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Origin, baseline contents, and vertical distribution of selected trace lithophile elements in soils from nature reserves, Russian Far East

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Abstract

Purpose Despite extensive studies, little is known about the natural trace lithophile element contents and the relationship between contents of these elements and soil properties in the natural environment. The objectives of this study are as follows: (i) to quantify the natural baseline total trace lithophile element contents in soils, (ii) to identify the main factors controlling the vertical distribution and accumulation of elements, and (iii) to evaluate the anthropogenic influence on the soils in the territory of reserves.

Materials and methods In this work, we collected 42 soil samples from conditionally pollution-free Dystric Cambisols of three large natural reserves on the coast of the Russian Far East. Soil samples were analyzed for total trace lithophile elements (Ga, Rb, Sr, V, Y, and Zr), total oxides of some major elements (Si, Al, Fe, and Mn), pH(KCl), organic C, total H, and clay content. The total contents of elements were determined via energy dispersive X-ray fluorescence spectroscopy. The correlations between soil properties and contents of the trace lithophile elements were analyzed. Estimation of additional inputs of trace lithophile elements from external sources was assessed by using corrected technogenic index (*Tg*) of the elements.

Results and discussion Natural baseline total element contents (mg kg^{-1}) were as follows: Ga (5.77–7.27), Rb (68.72–113.55), Sr (56.14–154.70), V (106.90–168.99), Y (18.02–20.98), and Zr (189.74–249.28). Rubidium and Y in soils from all reserves include additions from external sources. These elements tended to accumulate in the upper parts of the soil profiles. Contents of Rb and Y were dependent largely on organic C content, total H content, and Mn-containing compounds of soil. In the territories with the maximum levels of *Tg*, we identified increased associations of total soil Ga and Sr with organic C content and Mn-Fe-containing compounds, Zr with Fe-containing compounds. Distribution and accumulation of V were mainly controlled by natural soil-forming factors and were mostly dependent on Al_2O_3 and SiO_2 contents in soils.

Conclusions The levels of trace lithophile element contents in the soils from natural reserves depend on the mixed influence of natural environmental conditions (main soil-forming factors, peculiar geographic area) and additional inputs of elements originating from atmospheric deposition of long-distance transported pollutants. Technogenic index (*Tg*) indicated progressive contamination of soils from all reserves by Rb and Y, and local contamination of soils by Ga, Sr, and Zr. In our study, V was an uncontaminated element.

Keywords Cambisols · Contamination of soils · Technogenic index of elements · Trace lithophile elements

1 Introduction

Gallium (Ga), rubidium (Rb), strontium (Sr), vanadium (V), yttrium (Y), and zirconium (Zr) are trace lithophile elements (have an affinity for silicate phases) according to the Goldschmidt classification of the elements (White 2013). These elements naturally occur in varying contents in soils.

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Numerous studies have been shown that the contents of Ga, Rb, Sr, V, Y, and Zr are largely dependent on the mineralogical composition of the parent material of soils (Egli and Fitze 2000; Wang et al. 2009; Horbe and Anand 2011; Kabata-Pendias 2011). Most studies have demonstrated a low mobility of trace lithophile elements during chemical weathering and pedogenesis, and as such, they generally pose no risk to the natural environment (Adriano 2001; Tyler 2004; Muhs et al. 2007; Feng 2011). However, some studies have revealed a relationship between contents of Ga, Rb, Sr, V, Y, and Zr in soils and anthropogenic impacts on soils (Vodyanitskii et al. 2010; Molchanova et al. 2013; Reijonen et al. 2016). Soils in different parts of the world, particularly in urban and industrial regions, contain high contents of these elements. Galium, Rb, Sr, V, Y, and Zr may enter the air, water, and soil from anthropogenic sources such as steel production, copper metallurgy, glazed ceramic production, petrochemical plants, combustion of fuel-oil, fertilizers, and urban solid and liquid waste (Querol et al. 2007; Vodyanitskii et al. 2010; Scheib et al. 2013; Reijonen et al. 2016). Strontium and V are potentially dangerous for the natural environment. The toxic Sr level for biota has not been completely established because of insufficient evidence about deleterious effects on biota of the high levels of stable Sr in the biosphere (Kabata-Pendias and Pendias 2001; Sasmaz and Sasmaz 2009). Strontium has a similar action to Ca and Sr plays a similar role in many cellular metabolic possesses. Concentration of vanadium above than 2 ppm (for some bush beans above than 13 ppm) in plants and above than 140 ppm in the soil solution are toxic for the plants as high concentrations of V cause chlorosis and limit growth (Ivanov and Kashin 2010; Kabata-Pendias 2011). Vanadium with oxidation states +5 is more toxic for plant and biota, which may be attributable to the analogy of V(+5) with phosphate and consequently to inhibition of various phosphatases, ATPases, and other important enzymes (Leonard and Gerber 1994; Assem and Levy 2009). Vanadium (+5) is plant-available species of V in soils. Recently, it was shown that concentrations of this species of V increased with increasing total V contents in V-contaminated soils (Reijonen et al. 2016). The hazard class of Sr and V varies from low hazardous (in Russia) to most hazardous (UNEP), according to the toxicological classification of elements of different countries and organizations (Vodyanitskii 2012). Gallium, Rb, Y, and Zr are considered as “immobile elements” of soils, and a hazard class of these elements has not been established.

Studies of the trace lithophile element contents in soils have demonstrated the existence of dependence between distribution and accumulation of these elements in soil profiles and physical, physico-chemical, and chemical soil properties (Tyler and Olsson 2001; Fox and Doner 2002; Stiles et al. 2003; Ivanov and Kashin 2010; Feng 2011; Kabata-Pendias 2011; Jeske and Gworek 2012). Nonetheless, the main trends of behavior of trace lithophile elements in soils are currently unclear because of the location-specific environment and different pedogenic processes that affect both natural contents of elements and the dynamics of their anthropogenic flow. The contents of Ga, Rb, Sr, V, Y, and Zr have been examined in different soils and are documented in some literature sources (Poledniok and Buhl 2003; Tyler 2004; Mao et al. 2009; Vodyanitskii et al. 2010; Feng 2011; Kabata-Pendias 2011; Shahid et al. 2013; Reijonen et al. 2016). Such results have demonstrated the wide range of content levels of elements: Ga from 2 to 70 mg kg^{-1}, Rb from 5.9 to 1141 mg kg^{-1}, Sr from 12 to 3100 mg kg^{-1}, V from 10 to 500 mg kg^{-1}, Y from 2.7 to 100 mg kg^{-1}, and Zr from 12 to 366 mg kg^{-1}. Few soil-specific studies have shown that trace lithophile elements were associated with mineral and organic compounds of soils and the relationship with these elements varies depending on environmental conditions (Folkeson et al. 1990; Tyler and Olsson 2002; Stiles et al. 2003; Kabata-Pendias 2011; Sadeghi et al. 2013). Chemical, physical, and mineralogical compositions of soils depend on pedogenic processes. Therefore, the content, distribution, accumulation, and association of trace lithophile elements with reactive phase-carriers of soils may greatly vary among the soil types.

We examined soils (Dystric Cambisol) formed on the territory of three large reserves from the west coast of the Pacific Ocean (the Primorye Region of Far East Russia). Most studies of trace lithophile elements in soils from the Pacific region (e.g., from China and the Far East of Russia) have been performed on soils from urban and agricultural areas, and such data cannot provide comprehensive information about the natural background contents of trace lithophile elements and whether anthropogenic activities have altered element contents in soils. Cambisols that have formed in uncontaminated fields are ideal material for investigating the natural baseline trace lithophile element contents and migratory cycles of trace lithophile elements in the pedosphere under natural conditions. Generally, soils from reserves are regarded as having no known anthropogenic additions, but territories of reserves may be subject to deposition of different pollutants (including trace lithophile elements) that are transported over long distances with aerosols and wind-transported dust. The results of few studies have indicated inputs of many elements with atmospheric particulate matter in soils collected from areas that have had minimal exposure to anthropogenic activities (Tyler 2004; Querol et al. 2007; Scheib et al. 2013; Hardy et al. 2015). In a regional study, Chudaeva et al. 2008 and Kondrat’ev et al. 2017 documented the concentrations of Ga, Rb, Sr, and V in atmospheric precipitation using 71 sampling sites from across the Far East Russia. In their study, they noted increased concentrations of these elements in atmospheric precipitation under conditions of regional human-induced pollution (in the southern part of the Russian Far East) and under the influence of cyclones which were formed in the polluted atmosphere of East Asia and moved over the Yellow Sea and Sea of Japan. However, there are presently no comprehensive studies on the influence of atmospheric deposition on trace lithophile element contents in the soils in the territory of reserves. Cambisol is the prevalent soil type in the studied region, and data about the specific sorption of trace lithophile elements by the different soil phases can be extrapolated to Cambisol under different land uses.

The objectives of this study are as follows: (i) to quantify the natural baseline total trace lithophile element contents in soils from natural reserves; (ii) to identify the main factors controlling the vertical distribution and accumulation of elements in soil profiles; (iii) to evaluate the anthropogenic influence on the soils in the territory of reserves. We present new data about peculiarities of contents of trace lithophile elements in Cambisols from reserves and show that atmospheric deposition is the significant contributor to some trace lithophile element contents in the soils of these reserves.

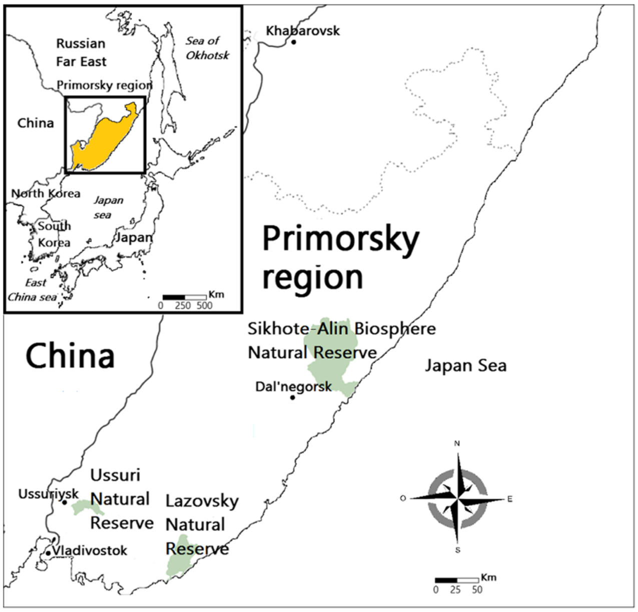

Fig. 1 Map showing sampling locations

2 Materials and methods

2.1 Site description

Soils were sampled from unpolluted areas on the coast of the Russian Far East (Fig. 1). The uncontaminated fields were located in the Sikhote-Alin Biosphere Nature Reserve territory, in the Lazovsky Nature Reserve territory, and in the Ussuri Nature Reserve territory (Table 1). Compared to other reserves, these territories are not influenced by any direct anthropogenic activities. The nature reserves were formed on the territory of a large massif of virgin coniferous–broadleaved forests, which are considered as natural and do not have analogues in North-East Asia (Seledets 2011).

The Sikhote-Alin Biosphere Nature Reserve is located in the central part of the Sikhote-Alin mountain chain. The central ridge of the Sikhote-Alin mountain chain divides the reserve into two large massifs: coastal, occupying the eastern slopes of the mountain chain, and continental, located on the western slopes of the mountain chain. Acidic effusive rocks, granites, sandstones, siltstones, gravelites, conglomerates, lenses siliceous–clayey shales, and limestones dominate this territory (Gracheva 2012; Kostenkov et al. 2016). The major part of the Lazovsky Nature Reserve territory is located in the eastern slope of the Sikhote-Alin mountain chain. The eastern part of this reserve is located at the coast of the Japan Sea. Soil formation materials are sandstone, siltstones, and granites in the mountainous territory and loamy and sandy–loamy derivatives of the Upper Cretaceous effusive rocks in the coastal territory (Semal et al. 2012) The Ussuri Nature Reserve is located in the southern part of the Sikhote-Alin mountain chain. Soil-forming materials are siltstones, sandstones, mudstones, alluvial deposits, limestones, and basalts (Semal 2007; Semal 2010).

The climate of the study area is influenced by the monsoon. In January, north, north-west, and west winds dominate whereas in July, the winds are from the south, south-east, and east. The winter climate is arid and frosty, with an average air temperature in January − 13 °C and a humidity of 26 to 48%. The summer monsoon climate is cloudy and rainy with an average air temperature in August of 19 °C and a humidity of less than 80%. Most precipitation occurs from August to September when the typhoons bring in significant rains. The hydrology is characterized by desiccation in spring and humidification in summer and at the beginning of autumn (Timofeeva et al. 2014).

2.2 Soil characterization

The soil used in this study is typical for the southern part of the Russian Far East. It is a Dystric Cambisol according to the World Reference Base for Soil Resources (World Reference Base for Soil Resources 2006). The Dystric Cambisol has formed in the territories of all studied reserves and is constituted by five horizons (A, Bw1, Bw2, BC, and C) (Fig. 2). The location of the soil favors regular saturation from atmospheric precipitation and surface runoff. Gley features (olive and whitish mottles) are absent in the soil profile, which points to short-term soil waterlogging (Timofeeva et al. 2014).

Table 1 Geographic and climatic data for Dystric Cambisols used in this study

Reserve	Geographic location	Ambient temperature (°C)		Annual precipitation (mm)
		January	August	
Sikhote-Alin Biosphere Nature Reserve	44° 95′ 80″ N 136° 55′ 19″ E 44° 95′ 03″ N 136° 55′ 15″ E 44° 95′ 91″ N 136° 558′ 586″ E 44° 97′ 52″ N 136° 56′ 93″ E	− 12,4	+ 19,1	from 650 to 800
Lazovsky Nature Reserve	43°30′18″ N 134° 00′ 05″ E 43° 28′ 29″ N 134° 05′ 39″ E 43° 26′ 91″ N 134° 02′ 32″ E 43° 25′ 67″ N 134° 00′ 29″ E	− 12,5	+ 19,4	from 667 to 731
Ussuri Nature Reserve	43° 61′ 93″ N 133° 41′ 74″ E 43° 67′ 51″ N 132° 49′ 34″ E 43° 68′ 40″ N 132° 71′ 14″ E 43° 61′ 49″ N 132° 36′ 45″ E 43° 61′ 82″ N 132° 36′ 51″ E 43° 55′ 03″ N 132° 85′ 34″ E	− 15,9	+ 19,7	from 700 to 800

2.3 Soil sampling

Soils were collected from May to September 2014 from 14 soil profiles. The soil pits were dug by hand and the soils were sampled from the main genetic horizons. Samples were ground using the planetary ball mill Pulverisette 5 (Fritsch GmbH) to obtain a powder. Prior to X-ray spectroscopy measurements, the powder was pressed into pellets (3.5 g) using a pressure of 8 to 15 Mg. The pellets were placed on circular sheets of Mylar X-ray polyethylene film. For the H content analysis, the powders were wrapped in tin capsules (5 × 8 mm).

2.4 Elemental analysis

Total SiO_2, Al_2O_3, Fe_2O_3, MnO, Ga, Rb, Sr, V, Y, and Zr contents were determined via energy dispersive X-ray fluorescence spectroscopy (EDX) using a Shimadzu EDX-800HS-P instrument (Shimadzu EUROPA GmbH) equipped with a rhodium X-ray tube (settings: vacuum, voltage 50 kV, current 100 mA, detection time 300 s, dead time 20%, and a collimator of 10 mm). Data were analyzed using PCEDX Shimadzu software. The elements were measured by K-line emission. Eight certified reference standard soil samples (901–76, 902–76, 903–76, 2498–83, 2499–83, 2500–83, 2507–83, 2509–83) from the Institute of Applied Physics of Irkutsk State University were used to obtain calibration curves and to assess the analytical recovery and precision. Soil standards with similar matrices were used for the construction of the calibration curves to avoid the matrix effect. Validation of calibration curves constructed for elements present in the standards was performed through analysis of standard reference materials. One standard soil sample (2499–83) was included for every five unknown samples. The certified values for the standard soil were as follows: SiO_2 (91.24%), Al_2O_3 (3.36%), Fe_2O_3 (0.99%), MnO

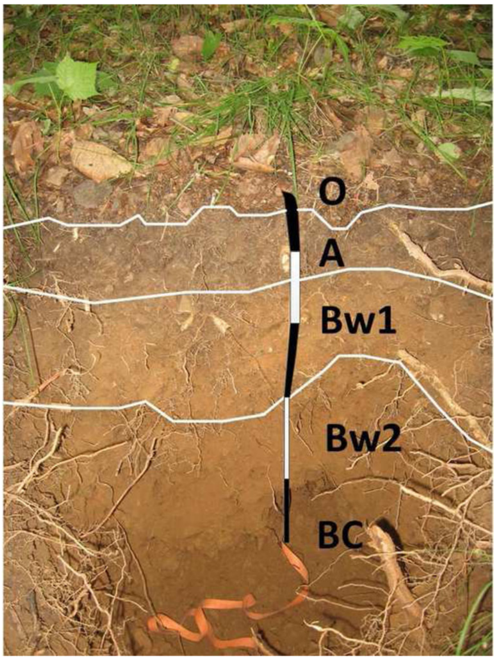

Fig. 2 View of the Dystric Cambisol profile

(0.011%), Ga (5 ppm), Rb (320 ppm), Sr (69 ppm), V (140 ppm), Y (13 ppm), and Zr (350 ppm). Acceptable recoveries for the standards were ± 9% of the certified values.

Analysis of total H content was performed using a Flash 2000 elemental analyzer (Thermo Scientific) with a CHNS configuration. Elemental data were analyzed using the Eager Xperience software. The samples were analyzed in a quartz reactor at 900 °C with a column temperature of 65 °C. Helium and oxygen flow rates into the reactor were 140 and 100 mL min^{-1}, respectively. The time cycle was 380 s and the oxygen injection time was 15 s. The organic analytical standard for Cystine (OAS 134139) and the K Factor calibration method were used for quality control. Organic C was determined on dried (105 °C) samples, using a TOC-L analyzer (Shimadzu) with a CSN configuration and a module for solid sample measurement, SSM-5000A.

2.5 Soil properties

The color of moist and dry soil samples was estimated using Munsell Soil Color Charts (Munsell Soil Color Charts 1990). The color of different samples was estimated simultaneously at comparable light conditions. Soil pH was measured electrometrically in a 1:2.5 soil/1 M KCl solution after shaking 10 g of air-dried soil powder for 1 h. The pipette method was used to determine particle size less than 2 μm distribution of each soil sample. The physico-chemical analysis procedures used in this study have been previously described in detail (Pansu and Gautheyrou 2006). Clay minerals were identified by X-ray diffraction analysis in dry soil powder. The samples were analyzed using a Rigaku MiniFlexII X-ray diffractometer (Rigaku).

2.6 Statistical methods

Each analysis was performed with three parallel probes to identify the adequate iteration number. The data were processed statistically (median value and regression analyses) using Microsoft Excel and SPSS software (SPSS Inc., version 16, 2007). Analysis of variance was used to determine significant differences and correlation matrices for the trace lithophile elements, major elements, and selected soil properties. The significance level (P) did not exceed 0.05. The corrected index of the technogenic (Tg) was calculated as the ratio of total element content in the upper horizons (A) of the soil profiles (MeA) to its content in the lower horizons (BC) of the profiles (MeBC) and normalized with the content of aluminum (Vodyanitskii et al. 2010):

$$Tg = 100\left[\frac{\left(\left(\frac{MeA}{AlA}\right):\left(\frac{MeBC}{AlBC}\right)-1\right)}{\left(\frac{MeA}{AlA}\right):\left(\frac{MeBC}{AlBC}\right)}\right]\%$$

3 Results and discussion

3.1 Soil properties

The mean value and range of the main chemical and physical properties and morphological characteristics of the Dystric Cambisols of the reserves are presented in Tables 2 and 3. Soil texture varied from heavy loam and light clay in the upper soil horizons to medium and heavy clay in the middle horizons. The content of clay was lowest in the lower horizons (BC). Lower soil horizons contained significant part weathered parent material which was estimated by field inspection from 45 to 70 vol.% in the BC horizons. The soils are characterized by significant weathering processes, increasing the accumulation of the clay fraction in the middle part of the soil profiles. The clay minerals of the Dystric Cambisols were largely represented by illite, kaolinite, and montmorillonite. Montmorillonite was observed in small quantities at a proportion of 1 (montmorillonite):5 (illite and kaolinite). Soil acidity varied from acidic to slightly acidic, with pH(KCl) ranging from 3.08 to 5.82. The level of pH depends on the content of H^+ ions in the soil solution, and a parameter that deserves to be mentioned here is total H content, which ranged from 0.10 to 0.95%. The quantitative distribution of total H in the soil was characterized by a sharp decrease from the upper to the middle and lower parts of the soil profile. Soil organic C varied greatly, ranging from 0.08 to

Table 2 Chemical, physico-chemical, and physical properties of the Dystric Cambisols

Soil properties	Horizon	pH(KCl)	Clay (g kg^{-1})	H (%)	OC (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)
Sikhote-Alin Biosphere Nature Reserve	A	3.91 (3.50–4.55)†	270.71 (246.83–320.58)	0.54 (0.39–0.71)	2.54 (2.28–3.38)	51.83 (51.74–52.68)	12.51 (12.30–13.07)	5.08 (4.64–6.28)	0.08 (0.08–0.09)
	Bw1	4.36 (4.04–4.82)	371.52 (339.16–408.36)	0.23 (0.14–0.37)	0.61 (0.32–1.15)	54.04 (51.16–57.77)	13.77 (12.37–16.21)	5.69 (5.25–7.05)	0.07 (0.06–0.09)
	Bw2	4.48 (4.16–5.07)	491.70 (441.18–547.21)	0.28 (0.24–0.39)	0.56 (0.22–1.06)	55.13 (52.77–58.20)	14.02 (11.92–16.80)	4.21 (4.10–5.27)	0.07 (0.06–0.08)
	BC	3.82 (3.26–4.23)	208.52 (177.12–243.53)	0.27 (0.20–0.37)	0.17 (0.10–0.25)	57.71 (52.13–64.69)	15.13 (14.02–16.49)	5.12 (4.32–5.60)	0.05 (0.04–0.06)
Lazovsky Nature Reserve	A	4.14 (4.06–4.43)	292.6 (261.66–336.71)	0.81 (0.77–0.95)	4.29 (3.62–6.10)	51.46 (45.57–64.62)	10.81 (9.50–12.76)	4.07 (3.39–5.33)	0.31 (0.21–0.45)
	Bw1	4.17 (4.14–4.28)	418.03 (354.99–492.65)	0.21 (0.18–0.29)	0.52 (0.37–1.16)	52.88 (37.66–69.31)	9.27 (7.63–11.19)	2.77 (2.35–3.06)	0.11 (0.10–0.14)
	Bw2	4.19 (3.94–4.54)	523.18 (479.04–571.47)	0.27 (0.26–0.28)	0.21 (0.25–0.5)	72.20 (71.66–73.78)	12.04 (11.22–13.81)	3.12 (3.17–3.64)	0.05 (0.05–0.06)
	BC	3.61 (3.08–4.19)	254.33 (216.99–299,95)	0.26 (0.18–0.38)	0.09 (0.08–0.11)	78.50 (72.89–86.08)	14.60 (12.97–16.51)	3.69 (3.22–4.40)	0.06 (0.05–0.07)
Ussuri Nature Reserve	A	4.76 (3.81–5.82)	281.13 (269.79–302.81)	0.59 (0.46–0.85)	2.44 (0.69–7.22)	54.31 (50.31–58.38)	11.93 (10.49–15.92)	5.79 (5.73–7.78)	0.11 (0.08–0.15)
	Bw1	4.58 (3.77–5.52)	452.49 (408.63–512.70)	0.27 (0.12–0.51)	0.60 (0.54–1.27)	59.36 (47.30–71.09)	12.77 (10.92–15.86)	6.03 (5.05–10.29)	0.08 (0.04–0.17)
	Bw2	4.55 (3.67–5.62)	561.82 (506.99–624.42)	0.28 (0.10–0.53)	0.47 (0.29–1.27)	58.66 (45.41–64.76)	13.91 (12.35–18.81)	6.47 (5.55–10.52)	0.07 (0.06–0.14)
	BC	4.09 (3.41–4.60)	185.69 (144.07–238.30)	0.28 (0.16–0.43)	0.12 (0.08–0.18)	66.12 (61.51–74.29)	15.01 (13.83–16.43)	6.82 (5.79–7.63)	0.05 (0.04–0.06)

† Mean values (in brackets total range)

7.22%. We observed an abrupt decrease in the organic C content from the surface horizon to the underlying layers. Contents of Si oxide and Al oxide ranged from 37.66 to 86.08% and from 7.63 to 18.81%, respectively. The contents of these oxides increased in the lower horizons. Iron and manganese oxide contents also varied greatly (from 2.35 to 10.52% and from 0.04 to 0.45%, respectively). The upper parts of the soil profiles had the highest contents of Mn oxide. We did not observe a clear relationship between Fe oxide and the depth of the soil horizons. A different vertical distribution of Fe oxide was observed at different sampling sites. The soils of the Sikhote-Alin Biosphere Nature Reserve and the soils of the Ussuri Nature Reserve had higher contents of Fe oxide in the medium and lower soil layers, and the soils of the Lazovsky Nature Reserve exhibited a higher content of Fe oxide in the upper parts of the soil profiles.

3.2 Trace lithophile element contents

The total contents of trace lithophile elements were determined using the EDX method. Results of numerous studies suggested that this method is acceptable for quantitative measurement of trace lithophile elements in soils and EDX method widely used across international projects such as "Geochemical mapping of agricultural and grazing land soils" (Stiles et al. 2003; Sadeghi et al. 2013; Scheib et al. 2013; Bezuglova et al. 2016).

The assessment of the trace lithophile elements contents is difficult because of the limited information about natural background contents for trace lithophile elements in soils of Russia. To our knowledge, contents of the studied elements have not been reported previously from natural soils of reserves in the Russian Far East. The soil chemistry is presented in Table 4. The average abundance of trace lithophile elements in the studied soils was as follows: Zr > Sr > Rb > V > Y > Ga.

The trace lithophile element contents in the Dystric Cambisols were compared with relevant literature data about mean values of elements in soils of Russia, reported by Vinogradov (1962). Additionally, we compared our results (i) with contents of elements in Swedish forest soils (Dystric and Eutric Cambisols) with similar main soil formation processes and little anthropogenic influence and (ii) with median values (for Y and Zr) in agricultural and grazing-land soils of Europe (Tyler and Olsson 2002; Sadeghi et al. 2013; Scheib et al. 2013).

Our data indicate that in the three natural reserves, the soil profiles show similar contents of Ga and Y. The contents of Rb, Sr, V, and Zr were highly variable among the soils collected from different locations. Contents of Y ranged

Table 3 Morphological characteristics of representative horizons of the Dystric Cambisols

Horizon	Medium thickness (cm)	Color moist	Color dry	Other characteristics
A	15	From dark gray 5YR 4/1 to dark reddish gray 5YR 4/2	Light gray 7.5YR 7/1	Homogenously colored; fine-loamy; fine-grained structured; loose; found a few slightly weathered parent material up to 2 cm; a clear color change, wavy boundary
Bw1	35	Reddish brown 5YR 4/3	Light brownish gray 10YR 6/2	Unevenly colored with a few reddish gray mottles; loamy; fine-grained structured; dense, bit; a lot of gruss and crushed rocks found slightly weathered parent material up to 5–6 cm; a clear color change, wavy boundary
Bw2	25	Dark gray 5YR 4/1	Reddish brown 5YR 5/2	Homogenously colored; loamy; a lot of gruss and crushed stone, found medium weathered fragment of rocks; a clear color change, wavy boundary
BC	15	Grayish brown 10YR 5/2	Brown 7.5YR 5/3	Unevenly colored with a numerous reddish brown mottles up to 3 cm; loamy; dense; found a crushed stone up to 3 cm; a clear color change, wavy boundary
C	–	Dark brown 7.5YR 3/4	Strong brown 7.5YR 5/6	Homogenously colored; dense; consisted of large pieces of the parent material

from 10.82 to 34.89 mg kg^{-1}; the content ranges of Y in soils from reserves are well within the range reported for the soils of Russia and Europe, with no statistically significant differences between the sampling sites. Levels of Ga and Sr ranged from 3.07 to 12.78 mg kg^{-1} and from 26.49 to 208.35 mg kg^{-1}, respectively. The soils of the Lazovsky Nature Reserve had low total contents of Sr. Mean values for Ga and Sr were approximately two times lower than those measured in Russian soils. These differences were probably due to differences in contamination inputs. The study by Vinogradov (1962) presented data for many regions of Russia, finding different contamination values, while the present study used data from territories that were far away from large cities and industrial areas. In our study, contents of V and Zr ranged from 79.22 to 277.56 mg kg^{-1} and from 118.02 to 331.40 mg kg^{-1}, respectively. The maximum content for V occurred in the Dystric Cambisols of the Ussuri Nature Reserve. Contents of V in our soils were higher than the ranges presented by Tyler and Olsson (2002) and were higher than mean values of V in soils of Russia in the territory of the Ussuri Nature Reserve. The higher V content is naturally derived from local parent material with mean values of this element from 148.59 to 184.81 mg kg^{-1} in the C horizons (Fig. 3). The mean values of Zr show similar concentrations in studied soils and agricultural and grazing-land soils of Europe, while the content of Zr in Swedish forest soils is lower than those in soils from reserves. Zirconium in soils shows an affinity for mineral phase of soils (i.e., sand and coarse silt fraction) (Stiles et al. 2003). The analysis of the content and distribution of Zr in the upper horizons of agricultural and grazing-land soils of Europe revealed that aeolian depositions with many very fine sand-sized zircon grains is the important source of Zr (Scheib et al. 2013). Rubidium levels ranged from 37.89 to 152.77 mg kg^{-1}. Elemental analysis revealed that soils from the Sikhote-Alin Biosphere Nature Reserve contained higher contents of Rb than soils of other reserves. Contents of Rb in the studied Cambisols were higher than the ranges reported for the forest soils of Sweden and for the soils of Russia. Kabata-Pendias (2011) found the highest mean Rb content in soils over granites, gneisses, and alluvial materials, while soils with less Rb had mainly developed on sandy and clayey deposits. The basic minerals composed of parent materials and the contents of Rb in the horizon C agree with tendency found by Kabata-Pendias (2011).

The C horizons were the least weathered horizon of the studied soils. It consisted of large pieces of the parent material. The total contents of trace lithophile elements in the C horizons were (mg kg^{-1}): Ga (6.34–6.79), Rb (75.17–101.48), Sr (121.72–185.64), V (148.59–184.81), Y (16.51–17.62), and Zr (208.41–271.30) (Fig. 3). The abundance of trace lithophile elements in the C horizons of studied soils is consistent with the contents of these elements in sedimentary rocks and in acid rocks. In general, the differences between the contents of trace lithophile elements in soils from different sampling sites are related to the contents of elements in the C horizons.

3.3 Trace lithophile element distribution profiles

The levels of most elements in the studied soils varied with depth (Fig. 3). Investigations of the depth profiles demonstrated that the contents of Rb and Y were highest at surface horizon A. Somewhat increasing Rb contents in the upper horizon have previously been shown for Haplic Podzol (south Sweden) that

Table 4 Comparison of average baseline trace lithophile element contents and ranges of the Dystric Cambisols with other published baseline contents in soils

Studies	Trace lithophile element contents					
	Ga mg kg^{-1}	Rb	Sr	V	Y	Zr
This study	Sikhote-Alin Biosphere Nature Reserve					
	6.67 (3.07–10.17)[†]	113.55 (84.99–152.77)	149.72 (104.83–181.55)	106.90 (79.22–134.83)	19.99 (10.82–34.89)	189.74 (118.02261.16)
	Lazovsky Nature Reserve					
	5.77 (3.43–9.52)	89.01 (62.44–122.53)	56.14 (26.49–88.15)	109.16 (86.14–163.50)	18.02 (12.48–32.18)	249.28 (174.30–331.40)
	Ussuri Nature Reserve					
	7.27 (4.13–12.78)	68.72 (37.89–112.36)	154.70 (102.72–208.35)	168.99 (116.94–277.56)	20.98 (12.51–31.44)	224.55 (175.51–284.39)
Contents of elements in Swedish forest soils (Tyler and Olsson 2002)	5.4 (2.2–7.9)	18.8 (5.9–51.0)	48.00 (11.0–190.0)	31.1 (12.9–59.3)	10.00 (4.9–17.6)	7.00 (1.8–12.1)
Contents of elements in agricultural and grazing-land soils of Europe (Sadeghi et al. 2013; Scheib et al. 2013)					26 (3.0-118.0)	281 (4.0–963.0)
Mean values of elements in soils of Russia (Vinogradov 1962)	17	60	300	100	20	300

[†] Mean values (in brackets total range)

had formed on a territory without major local sources of pollution (Tyler 2004). According to Nowack et al. (2001), greater contents of metals in the upper horizon relate to the cycling of metals in the soil–plant environment. However, the biological functions of Rb and Y are unconsidered. Several studies have reported accumulation of these elements in different types of plants, mosses, and lichens (Kabata-Pendias and Pendias, 1989; Tyler 2005). At the same time, high contents of elements in the upper horizons may be a result of atmospheric deposition (Suttona et al. 2002; Tyler 2004; Jolly et al. 2013; Hardy et al. 2015). In addition, Vodyanitskii et al. (2010) have observed that accumulation of Y in the upper part of the soil profile was related with increased contamination inputs in soils with techno-geochemical anomalies in Russia (Vodyanitskii et al. 2010).

Other trends of vertical element distribution were found for Ga, Sr, V, and Zr. The distribution of Ga throughout the soil profiles was homogeneous in the Dystric Cambisols of the Sikhote-Alin Biosphere Nature Reserve and the Lazovsky Nature Reserve. In the soils from Ussuri Nature Reserve, there is a tendency towards somewhat higher values of Ga in the upper horizons (Fig. 3). Strontium distribution in individual horizons exhibited different features for different sampling sites. Content of Sr were the highest in the upper horizons of the soils from the Lazovsky Nature Reserve. However, pronounced secondary peak of this element was found in the BC horizons. The Dystric Cambisols of the Ussuri Nature Reserve had relatively distinct content peaks of Sr in the Bw2 and BC horizons. Within profiles of soils in the Sikhote-Alin Biosphere Nature Reserve, contents of Sr slightly increased in the middle parts of the soil profiles (horizons Bw1, Bw2). It has previously been reported that Sr is easily mobilized during weathering processed in soils and that the distribution of Sr in soil profiles depends on the circulation of the soil solution (Kabata-Pendias and Pendias, 1989). However, enrichment of surface soils with Sr could be shown in industrial areas (input of polluting aerosols) and in coastal areas (input of sea salt) (Kabata-Pendias 2001; Vodyanitskii et al. 2010). Several studies of V distribution in different soil types have demonstrated accumulation of V in organic-rich layers of soil profiles (Tyler 2004; Feng 2011). In the present study, however, we did not observe such a trend. Figure 3 shows that the content of V increased with depth, and the highest amount was found in the middle and lower parts of the soil profiles. A similar behavior of V in soil has previously been indicated by Ivanov and Kashin (2010) in the landscapes of western Transbaikalia, where V was frequently co-associated with loam and clay (Ivanov and Kashin 2010). Analysis of the Zr distribution revealed increases of this element in the horizons BC of the soil profiles. Previous studies performed on uncontaminated soils have demonstrated higher solubility of Zr in the middle and lower parts of the profiles of Haplic Podzol (Tyler 2004). Zirconium is considered an immobile element in soils, and the distribution of Zr in the soil profile is related to weathering processes of primary minerals (Egli and Fitze 2000; Muhs et al. 2007). Highest total contents in the C horizons from all studied soils had Sr and V. In addition, Zr had its peak in this horizon in the Dystric Cambisols of the Ussuri Nature Reserve.

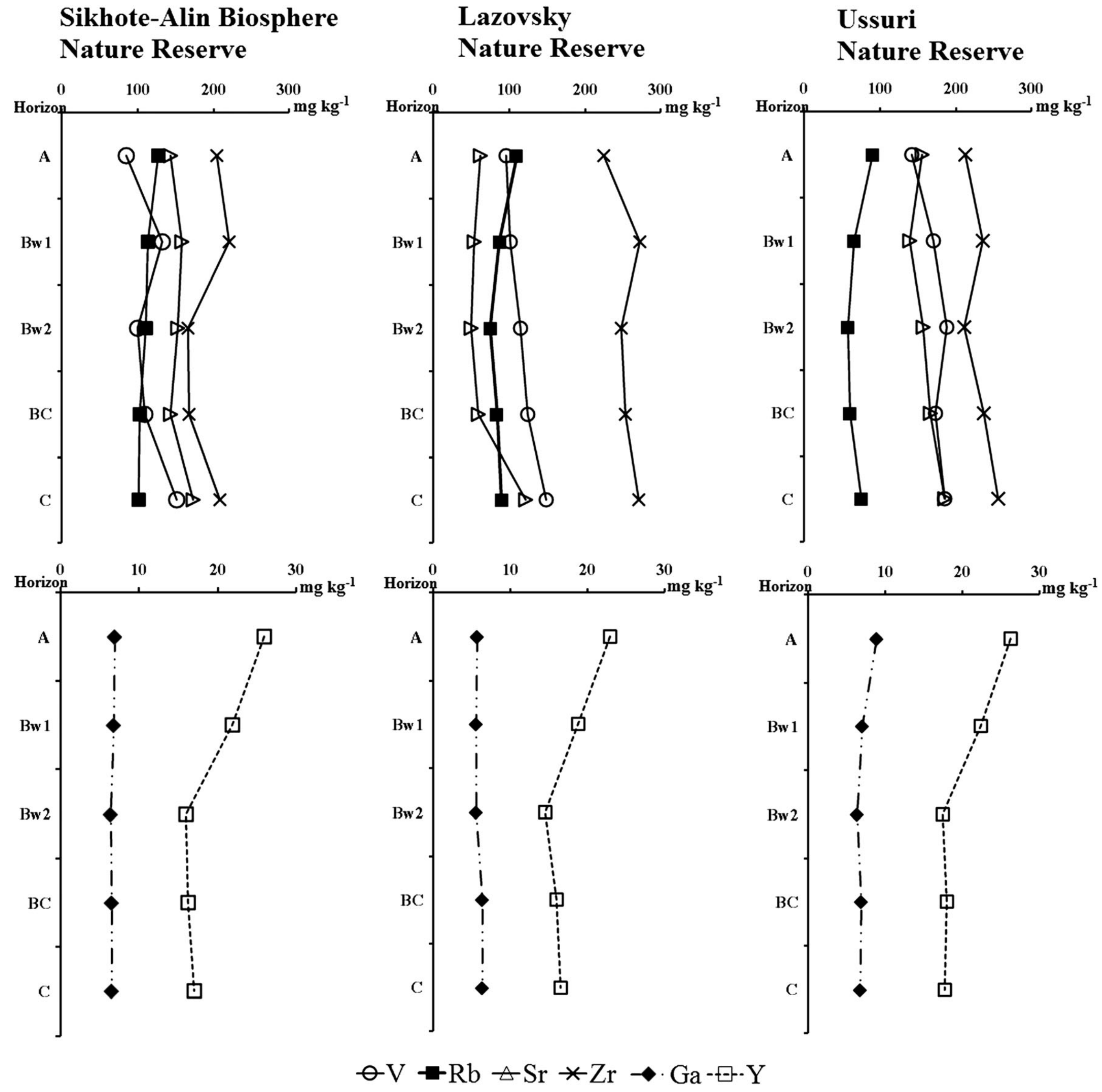

Fig. 3 Vertical distribution of trace lithophile elements in the Dystric Cambisols

3.4 Correlations of soil properties with trace lithophile elements

Analysis of the relationship between soil properties and contents of the trace lithophile elements revealed a complex relationship with different elements in different sampling sites (Fig. 4). In the present study, a similar trend of associations of Ga, Rb, and Y with soils properties was found for soils from all natural reserves. Significant correlations were observed between elements and several soil properties, including organic C content ($r_{\text{Ga-OC}}$ from 0.41 to 0.95; $r_{\text{Rb-OC}}$ from 0.95 to 0.97; and $r_{\text{Y-OC}}$ from 0.87 to 0.91), total H content ($r_{\text{Ga-H}}$ from 0.39 to 0.95; $r_{\text{Rb-H}}$ from 0.82 to 0.96; and $r_{\text{Y-H}}$ from 0.73 to 0.84), and total Mn content ($r_{\text{Ga-Mn}}$ from 0.43 to 0.84; $r_{\text{Rb-Mn}}$ from 0.90 to 0.97; and $r_{\text{Y-Mn}}$ from 0.75 to 0.96). In the Dystric Cambisols from the Sikhote-Alin Biosphere Nature Reserve and from the Lazovsky Nature Reserve, distributions of Ga, Rb, and Y were also controlled by Fe-containing compounds of soil ($r_{\text{Ga-Fe}}$ from 0.57 to 0.78; $r_{\text{Rb-Fe}}$ from 0.31 to 0.68; and $r_{\text{Y-Fe}}$ from 0.50 to 0.61). The main differences of soil from the Ussuri Nature Reserve were the positive correlation of Ga, Rb, and Y with pH ($r_{\text{Ga-pH}}$ 0.56; $r_{\text{Rb-pH}}$ 0.64; and $r_{\text{Y-pH}}$ 0.71). Increase in solubility of different elements correlates positively with pH in soils (Tyler and Olsson 2001, 2002). The peculiarity of the Dystric Cambisols from the Ussuri Nature Reserve indicated the affinity of Ga, Rb, and Y for the soluble compounds of soils. The Ga, Rb, and Y contents were negatively correlated with the contents of Al, Si, and clay; this suggests that complexation with organic matter and with Fe-Mn-containing compounds of soil would have played a major role in the distribution and accumulation of Ga, Rb, and Y in

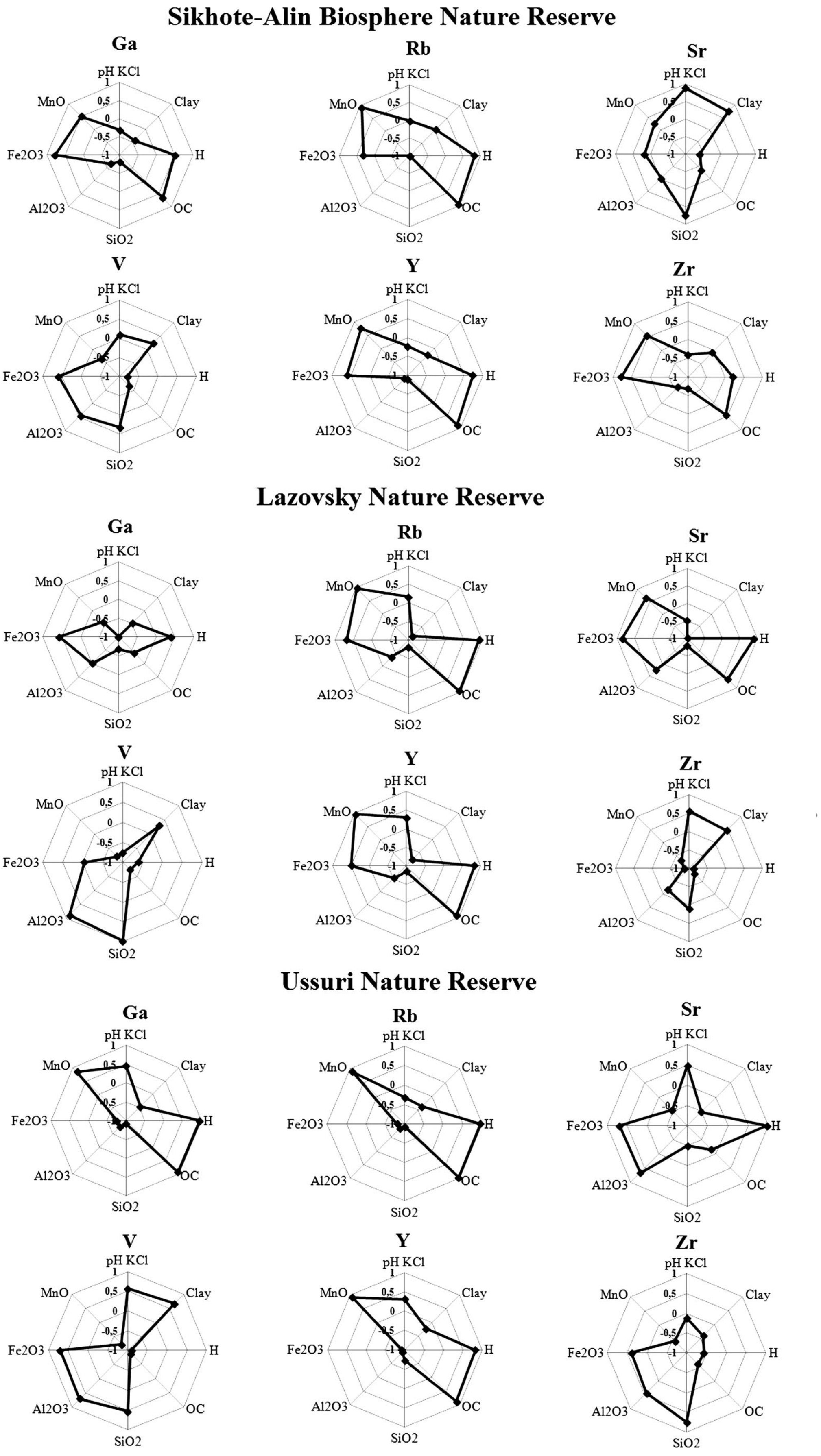

Fig. 4 Correlation coefficients between the contents of trace lithophile elements and chemical and physical properties of soils

soils from all reserves. Most previous studies have shown that the pedochemical behavior of Ga, Rb, and Y is not similar for all soils (Tyler and Olsson 2002; Mao et al. 2009; Feng 2011; Kabata-Pendias 2011). Likewise, Ga, Rb, and Y show large differences in geochemical parameters such as ionic radius (radius of Ga = 0.062 nm; radius of Rb = 0.149 nm; and radius of Y = 0.106 nm) and oxidation state (oxidation state of Ga and Y III; oxidation state of Rb I). Most likely, the similar behavior of Ga, Rb, and Y in the studied soils may have been caused by the influence of external sources containing mobile and reactive forms of these elements. This is supported by the observation that Rb is an element with very low ionic potential, which may be a soluble cation in soils (Mason and Moore 1982). Gallium and Y are the elements with intermediate ionic potential and tend to combine with hydroxyl groups (Muhs et al. 2007).

The relationships of Sr with soil properties were variable among the soils collected from different sampling sites. Total soil Sr content was largely dependent on clay ($r_{\text{Sr-clay}}$ 0.74) and Si ($r_{\text{Sr-Si}}$ 0.76) contents and pH ($r_{\text{Sr-pH}}$ 0.89) in the Dystric Cambisols from the Sikhote-Alin Biosphere Nature Reserve. Factors controlling the distributions of Sr in soils from the Lazovsky Nature Reserve were Mn ($r_{\text{Sr-Mn}}$ 0.66), Fe ($r_{\text{Sr-Fe}}$ 0.84), organic C ($r_{\text{Sr-OC}}$ 0.64), and H ($r_{\text{Sr-H}}$ 0.91). In soils of the Ussuri Nature Reserve, Sr showed an affinity with total Fe ($r_{\text{Sr-Fe}}$ 0.70), Al ($r_{\text{Sr-Al}}$ 0.66), and H contents ($r_{\text{Sr-H}}$ 0.96). Literature data about the relationship between contents and distributions of total Sr and soil properties are contrasting. Most of the previous studies have demonstrated that Sr is strongly fixed by organic matter in soils (Kabata-Pendias 2001). However, a recent study has shown that Sr formed non-stable complexes with organic matter and that in acid soils, Sr is transported by the soil solution throughout the soil profile (Dinu 2015). Some researchers suggest that Sr has a strong affinity to clay (Bascetin and Atun 2006; Khaleghpanah et al. 2010). The significant relationships of Sr with some soil properties in natural soils from reserves in our study were similar to the results reported by other researchers, but a clear relationship between total soil Sr and selected soil properties could not be recognized for the Dystric Cambisols from all reserves, suggesting the existence of different processes which control distribution and accumulation of this element in soil profiles.

The content of V was significantly correlated with the contents of Al and Si ($r_{\text{V-Al}}$ from 0.44 to 0.89; $r_{\text{V-Si}}$ from 0.32 to 0.98) in the soils from all reserves. The relationship of V with clay ($r_{\text{V-clay}}$ from 0.23 to 0.67) suggests that during weathering of primary minerals, V was partially incorporated into clay minerals and accumulated in the soil profiles during the main soil formation processes. According to van der Weijden and van der Weijden (1995), V in soils is frequently co-associated with Fe. A strong affinity between V and Fe was observed in soils of the Sikhote-Alin Biosphere Nature Reserve ($r_{\text{V-Fe}}$ 0.60) and in soils of the Ussuri Nature Reserve ($r_{\text{V-Fe}}$ 0.70). Our data indicated that V contents were negatively correlated with pH, contents of organic C, total H, and total Mn in the Cambisols from all reserves.

The content of Zr was poorly related to soil properties of the Dystric Cambisols from all reserves, with a few exceptions. We observed positive correlations between total soil Zr, clay, and pH ($r_{\text{Zr-clay}}$ 0.46; $r_{\text{Zr-pH}}$ 0.57) in soils of the Lazovsky Nature Reserve and a positive correlation between Zr and total Fe content ($r_{\text{Z-Fe}}$ 0.78) in soils of the Sikhote-Alin Biosphere Nature Reserve. In most cases, Zr showed low mobility during chemical weathering and pedogenesis, according to previously published results about Zr contents in highly resistant primary minerals (Egli and Fitze 2000; Tyler and Olsson 2001; Muhs et al. 2007; Scheib et al. 2013). However, several studies have indicated a more or less consistent relation between Zr contents in soils and in plants and between Zr and soil parameters such as soil organic matter and, partly, Mn levels (Tyler 2005; Kabata-Pendias 2011). Our results show that the contents of total Mn and organic C had some influence on the content of Zr in the Dystric Cambisols of the Sikhote-Alin Biosphere Nature Reserve ($r_{\text{Zr-OC}}$ 0.44; $r_{\text{Zr-Mn}}$ 0.56). Positive correlations between Zr and elements contained in primary minerals (Si and Al) were only found in soils from the Ussuri Nature Reserve ($r_{\text{Zr-Si}}$ 0.76; $r_{\text{Zr-Al}}$ 0.43). The distribution of Zr in the studied soils was not significantly controlled by the selected soil properties.

3.5 Technogenic index of the elements

Trace lithophile elements in natural soils from reserves, normalized to average content of elements in the earth's crustal rocks given by Greenwood and Earnshaw (1984), are shown in Fig. 5 (Greenwood and Earnshaw, 1984). Analysis of the trace lithophile element contents in soils revealed that three elements showed positive anomalies: Rb in the soils of the Sikhote-Alin Biosphere Nature Reserve and Lazovsky Nature Reserve, V in the soils of the Ussuri Nature Reserve, and Zr in the soils of all studied reserves. We used the corrected index of the technogenic origin (*Tg*) according to Vodyanitskii et al. (2010). This index separates values of the natural geochemical contents of trace lithophile elements from values of contents of elements of technogenic origin in soil. Here, *Tg* values above 20% indicate progressive contamination of the soil by elements of technogenic nature. The *Tg* of Rb varied from 33.47 to 46.50% (Table 5). For Rb, the *Tg* was higher in the Ussuri Nature Reserve than in the other reserves. The technogenic index of V had negative and lower values, indicating that V was a component of the primary suite of mineral phases inherited by parent materials, according to the rule described by Kabata-Pendias and Pendias (1989). The technogenic index of Zr exceeded 20% in the Dystric

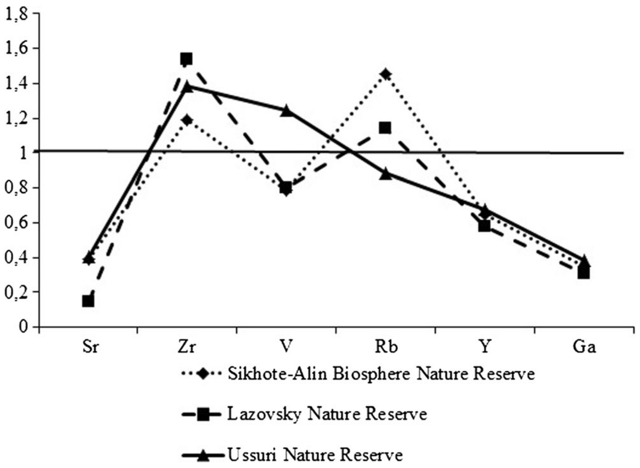

Fig. 5 Upper continental crust normalized distribution patterns of trace lithophile elements in the Dystric Cambisols from nature reserves. Upper continental crust data are cited from Greenwood and Earnshaw (1984)

Cambisols from the Sikhote-Alin Biosphere Nature Reserve only. The *Tg* of Zr varied from 11.14 to 31.89%. Compared with the element composition of the earth's crustal rocks, Ga, Sr, and Y showed negative anomalies. Nevertheless, *Tg* values of Ga ranged from 17.35 to 39.29%, with the largest values found in the Dystric Cambisols from the Ussuri Nature Reserve. The technogenic index of Sr was less than 20% in the soils from the Sikhote-Alin Biosphere Nature Reserve and from the Ussuri Nature Reserve. The *Tg* of Sr was 28.48% in soil from the Lazovsky Nature Reserve. Yttrium showed high technogenic index in soils from all natural reserves, with *Tg* values ranging between 45.52 and 48.40%.

In general, *Tg* values for Rb and Y in soils from all natural reserves and for Ga, Sr, and Zr in soils from some sampling sites suggest that soils of reserves at the coast of the Russian Far East were subjected to the influence of contamination inputs from external sources. Similar results were found by Vodyanitskii et al. (2010) and Molchanova et al. (2013) for Rb, Sr, Y, and Zr in a study on soils with urban activities and by Feng (2010) for V in a study of forest soils. Territories of natural reserves are characterized by the absence of direct contamination inputs from anthropogenic sources. Elements may have been imported through the weathering of soil primary minerals. As reported in the literature, the Rb/Sr ratio is a sensitive indicator of chemical weathering of soil parent material due to an effective fractionation of these elements during weathering of primary minerals. A geochemical relationship between Rb and Sr in rocks, weathered debris of rocks, and soils has been demonstrated in some studies (Chen et al. 1999; Mao et al. 2009; Wang et al. 2009). Figure 6 shows that the Rb/Sr ratio ranged from 0.36 to 1.77 in natural soils from the reserves. Different values of Rb/Sr ratio are likely to be related to diverse parent materials and geomorphic positions of various sampling sites. Where soils have been developed from alluvial deposits and are located in low-lying areas (Sikhote-Alin Biosphere Nature Reserve and Ussuri Nature Reserve), the Rb/Sr ratio is lower compared to that of soils developed from eluvial deposits (Lazovsky Nature Reserve). This indicates that for soils developed from eluvial deposits and located in the raised relief, elements were subjected to more intensive weathering processes.

The results of the Rb/Sr ratio calculation have revealed that the elements from the soil parent material are not significantly enriched of the soil profile from reserves. The high technogenic index values of Rb and Y in all sites is due to the fact that these elements may have entered the soils through atmospheric deposition by air, with a long-range transport of elements of unknown sources. Increases of *Tg* values for Ga, Sr, and Zr may point to local contamination sources in some sampling sites.

Atmospheric deposition plays an important role in the transportation of trace lithophile elements over long and intermediate distances (Tripathee et al. 2014; Hardy et al. 2015; Meyer et al. 2015). There are a few studies on the contents of Ga, Rb, Sr, V, Y, and Zr in atmospheric particulate matter in different regions of the world, suggesting that the most common source of such elements is atmospheric deposition through industrial activity (for Ga, V, Y, and Zr) and sea aerosols (for Rb and Sr) (Querol et al. 2007; Marx et al. 2014). In the studied region, atmospheric precipitation contained Ga, Rb, Sr, and V in dissolved and suspended forms of anthropogenic and maritime origin also (Chudaeva et al. 2008;

Table 5 Technogenic index (*Tg*) of trace lithophile elements in the Dystric Cambisols

Element	Sikhote-Alin Biosphere Nature Reserve %	Lazovsky Nature Reserve	Ussuri Nature Reserve
Ga	21.62	17.35	39.29
Rb	33.47	43.31	46.50
Sr	17.67	28.48	14.53
V	− 5.45	3.78	3.33
Y	48.40	48.36	45.52
Zr	31.89	16.57	11.14

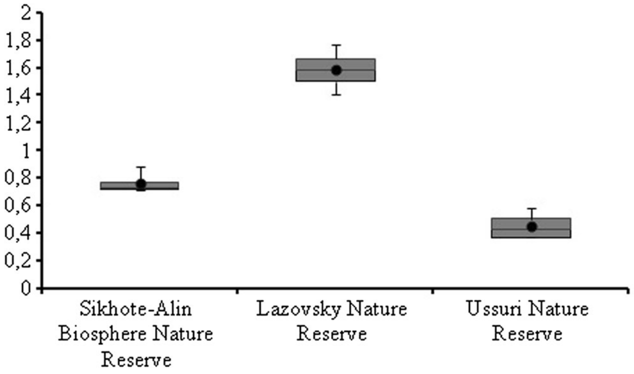

Fig. 6 The Rb/Sr ratios of the Dystric Cambisols

Kondrat'ev et al. 2017). The enrichment of atmospheric precipitation by trace lithophile elements of anthropogenic origin were the results of the increase of solid material content in precipitation. For example, Chudaeva et al. 2008 have shown that the mean values of Sr in the snowmelt water samples were 3.0 mg L^{-1} in uncontaminated areas, 9.6 mg L^{-1} in urban areas, and 17.5 mg L^{-1} in the samples of colored snow, falling from time to time in the Primorye Region. Additionally, the authors reported that concentrations of Ga, Rb, and V in samples of colored snow reached 0.7, 1.24, and 1.0 mg L^{-1}, respectively. In another study, Kondrat'ev et al. 2017 had demonstrated fallout of contaminated atmospheric precipitation, was brought from anthropogenic zone, over the distances about 100 km from source of contamination on the western slope of the Sikhote-Alin.

4 Conclusions

The levels of trace lithophile element contents in the Dystric Cambisols from natural reserves depend on the mixed influence of natural environmental conditions (main soil-forming factors, peculiar geographic area) and additional inputs of elements originating from atmospheric deposition of long-distance transported pollutants.

Dystric Cambisols have natural content of Rb above the average contents in soils of Russia. The mean values of Y in studied soils were similar to those found elsewhere in Russia. Nevertheless, the technogenic index evaluation reveals that both Rb and Y in soils from all reserves include additions from external sources. Content maxima of total Rb and Y occurred in surface horizon A in soils. Total Rb and Y contents were largely dependent on organic C content, total H content, and Mn-containing soil compounds. Average contents of Ga, Sr, and Zr in soils from reserves were lower than those in other soils of Russia. The technogenic index of Ga, Sr, and Zr indicated local contamination of the Dystric Cambisols by these elements. The main peculiarities of the soils with maximum technogenic index values for Ga were increased content of Ga in the upper horizons and increased association of Ga with organic C content, total H content, Mn oxides content, and pH values. Accumulation of Sr in the upper and middle parts of the soil profiles and association of this element with organic C content and Mn-Fe-containing compounds of soils increased in areas with high technogenic index values for Sr. Strontium was associated with Fe oxides, Al oxides, Si oxides, and levels of pH in the soils with minimal technogenic index values. In general, the content of Zr was weakly controlled by the studied soil properties, but mostly affected by total Fe contents in the areas with maximum technogenic index values for Zr. Vanadium was an uncontaminated element in the studied soils. Distribution and accumulation of total V in soil profiles is largely dependent on Al oxide and Si oxide levels.

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References

Adriano DC (2001) Trace elements in terrestrial environments: Biogeochemistry, bioavailability, and risks of metals. Springer-Verlag, New York

Assem FL, Levy LS (2009) A review of current toxicological concerns on vanadium pentoxide and other vanadium compounds: gaps in knowledge and directions for future research. J Toxicol Environ Health B Crit Rev 12:289–306

Bascetin E, Atun G (2006) Adsorption behavior of strontium on binary mineral mixtures of Montmorillonite and Kaolinite. Appl Radiat Isotopes 64(8):957–964

Bezuglova OS, Gorbov SN, Tischenko SA, Aleksikova AS, Tagiverdiev SS, Sherstnev AK, Dubinina MN (2016) Accumulation and migration of heavy metals in soils of the Rostov region, south of Russia. J Soils Sediments 16:1203–1213

Chen J, An ZS, Wang YJ, Ji JF, Chen Y, Lu HY (1999) Rb/Sr distribution in Luochuan profile in late 800 Ka and its paleoclimatic significance. Chin Sci 27:498–504 (in Chinese)

Chudaeva VA, Chudaev OV, Yurchenko SG (2008) Chemical composition of precipitation in the southern part of the Russian Far East. Water Resour 35(1):58–70

Dinu MI (2015) Interaction between metal ions in waters with humic acids in gley-podzolic soils. Geochem Int 53(3):265–276

Egli M, Fitze P (2000) Formulation of pedologic mass balance based on immobile elements: a revision. Soil Sci 165:437–443

Feng J-L (2011) Trace elements in ferromanganese concretions, gibbsite spots, and the surrounding terra rossa overlying dolomite: their mobilization, redistribution and fractionation. J Geochem Explor 108: 99–111

Folkeson L, Nyholm NEI, Tyler G (1990) Influence of acidity and other soil properties on metal contents in forest plants and animals. Sci Total Environ 96:211–233

Fox PM, Doner HE (2002) Trace element retention and release on minerals and soil in a Constructed wetland. J Environ Qual 31:331–338

Gracheva RG (2012) Sikhote-Alin Biosphere Natural Reserve name K.G. Abramov. In: Dobrovol'skiy GV (ed) Soils of the reserves and national parks of Russian Federation, "Ionosfera- NIA-Priroda", Moscow, pp 435–439 (in Russian)

Greenwood NN, Earnshaw A (1984) Chemistry of the elements. Butterworth-Heinemann, Oxford

Hardy A, Langley-Turnbaugh SJ, Murphy D (2015) Trace elements in high-elevation soils on six mountains in Maine, USA. Soil Horizons 53:31–37

Horbe AMC, Anand RR (2011) Bauxite on igneous rocks from Amazonia and southwestern of Australia: implication for weathering process. J Geochem Explor 111:1–12

Ivanov GM, Kashin VK (2010) Vanadium in the landscapes of western Transbaikalia. Geochem Int 48(3):295–299

Jeske A, Gworek B (2012) Chromium, nickel and vanadium mobility in soils derived from fluvioglacial sands. J Hazard Mater 238:315–322

Jolly YN, Islam A, Akbar S (2013) Transfer of metals from soil to vegetables and possible health risk assessment. SpringerPlus 2(385):1–8

Kabata-Pendias A, Pendias K (2001) Trace elements in soils and plants, 3rd edn. CRC Press, NY

Kabata-Pendias A, Pendias K (1989) Microelements in soils and plants. Mir, Moscow (in Russian)

Kabata-Pendias A (2011) Trace elements in soils and plants, 4rd edn. CRC Press, NY

Khaleghpanah N, Roozitalab MH, Majdabadi A, Mirkhani R (2010) The adsorption of strontium on soils developed in arid region as influenced by clay content and soluble cations. In: Gilkes R, Prakongkep N (eds) 19th world congress of soil Science, soil solutions for a changing world. Curran Associates, New York, pp 1925–1929

Kondrat'ev II, Mukha DE, Boldeskul AG, Yurchenko SG, Lutsenko TN (2017) Chemical composition of precipitation and snow cover in the Primorsky Krai. Russ Meteorol Hydrol 42(1):64–70

Kostenkov NM, Krasnopeev SM, Golodnaya OM, Zharikova EA, Oznobikhin VI (2016) The soils and soil cover of Sikhote-Alin Biosphere Natural Reserve name K.G. Abramov (with the soil Atlas). Dal'nauka, Vladivostok (in Russian)

Leonard A, Gerber G (1994) Mutagenicity, carcinogenicity, and teratogenicity of vanadium. Mutat Res 317:81–88

Mao LJ, Mo DW, Yang JH, Shi CX (2009) Geochemistry of trace and rare earth elements in red soils from the Dongting Lake area and its environmental significance. Pedosphere 19(5):615–622

Marx SK, Lavin KS, Hageman KJ, Kamber BS, O'Loingsigh T, McTainsh GH (2014) Trace elements and metal pollution in aerosols at an alpine site, New Zealand: sources, contents and implications. Atmos Environ 82:206–217

Mason B, Moore CB (1982) Principles of geochemistry, 4th edn. J. Wiley& Sons, New York

Meyer C, Diaz-de-Quijano M, Monna F, Franchi M, Toussaint M-L, Gilbert D, Bernard N (2015) Characterization and distribution of deposited trace elements transported over long and intermediate distances in north-eastern France using Sphagnum peatlands as a sentinel ecosystem. Atmos Environ 101:286–293

Molchanova IV, Mikhailovskaya LN, Pozolotina VN, Zhuravlev YN, Timofeeva YO, Burdukovskii ML (2013) Technogenic pollution of soil and plant cover in southern Primorye. Russ J Ecol 44(5): 371–374

Muhs DR, Budahn JR, Prospero JM, Carey SN (2007) Geochemical evidence for African dust inputs to soils of western Atlantic islands: Barbados the Bahamas, and Florida. J Geophys Res. https://doi.org/10.1029/2005JF000445

Munsell Soil Color Charts (1990) Munsell Color. Macbeth Div. of Kollmorgen Instruments, Baltimore

Nowack B, Obrecht JM, Schluep M, Schulin R, Hansmann W, Koppel V (2001) Elevated lead and zinc contents in remote Alpine soils of the Swiss National Park. J Environ Qual 30:919–926

Pansu M, Gautheyrou J (2006) Handbook of soil analysis mineralogical, organic and inorganic methods. Springer-Verlag, Berlin, Heidelberg

Poledniok J, Buhl F (2003) Speciation of vanadium in soil. Talanta 59:1–8

Querol X, Viana M, Alastuey A et al (2007) Source origin of trace elements in PM from regional background, urban and industrial sites of Spain. Atmos Environ 41:7219–7231

Reijonen I, Metzler M, Hartikainen H (2016) Impact of soil pH and organic matter on the chemical bioavailability of vanadium species: the underlying basis for risk assessment. Environ Pollut 210:371–379

Sadeghi M, Petrosino P, Ladenberger A, Albanese S, Andersson M, Morris G, Lima A, De Vivo B, GEMAS Project Team (2013) Ce, La and Y concentrations in agricultural and grazing-land soils of Europe. J Geochem Explor 133:202–213

Sasmaz A, Sasmaz M (2009) The phytoremediation potential for strontium of indigenous plants growing in a mining area. Environ Exp Bot 67:139–144

Scheib AJ, Birke M, Dinelli E, GEMAS Project Team (2013) Geochemical evidence of aeolian deposits in European soils. Boreas 43(1):175–192

Seledets VP (2011) Ecological assessment of the far east territory based on the state of vegetation. Dal'nauka, Vladivostok (in Russian)

Semal VA (2007) Soil cover patterns in the southern part of the Sikhote Alin Range (using the example of the Ussuri Nature Reserve). Eurasian Soil Sci 40(8):807–813

Semal VA, Tregubova VG, Nesterova OV (2012) Lazovsky Natural Reserve name L.G Kaplanov. In: Dobrovol'skiy GV (ed) Soils of the reserves and national parks of Russian Federation, Moscow, "Ionosfera- NIA-Priroda", pp 416–418 (in Russian)

Semal VA (2010) Properties of soils in southern Sikhote-Alin using the example of the Ussuri Reserve. Eurasian Soil Sci 3:278–286

Shahid M, Ferrand E, Schreck E, Dumat C (2013) Behavior and impact of Zirconium in the soil–plant system: plant uptake and phytotoxicity. Rev Environ Contam Toxicol 221:107–127

Stiles CA, Mora CI, Driese SG (2003) Pedogenic processes and domain boundaries in a vertisol climosequence: evidence from titanium and zirconium distribution and morphology. Geoderma 116:279–299

Suttona P, Maskalla J, Thorntonb I (2002) Contents of major and trace elements in soil and grass at Shimba Hills National Reserve, Kenya. Appl Geochem 17:1003–1016

Timofeeva YO, Karabtsov AA, Semal VA, Burdukovskii ML, Bondarchuk NV (2014) Iron-manganese nodules in udepts: the dependence of the accumulation of trace elements on nodule size. Soil Sci Soc Am J 78:767–778

Tripathee L, Kang S, Huang J, Sharma CM, Sillanpaa M, Guo J, Paudyal R (2014) Contents of trace elements in wet deposition over the central Himalayas, Nepal. Atmos Environ 95:231–238

Tyler G (2004) Vertical distribution of major, minor, and rare elements in a Haplic Podzol. Geoderma 119:277–290

Tyler G (2005) Changes in the contents of major, minor and rare-earth elements during leaf senescence and decomposition in a Fagus sylvatica forest. For Ecol Manag 206:167–177

Tyler G, Olsson T (2001) Contents of 60 elements in the soil solution as related to the soil acidity. Eur J Soil Sci 52(1):151–165

Tyler G, Olsson T (2002) Conditions related to solubility of rare and minor elements in forests soils. J Plant Nutr Soil Sci 165:594–601

van der Weijden CH, van der Weijden RD (1995) Mobility of major minor and some redox-sensitive trace elements and rare-earth elements during weathering of four granitoids in central Portugal. Chem Geol 125:149–167

Vinogradov AP (1962) The average content of chemical elements in the main types of igneous rocks of the Earth's crust. Geokhimiya 7:555–571 (in Russian)

Vodyanitskii YN (2012) Standards for the contents of heavy metals and metalloids in soils. Eurasian Soil Sci 45(3):321–328

Vodyanitskii YN, Savichev AT, Vasilev AA, Lobanova ES, Chashchin AN, Prokopovich EV (2010) Contents of heavy alkaline-earth (Sr, Ba) and rare-earth (Y, La, Ce) metals in technogenically contaminated soils. Eurasian Soil Sci 43(7):822–832

Wang X, Cheng G, Zhong X (2009) Trace elements in sub-alpine forest soils on the eastern edge of the Tibetan Plateau, China. Environ Geol 58:635–643

White WM (2013) Geochemistry. Wiley-Blackwell, NY

World reference base for soil resources (2006) A framework for international classification, correlation and communication. Intern. World Soil Resources Reports 103. FAO, Rome