggests that the STNP area studied is a relatively dangerous area because of the contamination observed.

Soils types do not generally affect the content of heavy metals in presence of a normal radionuclides background. The investigation carried out shows that the increased radionuclides background in the territory of the Atomic Lake, Degelen and the Test Field impacts slightly the maintenance of the soil micronutrients. The soils of STNP can be used for agricultural purposes in compliance to the ecological recommendations accepted.

REFERENCES

1. Yu. N. Vodyanitskiy, Heavy metals and non-7metals in soils M SSI, Dokuchaev Soil Institute of RAAS, 2008, p. 85, (in Russian).
2. V.V. Dobrovolsky, Fundamentals of biogeochemistry, Moskow, ACADEMIA, 2003, p. 397.
3. A.V. Evseev, T.M. Krasovskaya, Toxic metals in soils of the Russian North, Journal of geochemical exploration Part 1, 174, 2017, 128-131, (in Russian).
4. A. Kabata, X. Pendias, Trace Elements in Soils and Plants, Tr. from English, Moscow, 1989, p. 439.
5. D.S. Orlov, L.K. Sadovnikova, I.N. Lozanovskaya, Ecology and conservation of the biosphere at chemical pollution, Moscow, Higher School, 2002, p.334, (in Russian).
6. H.C. Ye, C.Y. Shen, Y.F. Huang, W.J. Huang, S.W. Zhang, X.H. Jia, Spatial variability of available soil microelements in an ecological functional zone of Beijing. Environmental monitoring and assessment, v. 187, 2015.
7. T.V. Minnikova, T.V. Denisova, S.S. Mandzhieva, S.I. Kolesnikov, T.M. Minkina , V.A. Chaplygin, M.V. Burachevskaya, S.N. Sushkova, T.V. Bauer, Assessing the effect of heavy metals from the Novocherkassk power station emissions on the biological activity of soils in the adjacent areas, J. of Geochemical Exploration, v. 174, March 2017, 70-78, (in Russian).
8. E.V. Salnikova, E.A. Osipova, A.V. Skalniy, T.I. Burceva, O.I. Boldyreva. Influence of micronutrients from the biosphere on the elemental status of a person, Bulletin of the Orenburg State University, 2013, No 10.
9. M.A. Yakovenko, O.B. Konstantinova, A.A.Kosolapova, L.V.Rogova, D.N. Alankina, Study of the content of heavy metals in the soil cover and vegetation of the reclaimed territories, Bulletin of the Kuzbass State Technical University, 2014, No. 3.
10. M.G. Mustafaev, A.B. Akhundova, Heavy metals in saline soils of the Salyan steppe of Azerbaijan, Bulletin of the Ryazan State Agrotechnological University named after P.A.Kostychev, 3, 19, 2013, (in Russian).
11. L. Boluspaeva, M.S. Panin, Heavy metals in the soils of Ust-Kamenogorsk city of the Republic of Kazakhstan, Siberian ecological journal, 2012, No 6, (in Russian).
12. A.D. Budaeva, E.V. Zoltoev, G.I. Khanturgaeva, B.S. Zhambalova, Sorption of copper and Zinc from model solutions of humic acids, J. Chemistry for Sustainable Development, v.16, 2008, 143-146.
13. G. Bakonyi, P. Nagy, I. Kadar, Long-term effects of heavy metals and microelements onnematode assemblage, Toxicology Letters, 140-141, 2003, 391-/401.
14. N. Grytsyuk, G. Arapis, L. Perepelyatnikova, T. Ivanova, V. Vynogradska, Heavy metals effects on forage crops yields and estimation ofelements accumulation in plants as affected by soil, Science of the Total Environment, 354, 2006, 224-231.
15. M. Kaplan, S.Orman, I. Kadar, J. Koncz, Heavy metal accumulation in calcareous soil and sorghum plant safter addition of sulphur-containing waste as a soil amendment in Turkey, Agriculture, Ecosystems and Environment, 111, 2005, 41-46.
16. Ji Cheol Kwon, Zahra Derakhshan Nejad, Myung Chae Jung, Arsenic and heavy metals in paddy soil and polished rice contaminatedby mining activities in Korea, CATENA, v. 148, Part 1, January 2017, 92-100.
17. G.V. Motuzova, T.M. Minkina, E.A. Karpova, N.U. Barsova, S.S. Mandzhieva, Soil contamination with heavy metals as a potential and real risk to the environment, Journal of Geochemical Exploration, v. 144, Part B, September 2014, 241-246.
18. Kang Tian, Wenyou Hu, Zhe Xing, Biao Huang, MengmengJia,Mengxue Wan, Determination and evaluation of heavy metals in soils under twodifferent greenhouse vegetable production systems in eastern China, Chemosphere, 165, 2016, 555-563.
19. G.S. Senesi, M. Dell'Aglio, R. Gaudiuso, A. De-Giacomo, C. Zaccone, O. DePascale, T.M. Miano, M. Capitelli, Heavy metal concentrations in soils as determined by laser-induced breakdown spectroscopy (LIBS), with special emphasis on chromium, Environmental Research, 109, 2009, 413-420.