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Satbayev University

Х А Б А Р Л А Р Ы

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ
НАУК РЕСПУБЛИКИ
КАЗАХСТАН
Satbayev University

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CONTENT OF COPPER IN DESERT SOILS AND PLANTS OF EAST KAZAKHSTAN REGION

Abstract. One of the ecological characteristics of heavy metals is the knowledge of the normal (background) content in soils and the parameters of its possible anthropogenic pollution. Knowledge of the level of background content of heavy metals, including copper in soils is practical importance. The soil cover and vegetation of desert zones are diverse, but the elemental and chemical composition has been poorly studied and requires ecological and geochemical research, since the territory has an economic value.

The article investigates the physico-chemical properties of the soils in the desert zone of East Kazakhstan region, as well as the content of the gross and concentration of the mobile form of copper (Cu). The copper content in the soils was determined by atomic absorption method. Statistical processing of the obtained data was carried out according to N.A. Plokhinsky using the Microsoft Excel program.

To determine the content of gross copper and its exchange form in the soil-forming rocks and soils of the East Kazakhstan desert zone, their ecological and geochemical assessment is given. The correlation dependence of copper on indicators of physical and chemical properties of soils is calculated.

The data obtained reflect the patterns of copper distribution in the desert soils of East Kazakhstan region and can be used to develop a strategy for rational nature management, improving the organization of ecological and geochemical monitoring.

Key words: soil, plants, desert zone, heavy metals, copper.

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ШЫҒЫС ҚАЗАҚСТАН ОБЛЫСЫНДАҒЫ ШӨЛДІ ТОПЫРАҚ ПЕН ӨСІМДІКТЕРІНДЕГІ МЫСТЫҢ ҚҰРАМЫ

Аннотация. Ауыр металдардың экологиялық сипаттамаларының бірі – олардың топырақтағы қалыпты (фондық) құрамын және оның ықтимал техногендік ластану параметрлерін білу. Ауыр металдардың, оның ішінде топырақтағы мыстың фондық құрамының деңгейін білудің тәжірибелік маңызы зор. Шөлді аймақтардың топырақ мен өсімдік жамылғысы әртүрлі болып келсе де, олардың элементтік-химиялық құрамы жеткіліксіз мөлшерде зерттелген және аумақтың шаруашылықта маңызы жоғары болғандықтан экологиялық-геохимиялық зерттеуді қажет етеді.

Мақалада ШҚО шөлді аймағы топырағының физикалық-химиялық қасиеттері, сондай-ақ мыстың жалпы және қозғалмалы формасының (Cu) концентрациясы зерттелген. Топырақтағы мыстың құрамы атомдық-абсорбциялық әдісімен анықталды. Алынған мәліметтерді статистикалық өңдеу Н.А. Плохинскийге сәйкес Microsoft Excel бағдарламасы көмегімен жүргізілді.

ШҚО шөлді аймағының топырақ түзуші жыныстары мен топырақтарындағы жалпы мыстың және оның қозғалмалы формасының құрамы анықталды, оларға экологиялық-геохимиялық баға берілді. Мыстың топырақтың физикалық-химиялық көрсеткіштеріне байланысты корреляциялық тәуелділік коэффициенттері есептелді.

Алынған мәліметтер ШҚО шөлді топырақтарындағы мыстың таралу заңдылықтарын көрсетеді және табиғатты тиімді пайдалану стратегиясын әзірлеу, экологиялық-геохимиялық мониторингті ұйымдастыруды жетілдіру мақсаттарында пайдаланылуы мүмкін.

Түйін сөздері: топырақ, өсімдік, шөл зонасы, ауыр металлдар, мыс.

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СОДЕРЖАНИЕ МЕДИ В ПУСТЫННЫХ ПОЧВАХ И РАСТЕНИЯХ ВОСТОЧНО-КАЗАХСТАНСКОЙ ОБЛАСТИ

Аннотация. Одной из экологических характеристик тяжелых металлов является знание нормального (фонового) содержания в почвах и параметры его возможного техногенного загрязнения. Знание уровня фонового содержания тяжелых металлов, в том числе меди в почвах имеет практическое значение. Почвенный покров и растительность пустынных зон разнообразны, но элементно-химический состав изучен слабо и требует эколого-геохимического исследования, поскольку территория имеет хозяйственно-ценное значение.

В статье исследованы физико-химические свойства почв пустынной зоны ВКО, а также содержание валовой и концентрация подвижной формы меди (Cu). Содержание меди в почвах определяли атомно-абсорбционным методом. Проведенная статистическая обработка полученных данных проводилась по Н.А. Плохинскому с использованием программы Microsoft Excel.

Определению содержания валовой меди и ее обменной формы в почвообразующих породах и почвах пустынной зоны ВКО дана их эколого-геохимическая оценка. Рассчитана корреляционная зависимость меди от показателей физико-химических свойств почв.

Полученные сведения отражают закономерности распределения меди в пустынных почвах ВКО и могут быть использованы для разработки стратегии рационального природопользования, совершенствования организации эколого-геохимического мониторинга.

Ключевые слова: почва, растения, пустынная зона, тяжелые металлы, медь.

Introduction. One of the ecological characteristics of heavy metals is the knowledge of the normal (background) content in soils and the parameters of its possible anthropogenic pollution. Knowledge of the level of background content of heavy metals, including copper in soils is of practical importance for the development of a strategy for rational nature management and improvement of the organization of soil-geochemical monitoring since the correctness of the assessment of the degree of soil pollution depends on it.

Some heavy metals such as Co, Cu, Fe, Mn, Ni, and Zn are required in low amounts by organisms. Nevertheless, high levels of these elements may become harmful for organisms (Chandrasekaran, 2015).

High concentrations of heavy metals are dangerous for living organisms, they can be accumulated inside of the organism and causes a severe form of poisoning (Avkopashvili, 2015), (Hanauer, 2011). Copper is a heavy metal toxic for plants and has a negative effect on human health (Woolhouse, 1981), (Turnlund, 2004).

Copper plays an important role in many physiological processes occurring in living organisms.

In plants, these are photosynthesis, hemoglobin synthesis, respiration, carbohydrate redistribution, nitrogen recovery, fixation, etc.

Animal organisms need copper for hemoglobin synthesis and participation in many biological processes similar to those described above for plants.

In animals and humans, copper deficiency (hypercuporosis) leads to anemia, a decrease in growth intensity, loss of body weight, an acute shortage of metal (less than 2-3 mg/day), rheumatic arthritis, and endemic goiter may occur (Ilyin, 2011).

At high concentrations, copper can become extremely toxic for plants causing symptoms such as chlorosis and necrosis, stunting, leaf discoloration, and inhibition of root growth (Borghi, 2008), (Cuypers, 2000). Heavy metals above allowable limits will often lead to disadvantageous effects in humans, other organisms and the environment at large (Mansourri, 2016).

The content of heavy metals in soil-forming rocks, soils, and plants of the East Kazakhstan region is considered in the works of (Panin, 1999), (Akhmetkaliyeva, 2018) and others.

The soil cover and vegetation of desert zones are diverse, but the elemental and chemical composition has been poorly studied and requires ecological and geochemical research. Since desert, soils and vegetation in the East Kazakhstan region are mainly used as land for pastures and haymaking.

The purpose of this study is to study the intra-profile and spatial distribution of copper in soils and plants of the desert zone of the East Kazakhstan region.

Materials and basic methods. The objects of the study were soil samples, plants selected in the desert zone (Alakol hollow) East Kazakhstan region. Objects of research: brown, meadow-brown, gray-brown soils, gray sail, meadow salt marshes, ridge-bumpy semi-fixed sands. Full-profile sections were laid on sites typical of nature in the system of conjugate landscapes, soil samples were selected according to genetic horizons. The physical-chemical properties of soils were determined by methods generally accepted in soil science. The gross content and concentration of the mobile form (extractant – ammonium acetate buffer, pH = 4.8) of copper in soils and plants were determined by the atomic absorption method using a spectrometer «Quantum-2A atomic absorption spectrometer».

Statistical processing of the data obtained during the study was carried out uses the Microsoft Excel program.

When processing the data, the following statistical indicators were used: n-the number of samples; $\bar{x} \pm S\bar{x}$ - arithmetic mean and its error; (mg/kg); C_V – coefficient of variation (%); lim – limits of fluctuations (mg/kg); σ – standard deviation (mg/kg); r – correlation coefficient.

Results. The soil-forming rocks of the studied soils are composed of clays, loams, sands, in places of crushed-pebble material and have a flat, less often hollow-hilly character with separate saline or takyrs hollow. The lake-alluvial plain occupies the lowest hollow of the plain and is composed mainly of the modern lake and partly river deposits (powdery and clay sands, occasionally with layers of pebbles, powdery sandy loams, and loams with variegated colored clays and semi-sandy soils).

The gross copper content in the soil-forming rocks of the region varies from 15.63 to 33.46 mg/kg with an average coefficient of variation of 18.64%. The average copper content in the whole set of soil-forming rocks is 23.49±0.65 mg/kg, which is lower than its Clark in the earth's crust. The lowest levels of copper content were found in sandy loam soil-forming rocks of 4.90 mg/kg. The highest copper content is characteristic of loamy deposits. In light loamy and sandy loam deposits, the copper content is 18.32 mg/kg.

Studies have established that the gross copper content in the studied soils in the hummus-accumulative horizon ranges from 17.58-35.47 mg/kg, averaging 25.57 mg/kg. The coefficient of variation of gross copper is 20.09%.

The average gross content and limits of fluctuations of copper in the soil cover of the studied territories are presented in Table 1.

Table 1 - Statistical parameters of copper content in desert zone soils

№	Soils	n	lim	$\bar{x} \pm S\bar{x}$	σ	C_V, %
			mg/kg			
1	Meadow-brown light loamy	5	15,63-21,97	18,40±0,33	2,08	11,28
2	Brown medium loamy	4	22,97-29,97	26,36±0,39	2,49	9,46
3	Brown light loamy	4	21,98-26,98	24,97±0,32	1,99	7,99
4	Serozems	5	17,58-19,49	18,62±0,11	0,69	3,71
5	Meadow-brown sandy loam	5	29,78-34,98	31,23±0,25	1,59	5,10
6	Gray-brown strongly skeletal loamy	3	32,96-35,47	33,96±0,16	1,00	2,95
7	The sands are ridge-bumpy semi-fixed	5	18,63-19,23	18,88±0,04	0,23	1,21
8	Meadow salt marshes are heavy loamy	4	19,59-27,98	22,71±0,46	2,92	12,87

Brown soils in the studied territories occupy a large area, are formed on proluvial deposits of sandy loam and sandy mechanical composition, under the cover of wormwood and boyalychovo-wormwood vegetation.

In brown light loamy soils, there is a decrease in the content of the element down the profile from 26.98 to 21.98 mg/kg, there is a relationship with a decrease in humus content. The behavior of the element in the soils under consideration is greatly influenced by humus, carbonates (r= 0.94; 0.83, respectively).

Serozems are formed under ephemeral sagebrush vegetation on the sloping slopes of the outliers and higher parts of the Alakol hollow at altitudes of 350-750 m, where they occupy significant areas. The total copper in these soils varies from 17.58 to 19.49 mg/kg, the coefficient of variation is 3.71%, the average content is 18.62 mg/kg.

Gray-brown strongly skeletal soils are confined to the slightly undulating inclined plain of the foothills of the Barlyk ridge. They are formed under highly sparse, poor species composition, desert vegetation on closely lying gravel-pebble deposits. The total copper in these soils varies from 32.96 to 35.47 mg/kg, the coefficient of variation is 2.95%, the average content is 33.96 mg/kg. The content of the element decreases along with the profile, there is a positive strong correlation with humus (r= 0.76) and a straight line of average strength with carbonates (r=0.58).

Meadow-brown sandy loam soils of the desert zone are formed among brown desert soils in relief hollows on homogeneous soil-forming rocks. The average copper content in them is 31.23, the coefficient of variation for meadow-brown sandy loam soils is 5.10%.

Desert-steppe bumpy sands fixed are confined to territories with semi-bumpy or bumpy relief, covered with grass-wormwood herbaceous or grass-shrub vegetation. The sands are composed of Aeolian deposits. Due to the deep (more than 6 m) occurrence of groundwater, insufficient atmospheric moisture, and high temperatures, vegetation cover is rare, contains very little organic matter (0.1-0.8%). The morphological profile of the sands is characterized by weakly isolated genetic horizons, structure less, loose addition. In the sands, there is a uniform content of the element along with the profile. The gross copper in the sands varies from 18.63 to 19.63 mg/kg, the average content is 18.88 mg/kg, the coefficient of variation is 1.21 mg/kg.

Salt marshes are formed under the influence of highly mineralized groundwater, lying at a depth of up to 1.5 m. under the cover of salt-resistant vegetation on medium-heavy loamy soil-forming rocks. The average concentration of copper in salt marshes of meadow soils is 22.71 mg/kg. There is a positive strong correlation with humus and a silty fraction (r=0.99; 0.93, respectively).

Important in the study of heavy metals in the soil is information about their mobility, i.e. the ability to transition from the composition of the solid phase of the soil to the liquid. Becoming mobile, chemical elements can migrate along with the soil profile up to groundwater, and which is very important, to transition into a form more accessible for absorption by plants. It is known that the physiological, agronomic, and ecological significance is not the gross content of trace elements, but their "mobile" forms in soils.

The concentration of the exchangeable form of copper in soils (extractant – ammonium acetate buffer, pH = 4.8) ranges from 0.09 - 0.99 mg/kg; the average content of this form is 0.41 mg/kg, which is 1.6% of the gross metal stock.

A plant, being a self-regulating system, having a powerful adaptive potential, can be an active component in the "soil-plant" system, the relationship in which is a complex problem.

The concentration of copper in the plants of the studied region ranges from 1.80 to 12.10 with an average content of 6.03 mg/kg and a coefficient of variation of 47.02%.

Table 2 - Statistical parameters of the copper content in desert zone plants

№	Soils	n	lim	$\overline{x} \pm S\overline{x}$	Σ	C_V, %
			mg/kg			
1	Paniculate wormwood (Artemisia scoparia)	5	5,1-10,95	8,86±0,33	1,32	29,78
2	Wormwood Lessing (Artemisia Lessingiana)	4	5,7-12,1	8,76±1,31	2,62	29,95
3	Wormwood Lerkhovskaya (Artemisia Lercheana)	4	6,55-9,2	7,83±0,77	1,33	16,95
4	Sandy wormwood (Artemisia Arenaria)	5	4,15-6,55	5,34±0,61	1,21	22,72
5	foxtail like sophora (Sophora alopecuroides)	5	4-7,18	5,08±0,71	1,43	28,14
6	Saltpeter wormwood (Artemisia nitrosa)	3	2,3-8,3	4,87±0,33	1,79	63,54
7	Caragana shrub (Caragana frutex)	3	4,7-4,7	4,7±0,00	0,00	0,00
8	Chingil (Halimodendron halodendron)	4	1,8-2,7	2,27±0,21	0,43	18,93

According to the value of the average copper content (mg/kg) in the total population of plants, the studied systematic groups are arranged in the following descending order: Artemisia scoparia. (8,86)> Artemisia Lessingiana. (8,76) > Artemisia Lercheana. (7,83) > Artemisia arenaria. (5,55) > Sophora alopecuroides. (5,08) > Artemisia nitrosa. (4,87) > Caragana frutex. (4,70) > Halimodendron halodendron (2,27) (Table 2).

Discussion. The found average copper content is lower than its Clark in the lithosphere (47 mg/kg) (Vinogradov, 1957), close to the estimate of its Clark in the soil (20 mg/kg) (Perelman, 1999), 2 times lower than the recommended maximum permissible levels (55.0 mg/kg), and 5 times lower than the approximate allowable concentration (120 mg/kg) (Motuzova, 2001).

Copper is quite intensively involved in the biological cycle and belongs to elements with a high accumulative capacity. Biogenic accumulation of copper in the humus horizon A is characteristic of all the studied soils of (Kazakhstan Assing, 1981).

The composition of the soil-forming rocks is one of the main factors determining the copper content in soils that are not subject to man-made impacts. In most of the soils of the desert zone studied by us, the biological accumulation of gross copper reserves in the upper horizons is observed. This shows a correlation with the results of previous studies. Figure -1.

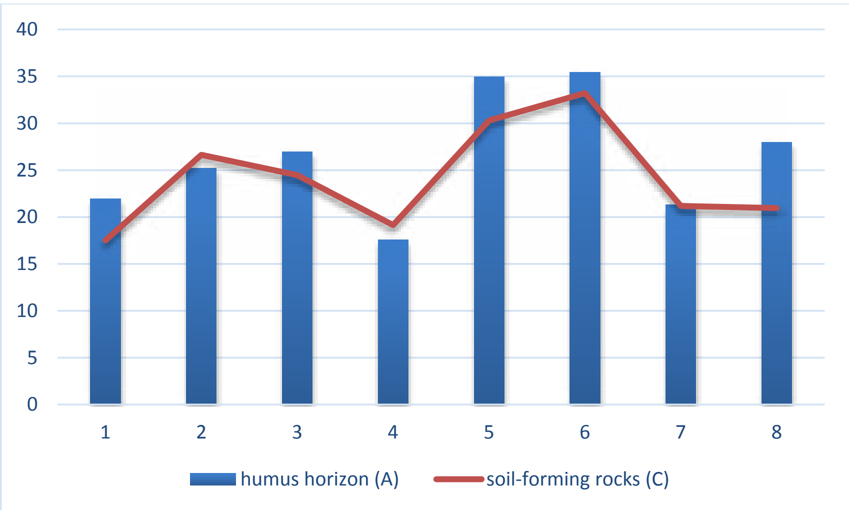

Figure - 1. The content of gross copper in the humus horizon (A) and soil-forming rocks
1 - Meadow-brown light loamy soils; 2 - Brown medium loamy soils; 3 - Brown light loamy soils; 4 - Light loamy gray soils; 5 - Meadow-brown sandy loam soils; 6 - Gray-brown strongly skeletal loamy soils; 7 - Ridge-bumpy semi-fixed sands; 8- Meadow salt marshes heavy loamy.

As can be seen from the data of Diagram – 1, humus-accumulative accumulation is characteristic of meadow-brown light loamy soils, brown light loamy, meadow-brown sandy loam, gray-brown strongly skeletal loamy soils, salt marshes of meadow heavy loamy. Brown medium-loamy soils, light-loamy gray soils, and ridge-bumpy sands inherit the level of content of elements of soil-forming rocks.

Most authors agree that the gross background content of chemical elements depends on the physical, chemical properties of the soil (physical clay, humus, the number of absorbed bases, etc.) and the near and far transport of substances (Ilyin, 2011).

As the results of the study showed, the average humus content in horizon A is 1.52%; ranging from 0.10- 3.41%. The CO^2 content in humus horizons ranges from 0.53-18.55%. The reaction of the soil solution in the upper horizons is highly alkaline, (the pH of the water is in the range of 8-9.8). The average content of the silty fraction over the entire soil profile is 12.82% and ranges from 0.16-30.86%.

In the course of our research, we revealed that the main factor in the accumulation and distribution of gross copper in the profiles of the studied soils is organic matter.

For most soils, a significantly high correlation was found between humus and gross copper: meadow-brown, light-loamy brown, gray-brown strongly skeletal, meadow salt marshes (r=0.97; r=0.94; r=0.76; r=0.99, respectively) (Table 3).

In soils with a low content of organic matter, an increase in bioaccumulation of the studied element in brown and gray-brown soils is caused by the aridity of the climate, non-washing water regime, and the alkaline reaction of the soil solution.

Table 3 - Correlations of the gross copper content in the soils of the studied territory with their main physical and chemical indicators

№	Soils	Humus	Carbonates	Muddy Fraction	Surroundings pH
1	Meadow brown slightly saline saline light loamy	0,97	-0,99	-0,75	0,36
2	Medium loamy brown	-0,79	-0,31	0,30	0,27
3	Light - loamy brown	0,94	0,83	-0,70	-0,69
4	Serozems	-0,91	-	-0,76	0,15
5	Meadow-brown sandy loam	0,97	-0,45	-0,46	-0,25
6	Grayish brown strongly skeletal loamy	0,76	0,58	-0,72	-0,33
7	The sands are ridge-bumpy semi-fixed	0,28	-0,36	0,86	-0,06
8	Meadow salt marshes are heavy loamy	0,99	-0,90	0,93	-0,81

As mentioned above, the average content of the exchange form of copper in soils (extractant - ammonium acetate buffer, pH=4.8) is 0.41 mg/kg. Thus, according to the recommended maximum permissible levels for the exchange form of copper (3 mg/kg) according to the revealed content of the element under study, the soils of the desert zone can be attributed to uncontaminated soils.

The average value of copper content in all plants studied by us does not exceed the Clarke value of copper in land vegetation (8.0 mg/kg). In 25% of the studied plant species, the copper content corresponds to the Clark values of copper, in other cases, the indicators are lower.

A critical low copper content in plants and feed is considered 3-5 mg/kg of dry matter. The results of our study have shown that in the shrubby plants of the desert zone, Caragana shrub (Caragana frutex), Chingil (Halimdendron halodendron), copper deficiency is observed.

The distribution of copper by morphological organs of plants of all studied species has a distinctly acropetal character – underground biomass accumulates copper 1.6 times more than aboveground.

Conclusion. 1. The average gross copper content in the soils of the studied territory does not exceed the generally accepted approximate permissible concentrations and recommended maximum permissible levels, below its Clark in the lithosphere, close to the estimate of its Clark in the soil.

2. The leading factor determining the concentration of gross copper in soils is organic matter. The content and distribution of gross copper in soils and the correlation dependence on the silty fraction, carbonates, pH of the medium in most cases have the opposite nature of dependence.

3. The exchange form of copper extracted by an acetate-ammonium buffer solution with a pH = 4.8 (mobile for plants) is less than 3 mg/kg for all studied soils.

4. The average copper content in the studied plants does not exceed its regional Clark.

The information obtained reflects the patterns of copper distribution in the desert soils of the East Kazakhstan region and can be used to develop a strategy for rational nature management, improve the organization of ecological and geochemical monitoring, since the studied area has an economically valuable value.

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