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ARTICLE



# Applicability of X-ray fluorescence spectrometry for assessing geochemical features and heavy metal contamination of soils: primary data

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## ABSTRACT

X-ray fluorescence spectrometry (XRF) has long been considered a convenient and powerful method for the determination of trace amounts of chemical elements in various types of natural materials. XRF is rapid, reliable, and non-destructive spectroscopic technique, allows performing a direct analysis of solid samples without pre-treatment. For the present report, we take advantage of the multi-elemental capability of the XRF-technique for the determination of major and trace amounts of rock-forming ( $S_{tot}$ ,  $Na_2O$ ,  $MgO$ ,  $Al_2O_3$ ,  $SiO_2$ ,  $P_2O_5$ ,  $K_2O$ ,  $CaO$ ,  $TiO_2$ ,  $MnO$ ,  $Fe_2O_{3(tot)}$ ) and trace (F, V, Cr, Co, Ni, Cu, Zn, Ga, Pb, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Nd) elements in environmental solid samples. Nowadays, study of the soil cover exposed by human-caused impact is an important aspect in understanding the geochemical processes occurring in it. Study object is the biggest territory of the Baikal region named Olkhon, which is a natural area of preferential protection of federal significance and a part of the Baikal National Park. In this study, we have determined chemical composition of the soil upper horizon (~0–15 cm) of meadow-stepper landscapes of the Baikal region (the Olkhon Island) to reveal their geochemical features and heavy metal pollution level. Three varieties of the steppe soils were distinguished: middle loamy, light loamy and sandy loam. For the first time, the influence of soil granulometric features on the content level of the rock-forming and toxic elements in them has been established. In addition, the primary data relating to the assessment of the soil heavy metal contamination have been presented.

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X-ray spectrometry; stepper soils; physico-chemical properties; granulometric features; elemental composition; chemical composition; heavy metals; rock-forming and toxic elements; contamination

## 1. Introduction

Soil is a main component of the environment including durable information about chemical element behaviour and simultaneously it is a physical-chemical barrier to heavy metal migration [1,2]. Numerous papers are dedicated to the study of the human-caused impact on soil cover in different parts of the world resulting in changes in their physicochemical properties [3–11]. This can appear for a long time, the elemental composition of the soil, namely the content of toxic elements and heavy metals, will significantly change.

Olkhon is the biggest island of Lake Baikal and a natural area of preferential protection of federal significance, and it is a part of the Baikal National Park, Russia. Moreover, this territory is the UNESCO World Heritage Site. Nowadays, the tourist and recreational development of the island is very extensive and constantly expanding. A time-consuming impact on the Olkhon soil cover activated a certain type of exogenous geological processes, which is appeared in the formation of small and large gorges on the slopes. In addition, a negative influence on human health is caused by the presence in the soil of various compounds of heavy metals that migrate along with the current of soil moisture, which over time can cause pollution of groundwater and soils in reduced relief elements, as well as the coastal zone of Lake Baikal. Thus, the study of the soil covers of the Olkhon Island, which is subject to the anthropogenic impact, is very important for understanding the geochemical processes occurring in it.

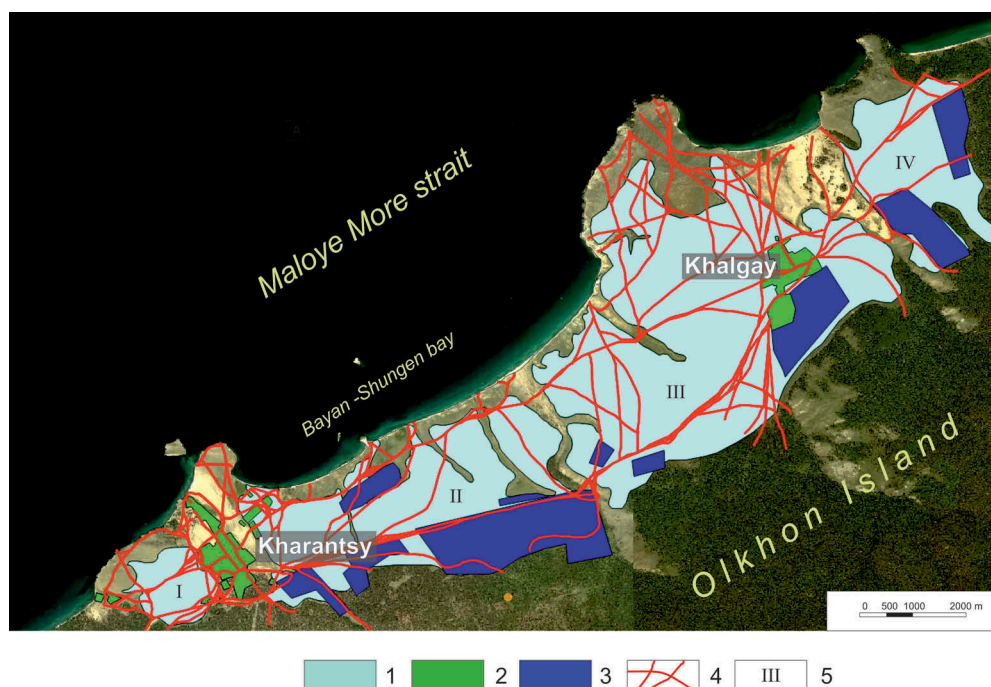
This report is a part of a large research devoted to the study of the ecological and geochemical state of the mountain-steppe landscapes of the Baikal region, which are experiencing modern anthropogenic impact. In this study, we suggest a new approach to the understanding geochemical processes occurring in the Baikal region soils with appliance of widely known in analytical practice, convenient, fast and non-destructive technique of X-ray fluorescence (XRF) spectrometry. The study involves the following steps: (i) obtaining the first data on the elemental composition of the steppe soils of the Olkhon Island using the XRF technique; (ii) revealing geochemical features of the soils examined; (iii) establishing the influence of the granulometric characteristics of the soils on the level of rock-forming and toxic elements in them; (iv) performing primary assessment of the soil metal contamination using indices such as geoaccumulation and degree of contamination.

## 2. Experimental

### 2.1. Study area and soil sampling

For a long time, the Olkhon area is experiencing human-caused impact caused by agricultural activity, especially, tourist. To a greater extent, it appears on the Olkhon Island. An indicator showing about violation of the ecological balance of the environment is the upper soil horizon (~0–15 cm). In 2015, zoning of the soils of the Baikal basin was carried out [12]. According to the map presented in [13], the study area refers to the distribution of chestnut stepper soils and is located between the settlements of Kharantsy and Khalgay as pictured in Figure 1. In accordance with the World Reference Base of Soil Resources [14], the chestnut steppe soils are Kastanozems. Soils from the surface soil horizon (~0–15 cm) and widespread within the meadow-steppe geosystems of the Olkhon Island were selected as the object of the study.

A total of 200 soil samples were carefully collected from the upper horizon (~0–15 cm) during dry summer season using stainless-steel spade at regular interval of 100 m. Such sampling depth is based on the fact that most of the heavy metals are accumulated in the surface of the soil cover [1,2]. All soil samples were sealed in polyethylene bags and kept in natural wet conditions during field work. The location of each collected sample was marked by GPS, and environmental conditions for each one were recorded. Next, the soil samples were transported to our laboratory and air-dried at ambient temperature for 72 h. Then, the



**Figure 1.** Map of the study area showing the following locations: 1 – stepper soil territories; 2 – village territories; 3 – former (abandoned) agricultural areas; 4 – modern tributary system; 5 – testing areas.

representative samples in an amount of 45 pieces were evolved from the collected amount for XRF after granulometric analysis.

All soil samples for XRF analysis were prepared in accordance with the requirements given in [15]. The preparation of the samples was performed as follows. The first step was the sieving and grinding the collected soil samples in the agate mortar for 1 h. Then, the ground material was mixed on a paper with a density of 250 grams per square metre (gsm). The mixing procedure was carried out by moving the sample material from one side to the other to avoid the segregation of coarse particles. The quartering method was applied for representative sampling. For the elimination of a particle aggregation during the milling process, a few drops of an ethyl hydroxide of high purity were added. Particle sizes of the powdered samples were defined using a laser particle-size analyser 'Analysette 22' COMPACT (FRITSCH, Germany). Particle size of the soil fraction is as low as 63  $\mu\text{m}$ . The second step was weighing procedure. Each sample powder weighing  $5 \pm 0.0001$  g and wax weighing  $1 \pm 0.0001$  g was taken using an analytic balance of AB-series (St. Petersburg, Russia). Then, these components were mixed and thoroughly shaken for two minutes. Prepared samples were pressed in tablets with a diameter of 30 mm using a HERZOG HTP-40 semiautomatic press with a pressure of 100 kN for further investigation.

## 2.2. Instrumentation

The concentrations of rock-forming ( $S_{\text{tot}}$ ,  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{MnO}$ ,  $\text{Fe}_2\text{O}_{3(\text{tot})}$ ) and trace (F, V, Cr, Co, Ni, Cu, Zn, Ga, Pb, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Nd)

elements were obtained by wavelength dispersive X-ray fluorescence (WDXRF) spectrometry. XRF is rapid, reliable, and non-destructive spectroscopic technique, allows performing a direct analysis of different solid samples, including environmental materials, without extensive pretreatment [16,17]. All measurements were carried out using an S8 TIGER spectrometer (Bruker AXS, Germany) connected to the SPECTRA<sup>plus</sup> software [18]. This instrument is equipped with a 4 kW power X-ray tube with a rhodium anode and a beryllium window of 75 µm thickness. Detailed information about the instrument features and measurement conditions can be found elsewhere [19,20]. For all measurements, the authors proposed to apply a universally usable crystal of LiF (200) which has higher reflectivity, sensitivity, and the X-ray spectrum contrast [20]. Measurement time of the analytical line and the background from each element was 60–100 s and 30–60 s, respectively. The matrix effects were taken into account using the influence coefficients ( $\alpha$ -correction equations) [20]. This spectrometer is located at the Centre for Geodynamics and Geochronology, Institute of the Earth's Crust (IEC), Siberian Branch of Russian Academy of Sciences (IEC, SB RAS, Russia, Irkutsk).

### 2.3. Reference materials

The analytical quality control and construct of calibration curves were performed by employing the International Certified reference materials (ICRMs) and in-house standard reference materials (HSRMs) of various types of soils and sediments [21,22]. The ICRMs were produced and certified by United States Geological Survey and Geological Survey of Japan [23,24], and HSRMs were produced by Bronnitskaya geological-geochemical expedition at the Federal State Unitary Enterprise 'Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements' in Russia [25], the Institute of Geochemistry, Siberian Branch of Russian Academy of Sciences [26].

### 2.4. Physical-chemical methods

The granulometric composition of the samples was determined by the pipette method in the modification N.A. Kaczynski [27], which is based on the speed of incidence of particles of different sizes in water. According to the classification accepted in the soil science [28], six fractions were determined: 0.50–0.25 mm (coarse middle-sandy); 0.25–0.05 mm (fine-thin sandy); 0.05–0.01 mm (coarse-silt); 0.010–0.002 mm (fine-silt); 0.002–0.001 mm (coarse-clay); <0.001 mm (thin clay).

The representative samples in an amount of 45 pieces were prepared for analysis in three ways: aggregate – maceration in water; semi-dispersed (standard) – soaking and boiling with the addition of ammonia; dispersed – soaking and boiling with sodium pyrophosphate. Moreover, three sample weights from each sample were taken. For soils and clay deposits, the most suitable are the results of particle size analysis with a semi-dispersed method of the preparation [28].

Water and hydrochloric acid extracts from the selected soil samples were studied. The composition of carbonate salts ( $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{FeCO}_3$ ), the total content of carbonates ( $S_{\text{carb}}$ ) and the total content of water-soluble salts ( $S_{\text{ws}}$ ) in the samples was determined by standard methods described in [29]. The calculated values of these contents are presented in Table 1. Concentrations of  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ , and  $\text{FeCO}_3$  were calculated from the

**Table 1.** The calculated values of analytical parameters for the soils examined, which were determined by standard methods described in [29].

Parameters	Middle loamy variety *n = 15	Light loamy variety *n = 15	Sandy loam variety *n = 15
Total content of carbonate salt (%), CaCO <sub>3</sub>	3.99	2.5	2.99
Total content of carbonate salt (%), MgCO <sub>3</sub>	not detected	0.59	0.76
Total content of carbonate salt (%), FeCO <sub>3</sub>	4.99	3.59	3.62
Total content of carbonates (%), S <sub>carb</sub>	8.98	6.68	7.37
Total content of water-soluble salts (%), S <sub>ws</sub>	0.26	0.23	0.12
Cation exchange capacity (pitch (eq kg <sup>-1</sup> ), CEC	78.6	41.92	31.44
Content of humus (%)	4.9	4.5	5.3
Medium reaction (pH)	6.8	7.3	6.8

\*Amount of representative samples for each soil variety, which were evolved from the collected amount (200 samples) for XRF after granulometric analysis.

obtained contents of CaO, MgO and  $\text{Fe}_2\text{O}_3$  from the hydrochloric acid extract of the studied soils. The determination of the CaO concentration was carried out by the bulk oxalate method, the MgO content – by the weight phosphate method. The colorimetric determination of the  $\text{Fe}_2\text{O}_3$  by the sulfosalicylic method was performed in an aliquot part of the hydrochloric acid filtrate from  $\text{SiO}_2$ . The concentrations of humus were determined by the method of I.V. Tyurin [29]. The determination of the composition of exchangeable cations and cation exchange capacity (CEC, pitch (eq)  $\text{kg}^{-1}$  of soil) was performed by adsorption of methylene blue in an aqueous solution. The pH values of soil samples are determined in a water extract by the potentiometric method using an EV-74 ionomer (Instrumentation Factory, Russia). When determining the pH in suspension, it is necessary to eliminate the influence of the diffusion potential.

### 3. Results and discussion

#### 3.1. Physical and chemical features of the studied soils

Surface soil horizon (~0–15 cm) of the Olkhon Island is characterised by a light and medium grain size distribution since its content of coarse-middle sandy, fine-thin sandy and coarse-silt fractions ranges from 64.6% to 82.2%. By the content of physical clay (particle size  $<0.001$  mm), according to the classification [27], we identified three types of the studied soils: middle loamy, light loamy, and sandy loam. The particle size of soils is determined by their chemical composition, and also depends on the nature of the soil-forming material (parent rocks) [30]. So, sandy soils are characterised by high water permeability, low water capacity, the absence of structural aggregates, low cation exchange capacity, and absorption. Coarse fractions prevail in the granulometric composition. Light and middle loamy soils are distinguished by high air and water permeability, retain moisture well, and they quickly and evenly warm up with the onset of heat. As shown in Table 1, loamy soils are characterised by higher CEC values than sandy loam. As seen from the Table, the value of CEC is 78.60 pitch (eq)  $\text{kg}^{-1}$  in the middle loamy variety, and in sandy loam soil – 31.44 pitch (eq)  $\text{kg}^{-1}$ .

Humus has a great influence on soil fertility, as well as on a number of their physical and chemical properties. The content of humus in samples varies within narrow limits: from 4.50 in light loamy to 5.30% in sandy loam as could be seen from Table 1. In the work of V.A. Kuz'min [2], the concentration of soil humus in the surface horizon within the steppe landscapes is 5.3%. This level of the humus concentration, in our opinion, despite the island's dry climate and constant winds that carry humus from the upper soil layer, is due to fertilisation and reclamation activities carried out in the area from 1955 to 1980.

Also, in Table 1 we can observe the following results. Values of the  $S_{\text{carb}}$  are in the range of 6.68–8.98%. Among carbonate salts in the samples,  $\text{CaCO}_3$  (2.50–3.99%) and  $\text{FeCO}_3$  (3.62–4.99%) are predominating, and  $\text{MgCO}_3$  (less than 1%) occurs in small amounts. In compliance with the classification [31], the studied soils belong to weakly carbonated. It is confirmed by the obtained values of the medium reaction (pH) of the aqueous extract, which vary from weakly acidic (6.8) to slightly alkaline (7.3). In soils with a weakly acidic, neutral and slightly alkaline reaction of the medium, the composition of exchangeable cations is generally favourable for the most agricultural plants. The total content of  $S_{\text{ws}}$  in the soils examined, obtained as a result of the chemical analysis of the aqueous extract, is



in the range from 0.12% in sandy loam to 0.26% in middle loamy soil. As a result, according to the water extract data, a low degree of salinity of the middle loamy soil was revealed in accordance with the classification [32]. The type of salinisation of this soil is sulphate (gypsum) since the value of the  $\text{Cl}^-/\text{SO}_4^{2-}$  anion ratio is 0.44 ( $<0.5$ ). The light loamy and sandy soils are non-saline since the total content of toxic ( $\text{Mg}(\text{HCO}_3)_2$ ,  $\text{MgSO}_4$ ,  $\text{MgCl}_2$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ ) and all water-soluble salts do not exceed the established toxicity threshold according to the classification [32].

Finally, despite the differences in the grain-size composition and physical-chemical properties, all studied samples belong to weakly carbonated, but in the middle loamy soil, a slight degree of sulphate (gypsum) salinisation was revealed. In addition, the soils examined have a positive potential [28] associated with a high content of humus, the optimal composition of exchangeable cations, as well as favourable pH values that have a great influence on the behaviour of various chemical elements in soil solutions.

### 3.2. Effect of granulometric features of the soils on their elemental composition

Equally important for the process of soil formation is the elemental composition of the soil. The granulometric features of the soil affect the level content of soil-forming elements and heavy metals [1]. When studying the rock-forming elements in the soils examined such as  $S_{\text{tot}}$ ,  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{MnO}$ ,  $\text{Fe}_2\text{O}_{3(\text{tot})}$ , the following was defined and presented in Table 2. The content of  $\text{SiO}_2$  in the stepper soils increases from 51.55% in the middle loamy to 57.36% in the sandy loam variety. It is related to the fact that the coarse sandy fractions (0.50–0.05 mm) are enriched with quartz and feldspars, the latter, in turn, are a source of alkaline elements (Na and K). Higher concentrations of  $\text{Fe}_2\text{O}_{3(\text{tot})}$  (7.64%),  $\text{MgO}$  (1.78%), and  $\text{TiO}_2$  (1.16%) are found in a middle loamy variety with a predominance of coarse clay (0.002–0.001 mm) and thin clay (silty) ( $<0.001$  mm) fractions. The minimum concentrations of these soil-forming oxides are present in the sandy loam variety with predominance of coarse-middle sandy (0.50–0.25 mm) and fine-thin sandy (0.25–0.05 mm) fractions. The MnO contents vary within narrow limits (0.12–0.13%), practically not changing during the transition from one variety to another.

**Table 2.** Analysis results found for the determination of the rock-forming element contents in the soils examined by means of the proposed XRF-technique.

Rock-forming elements	*Found (%), Middle loamy variety n = 15	*Found (%), Light loamy variety n = 15	*Found (%), Sandy loam variety n = 15
$\text{Na}_2\text{O}$	$0.35 \pm 0.006$	$0.67 \pm 0.006$	$0.88 \pm 0.009$
$\text{MgO}$	$1.78 \pm 0.004$	$1.55 \pm 0.009$	$1.51 \pm 0.01$
$\text{Al}_2\text{O}_3$	$17.71 \pm 0.04$	$14.60 \pm 0.05$	$13.49 \pm 0.11$
$\text{SiO}_2$	$51.55 \pm 0.15$	$56.68 \pm 0.12$	$57.36 \pm 0.10$
$\text{P}_2\text{O}_5$	$0.14 \pm 0.001$	$0.17 \pm 0.002$	$0.18 \pm 0.003$
$\text{K}_2\text{O}$	$1.10 \pm 0.006$	$1.66 \pm 0.006$	$1.88 \pm 0.011$
$\text{CaO}$	$2.09 \pm 0.014$	$2.53 \pm 0.012$	$2.50 \pm 0.004$
$\text{TiO}_2$	$1.16 \pm 0.004$	$0.85 \pm 0.005$	$0.82 \pm 0.005$
$\text{MnO}$	$0.12 \pm 0.001$	$0.12 \pm 0.002$	$0.13 \pm 0.002$
$\text{Fe}_2\text{O}_{3(\text{tot})}$	$7.64 \pm 0.041$	$5.47 \pm 0.027$	$4.75 \pm 0.020$
$S_{\text{tot}}$	$0.047 \pm 0.001$	$0.060 \pm 0.001$	$0.060 \pm 0.001$

\*Mean of 15 determinations of the selected soil samples for each rock-forming element (for 99.95% confidence level).



The general chemical features of the studied soils include high  $\text{Al}_2\text{O}_3$  contents (13.49–17.71%) as could be seen from Table 2. Furthermore, the maximum concentration of  $\text{Al}_2\text{O}_3$  (17.71%) is present in a middle loamy variety, characterised by a higher total content (20.70%) of coarse-clay (0.002–0.001 mm) and fine-clay (<0.001 mm) fractions. Aluminium is a part of both primary minerals (sillimanite, feldspar, muscovite, biotite, epidote) of large fractions with particle sizes of more than 0.05 mm, and secondary clay minerals (montmorillonite, kaolinite, illite, chlorite). The content of  $\text{Al}_2\text{O}_3$  in montmorillonite is 19.76% [33]. Thus, the given example shows the relationship between the  $\text{Al}_2\text{O}_3$  concentration and the contents of highly dispersed clay fractions, the mineral composition of which, apparently, to a greater extent affects the total aluminium content in the soils examined. Additionally, in all varieties of the steppe soils with weighting of the particle size distribution associated with an increase in the concentrations of finely dispersed clay fractions, there is an increase in the concentrations of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_{3(\text{tot})}$ ,  $\text{TiO}_2$ ,  $\text{MgO}$  and a decrease in  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{S}_{\text{tot}}$  from sandy loam to middle loamy variety.

The distribution of trace and toxic elements (F, V, Cr, Co, Ni, Cu, Zn, Ga, Pb, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Nd) in the soils examined has been studied, and a connection with their granulometric composition has been also established. The calculated concentrations of the trace and toxic elements are presented in Table 3. As it is obvious from the Table, sandy loam soil depleted in clay fractions is characterised by lower concentrations of V, Cr, Co, Ni, Cu, Zn, Nb, Y, La, Ce and Nd compared to the heavier middle loamy variety. Perhaps this is due to the high absorption capacity with respect to the various chemical elements of clay minerals of highly dispersed fractions, which are characterised by an increased content of organic matter [34].

An interesting element is gallium, which, as is well known, is a very rare element of the earth's crust and does not form its own minerals, but may be present in sphalerite, rich in iron, nepheline and bauxite (aluminium ores). Slightly elevated Ga concentrations were

**Table 3.** Analysis results found for the determination of the trace and toxic element contents in the soils examined by means of the proposed XRF-technique.

Trace and toxic elements	*Found (%), Middle loamy variety n = 15	*Found (%), Light loamy variety n = 15	*Found (%), Sandy loam variety n = 15
F	540 ± 19.0	494 ± 17.0	560 ± 25.0
V	237 ± 3.5	165 ± 3.2	140 ± 2.7
Cr	139 ± 2.8	96 ± 1.6	85 ± 1.7
Co	22 ± 1.7	15 ± 1.7	14 ± 1.3
Ni	76 ± 1.2	42 ± 0.5	35 ± 0.4
Cu	65 ± 0.5	40 ± 0.4	33 ± 0.4
Zn	155 ± 0.9	95 ± 0.9	77 ± 0.5
Ga	17 ± 0.6	14 ± 0.6	12 ± 0.5
Pb	20 ± 0.6	19 ± 0.9	18 ± 0.9
Rb	47 ± 0.4	57 ± 0.9	59 ± 1.2
Sr	228 ± 5.4	259 ± 11	281 ± 13
Y	30 ± 0.4	21 ± 0.6	17 ± 1.3
Zr	90 ± 3.1	115 ± 2.1	108 ± 3.7
Nb	9 ± 0.3	6 ± 0.4	5.6 ± 0.4
Ba	670 ± 10	730 ± 8	780 ± 10
La	27 ± 1.5	19 ± 1.5	18 ± 1.8
Ce	76 ± 4.9	61 ± 5.7	55 ± 5.5
Nd	37 ± 3.2	28 ± 3.4	26 ± 2.0

\*Mean of 15 determinations of the selected soil samples for each rock-forming element (for 99.95% confidence level).

found in the steppe soils of the Olkhon Island, especially in the samples of heavier particle size distribution ( $17 \text{ mg kg}^{-1}$ ). In these samples, elevated concentrations of  $\text{Fe}_2\text{O}_{3(\text{tot})}$  (7.64%) and  $\text{Al}_2\text{O}_3$  (17.71%) were determined, whereas the average gallium content in the soils of the Baikal region is only  $10.2 \text{ mg kg}^{-1}$  [35]. Probably, these mineral formations are present in small amounts in areas with an increased Ga concentration. The soils examined of a lighter granulometric composition (light loamy and sandy loam), which have elevated concentrations of coarse-middle sandy and coarse-silt fractions, are characterised by higher concentrations of Rb, Sr and Ba, unlike the middle loamy variety as it obvious from Table 3. It concerns with the isomorphic replacement of potassium in alkaline feldspars with barium, strontium and rubidium. The average Zr content in the soils of the Baikal region is  $36.9 \text{ mg kg}^{-1}$ . In all varieties of the steppe soils of the island, the Zr content is slightly variable in the range of  $90\text{--}115 \text{ mg kg}^{-1}$ , which is significantly higher than the average concentration but does not exceed its Clark value ( $170 \text{ mg kg}^{-1}$ ) [36]. The distribution of trace elements in the soils and some of their physicochemical properties are influenced by  $\text{Fe}_2\text{O}_{3(\text{tot})}$ , MnO and  $\text{CaCO}_3$ , the latter determines the pH value. The middle loamy soils of the Olkhon Island are enriched with  $\text{Fe}_2\text{O}_{3(\text{tot})}$  (7.64%) [2]. An increase in the concentrations of the elements of the iron group V, Cr, Co, Ni, Cu, and Zn agrees with [2].

### 3.3. Analytical figures of merit

Analytical figures of merit such as the relative standard deviation (RSD), limit of detection (LOD), instrumental limit of detection (ILD), repeatability of the WDXRF spectrometry and accuracy were carefully studied according to the recommendations from [16,37]. LOD was defined as being the smallest concentration of an analyte that can be reliably quantified analytical method with a 95.4% confidence level [16]. It was calculated from a series of 10 replicate specimens ( $n = 10$ ) prepared from the representative sample of the soil using the formula [20]. ILD was assessed as being the minimum net intensity of an analyte, which can be detected with a 99.95% confidence level using the following expression [16]. The obtained ILD and LOD values do not exceed  $5 \text{ mg kg}^{-1}$  for most elements determined, excluding Ba, Ni and Ce, for which these values are in the range  $7.0\text{--}15.8 \text{ mg kg}^{-1}$ . For fluorine, the calculated ILD value is  $55 \text{ mg kg}^{-1}$ .

In order to test repeatability of the WDXRF method, 10 tablets were prepared from the single representative sample of the soil and measured once, then one of the tablets was measured 10 times [20]. The RSD value of the measurement does not exceed 10–15%, which is admissible for the analytical XRF results of geological samples [15]. The relative percentage difference (RPD) between the certified and measured values was found to be satisfactory and ranged from 94% to 103%. The accuracy of the WDXRF method was checked by measuring the SGR-1b and Jk-1 ICRMs.

### 3.4. The assessment of the soil contamination

The preliminary assessment of the soil contamination was carried out using the contamination factor ( $C_f$ ) for a single element and contamination degree ( $C_{\text{deg}}$ ). The  $C_f$  factor was defined as the ratio of the heavy metal mean concentrations in the top soil horizon ( $\sim 0\text{--}15 \text{ cm}$ ) to the regional background. The regional background values for F, Pb, Cr, Co, V, Ni,

Cu, Zn for the calculation were taken from [35]. The  $C_f$  accounts for the contamination of single elements. To describe the contamination factor, we used the following ranges [38]:  $C_f < 1$  (low contamination factor, indicating low sediment pollution),  $1 \leq C_f < 3$  (moderate contamination factor),  $3 \leq C_f < 6$  (considerable contamination factor),  $6 \leq C_f$  (very high contamination factor).

The assessment of the overall pollution of soil was based on the degree of contamination ( $C_{deg}$ ), which was evaluated as the sum of all contamination factors for all elements examined, and four classes were recognised accordingly [38]. These classes are the following:  $C_{deg} < 8$  (low degree of contamination),  $8 \leq C_{deg} < 16$  (moderate degree of contamination),  $16 \leq C_{deg} < 32$  (considerable degree of contamination),  $32 \leq C_{deg}$  (very high degree of contamination).

The order of the mean  $C_f$  was  $F (3.0) > Pb (1.7) > V (1.6) > Zn (1.5) > Co (1.1) > Cr (1.0) > Cu (0.97) > Ni (0.92)$ . The maximum  $C_f$  was 3.0 for F, which indicates considerable pollution level of the environment. The highest values of  $C_f$  were 1.7 for Pb, 1.6 for V, 1.5 for Zn, 1.1 for Co and 1.0 for Cr, which gives evidence of moderate contamination level of the soils examined. For Cu and Ni, the  $C_f$  values were 0.97 and 0.92, respectively, which show low soil pollution. The degree of the contamination  $C_{deg}$  for all testing areas was 11.79, which denotes moderate degree of the pollution level of the environment [38].

### ***3.5. Comparison of heavy metal concentrations and fluorine with the values of regional background, Clark, average concentrations and maximum permissible concentrations in soils***

Comparison of the obtained F, V, Zn, Co, Cr, Cu, Ni and Pb concentrations in the soils examined with the values of regional background, Clark, average concentrations and maximum permissible concentrations (MACs) were carried out [35,39].

The average concentration of fluorine in the soil of the Baikal region is  $320 \text{ mg kg}^{-1}$ , Clark –  $200 \text{ mg kg}^{-1}$ , the regional background –  $175 \text{ mg kg}^{-1}$  and the MAC value –  $400 \text{ mg kg}^{-1}$  in accordance with [35,36]. Accordingly [39], the considerable contamination of the soils examined with this element was observed ( $C_f = 3.0$ ). The F content in soil and sedimentary rocks is considered to be  $500 \text{ mg kg}^{-1}$ ,  $500\text{--}1300 \text{ mg kg}^{-1}$  is critical [35]. According to these literature data, the F content ( $494\text{--}565 \text{ mg kg}^{-1}$ ) in the studied soils is on the border of the permissible level. The elevated concentrations of fluoride can be associated with the reaction medium (pH) of the aqueous extract of the studied soils, as well as with the accumulation in the parent rocks. Another reason for the increased fluorine content may be the use of phosphate fertilisers on the territory of the Olkhon Island, which caused it to enter the soil.

The average concentrations of Pb in the soils of the Baikal region are within the interval of  $11.0\text{--}11.6 \text{ mg kg}^{-1}$ , Clark –  $8 \text{ mg kg}^{-1}$ , the regional background is  $10 \text{ mg kg}^{-1}$  and the MAC value is  $32 \text{ mg kg}^{-1}$  in accordance with [35,36]. The Pb concentrations in all soil varieties are twice as high as these values, excluding the MAC value. Pb is a highly toxic element. Accordingly [39], the average level of the soil pollution with this element was defined ( $C_f = 1.7$ ) despite the MAC value. Presumably this is due to the organisation of illegal landfills on the territory of the Olkhon Island, and Pb migrates along with the current of soil moisture, which over time can cause pollution of groundwater and soils in reduced relief elements.

Vanadium belongs to the elements of high toxicity and affects the respiratory and nervous systems of humans. The regional background of V in the soils of the Baikal region is within the interval of 100–114 mg kg<sup>-1</sup> equal to the Clark value (100 mg kg<sup>-1</sup>) [35]. The average concentrations of vanadium are in the range of 110.4–121.0 mg kg<sup>-1</sup> and the MAC value is 150 mg kg<sup>-1</sup> [35]. The obtained V contents for all varieties are in the range of 140–237 mg kg<sup>-1</sup> that is above all established values. Accordingly [39], the moderate contamination of the soil with this element was observed ( $C_f = 1.6$ ). In obedience to [35], the elevated contents of vanadium in the Baikal region (127–255 mg kg<sup>-1</sup>) associated with the release of igneous rocks.

Zn is very important and in the same time toxic element, which is accumulated in the upper soil horizon (~0–15 cm) and it is in association with Pb and Cu. The average concentrations of Zn in the surface layers of soils of the World vary within the interval of 17–125 mg kg<sup>-1</sup>, Clark – 50 mg kg<sup>-1</sup>, the regional background is 87 mg kg<sup>-1</sup> and the MAC value is 110 mg kg<sup>-1</sup> in accordance with [35,36]. Accordingly [39], the moderate contamination of the soil with this element was observed ( $C_f = 1.5$ ). The obtained Zn concentrations in all soil varieties are within the interval of 77–155 mg kg<sup>-1</sup> as could be seen from Table 3, that exceed the regional background, Clark and MAC values. In addition to natural sources of zinc in the soil examined there are also human-caused sources, such as domestic waste landfills and leakage of wastewater from numerous tourist leisure bases located on the Olkhon Island.

From the geochemical point of view, an increase in the concentrations of vanadium and zinc is associated with the weighting of the particle size distribution of the soil from sandy loam to middle loamy varieties.

The average concentrations of Cu and Ni in the soils of the Baikal region are within the intervals of 42.5–46.7 and 42.0–44.7 mg kg<sup>-1</sup>, respectively [35]. The values of Clark for Cu and Ni are 20 and 40 mg kg<sup>-1</sup>, respectively [36]. The values of the regional background for Cu and Ni are 51 and 44 mg kg<sup>-1</sup>, and the MAC values are 55 and 85 mg kg<sup>-1</sup> in accordance with [35,36]. The calculated values of concentrations for Cu and Ni are in the ranges of 33–65 and 35–76 mg kg<sup>-1</sup>, respectively, which do not exceed the regional background values and slightly exceed the Clark and MAC values. In accordance with [39], the values of the  $C_f$  factor are equal to 0.97 for Cu and 0.92 for Ni, which are indicating low soil pollution.

The average concentrations of Cr and Co in the soils of the Baikal region are 101.9 and 17.0 mg kg<sup>-1</sup>, respectively [35]. The values of Clark for Cr and Co are 200 and 30 mg kg<sup>-1</sup>, respectively [36]. The values of the regional background for Cr and Co are 100 and 17 mg kg<sup>-1</sup> in accordance with [35]. The calculated values of the Cr and Co concentrations are in the ranges of 85–139 and 14–22 mg kg<sup>-1</sup>, respectively, which do not exceed the Clark values. The MAC values for Cr and Co equal to 64 and 40 mg kg<sup>-1</sup>, respectively, were used from the Canadian Council of Ministers of the Environment (CCME) [40] due to the absence of its values in the Russian Guide [39]. The obtained values of the Cr contents for all varieties exceed the MAC value and also slightly exceed the regional background and average concentrations for the Baikal region. In accordance with [39], the values of the  $C_f$  factor are equal to 1.00 for Cr and 1.10 for Co, which are indicating moderate soil pollution.

Thus, the comparison shows that the obtained values of the concentrations of all toxic elements in the soils examined exceed the values of the average concentration, regional

background, Clark and MAC, excluding Cu and Ni. These toxic elements indicate low level of the soil pollution.

### 3.6. Cluster analysis

Cluster analysis of R- and Q-types for all studied soil varieties was carried out in accordance with [28], allowed to identify groups of elements and analyse the correlation links between them. R-type cluster analysis revealed strong links ( $R = 0.98\text{--}1.00$ ) between Cr and Nd, V, Ce and La, Ni, Cu and Co, Zn and Y, Nb and Ga. Three groups of the elements are distinguished: (1) Cr, Nd, V, Ce, La; (2) Ni, Cu, Co, Zn, Y, Nb, Ga, Pb; (3) Rb, Ba, Sr, Zr. These groups are represented in Figure 2. As could be seen from the Figure, fluorine occupies an independent position and has a coefficient close to zero, which indicates on the disconnect with the clay component of the soil. Presumably, it has a different petrochemical nature and is introduced into the soil by anthropogenic means. There is a strong relationship between the first and second groups ( $R = 0.85$ ), the correlation coefficients are positive and close to 1.0 for all elements. The third group of the elements is associated with the first and second groups of feedback ( $R = -0.40\text{--}0.60$ ), that is, the interchangeability of the considered components takes place. At the

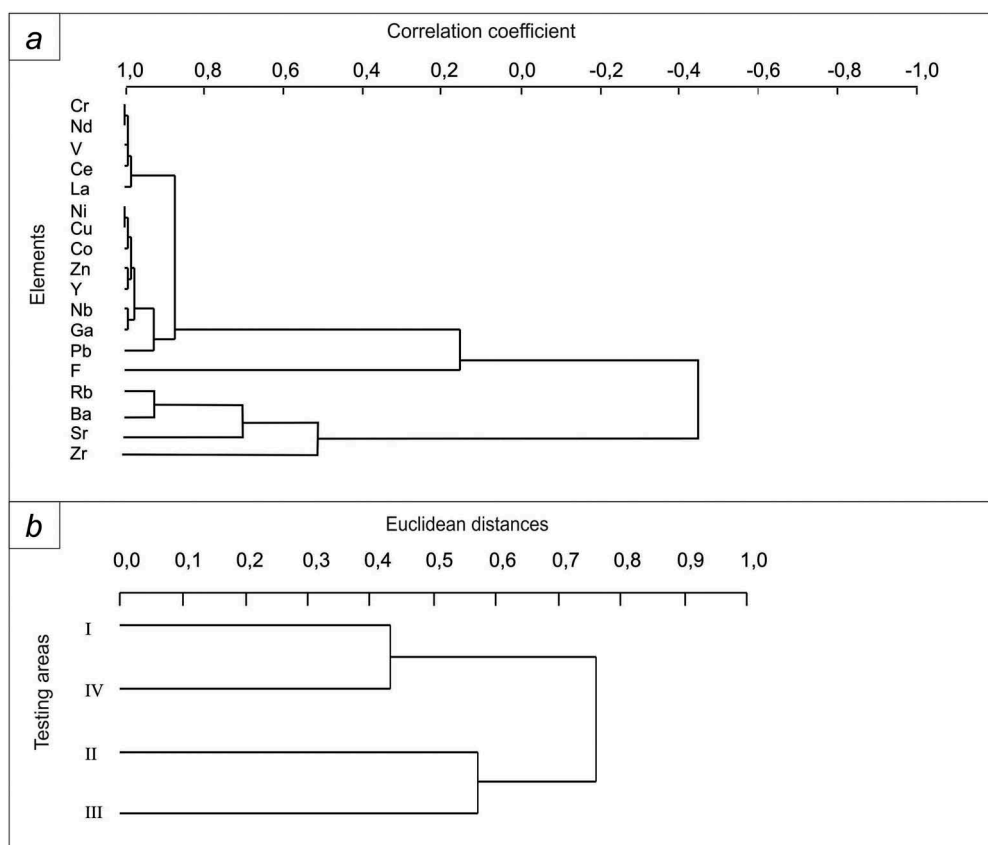


Figure 2. Dendrogram of cluster analysis on trace and toxic elements.

same time, with increasing contents of V, Co, Ni, Cu, Zn, La, Ce, and Nd, the concentrations of Sr and Ba decrease, this is determined experimentally for sandy loam soil. Elements that accumulate in various clay minerals of the soil were attributed to the first group.

Elements of the second group are closely associated with various iron minerals in soils, including ore. There is a strong correlation between the first and second groups ( $R = 0.85$ ), since the minerals of iron oxides and hydroxides are present in the composition of the fractions ( $<0.001$  mm) of the soil. Taking into account a number of chemical properties of all these elements of the second group, it can be assumed that Y, Nb and Ga can be part of the iron ore minerals.

The third group of elements is associated with the first two feedbacks ( $R = -0.40-0.60$ ), since typical components (Ba, Sr, and Zr) prevail here. Rubidium, presumably, replaces barium isomorphically, since it is a scattered element that practically does not form its own minerals in nature.

The Q-type cluster analysis revealed two groups of the steppe soil samples based on certain differences in their granulometric, chemical and microelement composition. The first combined samples of middle loamy and light loamy varieties, distributed in regions II and III, and characterised by high average concentrations of V, Cr, Ce, as well as lower Ba, Sr, and  $S_{\text{tot}}$ . The second group identified sandy loam and light loamy soils close to it in terms of trace elements, which are common in regions I and IV.

Light and middle loamy and sandy loam soils distinguished by the granulometric composition differ in the content of the heavy metals. In middle loamy soil, the heavy metals are contained in a greater amount than in light loamy and sandy loam varieties due to differences in the concentrations of coarse (0.002–0.001 mm) and fine clay (clay) ( $<0.001$  mm) fractions.

Thus, the R-type cluster analysis made it possible to identify correlation relationships between individual trace elements and their groups, as well as to establish localisation centres for certain chemical elements. In turn, the Q-type cluster analysis, along with the separation of the samples of the studied soils into groups, confirmed experimentally established differences in the properties and chemical composition of the soils examined in terms of the cation exchange capacity of the CEC, the total content of water-soluble salts, the level of concentrations of the elements determined, the results of the particle size analysis.

#### 4. Conclusions

In this work, we applied the suggested approach to the understanding geochemical processes occurring in the Baikal region stepper soils with using a convenient, rapid, reliable, and non-destructive spectroscopic XRF-technique without extensive sample treatment. The proposed technique has been applied for the determination of major, trace, and toxic elements in environmental solid samples. For the present report, the determination of rock-forming ( $S_{\text{tot}}$ ,  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{MnO}$ ,  $\text{Fe}_2\text{O}_{3(\text{tot})}$ ), trace and toxic (F, V, Cr, Co, Ni, Cu, Zn, Ga, Pb, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Nd) elements in the selected soil samples was carried out by means of the XRF-technique.

Three varieties of the steppe soils were distinguished: middle loamy, light loamy and sandy loam. In addition, the primary data relating to the assessment of the soil heavy metal contamination have been presented. Despite the differences in the grain-size composition and physical-chemical properties, all studied samples belong to weakly carbonated, but in the middle loamy soil, a slight degree of sulphate (gypsum) salinisation was revealed. In addition, the soils examined have a positive potential associated with a high content of humus, the optimal composition of exchangeable cations, as well as favourable pH values that have a great influence on the behaviour of various chemical elements in soil solutions. The work shows that the chemical composition is of no small importance for the process of soil formation. For the first time, the influence of soil granulometric features on the content level of the rock-forming and toxic elements in them has been established. In all varieties of the steppe soils with weighting of the particle size distribution associated with an increase in the concentrations of finely dispersed clay fractions, there is an increase in the concentrations of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_{3(\text{tot})}$ ,  $\text{TiO}_2$ ,  $\text{MgO}$  and a decrease in  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $S_{\text{tot}}$  from sandy loam to middle loamy variety.

The obtained ILD and LOD values do not exceed  $5 \text{ mg kg}^{-1}$  for most elements determined, excluding Ba, Ni and Ce, for which these values are in the range  $7.0\text{--}15.8 \text{ mg kg}^{-1}$ . For fluorine, the calculated ILD value is  $55 \text{ mg kg}^{-1}$ . The RSD value of the measurement does not exceed 10–15%. The RPD between the certified and measured values was found to be satisfactory and ranged from 94% to 103%.

The preliminary assessment of the soil contamination showed the following results. The order of the mean  $C_f$  was  $\text{F} (3.0) > \text{Pb} (1.7) > \text{V} (1.6) > \text{Zn} (1.5) > \text{Co} (1.1) > \text{Cr} (1.0) > \text{Cu} (0.97) > \text{Ni} (0.92)$ . It indicates considerable and moderate pollution levels of the environment excluding Cu and Ni. The  $C_{\text{deg}}$  value for all testing areas was 11.79, which denotes moderate degree of the pollution level of the environment.

Additionally, a comparison of the obtained F, V, Zn, Co, Cr, Cu, Ni and Pb concentrations in the soils examined with the values of regional background, Clark, average concentrations and MACs was carried out. It showed that the obtained values of the concentrations of all toxic elements in the soils examined exceed these values, excluding Cu and Ni. These toxic elements indicate low level of soil pollution.

Cluster analysis of R- and Q-types for all studied soil varieties allowed to identify groups of elements and analyse the correlation links between them. The Q-type cluster analysis revealed two groups of the steppe soil samples based on certain differences in their granulometric, chemical and microelement composition. The R-type cluster analysis made it possible to identify correlation relationships between individual trace elements and their groups, as well as to establish localisation centres for certain chemical elements.

The paper presents primary data on the elemental composition of steppe soils of the Olkhon Island, the Baikal region. This study was carried out within the framework of project IX.124.1.2 (PK AAAA-A17-117022250064-6) and is a part of large paleogeodynamic and ecological-geochemical study of the territory included in the UNESCO World Heritage Site.

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## Disclosure statement

No potential conflict of interest was reported by the authors.

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