Natural and Anthropogenic Factors of Soils Chemical Composition on Shikotan Island (Kuril Islands)

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Abstract—The chemical composition of the soils (Haplic Andosols) of Shikotan Island (Lesser Kuril Chain) formed on volcanic rocks of different compositions and ages has been studied. The background content of metals (Ba, Mn, Zn, Cu, Ni, Co, Pb, Cd, Cr, Fe, V, Sc, K, Sr, Na, Ca, Mo) in soils was estimated using inductively coupled plasma mass spectrometry with complete acid digestion of samples. Bulk contents of chemical elements undergo abrupt changes and depend on bedrock composition, zonal and azonal geochemical landscape differentiation, influence of oceanic air masses, and the composition of plant communities. High natural concentrations (exceeding element abundances in the Earth's crust (clarkes)) of femaphile elements (Sc, V, Fe, Cu, Zn) are typical for the soils. The concentrations of Ca, Mo, Cd, and Pb are comparable to the clarkes and concentrations of K, Cr, Ni, Sr, and Ba are lower than their clarkes. The main factor of migration and accumulation of chemical elements in the studied soil is soil acid—base conditions depending on the ratio between intermediate and mafic rocks. Humid climate and contrasting relief of the island cause intensive migration of chemical elements not only in dissolved but also in particulate forms. This leads to different distribution of lithophile and siderophile elements along soil catenas. Thus, Cr, Co, and Ni are fixed in topsoil of subordinate positions, while Cd and Pb are abundant in topsoil of autonomous positions. Statistical data processing included correlation, cluster, and principal component analyzes (Statistica 12.0). The results indicate local chemical contamination of soil within the settlement of Krabozavodskoe and in some areas affected by educational tourism. Vehicles are the main source of contamination.

Keywords: regional geochemical background, lateral migration, anthropogenic pollution

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INTRODUCTION

Currently, much attention is paid to the development of the Kuril Islands, strengthening the economy, and creating new jobs in the region. According to the *Strategy for Socio-Economic Development of the Sakhalin Region for the period up to 2035*, the Kuril Islands are classified as a territory of priority socioeconomic development. However, they belong to little-studied areas in terms of assessing the landscape-geochemical situation and the degree of anthropogenic disturbance of the territory. Along with natural hazards (seismic and volcanic activity, tsunamis), industrial development can lead to an increase in human load on the environment.

Therefore, rational nature management should be based on a scientifically verified assessment of the environmental sustainability and environmental risks of natural and anthropogenic origin. Data on the environmental geochemistry of the Kuril Islands are insufficient; in particular, the processes of geochemical differ-entiation and the background contents of chemical elements attract attention. Along with the established of maximum permissible concentrations (MPCs) and tentative permissible concentrations (TPCs) [27], to assess possible changes in the chemical composition of soils under the anthropogenic impact, it is necessary to know natural background concentrations, especially in the areas with complex geological structure. Major international and national projects (Barents Region, GEMAS, DEQ, Envirolink, NGSA, etc.), Russian [10, 11, 14, 18, 20] and foreign studies [32–37, 40–42] have been devoted to these issues. Data on the chemical composition of the soils of the Kuril Islands and adjacent regions are scarce [9, 13, 23, 30]; often, they have been obtained using an approximate emission spectroscopy analysis [5] and require refinement with the use of modern analytical methods. At present, there are publications on the soil cover of the Kunashir and Iturup Islands, acid–base soil properties, and concentrations of some trace elements [7, 8, 23, 30], whereas informa-

Table 1. The content of rock-forming elements in the volcanic complexes of the Lesser Kuril Ridge [22], wt %

Oxide	Complex		
	Matakotan	Shikotan	Notoro
SiO_2	49.16	51.63	52.72
TiO_2	0.82	0.65	0.80
Al_2O_3	17.75	16.77	17.23
Fe_2O_3	6.04	4.98	4.78
FeO	4.14	3.45	3.9
MnO	0.19	0.16	0.16
MgO	4.88	5.86	5.83
CaO	8.80	7.87	8.14
Na_2O	3.36	3.45	3.43
K_2O	1.18	1.28	1.12
P_2O_5	0.19	0.14	0.009
H_2O	0.42	1.38	0.37
Sum	98.42	98.28	98.73
Number of samples	106	50	46

tion on the bulk elemental composition of the soils of Shikotan Island is missing. Under these conditions, the acquisition of new data and the establishment of major features of the chemical composition of soils and the influence of natural and anthropogenic factors on it are of particular importance.

The aim of this study is to determine the distribution of metals in the soils of Shikotan Island and to establish the regional geochemical background for using these data in the environmental monitoring programs. The particular objectives of the research are as follow:

(1) to determine the main landscape-geochemical conditions of soil formation on Shikotan Island;

(2) to reveal the role of natural factors in the formation of the chemical composition of soils;

(3) to determine the patterns of radial and lateral migration of chemical elements in the soil-geochemical catenas; and

(4) to assess changes in the chemical composition of soils under the impact of anthropogenic load.

OBJECTS AND METHODS

Research objects. Shikotan is the largest in the Lesser Kuril Chain of islands; its area reached 260 km^2 (Fig. 1). The length from northeast to southwest is 28 km, the average width is 10 km. Shikotan is characterized by a complex geological structure. It is com-

posed of volcanic and volcanogenic-sedimentary formations of basic and intermediate composition of the Late Cretaceous and Paleogene ages. According to Gavrilova and Solov'eva (1973) with additions by Govorov and Piskunov (2004), they are divided into three main complexes: Matakotan and Shikotan volcanogenic-molasse and Tomari–Notoro volcanic. The Matakotan complex in the western part of Shikotan contains volcanic breccias replaced by conglomerates in the upper part. There are composed of basaltic and basaltic-andesite lavas, lava breccias, agglomerate tuffs, coarse and fine clastic volcanic sedimentary rocks. They are characterized by increased contents of total Fe, MnO, and CaO, and decreased contents of MgO and SiO_2 (Table 1). Within the Matakotan complex, the Krabozavodsk formation is distinguished; it composes the coastal cliffs of the Krabovaya Bay and is represented by basalts with globular and pillow structures [15].

The Shikotan complex is mainly found in the east of the island. It is composed of effusive-pyroclastic formations: basalts and basaltic andesites, which are combined with layers of massive basalts and conglomerate-breccia lenses. According to their chemical composition, they belong to rocks with normal alkalinity, low contents of TiO_2, CaO, and Fe oxides, and high content of MgO. This complex is complicated by gabbroid dikes (Shikotan gabbroid complex) and dolerites and basalts (Dimitrov dike complex) in the northern and southern parts of Shikotan [15, 28].
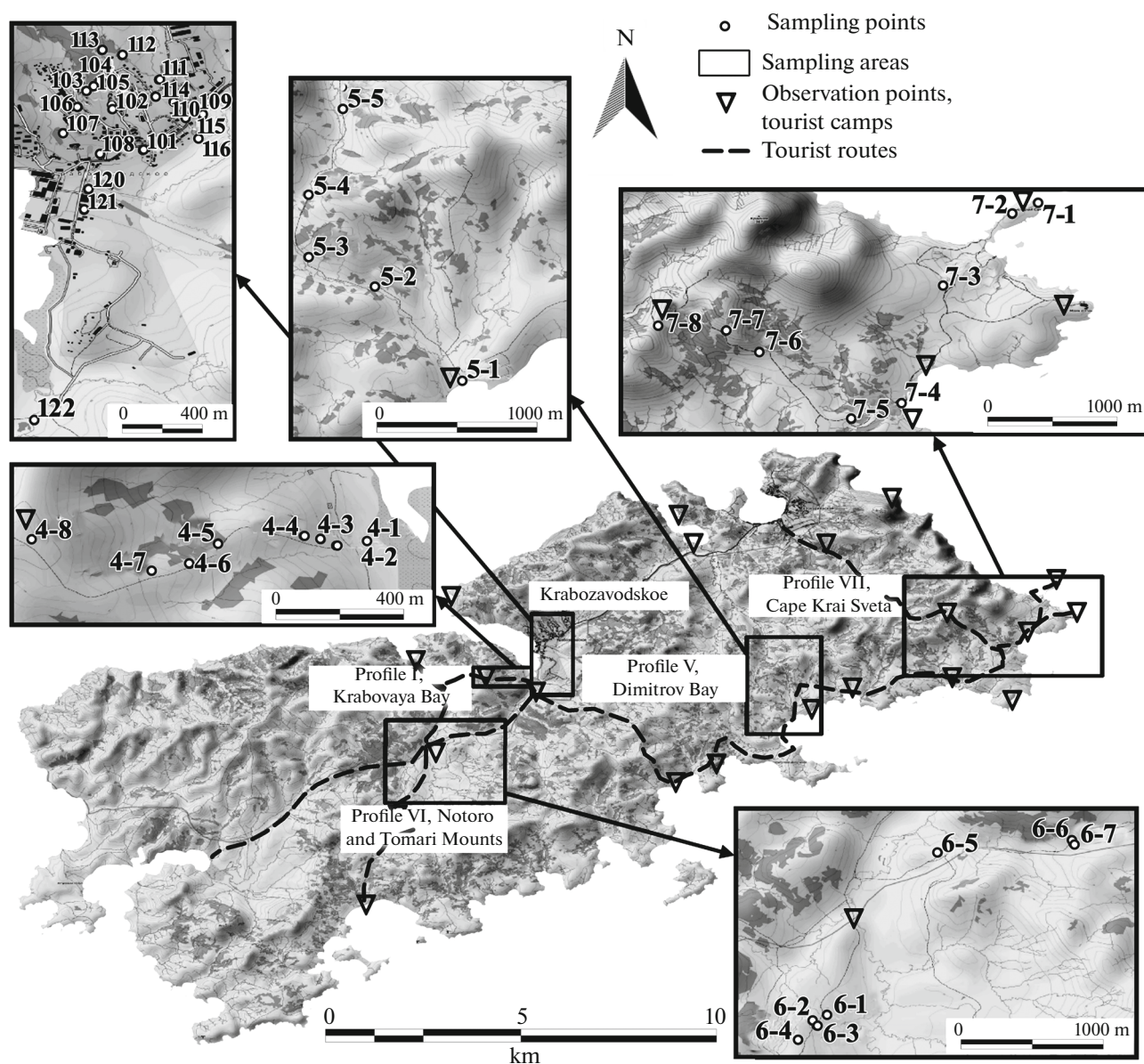
Fig. 1. Schematic map of sampling points on Shikotan Island, Lesser Kuril Chain.

The Tomari-Notoro complex in the central part of Shikotan is composed of lavas and lava breccias of basalts, basaltic andesites, and andesites. The presence of subalkaline potassium rocks of the absarokite — shoshonite series of more acidic composition (Lesser Kuril complex according to [15]) is characteristic of this complex. In general, the rocks of the complex have high contents of SiO_2, CaO, and Al_2O_3 and moderate contents TiO_2, MgO, and alkalis with a significant predominance of Na.

The relief of the island is represented by accumulative−denudational and tectonic forms: strongly dissected elevated plateaus and mesas of andesitic and basalt (less often, tuff) compositions [1].

Shikotan is located in a temperate maritime monsoon climate with strong and prolonged winds, high precipitation, and frequent fogs. The winter season is relatively mild, the spring season is long and rainy, the summer season is with little sunshine and heatless, and the autumn season is relatively dry [12, 17, 24].

The island is part of the South Kuril botanical-geographical province of the South Sakhalin−South Kuril−Hokkaido subregion of the Far East coniferous−broadleaved forest region. Spruce−fir forests with Ayan spruce *Picea ajanensis* (Lindl. & Cord.) Fisch. ex Carr. and Sakhalin fir *Abies sachalinensis* fr. Schmidt, as well as groves of stone birch *Betula ermanii* Cham. and white birch *Betula platyphylla* Sukacz. and
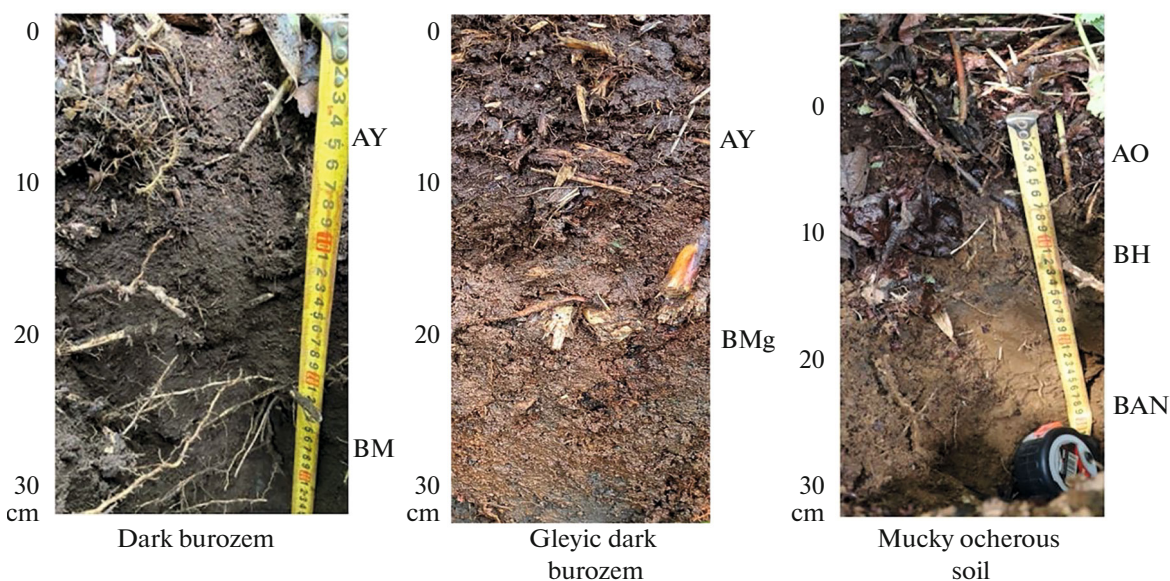
0
10
20
30 cm
AY
BM
Dark burozem

0
10
20
30 cm
AY
BMg
Gleyic dark
burozem

0
10
20
30 cm
AO
BH
BAN
Mucky ocherous
soil

Fig. 2. Soils of Shikotan Island.

thickets of low-growing (50−70 cm) Kuril bamboo *Sasa kurilensis* (Rupr.) Makino & Shibata predominate [3]. Sakhalin cork tree *Phellodendron sachalinense* (F. Schmidt) Sarg., Kuril larch *Larix kurilensis* Mayr., mountain ash *Sorbus commixta* Hedl., and yew *Taxus cuspidata* Siebold et Zucc. trees can also be found [1, 26].

In terms of soil zoning schemes, Shikotan belongs to the South Kuril region [16]. According to the Russian soil classification system of 2004, soils developed from volcanic sediments are classified as stratified ocherous soils [31]; in the WRB system, they belong to Haplic Andosols [38]. These soils are characterized by a specific mineralogical composition with a predominance of weatherable minerals and an abundance of amorphous mineral phases, such as allophane and organomineral compounds. They have specific water-physical properties: high intra- and inter-aggregate porosity and high infiltration capacity against the background of high water-retention capacity [31].
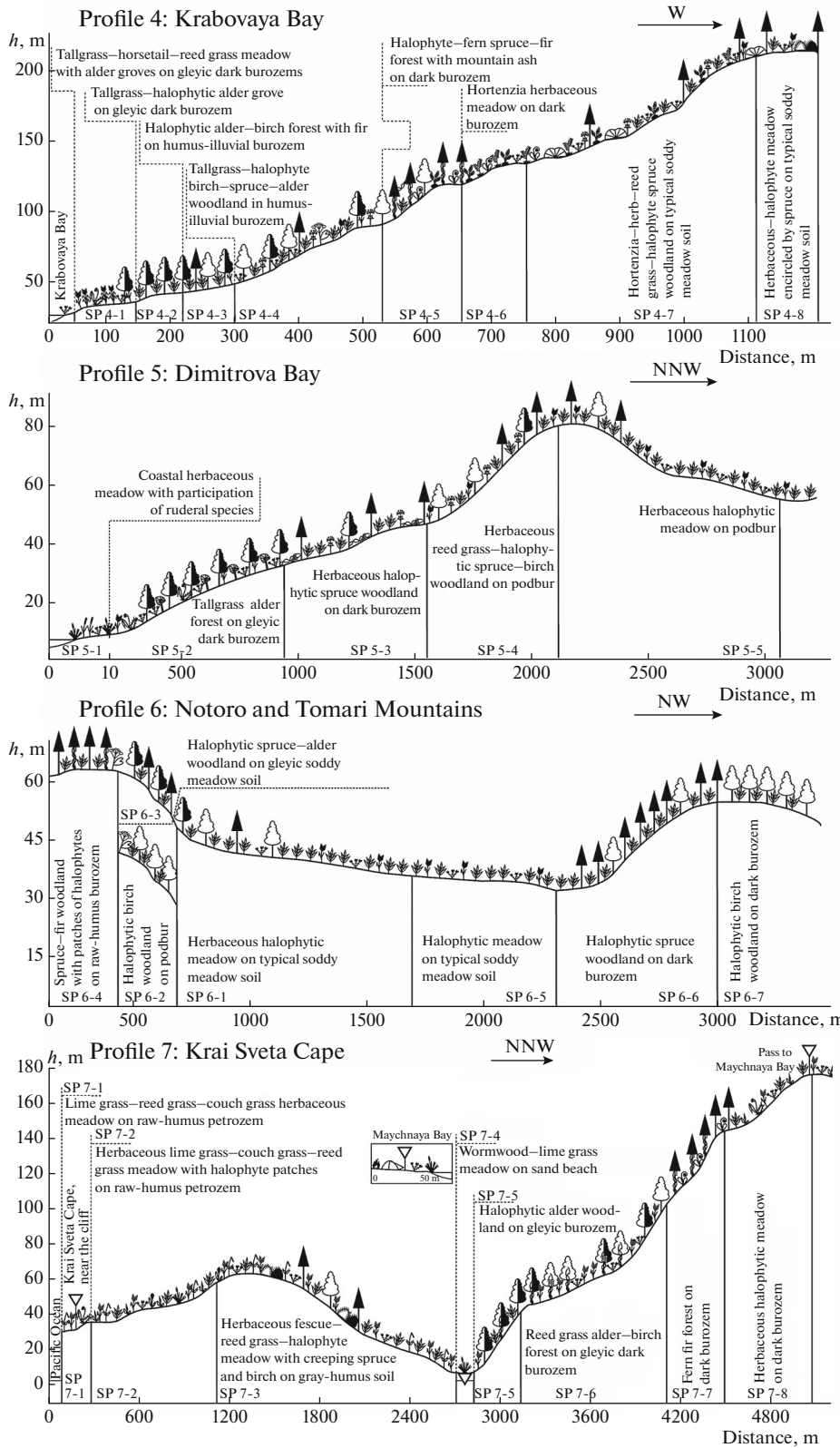
Despite the absence of present-day volcanism, volcanic ashes coming from eruptions on adjacent islands take an active part in the soil-forming processes on the island. Thus, as a result of the joint manifestation of the zonal and synlithogenic pedogenesis, soils have a complicated morphology of the profile. These are layered polygenetic soils with buried horizons and with a high content of organic matter throughout the profile. According to the *Atlas of the Kuril Islands* [1], dark gleyic burozems (27.7% of the island area) and soddy (gray-humus) soils (24.2%) predominate. A significant area is occupied by raw-humus burozems [16] (Fig. 2).

The complex geological structure, contrasting relief, and diversity of vegetation contribute to the fragmentation of the soil cover and frequent changes in soil varieties. In addition, the input of fine tephra during volcanic eruptions on the Greater and Lesser Kuril Ridges, Kamchatka, and the Japanese Islands has a certain effect on the chemical composition of soils. Thus, a peatland in the middle reaches of the Gorobets River contains ash layers with eruptions of volcanoes of Komagatake, Tarumai, and Mashu on Hokkaido; L'vinyi Zev volcano on Iturup, etc. [25].

Materials and methods. In August 2021, multiple landscape-geochemical studies were carried out on Shikotan. We surveyed background areas along four landscape profiles (PR) in different parts of the island within the main geological complexes and an anthropogenically modified area within the settlement of Krabozavodskoe. Overall, 45 sampling points (SP) encompassing the maximum natural diversity in different geochemical positions were studied (Figs. 1 and 3).

Profile 4 (PR4) was laid on the northern slope of Mount Gorobets towards the Krabovaya Bay and included 8 sampling points. Its length was 1100 m, and the difference in heights reached 203 m. Dark burozems predominated on the lower and middle parts of the slope; soddy meadow soils, on the upper part. The soils were formed on the colluvium of tuff conglomerates and mafic (basaltic) mictites of the Krabozavodskaya suite.

Profile 5 (PR 5) from the Dimitrov Bay along the western slope towards local summit had a length of 1100 m and a vertical difference in heights of 97 m; it included 5 sampling points. In the lower part, soils

Profile 4: Krabovaya Bay

Tallgrass—horsetail—reed grass meadow with alder groves on gleyic dark burozems

Tallgrass—halophytic alder grove on gleyic dark burozem

Halophytic alder—birch forest with fir on humus-illuvial burozem

Tallgrass—halophyte birch—spruce—alder woodland in humus-illuvial burozem

Halophyte—fern spruce—fir forest with mountain ash on dark burozem

Hortenzia herbaceous meadow on dark burozem

Hortenzia—herb—reed grass—halophyte spruce woodland on typical soddy meadow soil

Herbaceous—halophyte meadow encircled by spruce on typical soddy meadow soil

Krabovaya Bay

SP 4-1 SP 4-2 SP 4-3 SP 4-4 SP 4-5 SP 4-6 SP 4-7 SP 4-8

Profile 5: Dimitrova Bay

Coastal herbaceous meadow with participation of ruderal species

Tallgrass alder forest on gleyic dark burozem

Herbaceous halophytic spruce woodland on dark burozem

Herbaceous reed grass—halophytic spruce—birch woodland on podbur

Herbaceous halophytic meadow on podbur

SP 5-1 SP 5-2 SP 5-3 SP 5-4 SP 5-5

Profile 6: Notoro and Tomari Mountains

Halophytic spruce—alder woodland on gleyic soddy meadow soil

SP 6-3

Spruce—fir woodland with patches of halophytes on raw-humus burozem

Halophytic birch woodland on podbur

Herbaceous halophytic meadow on typical soddy meadow soil

Halophytic meadow on typical soddy meadow soil

Halophytic spruce woodland on dark burozem

Halophytic birch woodland on dark burozem

SP 6-4 SP 6-2 SP 6-1 SP 6-5 SP 6-6 SP 6-7

Profile 7: Krai Sveta Cape

SP 7-1
Lime grass—reed grass—couch grass herbaceous meadow on raw-humus petrozem

SP 7-2
Herbaceous lime grass—couch grass—reed grass meadow with halophyte patches on raw-humus petrozem

Krai Sveta Cape, near the cliff

Pacific Ocean

Maychnaya Bay

SP 7-4
Wormwood—lime grass meadow on sand beach

SP 7-5
Halophytic alder wood-land on gleyic burozem

Pass to Maychnaya Bay

Herbaceous fescue—reed grass—halophyte meadow with creeping spruce and birch on gray-humus soil

Reed grass alder—birch forest on gleyic dark burozem

Fern fir forest on dark burozem

Herbaceous halophytic meadow on dark burozem

SP 7-1 SP 7-2 SP 7-3 SP 7-5 SP 7-6 SP 7-7 SP 7-8

Legend

Picea ajanensis, Abies sachalinensis		*Pinus pumila, Juniperus sargentii*	
Betula ermanii		*Duschekia fruticosa*	
Alnus hirsuta		*Hydrangea paniculata*	
Actinidia kolomikta		*Eubotryoides grayana*	
Vitis coignetiae		*Matteuccia struthiopteris*	
Eupatorium glehnii		*Carex dispalata, C. lyngbyei*	
Aralia elata		*Sanguisorba tenuifolia*	
Sasa senanensis		*Leimus mollis*	
Calamagrostis langsdorffii		*Ligularia hodgsonii*	
Phragmites australis		*Artemisia montana, A. japonica*	
Cirsium weyrichii, C. kamtschaticum		*Plantago asiatica, P. camtschatica*	
Petasites japonicus			
Observation site		Camping area	

Fig. 3. Schemes of landscape profiles studied on Shikotan Island.

develop from the colluvium of mafic rocks (Dimitrov dike complex of dolerites and basalts [15]); in the upper part, from subvolcanic formations of the Lesser Kuril complex of more acidic composition. Raw-humus burozems, dark burozems, dark gley burozems, and podburs were described in sampling points.

Profile 6 (PR6) crossed outcrops of the Tomari-Notoro volcanic complex and volcanic-sedimentary rocks of the Lesser Kuril complex. It consisted of six sampling points, had a length of more than 3500 m, and height difference of 19 m. The profile crossed a step-like accumulative marine plain between marginal parts of the central plateau. Dark burozems, podburs and meadow-soddy soils formed on a stratum composed of lavas and lava breccias of andesites and basaltic andesites were described along this profile.

Profile 7 (PR7) in the northeastern part of Shikotan extended from Cape Krai Sveta to Mayachnaya Bay and from the Pacific Ocean's water edge along the slope of the western exposure to the top of the pass. Its length was 4800 m and the difference in heights reached 128 m. Raw-humus burozems, dark burozems, gray-humus soils, and raw-humus petrozems developed from Shikotan complex rocks were described along this profile.

In the area of the Krabozavodskoe settlement, 19 sampling points evenly distributed over the area of residential development were studied.

At each sampling point, detailed physiographic description of the landscape conditions was made, including the description of soil profiles in shallow pits (to the middle-profile horizon) and vegetation (main layers, synusia, species composition, projective cover and abundance of plant species, phenological state, vitality, etc.). Special attention was paid to potential sources of anthropogenic impact, their location, possible spread of pollutants in the catenary structure, environmental disturbance, etc.

Soils were sampled from two genetic horizons: surface accumulative (A) and middle-profile (BF, BHF, BG). Overall, 72 soil samples were taken and analyzed, including 19 samples from the technogenically modified territory. In soils of natural moisture in the field, the pH value was determined using a pH meter (Horiba LAQUAtwin B-712) with a horizontal electrode for measuring in solid sediments, gels, and liquids.

One of the objectives of the research was an assessment of soil pollution related to the economic activities and unorganized educational tourism. For this purpose, surface soil samples were taken in the Krabozavodskoe settlement on observation points of tourist routes. In addition, the studied profiles partially crossed major tourist routes.

The analysis of the bulk contents of metals (Na, K, Ca, Mg, Cu, Zn, Fe, Pb, Cd, Ni, Co, Cr, Ba, Sr, and Cd) in the soil samples was performed in the Central Laboratory of the Karpinsky All-Russia Geological Research Institute using inductively coupled plasma mass spectrometry on an ELAN-6100 DRC instrument.

Data on the average contents of the studied metals in the urbanized area (Krabozavodskoe settlement) were compared with data from the background natural landscapes unaffected by economic activity.

The background concentrations of heavy metals in soils were calculated using the minimum anomalous concentration of the element related to the technogenic pollution or errors in sampling and sample preparation:

$$x_{\text{min.an}} = \bar{x} \pm t\delta,$$

where $\bar{x}$ is the average content of a chemical element, δ is the standard deviation, and t is Student's coefficient (its values are tabulated depending on the level of significance and the number of samples).

The value of the Student's coefficient with a confidence interval of 95% for the studied samples ($n \geq 26$) is about 2.0. Thus, the final formula takes the form: $x_{\text{min.an}} = \bar{x} \pm 2\delta$. All values beyond these limits were excluded from the calculation of the regional background concentrations, which were determined for "clean" samples.

The methods of descriptive statistics were applied using Excel software. For multivariate statistical analysis of geochemical data, cluster analysis and principal component analyses (PCA) were performed using Statistica 12.0 software package (StatSoft). Cluster analysis was performed using a hierarchical agglomerative method (tree clustering) according to the single link rule (Single Linkage) with a preliminary standardization (Standartize) of concentrations for two samples characterizing element contents in the humus and middle-profile horizons. The measure of similarity between elements was determined as the Euclidean distance. The PCA was performed for three statistical samples with 17 variables (metal contents) for 72 soil samples.

To assess the natural geochemical heterogeneity and intensity of element migration in soil catenas, the coefficients of lateral differentiation were calculated (the ratio of the element content in the upper horizon of the subordinate landscape to its content in the same soil horizon of the geochemically autonomous landscape, *L)* [6]. Because of the high heterogeneity of the parent materials, the geological structure of the territory was taken into account in the calculation. This was done on the basis of a comparison of the content of the element in the middle-profile horizons of the

same soils, since the formation of their chemical composition is greatly influenced by parent rocks. In these horizons, the coefficient of heterogeneity of the geological structure (KHGS) was determined:

$$\text{KHGS} = \frac{c_{i1}}{c_{i2}},$$

where c_{i1} and c_{i2} are the metal concentrations (mg/kg) in the middle-profile horizons in the autonomous (upper) and subordinate (lower) catenary positions, respectively. Then, the coefficient of lateral migration was normalized to this coefficient by dividing L by the coefficient of heterogeneity of the geological structure (KHGS). This approach made it possible to partially remove the influence of the composition of parent rocks on the L value. However, it should be born in mind that its use is advisable in the case when the influence of soil-forming processes on the accumulation and removal of the elements under consideration, especially their radial migration, are of the same type in the compared landscapes. A comparative assessment of the level of soil pollution was based on the calculation of the total index of soil pollution (Z_c) [27]. Based on the similarity of the geological structure of the territories, the average metal contents in the organogenic (humus) soil horizons of PR4 and of PR6 (for the central part of the island) were taken as reference background values. To remove the possible influence of the heterogeneity of the geological structure, the calculation was carried out only for metals, which, based on statistical analysis, were classified as potential pollutants.

RESULTS AND DISCUSSION

Acid–base soil properties. Soils of Shikotan are characterized by a neutral or slightly acid reaction (pH 5.10–7.52). This significantly affects the mobility of chemical elements in the landscape. In a neutral medium, most chemical elements have a low migration capacity; with acidification of the soil solution, element mobility sharply increases [19, 21, 39]. The main factor determining the change in the acid–base index is parent material. The lowest pH values were noted in soils forming in the central part of Shikotan (PR6 crossing the Tomari-Notoro and Lesser Kuril rock complexes), as well as in soils on volcanogenic-molasse complex (PR5 towards Dimitrova Bay) and soils on lavas and lava breccias of intermediate composition in the northwestern part of PR7. Soils developing from basalt rocks on the slope of Mount Gorobets, as well as soils on tectonites of mafic rocks on the macroslope in Dimitrov Bay and Krai Sveta Cape have a neutral and slightly alkaline reaction. In the transition from the humus to the middle-profile horizon, an increase in pH is observed in most soils in the interior of the island. In the soils of marine terraces, where the influence of oceanic air masses is significant, an increase in pH in the organic horizon is noted.

In addition, within one geological complex, a change in the pH value occurs when the dominants of plant communities change. Acidification of the surface horizon was found for the soils under spruce–fir forests because of the needle litter containing a large amount of resin acids.

Content and associativity of chemical elements in soils. An analysis of the content of chemical elements in the soils of Shikotan indicates the heterogeneity of the samples due to the complex geological structure of the territory. The content of most metals is rather variable. Close relationships between the chemical compositions of soils and rocks are known for the Kuril Islands [23]. As noted above, the geological structure of the island is dominated by mafic and intermediate effusive rocks. Table 2 shows the average content of metals in the studied soils, which suggests that the mafic rocks are represented to the maximum extent in the Matakotan (Krabozavodskaya Formation) and Shikotan volcanogenic–molasse complexes of basaltoid rocks (PR4, PR5, PR7). The rocks of the Tomari–Notoro and Lesser Kuril complexes (PR6) are closer to the composition of andesites and more acidic rocks (subalkaline potassium varieties). The Shikotan complex in the northeastern part of the island (in the area of PR5 and PR7) is characterized by a significant heterogeneity, as evidenced by the wide range of metal contents in the middle-profile soil horizons. This is due to the overlay of the dike complex of gabbroids, dolerites, and basalts.

The geochemical features of soils and soil-forming rocks were considered using PCA analysis of data on metal contents in the middle-profile horizon (Table 3). In general, all variations in the chemistry of the studied soils are described by three associations. The first principal component includes about 50% of the total variance. It reflects the differentiation of soils by the types of soil-forming rocks. Felsiphile metal association (Mo–Pb–Cd) with positive values of factor 1) is related to felsic rocks, and parageneses of siderophile and lithophile metals (negative values of factor 1) are associated with mafic rocks. The second component (weight 25%) reflects the differentiation of mafic rocks into a femaphile group of elements (metals of mafic and ultramafic rocks: Fe, V, Mg, Sc, Ni, Co, etc.) and alkali metals. It is believed [22] that all basaltoids of the island belong to the normal alkaline series, but their alkalinity (the sum of sodium and potassium oxides) differs, and its maximum is noted in the rocks of the Shikotan complex. The subalkaline rocks of the Lesser Kuril Complex (PR6) tend to the alkaline series.

Table 2. The content of metals (mean ± confidence interval at 5% significance level) in the studied soils of the island Shikotan, mg/kg

Metal	Profile/sampling area				
	4	5	6	7	Krabozavodskoe
	Organogenic horizon				
Na	9300 ± 400	9300 ± 4800	5800 ± 1700	13400 ± 2400	10900 ± 1800
Mg	10300 ± 750	9950 ± 7100	5100 ± 1650	14150 ± 5050	13750 ± 3300
K	5800 ± 300	4900 ± 2100	4200 ± 1300	6500 ± 1300	9400 ± 1200
Ca	16100 ± 2000	14700 ± 8300	11100 ± 4500	24000 ± 8100	17900 ± 2700
Sc	17 ± 1.4	11.6 ± 7.3	8.6 ± 3.0	17.0 ± 2.0	18.6 ± 2.67
V	175 ± 13	103 ± 66	76.5 ± 28	163 ± 25	186 ± 27
Cr	27 ± 19	40.9 ± 42	11.8 ± 7.4	49.5 ± 30	39 ± 9.4
Fe	53500 ± 3200	31600 ± 19200	23800 ± 8600	46500 ± 5600	55700 ± 5400
Co	16 ± 1.6	11.4 ± 7.9	7.79 ± 2.6	16.1 ± 4.7	20.8 ± 3.2
Ni	10 ± 1.5	20.7 ± 22	6.94 ± 3.0	17.8 ± 9.0	23.5 ± 4.6
Cu	54 ± 7.5	43.8 ± 29	30.4 ± 6.4	65.2 ± 24	100 ± 17.6
Zn	100 ± 10	71.2 ± 23	73.2 ± 22	80.9 ± 10	162 ± 36
Sr	118 ± 11	148 ± 81	95.3 ± 29	251 ± 110	229 ± 36
Mo	1.56 ± 0.10	1.17 ± 0.55	1.04 ± 0.19	1.42 ± 0.36	1.40 ± 0.27
Cd	0.32 ± 0.05	0.23 ± 0.05	0.31 ± 0.09	0.26 ± 0.07	0.33 ± 0.06
Ba	216 ± 21	210 ± 142	167 ± 52	278 ± 71	583 ± 124
Pb	16 ± 2.6	17.2 ± 5.0	19.0 ± 3.5	17.3 ± 4.0	147 ± 242
pH	6.63 ± 0.36	5.94 ± 0.66	5.36 ± 0.22	6.00 ± 0.44	5.63 ± 0.65
	Middle-profile horizon				
Na	7000 ± 1100	11900 ± 2600	10000 ± 600	12800 ± 2200	–
Mg	14950 ± 2700	11100 ± 5900	7650 ± 1200	15350 ± 6150	–
K	6500 ± 1200	6000 ± 1600	5900 ± 1400	7200 ± 2500	–
Ca	14700 ± 1200	15200 ± 2000	13800 ± 2400	22100 ± 7900	–
Sc	22.3 ± 0.9	18.8 ± 1.5	17.2 ± 2.7	20.7 ± 3.0	–
V	238 ± 23	173 ± 14	151 ± 20	196 ± 26	–
Cr	28.9 ± 8.3	32.4 ± 36	16.6 ± 6.4	43.9 ± 22	–
Fe	68300 ± 4700	56700 ± 4300	49500 ± 5200	58400 ± 4300	–
Co	25.5 ± 3.5	15.8 ± 5.3	14.4 ± 1.5	19.7 ± 3.5	–
Ni	18.0 ± 4.8	18.2 ± 24	7.51 ± 3.1	17.8 ± 8.4	–
Cu	96.9 ± 25	56.8 ± 25	41.8 ± 6.5	69.4 ± 20	–
Zn	105 ± 9.2	81.3 ± 3.8	85.8 ± 12	87.4 ± 12	–
Sr	102 ± 24	146 ± 56	116 ± 11	247 ± 136	–
Mo	1.16 ± 0.26	1.83 ± 0.67	1.82 ± 0.10	1.48 ± 0.40	–
Cd	0.27 ± 0.04	0.24 ± 0.05	0.24 ± 0.02	0.21 ± 0.03	–
Ba	271 ± 60	249 ± 132	204 ± 47	280 ± 83	–
Pb	9.7 ± 0.8	13.2 ± 1.9	14.9 ± 2.0	11.4 ± 2.4	–
pH	7.01 ± 0.20	6.00 ± 0.48	5.8 ± 0.30	5.87 ± 0.24	

Table 3. Parageneses of chemical elements in generalized factor load responsible for the distribution of metals in the soils of Shikotan. Above the line—positive coefficients of factor load; under the line—negative coefficients of factor load (in the formulas, the values of the loads multiplied by 100 are given)

Factor	Name	Paragenesis	Factor share, %
		Total content of metals in the organogenic horizon of soils, $n = 28$	
I	Parent material	$\dfrac{Mo_{43}}{Mg_{97}Sc_{92}Ba_{90}Co_{88}Ni_{88}V_{88}Ca_{86}Na_{86}K_{82}Sr_{82}Cr_{75}Fe_{74}}$	54.8
II	Organogenic	$Cu_{83}Cd_{75}Zn_{69}Pb_{66}Fe_{46}$	17.4
		Total content of metals in the organogenic (surface) horizon of soils on the profiles and the Krabozavodskoe site, $n = 46$	
I	Parent material	$Mg_{95}Sc_{90}Co_{87}Ni_{87}V_{85}Ca_{80}Sr_{79}Fe_{73}Cr_{69}K_{67}Na_{66}Ba_{49}$	45.9
II	Technogenic	$Cu_{78}Cd_{68}Pb_{67}Zn_{57}Ba_{50}$	16.7
		Total content of metals in the middle soil horizon, $n = 26$	
I	Parent material	$\dfrac{Mo_{88}Pb_{80}Cd_{40}}{Mg_{97}Co_{88}Cu_{87}Ba_{87}Ni_{81}Cr_{81}V_{75}K_{71}Sr_{60}Fe_{57}Ca_{52}Sc_{41}}$	49.8
II	Formational	$\dfrac{Na_{89}Sr_{68}Ca_{54}}{Fe_{74}Sc_{65}Zn_{65}V_{57}Cd_{57}Co_{41}}$	24.8

In order to identify the features of the chemical composition of the middle-profile horizons in the studied catenas and link them to the main geological complexes, soil samples were evaluated according to factor loads. Within the Matakotan complex of the Krabozavodskoe series (PR4), burozems and podburs are characterized by a homogeneous elemental composition and tend to the femaphile elements (negative loads on factors I and II). Soils of PR6 (dark burozems, podburs, and meadow-soddy soils) have maximum loads on the association of intermediate effusives (positive loads on factors I and II). Sampling points of PR5 and PR7 belonging to the Shikotan complex are distinguished by the considerable heterogeneity. Part of samples PR7 from Cape Krai Sveta (raw-humus petrozems and dark gleyic burozems) and sampling point 2 from PR5 in Dimitrov Bay (dark gleyic burozem) are characterized by maximum loads on alkaline basaltoids (negative load on factor I and positive load on factor II). Away from the coast towards higher hypsometric levels, that is, from superaquatic beach deposits to transeluvial positions with dark burozems, both profiles intersect rocks of a more felsic composition similar in chemistry to the rocks of the Lesser Kuril complex. They are represented by the association of felsiphile elements (positive loads on factor I).

In general, factor analysis indicated that metal contents in the middle-profile horizons are characterized by paragenesis of femaphile and alkaline metals. The total contents of elements of these groups are characterized by high values significantly exceeding element abundances in the Earth's crust (clarkes). Chalcophile metals (Cu, Zn, Cd, Pb) in the middle-profile horizon do not show paragenetic affinity with one another, which can be associated with the absence of sulfide rocks in the study areas, as well as by the low mobility and degree of involvement of these metals in the biogeochemical cycle [19]. This is mainly due to neutral soil reaction and approximately clarke levels of metal concentrations.

Metal concentrations in the organogenic horizon differ from those in the middle-profile horizons, which is also confirmed by the PCA. The first factor explaining 55% of the total variance reflects the accumulation of femaphile metals, which are characteristic of mafic effusive rocks. An independent association of felsiphile elements found in the middle-profile horizon is absent in the upper horizon. The second factor explaining 17% of the total variance is related to chelate formation with participation of chalcophile elements (Cu, Cd, Pb, Zn) and iron. These metals are complex-forming elements and are part of the organo-mineral compounds that make up a significant proportion of the soil adsorption complex. In the middle-profile horizon, these metals are included in the association of trace elements of volcanic rocks and, as noted above, do not display significant correlation with one another. The soils of PR4 have the maximum loads on the second component, which indicates the activity of chelation processes and the high degree of participation of these metals in organo-mineral complexes. In this regard, it seems interesting that felsiphile metals (Cd and Pb) and femaphile metals (Cu, Zn, and Fe) are associated in this par-
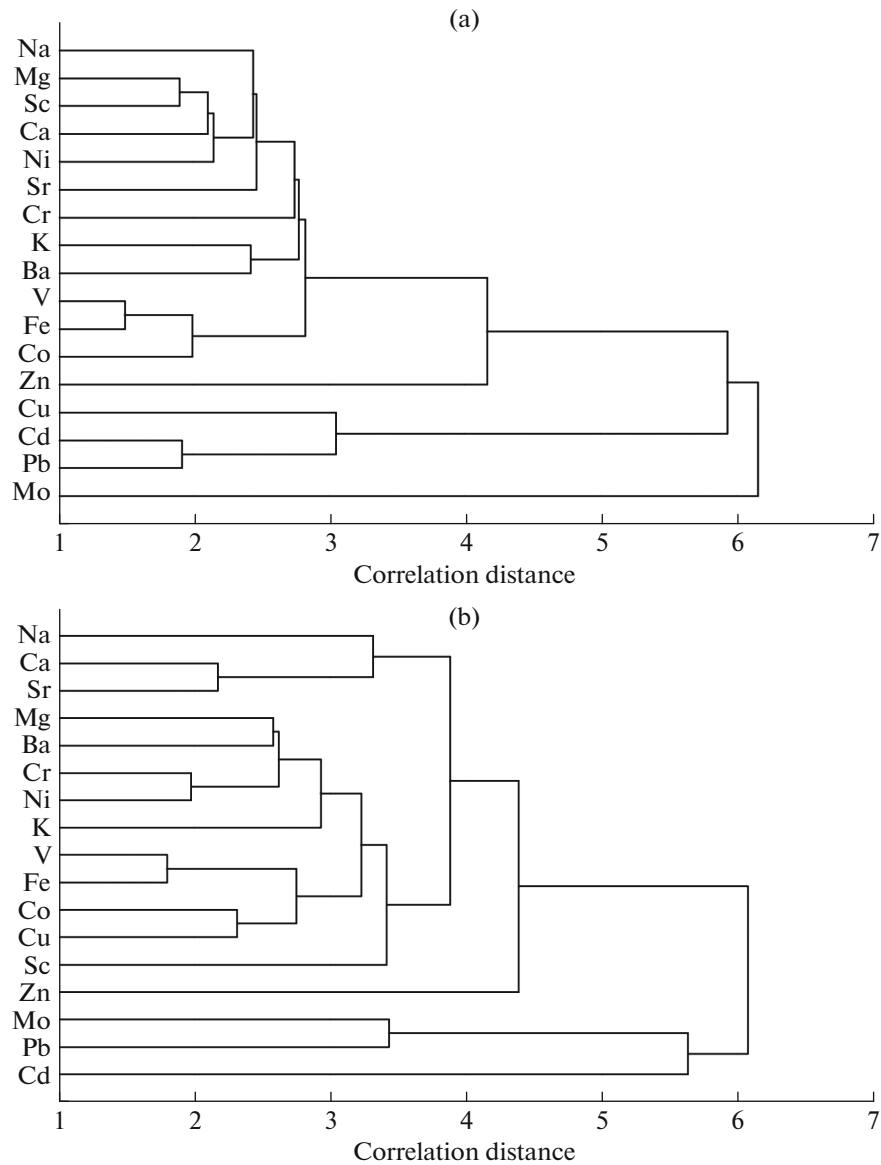
Fig. 4. Dendrogram of the hierarchical cluster analysis of metal concentrations in (a) organogenic and (b) illuvial horizons of soils.

agenesis. This indicates a significant role of soil-forming processes in the formation of the chemical composition of the humus horizon.

The regularities established above are confirmed by the results of cluster analysis of the general sample representing both humus and middle-profile horizons. At the first clustering step, Fe and V are combined, then Co is added to them, then Sc (Fig. 4). The Pearson pair correlation coefficient between Fe and V concentrations is 0.96 for the humus horizons and 0.94 for the middle-profile horizons. The strong correlation between V and Fe in soils is confirmed by the literature data [2]. The coefficient of pair correlation between Fe and Co concentrations is 0.89 for the

humus horizons and 0.76 for the middle-profile horizons. Vanadium has a stronger relationship with cobalt: the correlation coefficients are 0.92 and 0.85 for organogenic and illuvial horizons, respectively. A close relationship is found between Mg and Ni, which then combine with the previously listed metals to form the femaphile association. Chalcophile elements (Cu, Cd, Zn, Pb) have low pairwise correlation coefficients and large clustering distance.

Geochemical characterization of soil types. As is known, the chemical composition of soils is determined not only by the characteristics of soil-forming rocks but also by pedogenetic processes. Comparative analysis of data on metal concentrations in different
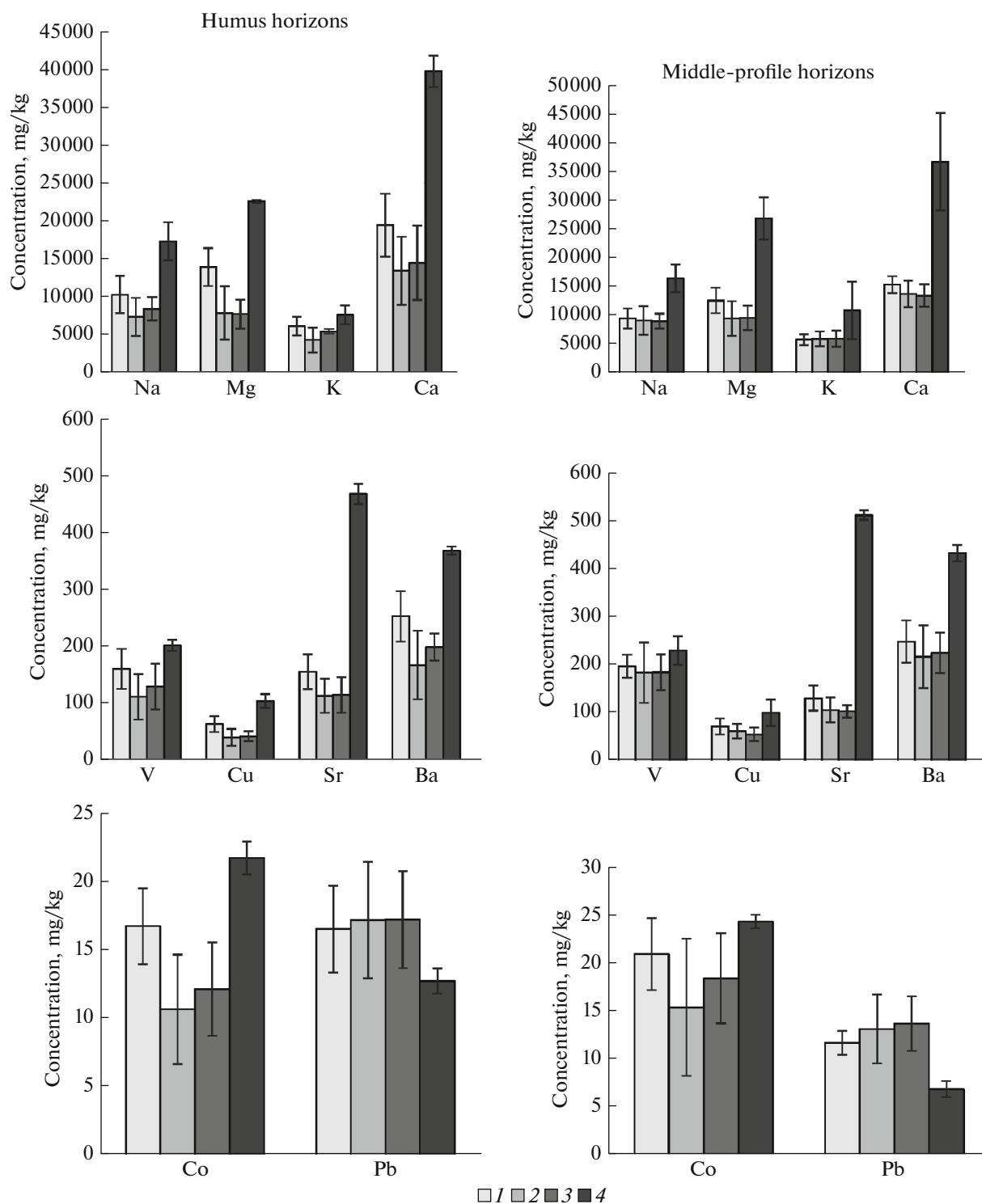
Fig. 5. Metal concentrations in different soils: (*1*) burozems, (*2*) podburs, (*3*) soddy meadow soils, and (*4*) petrozems.

genetic types of soils indicates that petrozems are characterized by generally higher concentrations of Na, Mg, K, Ca, V, Co, Cu, Sr, and Ba both in the top-soil and middle-profile horizons (Fig. 5). The accumulation of Pb is observed in meadow-soddy soils under meadow communities (the Pb content is 2.5–3.0 times higher than in other types of soils in the humus horizons and 1.2–2.3 times higher in the middle-profile horizons). At the same time, meadow-soddy gleyic soils are significantly depleted in calcium
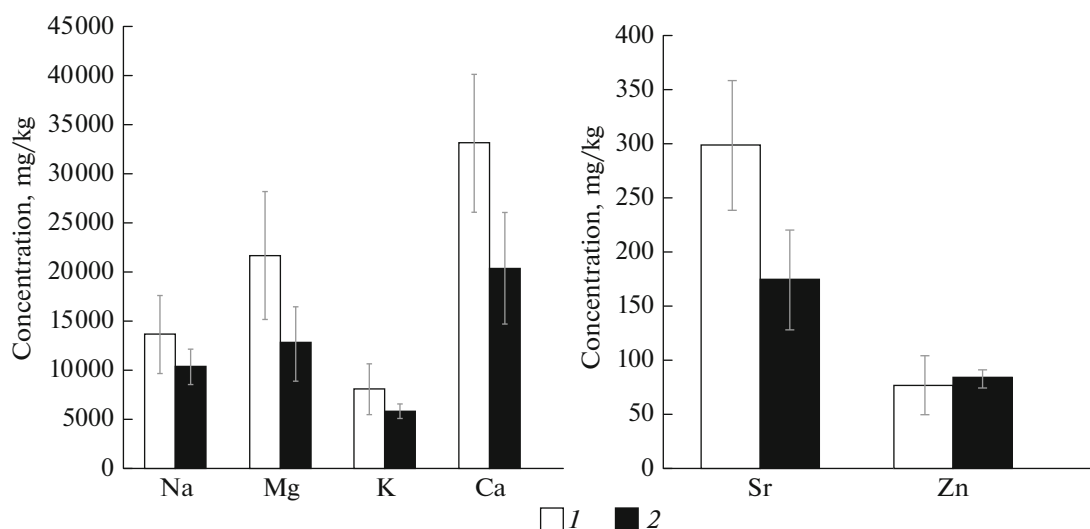
Fig. 6. Concentrations of alkali metals in the humus horizons of soils of coastal areas of Shikotan: (*1*) sampling points on the ocean coast and (*2*) general sample.

(2.6 times less Ca in the humus horizons and 1.5 times less in the middle-profile horizons) compared to typical meadow-soddy soils. In burozems and podburs, the concentrations of metals approximately correspond to the average background values (Fig. 5).

The noted differences are explained, first of all, by the specificity of soil morphology and properties. Petrozems are characterized by the low humus content compared to podburs, burozems, and meadow-soddy soils. A small amount of organic matter and an underdeveloped profile with shallow bedrock contribute to a significant effect of parent rocks on the elemental composition of the soil, including an increase in the concentration of typical femaphile metals. This again emphasizes the significant influence of volcanic rocks on the chemistry of not only petrozems but also other soils of Shikotan.

It is important to note the oceanic influence on the chemical composition of the topsoil horizon of soils on plots located in relative proximity to the Pacific coast (sampling points 7-1, 7-2, 5-1, and 5-2), in which the concentrations of Na, Mg, K, and Ca cations (typical of seawater) is 1.5–2.0 times higher (Fig. 6).

In addition, changes in the contents of metals in the humus horizons are related to changes in plant communities (alder, birch, fir–spruce forests and herbaceous meadows). Thus, soils under alder forest are characterized by higher (by a factor of 1.5–1.9) Co concentrations compared to soils under fir–spruce, birch, and meadow communities. This may be caused by the influence of Co on the capacity of alder species to fix nitrogen from the air [39]. Along with this, in podburs and burozems developed under alder communities, the concentrations of Mg, K, V, Fe, Ni (1.7–

3.5 times), Cu, Ba, and Zn (1.5–2 times) are also higher. Soils under fir–spruce communities are characterized by the high Cr content. In meadows, Na, Ca, Sr, and Pb are concentrated in the soils.

Redistribution and migration of metals in the soil catenas. Comparison of the contents of metals in the topsoil and middle-profile horizons using statistical criteria (Student's test) indicates that their ratio depends on the type of soil and geological structure. The highest differentiation of metals between the genetic soil horizons was found within the Matakotan Complex (PR4). In the middle-profile horizon, significant accumulation of Mg, Sc, V, Fe, Co, Ni, and Cu takes place in comparison with the topsoil. At the same time, Na, Mo, and Pb accumulate in the topsoil. In the areas of the Tomari–Notoro and Lesser Kuril complexes (PR6), the vertical redistribution of Na, Mg, Sc, V, Fe, Co, Ni, Cu, and Mo generally repeats the differentiation of metals in the soils of PR4, but only Pb accumulates in the organogenic horizon. In the soils formed within the area of the Shikotan complex (PR5 and PR7), there are no statistically significant differences in the contents of metals between the topsoil and middle-profile horizons, except for some accumulation of Fe in the middle-profile horizon (on both profiles) and Pb in the topsoil in profile PR7. Probably, the absence of statistically significant differences in the concentrations of metals in the genetic soil horizons in these areas is explained by their high variability, as was already noted earlier.

The calculation of the coefficients of lateral migration (*L*) showed that the migration activity of the elements varies significantly from eluvial (autonomous) to superaquatic (subordinate) landscape-geochemical

Table 4. Coefficients of lateral migration of metals in the landscape-geochemical catenas of Shikotan

Metal	Profile (altitude difference)					Average
	4 (203 m)	5 (57 m)	5 (40 m)	6 (19 m)	7 (128 m)	
Na	0.67	3.87	4.94	3.00	0.90	2.69
Mg	1.77	2.89	5.95	3.08	2.04	3.15
K	0.92	1.96	2.23	1.83	1.03	1.60
Ca	0.88	5.1	6.90	2.86	0.91	3.38
Sc	1.33	5.7	8.56	3.84	0.84	4.02
V	1.74	6.46	7.74	3.81	0.97	4.14
Cr	3.04	2.71	10.20	1.89	1.77	3.92
Fe	1.62	6.44	6.80	3.88	0.95	3.94
Co	2.08	3.94	7.17	3.65	1.91	3.75
Ni	2.22	1.36	6.15	1.37	1.57	2.53
Cu	2.12	2.24	3.89	2.03	1.80	2.42
Zn	1.17	1.44	1.86	1.72	0.77	1.39
Sr	0.54	2.47	3.38	2.41	1.12	2.00
Mo	0.49	1.1	1.43	1.81	0.38	1.04
Cd	0.62	0.9	1.02	1.42	0.53	0.90
Ba	0.90	2.39	3.33	2.31	1.52	2.09
Pb	0.49	0.5	0.73	1.13	0.49	0.67

positions (Table 4). The distribution of metals by elements of the relief is controlled by the geological and geomorphic factor and acid−base conditions. Thus, at PR4, the elevation difference reaches 200 m, and the average soil pH is 6.80. The most active lateral migration ($L > 2$) is noted for Cu, Ni, Cr, and Co. At PR5, L was estimated for two landscape-geochemical catenas with height differences of 57 and 40 m. With the exception for Mo, Cd, Pb, and Zn, metals had high values of the coefficient of lateral migration ($L = 2-10$) with maximums for Cr, Fe, Co, V, Ca, and Sc. The average pH was 6.14 and 5.41 for the first and second catenas, respectively. Characteristically, under homogeneous geological and geochemical conditions, the values of L increase at lower pH values, which is in good agreement with the increase in the mobility of most metals upon acidification of the soil solutions [19, 39]. At PR6 with a small height difference (19 m), relatively low values of L (1.1−3.9) have been noted. The most active lateral migration is characteristic of siderophile metals. In profile PR7 from the pass to Mayachnaya Bay to sampling point SP4, the height difference reaches 128 m, and the average pH value is 5.63. Here, the L values indicate a very low degree of the lateral metal migration: L somewhat exceeds 2 only for Mg.

In general, the lateral migration of metals in the landscape-geochemical catenas Shikotan can be characterized by the following decreasing sequence (according to L values): V (4.1) > Sc (4.0) > Fe (3.9) > Cr (3.9) > Co (3.8) > Ca (3.4) > Mg (3.2) > Na (2.7) > Ni (2.5) > Cu (2.4) > Ba (2.1) > Sr (2.0) > K (1.6). The lateral migration of Zn, Cd, Pb, and Mo in the studied soils is very weak. High value of L for generally slightly mobile Sc, V, and Cr indicate that, within the dissected relief, the migration of metals is possible not only in the form of soluble salts but also in a mechanical form together with soil particles. It is necessary to note the general regularity of migration, i.e., its dependence on the soil pH. The lowest L values are typical of PR4 with an average pH 6.80 (low metal mobility), and the highest L values are observed at PR5 with an average pH 5.41 (relatively high mobility of cationic metals). Based on the results obtained, it can be concluded that under conditions of a highly dissected relief, a direct relationship between the intensity of metal migration and an increase in the height difference and slope of the surface disappears.

The revealed relationship between the intensity of lateral migration and pH is of great importance in determining landscape tolerance towards chemical pollution. In turn, pH in the landscape-geochemical

Table 5. Background metal concentrations (mean ± confidence interval at 5% significance) in the soil horizons of Shikotan, mg/kg

Element	Horizon A (n = 27)	Horizon B (n = 26)	Soil clarke [2, 9]
Na	9300 ± 1300	10 200 ± 1300	5000
Mg	10 650 ± 2450	12 650 ± 2450	5000
K	5700 ± 670	6100 ± 600	14000
Ca	17 000 ± 3300	16 600 ± 2600	15000
Sc	16.3 ± 2.4	20 ± 1.3	7.0
V	158 ± 21	190 ± 15.4	90
Cr	33 ± 12.8	31 ± 9.9	70
Fe	46 300 ± 5300	58 100 ± 3200	40000
Co	14.8 ± 2.4	18.9 ± 2.3	8.0
Ni	14.1 ± 4.4	13.5 ± 3.6	50
Cu	51 ± 9.4	69 ± 13.3	30
Zn	84 ± 8.0	91 ± 6.2	90
Sr	139 ± 26	122 ± 16.4	250
Mo	1.3 ± 0.16	1.5 ± 0.18	1.2
Cd	0.31 ± 0.08	0.24 ± 0.02	0.35
Ba	241 ± 39	243 ± 35	500
Pb	16.4 ± 2.0	12.0 ± 1.2	12

catenas of Shikotan to a certain extent depends on the ratio of mafic and intermediate rocks: an increase in the proportion of andesites leads to a decrease in soil pH and an increase in the migration potential of metals; mafic rocks (basaltoids) alkalinize soil solutions and reduce the mobility of metals.

Regional geochemical background (tentative estimate for the soils). The calculation was carried out for the entire soil cover of the island, taking into account approximately even distribution of sampling points by geological complexes and soil types. The regional geochemical background for the humus and middle-profile horizons reflects the highly contrasting natural conditions and geological structure of the island (Table 5).

The soils of Shikotan are characterized by the high contents of Na, Mg, Sc, V, Fe, Co, and Cu, which exceed the clarke for soils [29] by 2−5 times; this is generally typical of the areas with mafic volcanism [23]. The concentrations of K, Cr, Ni, Sr, and Ba are 2−3 times lower than corresponding soil clarke values, and the concentrations of Ca, Zn, Mo, Cd, and Pb are comparable with clarke values. High concentrations of V and Sc throughout the island are associated with mafic volcanic rocks (basalts, gabbro). Important indicators of rock variability are Mg and Fe, the con-

tents of which in soils range from 2400 to 44400 and from 6300 to 81900 mg/kg, respectively. An increase in their concentration occurs in the areas of basaltic rocks serving as soil parent materials.

Technogenic pollution of soils. A conjugated analysis of the chemical composition of soils, landscape-geochemical conditions, and sources of anthropogenic impact showed that, along with natural factors, there is local anthropogenic pollution, which determines the variation in the content of metals in the soils of the study area. On the territory of Krabozavodskoe, sources of pollution include vehicles, a boiler house, a fish processing plant, a heliport, and residential infrastructure.

Profile 4 and the Krabozavodskoe area are located in homogeneous geological conditions; these samples were used to compare the statistical characteristics of the metal content in the surface soil layer. According to the results of the analysis, a statistically significant excess of the content of metals in the urbanized area in relation to the background values was revealed for Co, Ni, Cu, Zn, Sr, Ba, and Pb. This is the reason to consider these metals as potential pollutants entering the soil as a result of economic activities in the village. The level of soil contamination with these metals within the development area can be represented by the following series (in parentheses, the ratio of the average
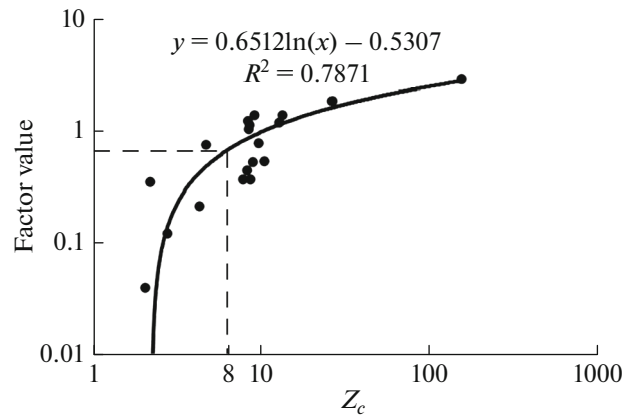
Fig. 7. Regression dependence of the total indicator of soil pollution (Z_c) and the values of the technogenic factor.

values of the content of elements in the organic soil horizons in the urbanized area and in PR4): Pb (144) > Ba (6.0) > Ni (4.0) > Zn (3.7) > Cu (3.4) > Sr (3.2) > Co (2.1). As a rule, pollution is local in nature with a relatively low background excess. An exception is Pb with an abnormally high concentration (2370 mg/kg) in one of the residential areas.

In order to clarify the geochemical structure and identify contaminated areas, a factor analysis of metal concentrations in the topsoil was performed for all samples, including those from the Krabozavodskoe site. In general, the associativity of metals in the coordinates of the main factors in the topsoil for the background areas and the Krabozavodskoe site is close to one another. The first component almost completely repeats the rock factor of metal contents in conventionally background areas. However, in the second factor, with the leading role of chalcophile metals, their association expands due to barium, which, based on statistical calculations, was assigned to the group of potential pollutants. This allows us to consider this factor as a technogenic one. According to the maximum loads on the second factor, soils characterized by the technogenic pollution are easily distinguished. These soils include 14 surface samples from an urban area. These samples show widespread contamination with Cu (up to 185 mg/kg), Zn (up to 376 mg/kg), Pb (up to 2370 mg/kg); some samples are contaminated with Ni (42.4 mg/kg), Co (34.8 mg/kg), Ba (1300 mg/kg), Sr (375 mg/kg), and Cd (0.74 mg/kg). Within the studied profiles along the tourist routes, two areas with pronounced metal contamination have been identified. First, it is the soil in the superaquatic (floodplain) position sampled in close proximity to a dirt road at PR4. It is contaminated with Cu (199 mg/kg) and has a slight excess of the content of Co (35.8 mg/kg). The second area is in the lower position of PR6, which is a recreation area for partic-

ipants in unorganized educational tourism. This topsoil sample is contaminated with Cu (389 mg/kg), Cd (1.24 mg/kg), and Pb (189 mg/kg).

The calculation of Z_c for the listed samples indicates that the soils are characterized by a low level of pollution ($Z_c = 8-16$); at the lower positions of PR6, soils have a moderate degree of pollution ($Z_c = 26$); in one of the urbanized areas, where the content of Pb in the topsoil is 2370 mg/kg, the pollution category is assessed as very severe ($Z_c = 156$).

Correlation and regression analyses confirmed the correctness of the interpretation of the technogenic factor. Correlation coefficient between the value of Z_c and loads on the technogenic factor is 0.78 (the critical value is 0.46 at $p = 0.05$). The regression analysis indicates that this dependence is approximated by a logarithmic function with the coefficient of determination $R^2 = 0.79$ (Fig. 7).

Thus, we can talk about the anthropogenic contamination of soils at sampling points 101, 103, 109, 110, 113, 114, and 122 in the area of the Krabozavodskoe settlement, as well as at sampling points 4-1 (Krabovyi Bay–Mount Gorobets) and 6-1 (central part of Shikotan, near Notoro and Tomari mounts). The points mentioned adjoin well-trodden roads; at PR4, the road leads to the old defensive fortifications. Point 6-1 is located near the parking lot on the way to Tserkovnaya Bay. The road is actively used by local residents and tourists, the presence of bonfires and parking spaces has been noted. Sampling point 101 (2 Torgovaya Street) is located in close proximity to administrative buildings, a bus stop, the private residential sector, and cattle grazing areas. Soil contamination with Cu, Pb, and Ba has been revealed. There are no significant infrastructure facilities near sampling point 103 (Krabozavodskoe settlement, corner of the Dachnaya Street and the local stream), except for the private res-

idential sector with wooden houses and metal structures, as well as a bridge over the stream. Pb, Zn and Cu pollution is probably associated with the traffic and parking of cars that drive up to the water intake point (well). An increased concentration of Lead indicates long-term contamination of the soil, copper is part of the anti-corrosion coatings of cars, zinc is used in the vulcanization of tires. Pollution at sampling site 109 (Krabozavodskoe, south of Torgovaya Street, area between Molodezhnaya and Stroitelei streets) is explained by its location a few meters from the helipad. Near sampling point 110 (bank of the stream between Lesnaya and Stroitelei streets), where littering with household waste was found, the soils are characterized by an increased content of Cu and Ba. There are no infrastructure facilities, it is possible that pollutants enter from the territory located hypsometrically higher, since the nearest buildings and the road are at a distance of a few tens of meters. At sampling point 122 (source of the Anama River), Cu inflow is caused by the oxidation of metal structures stored nearby.

According to the results of comparison of the total content of metals in soils of the Krabozavodskoe settlement and background areas, the main indicators of anthropogenic load are Cu, Zn, and Pb.

CONCLUSIONS

(1) The chemical composition of soils in Shikotan is characterized by significant contrasts and depends on the composition of parent rocks, landscape-geochemical position, and, to some extent, oceanic influence. The soils have high natural contents of femaphile elements Sc, V, Fe, Cu, and Zn exceeding corresponding clarke values. The concentrations of K, Cr, Ni, Sr, and Ba are below clarke valuers, and the concentrations of Ca, Mo, Cd, and Pb are comparable to clarke values.

(2) The leading factor determining the migration and accumulation of elements in the soils of Shikotan is the soil pH, which depends on the proportion between mafic and intermediate rocks in the composition of parent materials. On basaltoids, alkalization of soil solutions is noted, which reduces the migration of metals and leads to an increase in soil tolerance towards chemical pollution. On andesites (basaltic andesites), acidification of soils and a decrease in their buffer capacity are pronounced.

(3) Landscape and geochemical differentiation of the territory is determined by different types of soils and diversity of plant communities. The maximum concentrations of Na, Mg, K, Ca, V, Co, Cu, Sr, and Ba are characteristic of petrozems (both in organic-accumulative and in the middle-profile horizons). In

meadow-soddy soils under halophytic communities, accumulation of Pb is noted. In burozems and podburs, the concentration of metals mainly corresponds to the average background values. The change in the content of metals in the humus horizons is due to the change in plant communities (alder, birch, and fir–spruce forests and halophytic meadows). In podburs and burozems under alder communities, the concentrations of Co, Mg, K, V, Fe, Ni, Cu, Ba, and Zn are higher. Soils under fir–spruce forests are characterized by the high Cr content. Soils of halophytic meadows concentrate Na, Ca, Sr, and Pb.

(4) Under conditions of a humid climate and dissected relief, lateral migration of metals proceeds not only in the form of soluble salts but also in the mechanical form leading to differentiation of lithophile and siderophile elements along the catena. Cr, Co, and Ni are fixed in the humus horizons of subordinate landscapes, while Cd and Pb tend to accumulate in the surface horizons of autonomous landscapes. In the soils of marine terraces, where the influence of oceanic air masses is significant, there is an increase in the acid–base index and in the concentration of metals, the cations of which are part of sea water: Na, Mg, K and Ca.

Anthropogenic pollution of soils, identified on the basis of statistical analysis, is of a local nature. Among the studied metals, potential pollutants on the Shikotan island are Co, Ni, Cu, Zn, Sr, Ba, and Pb. Most of the soil samples from the urbanized area and two samples from the tourist trails are characterized by the high contents of metals. Motor vehicles are the main source of pollution.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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