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Copper in the Main Components of Western Transbaikalia Landscapes

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Abstract—Copper content was analyzed in the parent rocks, soils, natural waters, and plants of the taiga and steppe terrains of Transbaikalia. The concentration of copper appeared to be low in the taiga terrains compared with the steppe ones. Extensive biogenic accumulation of copper was detected in the plants of steppe communities. It was shown that copper is selectively absorbed by different plant species from the same habitat and by a single species in different environment conditions.

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THEORETICAL ANALYSIS

On the one hand, copper is a biologically important trace element if present in small amounts, and on the other hand, it is a hazardous toxicant for living organisms at high concentrations. The significance of copper for the normal activity of plants, animals, and humans is high and diverse. It occurs in a number of enzymes: oxidase–cytochrome oxidase, ceruloplasmin, superoxide dismutase, urate oxidase, and others [1, 2]. Copper takes part in biochemical processes as a constituent of enzymes responsible for the reactions of oxidation of organic substances by molecular oxygen. Copper plays a role of the active center in enzymes as an acceptor or a donor of electrons at the changes in its oxidation state.

Copper is an essential trace element for living organisms. Its insufficient supply to plants results, in particular, in the Gramineae family, in drying of leaf tips, distortion of the formation of generative organs, absence of grains in spikes, which is the "tilling decease" widespread in various countries of Western Europe, Russia, USA, Australia, and New Zeland in soils with low concentration of copper available for plants [3].

High copper concentrations cause the poisoning of living organisms with a decrease in the activity and biosynthesis of some enzymes.

In 1980, the United Nations Environment Program (UNEP) classified copper as the most toxic element, along with seven other elements—mercury, cadmium, lead, chromium, nickel, and arsenic.

The migration properties of copper are controlled by its valence state. The compounds of monovalent copper are insoluble, whereas divalent copper forms both highly soluble sulfates and low soluble sulfides. Copper is most actively transported in landscapes with the sulfate class of water migration. The oxidation of Cu_2S and CuS under such conditions results in the formation of a highly soluble copper sulfide, $CuSO_4 \cdot 5H_2O$, which significantly increases the content of mobile copper in soils and waters of such terrains. However, at pH 5.5, copper hydroxide $Cu(OH)_2$ precipitates and is adsorbed during the neutralization of the environment by clays, manganese hydroxides, humus, and silica, which results in its active involvement into the biological cycle. Copper may form easily soluble carbonate complexes in soda–solonetz terrains [4].

Thus, the problem of copper in the biosphere has two important aspects: biological and ecological–toxicological, which requires permanent monitoring in various parts of the biochemical food chain.

The goal of this work was to study the character of the migration and accumulation of copper in the main components of landscapes: parent (soil-forming) rocks, natural waters, main soil types, and predominant plant species, and its biological activity in the environments of Transbaikalia.

METHODS

The investigations were conducted in the landscapes of the intermontane depressions of western Transbaikalia in the most populated areas of the Buryat Republic. Sampling sites, plots 100 × 100 m, were located in the typical areas of grassland, meadow, and fields of cultural plants in taiga, forest steppe, and steppe landscapes. One main soil column with a complete description of the soil profile and 3–5 additional columns were obtained at each site. Soil horizons and parent rocks were sampled simultaneously with particular plant species and total phytomass yields from an area of 1 m^2 during the bloom period of dominant plants. Water samples were collected five times during the low water period of August–September.

Soil samples were collected into polyethylene bags using a universally accepted procedure, which was repeated 5–9 times. In order to determine the bulk copper contents of rocks and organogenic horizons (from A to BC), 5 g of material were dried, powdered in an agate mortar, incinerated in a platinum crucible in an electric furnace at a temperature of 550°C to a constant mass of ash, and decomposed in a mixture of concentrated sulfuric and fluoric acids. The residue after incineration was dissolved in 5 ml of concentrated HCl and diluted with double-distilled water up to a volume of 50 ml. The results were recalculated to the initial sample weight [5].

In order to determine copper contents in plants and water, 10 g of air dried material were incinerated and 1 l of water was evaporated, after which the residues were annealed in the furnace and dissolved.

Copper was analyzed in triplicate by atomic absorption spectrometry. The precision of analyses was 4–7%.

The mathematical processing of the analytical results included the calculation of the arithmetic mean contents for air dried materials, standard deviation, correlation coefficients (r), variance (V), eluvium accumulation coefficient (K_{ea}), and biologic absorption (K_b) [6].

RESULTS

Copper Content in Parent Rocks

As was mentioned above, the region under investigation is made up of various rocks, the most common being ancient schists, granites, gneisses, granite porphyries, and basalts, as well as limestones, sandstones, and shales. The rocks alternate in space and are expose as cliffs and taluses [7].

The concentration of copper in the parent rocks of Transbaikalia is strongly variable. As can be seen from the experimental results given in Table 1, the lowest copper content is characteristic of glacial sandy loams and alluvium deposits. Low copper content was also detected in sandstones and schists of the Baikal–Patom upland [10].

Table 1. Concentration of copper in the parent rocks and soils (0–20 cm) of Transbaikalia (n = 20–80)

Column	Parent rock	Soil			Copper, ppm			
		type	humus, %	pH_{aq}	rock		soil	
					lim	$M \pm m$	lim	$M \pm m$
Taiga landscapes								
38k, 53kzh, 103pb-87, 43k, 20t, 24t-87	Ancient lacustrine loam	Gray wooded	1.7–2.3	6.2–6.9	18–28	26 ± 3	17–29	25 ± 3
52kzh, 59d, 100kb, 104pb-87	Alluvium deposits	Alluvium meadow	2.1–2.7	7.0–7.4	17–19	18 ± 3	21–28	24 ± 3
Forest steppe landscapes								
32b, 22t, 29t, 101kb, 28t-87	Glacial loam	Gray wooded	2.0–2.4	6.2–7.0	24–30	28 ± 2	18–28	25 ± 2
19k, 56z, 62kh, 30b-87	Alluvium deposits	Alluvium meadow	2.2–2.6	6.9–7.3	18–20	19 ± 3	17–28	26 ± 3
Steppe landscapes								
25t, 35m, 54kzh, 59d, 64kh, 58d-88	Ancient lacustrine loam	Chernozems	3.2–3.7	7.0–7.2	26–30	28 ± 3	36–72	53 ± 7
20t, 44k, 40k, 24t-87	Alluvium deposits	Alluvium meadow	2.2–2.6	6.9–7.1	18–21	20 ± 2	19–26	25 ± 3
Dry steppe landscapes								
21t, 31b, 33m, 37s, 61kh, 58d-88	Glacial sandy loam	Chestnut	1.4–1.9	7.1–7.8	18–21	20 ± 2	10–34	22 ± 2
34m, 36s, 34m, 12s-86	Alluvium deposits	Alluvium meadow	2.3–2.6	6.8–7.0	14–17	16 ± 2	14–18	23 ± 3
Floodplain landscapes								
12s-86-104pb-87	Alluvium deposits	Alluvium meadow (all data)	2.1–2.7	6.8–7.4	14–21	18 ± 2	14–28	24 ± 3
Global average content [8]						53		30
Maximum admissible content [9]								100

Table 2. Copper content in the natural waters of Transbaikalia

Water source, sampling site	n	Copper, μg/l	
		$M \pm m$	lim
Rivers	25	2.98 ± 0.2	
Selenga (Shigaevo village)	5	2.2 ± 0.1	2.0–2.4
Dzhida (Dzhida village)*	5	2.1 ± 0.2	2.0–2.3
Itantsa (Turuntaevo village)**	5	3.2 ± 0.1	3.1–3.3
Angyr (Zyryansk village)**	5	2.3 ± 0.1	2.2–2.3
Bichura (Bichura village)*	5	5.1 ± 0.2	5.2–5.3
Freshwater lakes	15	1.9 ± 0.2	
Ranzhurovo village**	5	2.1 ± 0.1	2.0–2.2
Baikal (Istomino village)**	5	3.2 ± 0.1	3.1–3.3
Gusinoe (Gusinoozersk)*	5	0.4 ± 0.02	0.2–0.6
Solenoe (Borgoi village)*	7	3.1 ± 0.2	3.0–3.3
Ground water (wells)	20	4.95 ± 0.2	
Tarbagatai village*	5	6.2 ± 0.2	6.1–6.4
Bichura village*	5	9.3 ± 0.1	9.2–9.4
Istomino village**	5	2.2 ± 0.2	2.1–2.5
Zyryansk village**	5	2.1 ± 0.1	2.0–2.3
Subsurface waters (boreholes)			
N. Torei village*	5	3.2 ± 0.1	3.2–3.3
Dzhida road	5	3.3 ± 0.2	3.1–3.4
Average for boreholes with high contents	10	3.25 ± 0.1	
Zyryansk village**	5	2.1 ± 0.2	2.0–2.3
Kabansk village**	5	2.2 ± 0.1	2.1–2.3
Turuntaevo village**	5	2.1 ± 0.1	2.0–2.2
Average for boreholes with low content	15	2.13 ± 0.2	
Maximum admissible content [12]		1000	

*Zone of steppe and dry steppe landscapes.
**Zone of taiga and forest steppe landscapes.

The variations in the copper content of parent rocks are related to their lithologic and geochemical characteristics, i.e., various copper abundances in the bedrocks and physicochemical processes promoting transitory migration. The diversity of parent rocks from Transbaikalia in the copper content is responsible for the spatial variations of its accumulation in soils [11].

The concentration of copper in the rock of coarse grain-size composition is 2–3 times lower than that of loamy varieties. The reason is that an increase in the fineness of grain-size composition and the total specific surface of particles enhances trace-element sorption on their surface owing to electrostatic forces, as well as incorporation into the interlayer space. The content of the clay fraction in the parent rocks of Transbaikalia varies by a factor of about three, from 5 to 15%. An important factor for the estimation of the level of copper concentration in the rocks and soils is also the relationships of the major components of their chemical composition, silicon oxide (SiO_2) and the sum of other oxides. The higher the SiO_2 content is, the lower the concentration of trace elements is. The concentration of SiO_2 in the parent rocks of Transbaikalia ranges from 61 to 73%, and the total of other oxides ranges from 27 to 39%. Therefore, variations in the content of clay particles and the ratio of SiO_2 to other elements exert a significant influence on the concentration of copper in rocks and control its mosaic spatial distribution [7, 11].

Copper in Natural Waters

The concentration of copper in the water of three freshwater lakes (Table 2) ranged from 0.4 to 3.2 μg/l. The water of closed saline lake Beloe near the settlement of Borgoi contains no more than 3.3 μg/l of copper and 3.1 μg/l on average, which is higher by a factor of 1.6 than in the water of small freshwater lakes. High copper concentrations were reported from the waters of strongly mineralized lakes (6.1×10^{-3} mg/l) in southeastern Transbaikalia by Filippova et al. [13] at an average pH value of 8.7. Copper hydroxide precipitates at such pH values, if the concentration of copper ions is higher than 1.54×10^{-2} mg/l. The concentration of copper in lake water never reached such high values. Moreover, metals occur in the waters not only as simple ions, but also as organomineral complexes, suspensions, and colloids [14]. Because of this, the pH value only partially controls their contents in natural waters.

The subsurface waters (Table 2) are enriched in copper with respect to the fresh surface waters. Ground waters from wells contain from 2.1 to 9.3 μg/l copper, varying by a factor of 4.4 with an average of 4.95 μg/l. The copper content of ground waters from boreholes in the taiga landscape is 2.1–2.2 μg/l, and that of waters from the dry steppe landscape is 2.4 times higher reaching maximum values of 5.1–9.3 μg/l.

An analysis of the copper distribution in various water sources of Transbaikalia revealed a higher concentration in the waters of dry steppe landscapes compared with taiga landscapes. The difference was especially high (2–4 times) in subsurface waters (in contrast to river water). The reason for different copper contents in the natural waters of dry steppe and taiga landscapes (by a factor of 2.8) is the distinctive copper contents in the drained rocks, which supply this element into natural waters. The concentration of copper in the parent rocks of the dry steppe landscape (sediments) is 1.8 times higher than in the rocks of the taiga landscape (granitoids) [7].

Thus, the average copper content in the natural waters of Transbaikalia show considerable variations, from 2.0 to 9.4 μg/l or by a factor of 4.7. The natural waters form the following sequence in average copper content (μg/l): lake (1.90) < subsurface (2.69) < river < ground waters (4.95).

The concentration of copper in the drinking water of Transbaikalia is much lower than the maximum admissible concentration defined by hygienic norms (1000 μg/l) [12].

Copper in Soils

The concentration of copper in chestnut soils ranges from 10 to 34 ppm or by a factor of 3.4 (Table 1). The variations at similar pH values are mainly related to the differences in granulometric composition, which ranges from sand to sandy loam, and the content of the <0.01-mm fraction is between 8.0 and 24%. The average copper content of these soils is 22 ppm. Given the average copper abundance in soils of 30 ppm reported by IMGRE in 2002 [8], the chestnut soils of the sites studied have bulk copper contents of 0.73–1.13 of the average value.

Soil solutions from the floury–carbonate Chernozems of steppe landscapes show a neutral pH value. Their copper content varies depending on the grain-size composition (13–32% of <0.01-mm fraction) from 36 to 72 ppm, averaging 53 ppm. The Chernozems of 50 key sites contain 1.2–2.4 times the average copper content [8].

Gray wooded soils are formed in forest steppe and taiga landscapes. Their pH value is 6.2–7.3, and coarse- and medium-grained loamy varieties are most common (18–38% of <0.01-mm fraction). Depending on the grain-size composition and the pH value of the medium, the concentration of copper ranges in these soils from 17 to 29 ppm, averaging 25 ppm. The gray wooded soils contain 0.57–0.97 of the average soil copper abundance. This is related to the weakly acidic pH value of some soils and their confinement to northern slopes, which have elevated moisture contents favorable for copper leaching and migration.

Meadow soils are formed on alluvium deposits along river valleys of the Baikal basin and show pH 6.4–8.4. Their grain-size composition ranges from sandy loam to medium-grained loam (12–35% of <0.01-mm fraction). The copper concentration ranges from 21 to 30 ppm, which is 0.7–1.0 of the average soil abundance.

Thus, the average copper content of various soil types of Transbaikalia ranges from 10 to 72 ppm, or by a factor of 7.2. This is higher than the variability of copper content in the parent rocks (by a factor of 2.1) (Table 1). The main reason for the low copper content in some soils of Transbaikalia is its low concentration (significantly lower than the average lithospheric value) in the parent rocks, which are the main source of copper in soils.

Copper in Plants

Our determinations of K_b for copper of various plant communities (bulk crops, recalculated to ash, which is a common practice in the biogeochemistry of plants [15]) from various environmental conditions (landscapes, soil types, and moisture conditions) showed that this parameter was much higher than 1.0 and varied within 1.9–6.4 with an average variance coefficient of 23–28%. This indicates that copper is an element with a medium degree of accumulation in plants. It should also be noted that there is a significant difference between the average K_b values of the steppe (5.0 ± 0.4) and meadow (4.0 ± 0.3) communities. The reliability factor of the difference in K_b between these plant communities is 2.1 at a 95% confidence level, which corresponds to its theoretical value. According to our data, the K_b of molybdenum, an element of strong accumulation, is 21, and that of weakly accumulated elements (nickel, iodine, and lead) is lower than 1.0.

Figure 1 shows copper accumulation in plants of various communities depending on its content in soil. Copper is more extensively accumulated by mixed grass–Gramineae and mixed grass communities in

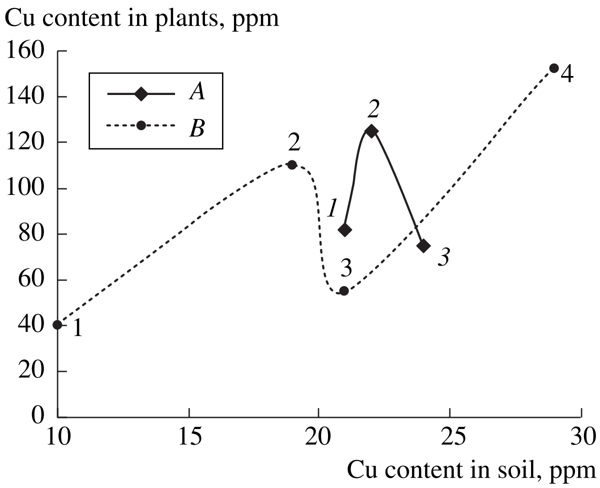

Fig. 1. Copper accumulation by plants of various phytocenoses as a function of copper content in the soil: *A*, meadow phytocenoses with (*1*) mixed grass, (*2*) mixed grass–Grameneae, and (*3*) Gramineae communities; *B*, steppe phytocenoses with (1) Gramineae–feather grass, (2) cold wormwood, (3) hard sedge, and (4) mixed grass communities.

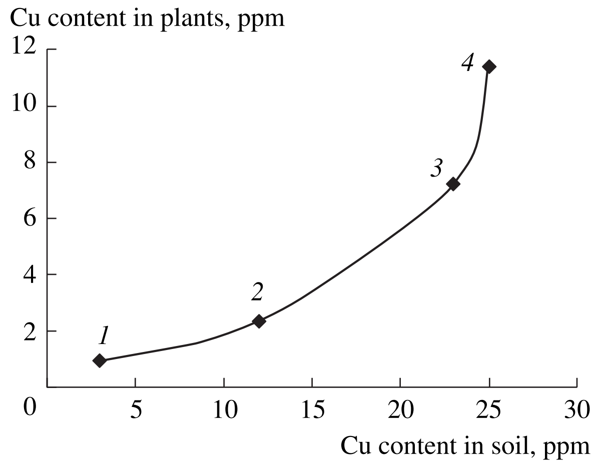

Fig. 2. Copper content in the bulk crop of meadow plants from the floodplain–sod soils of the Selenga valley with various copper contents: (*1*) with predominance of sedge on the peat-bog soil; (*2*) and (*3*) with predominance of grass and legumes; and (*4*) with predominance of mixed grass.

meadow areas and mixed grass and cold wormwood communities in steppe area.

A single plant species may show very different copper contents in different environments. Among the 47 plant species investigated by us, the ratio of the maximum and minimum copper contents in a single species ranged from 1.4 for *Dactylorhiza salina* (19.2–27.0 ppm) and *Artemisia dracunculus* (5.4–7.6 ppm) to 8.5 for *Galium verum* (2.6–22.0 ppm) and 8.4 for *Vicia venosa* (2.0–16.8). These data illustrate considerable variability in copper accumulation by plants grown under different conditions. High variability in copper content is characteristic of plants with a considerable ecological amplitude of growth. They occur in the taiga, forest steppe, and steppe terrains of Transbaikalia, which show different copper contents in the soils. Such plants can be used as biological indicators for a deficiency or excess of an element in soils in the system of ecological and biogeochemical monitoring of the environment.

Distinct differences in copper accumulation in particular plant species and in bulk crops of phytomass depending on environmental conditions and, primarily, the content and bioavailability of copper in soils were detected by us during soil sampling in various landscapes of the Selenga River valley, the main tributary of Lake Baikal (Fig. 2). For instance, the copper content in the bulk crops was 0.93 ppm on the peat-bog soil, 2.37 ppm on the floodplain–sod soil of the taiga zone, 11.4 ppm in the forest steppe zone, and 7.22 ppm in the dry steppe zone. The normalization of these contents to the lowest value of 0.93 ppm gives 1.0, 2.5, 12.2, and 7.7, respectively, i.e., the maximum and minimum values differ by a factor of 12.2.

The concentration of copper in the biomass crops of steppe and meadow vegetation of Transbaikalia shows a very contrasting distribution, and varies from 0.9 to 11.4 ppm (Table 3). The analysis of data and comparison with norms for the copper supply of animals (6.7–11.4 ppm) suggest that the steppe and meadow vegetation of the key sites in the Kyakhta, Mukhorshibir, Bichura, and Tarbagatai districts of Buryatia are sufficiently supplied with copper. The bulk copper content in the soils of these districts ranges from 21 to 34 ppm. The vegetation of the Dzhida, Ivolginskii, Selenga, Zaigraevskii, Khorinskii, and Kizhinginskii districts is insufficiently supplied with copper (2.0–5.0 ppm, which corresponds to a deficit of 30–50% relative to the norm, except for a few key sites). Two groups of districts can be distinguished in terms of bulk copper content in soils. The concentration of copper in the soils of three southern districts (Dzhida, Selenga, and Ivolginskii) (19–34 ppm) is much higher than in northern ones. However, the availability of copper to the plants in the carbonate soils of the dry steppe zone (pH 7.6–8.2) is very low, which results in low copper concentrations in plants. According to the available data, the total solubility of cation and anion copper species decreases at pH values of about 7–8 [17] and increases at pH values below 7. The bulk copper content in the soils of three northern districts is low, 10–18 ppm, but the bioavailability for plants is higher, because the pH values of these soils are below 7.

Extremely low copper content was detected in the meadow vegetation of the Pribaikal'skii and Kabanskii districts, which are situated in the taiga zone adjacent to Lake Baikal (0.9–3.7 ppm). Compared with the lower boundary of the norm (6.0 ppm), the supply of copper

Table 3. Concentration and accumulation of copper in the aboveground biomass of steppe and meadow vegetation from southwestern Transbaikalia

Vegetation, sampling site	Copper, ppm	Biological productivity, 100 kg/ha	Copper accumulation, g/ha
Normal supply of plants with copper (Kyakhta, Mukhorshibir, Bichura, and Tarbagatai districts)			
Cold wormwood steppe, Ust'-Kyakhta village	9.3	5.0	4.65
Mixed grass meadow, Ust'-Kyakhta village	7.2	50.4	36.3
Mixed grass meadow, B. Lug village	7.4	56.0	41.4
Mixed grass–Graminaea meadow, Oktyabr'skoe village	9.6	n.d.	n.d.
Mixed grass meadow, Tugnui village	8.9	54.0	48.1
Grass meadow, M. Kunalei village	6.7	n.d.	n.d.
Mixed grass meadow, Tarbagatai village	11.4	41.2	47.0
Mixed grass meadow, Nadeeno village	6.5	48.8	31.7
Poor supply of plants with copper (Dzhida, Ivolginskii, Selenga, Zaigraevskii, and Khorinskii districts)			
Hard-sedge steppe, Belozersk village	4.0	n.d.	n.d.
Mixed grass–fescue steppe, Borgoi village	4.7	4.2	1.97
Sedge steppe, Borgoi village	6.4	5.4	3.46
Grass–cold wormwood steppe, Ivolginsk village	5.8	9.8	5.68
Grass–wormwood steppe, Atsagat village	4.0	n.d.	n.d.
Grass steppe, Tokhoi village	2.0	–	–
Grass–legume steppe, Tokhoi village	5.4	–	–
Grass–sedge meadow, Yagodnoe village	4.4	31.2	13.7
Grass–sedge meadow, Zhargalantui village	3.7	54.6	20.3
Very low supply of plants with copper (Pribaikal'skii and Kabanskii districts)			
Sedge meadow, Istok village	0.9	n.d.	n.d.
Grass meadow, Korymsk village	1.1	–	–
Grass–sedge meadow, Korymsk village	1.7	–	–
Sedge meadow, Korymsk village	1.5	–	–
Grass meadow, Turuntaevo village	2.0	30.6	6.12
Grass–sedge meadow, Turuntaevo village	3.7	n.d.	n.d.
Sedge meadow, Turuntaevo village	1.7	–	–

Note: Norm of supply [16] 6–10. Deficit [17] <5. Excess [17] >20.

to plants is usually only 15–30% in these districts. This is related to the very low copper content in the soils: 1.5–3.0 ppm in the peat-bog soil and 10–12 ppm in the floodplain–meadow soil, in contrast to 20–34 ppm in the soils of the steppe zone.

The relatively low copper content in the forage plants of the Dzhida, Zaigraevskii, and Kizhinginskii districts is the reason for enzootic ataxia, a decease of agricultural animals observed in these regions [18]. The disease affects sheep, cattle, and pigs.

The accumulation of copper in plants per unit area depends primarily on biologic productivity. The amount of copper in steppe vegetation is 2.0–5.7 g/ha, in contrast to 12.7–48.1 g/ha in meadow vegetation, the productivity of which is 6–11 times higher.

CONCLUSIONS

Our study demonstrated the following.

—Low copper contents were detected in parent rocks (0.3–0.53 of the global average abundance) and soils (0.80–0.87 of the global average abundance), except for the Chernozems containing 1.2–1.8 of the global average abundance.

—Contrasting copper distribution was observed in the natural waters: from 2.0 μg/l in river, lake, and subsurface waters to 9.4 μg/l in the ground water from wells. The concentration of copper in the natural waters decreases in the sequence lake water < subsurface water < river water < ground water.

—The biogenic accumulation of copper in the humic horizons of soils is characterized by a strong direct correlation in the Chernozems (r = 0.84) and moderate direct correlations in the floodplain (r = 0.58), chestnut (r = 0.39), and gray wooded soils (r = 0.37) at tr and t_{fact} of 13.7, 6.1, and 3.4, respectively, and t_{theor} of 2.0.

—Under similar conditions, various plant species show selective copper accumulation related to their biological characteristics. The ratio of the maximum and minimum concentrations is up to 4.4. A particular plant species accumulates different amounts of copper when growing in different soils.

—The meadow plant communities accumulate 13–48 g/ha of copper, in contrast to the low productivity steppe plant communities accumulating 2.0–5.7 g/ha of copper.

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