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Cobalt Ecosystems in the Inland Delta of the Selenga River

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Abstract

The contents and distribution of cobalt in soils and plants of the Selenga River delta (the Western Transbaikalia) have been studied. It is shown that the cobalt content in the studied soils does not exceed the clarke value and is somewhat higher than the regional background value. Its distribution in the soil cover of the region is rather uniform. The concentration of cobalt in the aboveground phytomass is usually lower than its normal concentration in the vegetation of the world.

Keywords: Cobalt, soils, plants, delta, Transbaikalia.

Introduction

Cobalt is a biologically active element that is always present in plants and animals [1]. Being a component of the B_{12} water-soluble vitamin (cyanocobalamin), it affects the consumption of nitrogen by plants and increases the contents of chlorophyll and ascorbic acid in them. This vitamin also affects the carbohydrate and fat exchange processes and participates in hematogenesis. Cobalt is a component of a number of enzymes enhancing the biosynthesis of methionine, nucleic acids, and nitrogen of protein. Microdoses of Co are necessary for the normal vital activity of plants and animals. Insufficient Co concentrations in animals' diets result in negative effects (a cobalt deficit, allotriophagy, anemia, hypo- and avitaminosis of B_{12}, and enhancement of goiter endemia). A high content of Co compounds exerts toxic effects (damping of the synthesis of the B_{12} vitamin and other processes) [1, 14].

The study of the contents of heavy metals (HMs) in soils and plants under particular soil-geochemical conditions is of great importance, particularly for the areas of specific nature use, such as the Selenga River delta.

The cobalt content in the ecosystem components of the Selenga River delta remains insufficiently studied. There are some data on its content in the water and bottom deposits of Lake Baikal [5, 21].

The aim of this investigation is to determine the Co content in the soils and plants of the Selenga River delta and to assess its ecological effect.

1. Objects and Methods

A field survey was performed in the Selenga River delta in 2001-2002. The study area is found on the southeastern part of the Lake Baikal coast (the Buryat Republic). The Selenga delta advances into the lake and includes numerous branches. Its total area is 1120 km^2. The modern floodplain represents a swampy plain surface elevated about 0.25-1.0 m above Lake Baikal. It is dissected by numerous channels and oxbow lakes.

Three terrace levels are clearly distinguished in the delta. The relative elevation of the first terrace (the Kabansk terrace) is about 2 m above the lake level. This is a plain with small depressions and hollows left by the ancient channels of the Selenga River. The plain is slightly inclined to the northeast.

The second terrace (the Kudarinsk terrace) is elevated about 20 m above the lake level; it is most pronounced on the right bank of the Selenga River, and its fragments are seen on the left bank. Its slightly undulating surface is covered by steppe vegetation with separate groves of mixed forest. Some areas are used for crop growing. The upper layers of the terrace are composed of loess-like loams, gravelly deposits, and quartz sands and sandy loams.

The third terrace (the Fofonovo terrace) is elevated about 80 m above the lake level. It is better pronounced on the right bank of the Selenga River near the settlement of Fofonovo. The terrace is composed of uniform fine-grained sand with thin interlayers of sandy loam. The slightly undulating surface with gentle slopes is covered by mixed forest and shrubs.

Some part of the delta is covered by meadow vegetation; it represents the most valuable agricultural land used for crop cultivation, haymaking, and pasturing [4, 23].

The diverse ecological conditions are responsible for the development of the different soil types and plant communities in the delta.

We studied swampy, meadow-swampy, meadow, and soddy alluvial soils and gray forest soils. The alluvial soils have a neutral or slightly alkaline reaction and a low content (0.4-4.5%) of organic matter (except for the swampy alluvial soils with up to 8.9% organic matter). Calcium predominates among the exchangeable cations. The soils are moderately and poorly provided with available phosphorus and potassium (1.9-3.9 and 2.6-10.0 mg/100 g of soil, respectively). The soil texture varies from sand to medium loam.

Samples from the genetic soil horizons were taken; the chemical analyses were performed by routine methods [2].

Samples of the aboveground phytomass of particular plant species and of the entire vegetation (herbs) growing on the area of 0.25 m^2 were taken in twofold replicates (39 samples).

The total Co content in the soil samples was determined in an HC1 solution after decomposition of the calcined soil by HF in the presence of H_2SO_4 by the AAS method (using an AAS SOLAAR M device). We also determined the contents of Co in an acetate ammonium buffer (pH 4.8) (exchangeable Co) and in a IN HC1 extract (acid-soluble Co); the soil-to-extractant ratio was 1 : 10 in both cases. The cobalt content in the plants was determined using the AAS method after dry ashing in a muffle furnace at 500°C and further dissolution of the ash in HC1.

The names of the soils are given according to *Klassifikatsiya i diagnostika pochv SSSR* (Classification and Diagnostics of Soils in the USSR) (1977). The soil grouping with respect to the total Co content was performed according to [10], and the soil grouping with respect to the content of exchangeable Co was performed according to [11]. The species composition of the plants was determined according to [12]. The statistical treatment of the data (the calculation of the arithmetic mean and the error of the mean) was performed with the help of Microsoft Excel.

2. Results and Discussion: Cobalt in the Soil-Forming Rocks and Soils

The soils in the Selenga River delta are mainly developed from the alluvial and loose sedimentary Quaternary deposits with a predominance of quartz, feldspars, hornblende, minerals of the epidote group, and yellowish green mica [8]. The content of trace elements in these rocks is low. The total Co content in the parent materials of the studied soils averages 8.3 mg/kg (Table 1), which is lower than the clarke value (23 mg/kg) [19]. It should be mentioned that the mineralogy and texture of the parent materials affect the total Co content in them. The highest Co content is in the alluvial sandy loam (10.1 mg/kg), and the lowest one is in the sandy deposits under pine forests (2.0 mg/kg).

Table 1: The cobalt contents in the parent materials of the Selenga River delta in mg/kg (for the exchangeable and acid- extractable forms, their percentages of the total Co are given under the line)

Soil-forming rock (soils)	Total	Cobalt compounds	
		exchange able	acid-extract able
Alluvial sandy loam (swampy and meadow, n = 4)	10.1	0.2 2.0	1.7 17
Loose sand loam (soddy, n - 1)	6.5	0.2 3.1	1.2 19
Loose sand (gray forest, n = 1)	10.3	Absent	0.2 1.9
Sand (sand under pine forest, n = 2)	2.0	0.06 3.1	0.8 40
Mean for the delta	8.3	Not dent	

The data on the total contents of chemical elements in the soil-forming rocks and soils are insufficient for the detailed characterization of the pedogeochemical and biogeochemical conditions in the studied areas. Data on the particular forms of chemical elements in the parent materials and soils are necessary because they characterize the availability of elements for plants and their water migration capacities [18].

The water-soluble compounds of elements are most available for plants and animals [18]. The water-soluble compounds include three major groups of HM compounds: (1) readily soluble compounds, (2) difficultly soluble compounds, and (3) HM compounds with organic and inorganic ligands soluble in water [9].

The portion of water-soluble Co in the studied soil- forming rocks does not exceed 1.7% (up to 0.2 mg/kg) of its total content. In the sandy deposits under gray forest soils, water-soluble Co has not been detected.

The exchangeable compounds extracted by the acetate-ammonium buffer (pH 4.8) correspond to a wide range of the particular forms of HMs in the soils. These are ions entering inner and outer spheres of surface complexes, surface precipitates fixed on the defective parts of crystalline lattices, and others [9].

The content of exchangeable Co in the soil-forming rocks of the delta varies from trace amounts to 0.5 mg/kg and does not exceed 8% of the total Co content.

The potential reserves of available elements are judged from the amounts of elements extracted by 1 N HC1 or HN03 [18]; these agents extract heavy metals bonded to different soil components (clay minerals; humic compounds; iron, manganese, and aluminum compounds; and primary minerals) and having different migration capacities [9].

The portion of acid-extractable Co in the soil-forming rocks comprises 12-20% (1.4-2.0 mg/kg) of the total Co content, except for the loose sand deposits, in which the amount of acid-extractable Co does not exceed 0.2 mg/kg or 1.9% of its total content.

The low Co content in the parent materials is responsible for its low content in the soils of the Selenga River delta. The total Co content in the investigated soils (Tables 2, 3) does not exceed the clarke value for the world soils (10 mg/kg according to [3]), except for the peat gley alluvial soil (pit 1) and gray forest soil (pit 3), in which it is somewhat higher. The total Co content in the upper 20 cm of the studied soils varies from 2.0 to 21.0 mg/kg with the highest value being in the peat gley alluvial soil (pit 1) and the lowest value in the sandy soil of the pine forest (pit 18). The soils of accumulative landscapes (swampy and some meadow alluvial soils) are relatively rich in this element (Tables 2 and 3). This is explained by the physicochemical features of these soils (the high moisture content, heavy texture, and relatively high content of organic matter) favoring the fixation of Co and by the additional input of this element from the surrounding areas.

The total Co content in the soils of the Selenga River delta is higher than that in the regional background soils (5.5 mg/kg, as calculated by us from earlier published data [16]) (Table 3).

According to a scale suggested for soils of Siberia and the Far East [10], the soils of the Selenga River delta contain a moderate amount of total Co.

The distribution pattern of the Co in the delta soils is rather uniform; its variability in the upper 20 cm of the soil profiles (except for the profiles with the highest variability (the peat gley alluvial soil in pit 1) and the lowest (the gray forest soil under the pine forest in pit 3) Co contents) does not exceed two times. A relatively high Co content is typical of the soils in the western and southwestern parts of the delta, where loamy swampy and meadow-swampy alluvial soils predominate.

The content of water-soluble Co in the soils of the Selenga River delta does not exceed 2.6% of its total content (Table 2). The minimum values (0.03-0.05 mg/kg, or 0.2-0.6% of the total Co content) are typical of the swampy alluvial soils, and the maximum values (0.13-0.19 mg/kg, or 1.3-2.6% of the total Co content) are seen in the meadow alluvial soils. The low content of water-soluble Co in the swampy soils is probably explained by its presence in the exchangeable form and in the form of organomineral and iron-manganic complexes. The content of water-soluble Co in the gray forest soils varies from 0.08 mg/kg (plowland) to 0.18 mg/kg (forest), or within 1.0-1.5% of the total Co content.

The portion of exchangeable Co (Table 2) does not exceed 4.6% of its total content, except for the peat gley alluvial soil (pit 9), where it reaches 30% (1.7 mg/kg) of the total Co content. The relatively high content of exchangeable Co in the peat gley alluvial soils is explained by the excessive moistening of these soils and the transformation of crystalline iron and manganese oxides into amorphous compounds binding Co. A decrease in the degree of crystalline of hydroxides and a rise in the degree of their dispersion result in a considerable increase in the number of exchange sites, from which the adsorbed Co cations may be replaced by cations in the solution interacting with the soil [13].

Table 2: Contents of different cobalt compounds in the surface (0-20 cm) soil layer of the Selenga River delta (mg/kg is above the line and the % of the total content is under the line)

Pit no., soil (sampling site)	Total	Compounds		
		water-soluble	exchangeable	acid-extractable
1, alluvial peat gley (Istok settlement)	21.0	0.05 / 0.2	0.6 / 2.6	5.6 / 21
9, alluvial peat gley (Dubinino settlement)	5.7	0.03 / 0.6	1.7 / 30	1.9 / 37
19, alluvial meadow-swampy (Stepnoi Dvorets settlement)	6.8	Not det.	0.3 / 4.6	3.2 / 46
20, alluvial peaty gley (Shamanka Island)	10.5	»	0.25 / 1.6	2.5 / 25
21, alluvial peat gley (Semenovskii Island)	9.3	»	0.15 / 1.6	3.0 / 33
12, alluvial meadow stratified (Kudara settlement)	9.1	»	Not det.	2.3 / 25
4, alluvial meadow saturated (Murzino settlement)	12.6	0.13 / 1.0	0.3 / 2.0	3.7 / 25
10, alluvial meadow calcareous (Krasnyi yar settlement)	8.4	Not det.	0.1 / 1.2	3.8 / 46
16, alluvial meadow calcareous (Bazhenovsk)	7.8	0.13 / 1.7	0.15 / 1.9	3.0 / 38
16k*, alluvial meadow calcareous (Bazhenovsk)	7.4	0.19 / 2.6	0.3 / 4.0	2.1 / 28
15, alluvial meadow calcareous (Shustovskii Island)	5.6	Not det.	0.1 / 1.8	1.8 / 32
11, alluvial soddy steppe (Fofonovo settlement)	10.0	»	0.2 / 1.9	4.1 / 42
2, gray forest (plowland, Istoko-Tvorogovsk Upland)	5.2	0.08 / 1.5	Not det.	0.6 / 12.1
3, gray forest (forest, Istoko-Tvorogovsk Upland)	16.8	0.18 / 1.0	0.3 / 1.5	0.7 / 4.2
Sand soil under pine forest (Stepnoi Dvorets settlement)	2.0	Not det.	0.07 / 3.5	0.8 / 40
MPC (total according to [3], exchangeable according to [15])	50	»	5.0	Not det.

According to a scale suggested in [11], the soils of the Selenga River delta are poorly provided with exchangeable Co. The only exception is represented by the swampy alluvial soils with a high content of exchangeable Co.

The content of acid-extractable Co in the upper 20 cm of the alluvial soils varies from 1.8 to 5.6 mg/kg, which comprises 21-46% of the total Co content (Table 2). The average content of acid-extractable Co in the upper meter of the alluvial soils is 2.7 mg/kg, or 30% of the total Co content (Table 3). A low content of acid- extractable Co is typical of the gray forest soils (14% of the total Co content).

Table 3: Statistical characteristics of the Co contents in the 1-m-thick soil layer in the Selenga River delta, mg/kg (P = 0.95)

Soil type	Total content				Acid-soluble compounds				
	mean	variation limits	confidence interval	variation coefficient	mean	variation limits	confidence interval	variation coefficient	% of the total
Swampy alluvial (n = 21)	9.8±1.3	4.3–27.2	7.2–12.6	59	2.7±0.3	0.3–6.5	1.8–3.3	63	28
Meadow alluvial (n = 26)	8.7±0.5	5.2–14.8	7.7–9.8	29	2.5±0.2	0.9–5.6	2.1–3.0	41	29
Soddy alluvial (n = 8)	9.4±0.9	6.3–12.6	7.5–11.2	24	3.0±0.4	1.3–4.6	2.2–3.8	33	32
Gray forest ("= 13)	9.7±1.7	3.2–18.6	5.8–13.4	65	0.9±0.2	0.3–1.6	0.7–1.2	49	14
Sand soil of pine forest (n = 4)	2.2±0.2	1.8–2.8	1.6–2.7	16	0.7±0.1	0.5–1.0	0.5–1.0	24	31
Average for the delta (n = 68)	9.4±1.1	3.2–27.2	8.4–10.6	47	2.7±0.2 (n = 51)	1.1–6.5	2.4–3.0	43	30

This is obviously related to the fact that the Co in the gray forest soils is mainly firmly bound to mineral complexes (primary and secondary minerals and mineral neoformations in the soils). In the alluvial soils, Co is bound to organic, organomineral, carbonate, and iron-manganic complexes that are easily destroyed under the impact of 1 N HC1.

The cobalt distribution patterns in the soil profiles depend on the soil type (figure). In the swampy alluvial soils, the total Co content reaches its maximum in the peat horizons and decreases down the soil profile. In the meadow alluvial soils, the distribution of Co has bimodal patterns with maximums in the upper mucky-humus and in the gleyed carbonate horizons. In the meadow and soddy alluvial soils, the highest Co content at a depth of 30-60 cm may be related to the somewhat heavier soil texture at this depth.

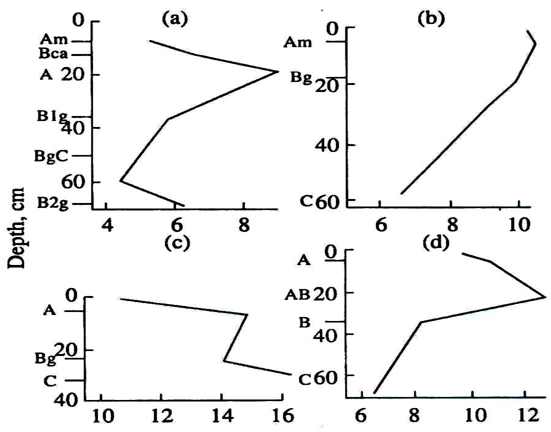

Figure: Distribution patterns of Co in the soils of the Selenga River delta (a) pit 9, peal gley alluvial soil; (b) pit 20, shallow peat gleyed alluvial soil; (c) pit 4, meadow saturated alluvial soil; and (d) pit II, soddy steppe alluvial soil

At present, the Co concentrations in the soils of the Selenga River delta correspond to the background level, which attests to the normal ecological status of the soil cover. Changes in the nature management may affect the content and distribution of Co in the soils of the delta in the future.

2.1 Cobalt in Plants

The concentration of Co, as well as other microelements, in plants depends on the contents of Co and its particular compounds in the soils, the phenological phase of the plant development, and other factors [17, 22].

The activity of the element migration in the soil- plant system can be judged from the coefficient of biological accumulation (CBA) representing the ratio between the element content in the plant ash and in the soil on which the plant grows. For most of the studied plants, the CBA for Co in the aboveground phytomass varies from 0.01 to 1.25 (Table 4). The highest value of this coefficient is typical of the plants growing on meadow alluvial calcareous soil (pit 15). The lowest CBA for Co has been determined in sedges growing on the swampy alluvial soils. According to the range of biological accumulation of elements suggested by Perel'man (cited from [15]), Co is assigned to the group of elements with moderate biological accumulation. According to our data (Tables 4 and 5), the biological accumulation of Co in the plants of the Selenga River delta is relatively low, so Co can be qualified as an element with weak biological accumulation.

Table 4: Cobalt concentrations in the aboveground phytomass of the Selenga River delta (mg/kg of dry matter) and the coefficient of its biological accumulation (CBA)

Plant, pit, soil	Cobalt	CBA
Meadow clover (*Trifolium pratense* L.)		
pit 1, alluvial peat gley	0.15	0.10
pit 4, alluvial meadow saturated	0.19	0.21
pit 9, alluvial peat gley	0.03	0.01
pit 10, alluvial meadow calcareous	0.16	0.09
pit 11, alluvial soddy steppe	0.14	0.22
Timothy grass (*Phleum pretense* L)		
pit 10, alluvial meadow calcareous	-	-
pit 11, alluvial soddy steppe	-	-
pit 16, alluvial meadow calcareous	0.11	0.16

Sedge (Carex curaica *Kunth)*		
pit 1, alluvial peat gley	0.02	0.02
pit 19, alluvial meadow-swampy	0.42	0.74
pit 21, alluvial peat gley	0.34	0.04
*Common horsetail (*Equisetum arvense)		
pit 9, alluvial peat gley	-	-
pit 10, alluvial meadow calcareous	0.07	0.04
pit 11, alluvial soddy steppe	-	-
pit 16, alluvial meadow calcareous	0.34	0.20
pit 15, alluvial meadow calcareous	0.51	0.48
Bent grass (*Agrostis mongolica* Roshev)		
pit 15, alluvial meadow calcareous	0.34	0.68
Wormwood (*Artemisia mongoliaca* Fisch.ex Nakai)		
pit 15, alluvial meadow calcareous	0.53	1.25
Wormwood (*Artemisia scoparia* Waldst.et Kit)		
pit 15, alluvial meadow calcareous	0.29	0.57
*Sanguinary (*Achillea millefolium *L.)*		
pit 15, alluvial meadow calcareous	0.08	0.18
Caraway (Carum carvi *L.)*		
pit 15, alluvial meadow calcareous	0.36	1.12
Meadow geranium (*Geranium pretense* Peschkova)		
pit 15, alluvial meadow calcareous	0.26	0.45
*Meadow pea (*Lathyrus pratensis *L.)*		
pit 15, alluvial meadow calcareous	0.46	1.03
The mean Co content in terrestrial vegetation [6]	0.5	
Norm [7]	0.5-3.0	

Note: The dashes stand for "not detected".

The cobalt concentrations in the aboveground phytomass of the studied plants vary from trace amounts to 0.53 mg/kg of dry matter (Table 4). The highest Co concentration is typical of the plants growing on the meadow calcareous alluvial soil (pit 15). The minimum Co concentration is typical of timothy and horsetail growing on the meadow calcareous alluvial soil (pit 10) and on the soddy alluvial soil (pit 11).

Table 5: Cobalt distribution in the aboveground phytomass in the Selenga River delta

Plant association, pit, soil	Co, mg/kg		CBA	Biological productivity, t/ha	Accumulation, g/ha
	of dry matter	of plant ash			
Horsetail, pit 20, alluvial peat gley	0.05	0.34	0.03	92.4	0.46
Herbs, pit 10, alluvial meadow calcareous	0.17	1.60	0.19	24.0	0.41
pit 12, alluvial meadow stratified	0.06	0.72	0.08	55.2	0.33
Forb-sedge, pit 9, alluvial peat gley	0.15	1.27	0.22	27.6	0.41
pit 21, alluvial peat gley	0.01	0.04	0.004	67.1	0.07
Sedge-grass, pit 4, alluvial meadow saturated	0.07	0.83	0.07	27.2	0.19
Grass-sedge, pit 1, alluvial peat gley	0.08	1.14	0.05	50.0	0.40
Horsetail-sedge-forb, pit 19, alluvial meadow swampy	0.16	1.13	0.17	25.2	0.40
Horsetail-grass-forb, pit 15, alluvial meadow calcareous	0.25	2.33	0.42	50.8	1.28
sedge-forb, pit 16, alluvial meadow calcareous	0.04	0.35	0.05	30.6	0.12

Different plant species are characterized by selective Co accumulation even under similar ecological conditions (pit 15) (Table 4). For example, legumes and *Compositae* plants accumulate Co more intensively than grasses and horsetails. The differences in the Co contents in the species of sedges, legumes, grasses, horsetails, and forbs are considerable (7.3 times).

There is an opinion [20] that the specific features of the accumulation of heavy metals and microelements in different plant species under conditions of their similar contents in the soils are related to the selective Co adsorption by plant root systems and metabolic processes in plant tissues. At the same time, the same plant species may accumulate different amounts of Co in different habitats, which is probably explained by the differences in the bulk contents and the biological availability of the element in the soils.

The uptake of heavy metals by plants depends on the chemical and physical soil properties, the acid-base and oxidation-reduction conditions, and the microbiological activity [15].

The Co content in the undifferentiated samples of the aboveground plant phytomass cut from the test plots varies from 0.01 to 0.25 mg/kg of dry matter (Table 5).

The accumulation of Co in the aboveground phyto- mass is estimated at 0.07 to 1.28 g/ha (Table 5). It depends on the productivity and the species composition of the phytocenoses. The highest accumulation of Co is typical of the forb-grassy cenoses on the meadow calcareous alluvial soil (pit 15). The lowest accumulation of Co is seen in the sedge-forb cenoses on the peat gley alluvial soil (pit 21).

The low Co concentration in the plants of the investigated region is related to the low content of exchangeable Co in the soils, though the soil supply with total Co is sufficient. The low concentration of Co in the above- ground phytomass makes it possible to assign the Selenga River delta to the areas with a Co deficiency.

Conclusions

(1) The Co content in the soils of the Selenga River delta is close to the clarke value calculated for the soils of the world and is higher than the regional background content of this element. According to the scale suggested for the soils of Siberia and the Far East, the investigated soils are characterized by a medium content of total Co.
(2) The Co content in the plants of the delta is lower than the clarke value for the plants of the world. Its accumulation in the aboveground phytomass depends on the species composition of the plants and on the soil conditions.
(3) The Selenga River delta may be assigned to the areas with a Co deficiency.

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