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ARTICLE



Assessment of soil pollution level using environmental indices in the Olkhon Island, Lake Baikal, Russia: primary data

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ABSTRACT

This work is dedicated to the study of ecological and geochemical state of mountain-stepper landscapes of the Olkhon Island, Lake Baikal, which are influenced by modern human-caused impact. The main goal of our research is the assessment of the soil pollution level caused by entry of heavy metals into soil cover. We studied the distribution of toxic elements such as Hg, As, Cd, Pb, Cr, Co, Ni, Cu, Zn, which is based on atomic absorption and X-ray fluorescence methodology. To evaluate the contamination of the soils examined, we applied geoecological indices used in ecological-geochemical assessment such as enrichment factor, contamination factor, degree of the contamination and pollution load index were applied. During the research, we made the following conclusions. The tests revealed the elevated contents of Cd, Co, Pb, Ni, Zn in the soils examined. Namely, the degree of the contamination for the mean metal contents in all five profiles (A, B, C, D, E) indicated moderate pollution level of the environment. The pollution load index for all profiles denoted that C profile was heavily polluted; A, B, D and E profiles were moderately polluted. Thus, the obtained primary results indicated the moderate soil pollution level at all profiles in the island. Finally, we emphasise that the increase of the contribution of metals from the anthropogenic sources in soils plays an important role in the environment of the island.

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Lake Baikal; stepper soils; heavy metals; soil pollution level; contamination indices; X-ray fluorescence and atomic absorption spectrometry

1. Introduction

In our research, the main attention was paid to the study of geochemical and ecological state of the mountain-stepper landscapes of the biggest island of Lake Baikal, which are influenced by modern human-caused impact. The study object is a territory included in the UNESCO World Heritage Site, as well a part of the Baikal National Park [1].

Soil is the main component of the natural environment, which carries long-term information on the behaviour of chemical elements determined by the composition of parent rocks, the topography, climate and technological impact. Simultaneously, soil acts as the main physicochemical barrier to the migration of heavy metals [2–4]. Soil is considered primarily as a component of the landscape changing or evolving over time [2]. A wide variety of natural landscapes is characteristic in general for the entire Baikal region. Outstanding interest is to study territories associated with arid mountain zoning

(position in the rain shadow), on which steppe soils are widespread. The lack of atmospheric moistening and high infiltration of water of these soils reduce their biological productivity. Obviously, this leads to the degradation of soil-vegetation cover. During a long time, the territory around Lake Baikal has been experiencing anthropogenic pressures caused by housekeeping, agricultural and, largely, tourism activities, especially on the Olkhon Island. An indicator showing a violation of the ecological balance of the environment is the upper soil horizon. The human-caused impact on the soil cover in the Olkhon Island activated a certain type of exogenous geological processes, which occurred in the formation of small and large gullies on the slopes. At the same time, these territories are exposed to contamination with various consumer wastes due to illegal landfill organisation and leakage from the sewage system of resorts, containing heavy metals. Various compounds of the heavy metals migrate in the soil along with the current of soil moisture and over time can cause pollution of groundwater and soil in a low relief feature, as well as the coastal zone of Lake Baikal [5]. Nowadays, the investigation of the Baikal region geological environment by different geochemical techniques gives rise to a great interest of scientists because of the increase of industrial load [6–8].

The objective of the work is to determine toxic element contents in the steppe soils of the island to perform a preliminary assessment of soil pollution level. To achieve this, we used the following approaches: (1) determination of the heavy metal contents such as Hg, Cd, As and Pb by Atomic Absorption Spectrometry (AAS) and Cr, Co, Ni, Cu, Zn, As and Pb by X-ray fluorescence (XRF) spectrometry in the selected soil samples; (2) comparison of the obtained data with regional background values [6,9], and the guideline values taken from Russian Guide – Hygienic Standards (HS) [10] and the Canadian Guide – Canadian Council of Ministers of the Environment (CCME) [11] for the elements examined; (3) assessing the soil pollution level using various indices such as contamination factor, normalised enrichment factor, pollution load index and degree of the contamination.

2. Experimental

2.1. Study area and soil sampling

Administratively, the Olkhon Island is a part of the Irkutsk region of the Olkhon area with the centre located in Huzhir village (53°11'36" N and 107°20'38" E). The length of the island between the capes Khoboj and Umysh-Tame is 73 km, a width is up to 15 km, and an area is about 700 km² [12].

Nowadays, the human-caused impact on the soil cover of the island is very extensive and caused by tourist and recreational development. As previously noted, the entry of various heavy metal compounds into the soil cover brings about a change in its chemical composition and physicochemical properties, which is hazardous for the land and water resources of the island. The heavy metal compounds accumulated in the topsoil horizon (15 cm) are the indicator showing the violation of ecological balance of the environment. Thus, the topsoil horizon of piedmont dry steppes of the Olkhon Island was chosen as the study object. According to the Ecological Atlas [12], on the territory of the Olkhon Island, three types of soils were distinguished: mountain dark-chestnut thin rubbly, chestnut (Kastanozems) under steppe vegetation and sod-podbur (Retisols) under forest

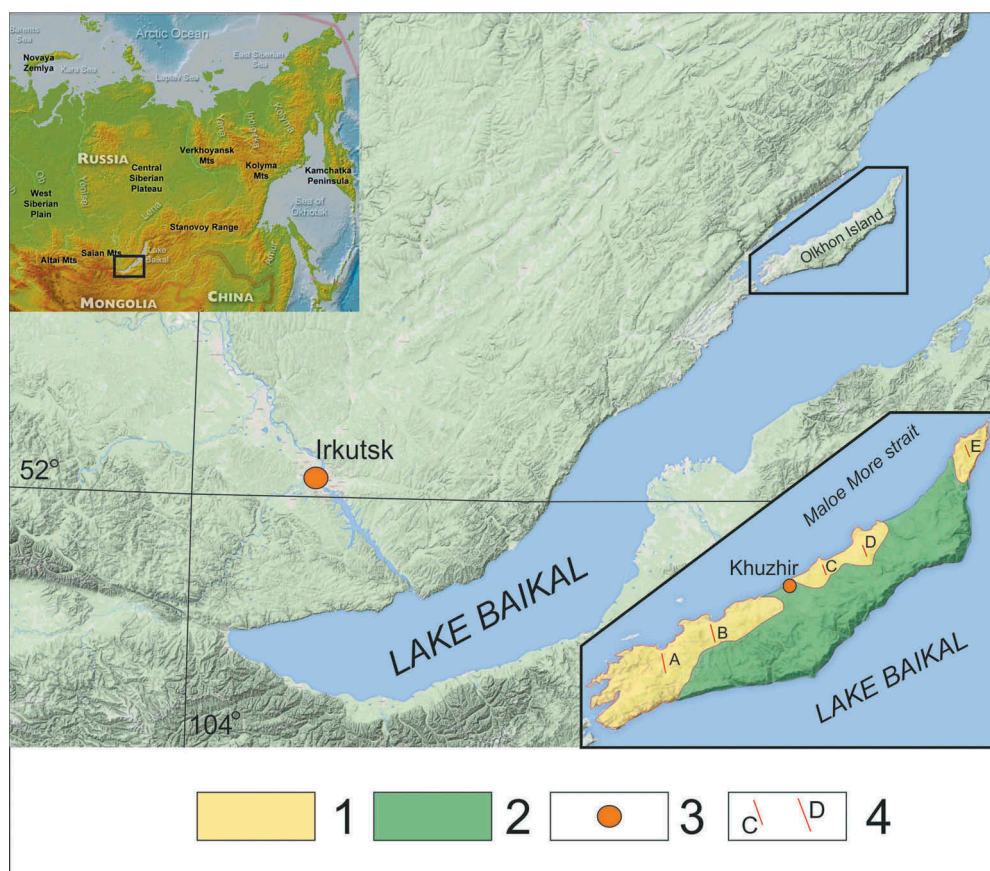


Figure 1. The study area: 1 – Mountain dark-chestnut thin rubbly, chestnut (Kastanozems) under steppe vegetation; 2 – Sod-podbur (Retisols) under forest vegetation; 3 – Huzhir village, centre of the Olkhon Island; 4 – five profiles discussed.

vegetation as presented on [Figure 1](#). In accordance with the World Reference Base for Soil Resources – WRB [13], these steppe soils are Kastanozems. These soils spread within meadow-steppe geosystems, the total area is 219.5 km². These territories are located in the travel and transport zones.

All soil samples refer to the stepper soils, which were exposed by the human-caused impact. These samples in an amount about 25 pieces were selected from each of five key profiles (A, B, C, D, E) by the classic envelope method with a step of 100 m, as seen in [Figure 1](#). The sampling area has been divided into various portions. Then from the different sport, samples were taken and merged as composite sample for different sites A, B, C, D, E. These profiles include all types of the human-caused impact. All soil samples were collected from the depth of 15 cm using a stainless steel spade. The collected samples were sealed in polyethylene bags and kept in natural wet conditions during fieldwork. The location of each collected sample was marked by GPS, and environmental conditions for each sample were recorded. The soil samples were transported to our laboratory, and air-dried at ambient temperature for 72 h, carefully crushed, ground in an agate mortar and sieved before performing analysis.

2.2. Instrumentation and reference materials

The measurement of the Cr, Co, Ni, Cu, Zn, As and Pb intensities has been carried out in a vacuum condition using a wavelength dispersive (WD) XRF spectrometer S8 TIGER (Bruker AXS, Germany). The instrument is equipped with a 4 kW power X-ray tube with a rhodium anode. Detailed information about the WD XRF-spectrometer features can be found elsewhere [14]. Processing the X-ray spectra and correction of the matrix effects were performed using the software SPECTRA^{plus} [15] linked to the equipment. 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 (Irkutsk, Russia).

The analytical quality control of the heavy metal contents was carried out using the Reference Materials (RMs) of different types of soils and sediments: SSK-2 (industrial soil), SDPS-1 (background soil), SDPS-2 (industrial soil), OOKO303 (carbonaceous background silt), OOKO302 (anomalous silt). These RMs were produced and certified by the Institute of geochemistry after A.P. Vinogradov of SB RAS and the laboratory of the Research Institute of Applied Physics at Irkutsk State University in Russia [16]. The calibration set of the RMs and Certified Reference Materials (CRMs) contains the soils and sediments of various compositions, and calibration curves were constructed using these reference materials. All RMs, CRMs and soil samples for XRF analysis were prepared in accordance with requirements given in Industrial standard – OST [17]. Values of the element contents in these RMs and CRMs vary within wide ranges (Table 1). The matrix correction method using fixed alpha-coefficients has been performed by the software SPECTRA^{plus} [15]. Table 1 presents the calibration data obtained for the sediment and soil matrices. The standard deviation (SD) of the measurement characterises a dispersion point around the calibration line. As it can be seen from Table 1, the comparison indicated that the SD values obtained applying the fixed alpha-coefficients were less than the SD values achieved without the matrix correction by 1.3–5.4 times.

Statistical processing of the XRF results was performed in accordance with the recommendations given at a 95% confidence interval [18]. The instrumental limit of detection (ILD) was defined as being the minimum net intensity of an element, which can be detected by an instrument in a given analytical context with a confidence level from

Table 1. Calibration data obtained for the soil and sediment matrices and the accuracy of the element determinations in the CRM SGR-1b.

Element	Number of the CRMs and RMs	Calibration range, mg kg ⁻¹	Line overlap correction	Influence coefficients (alpha-correction)	SD ^a , mg kg ⁻¹		SGR-1b CRM (Green River Shale)	
					I ^b	I ^c	^d C _{XRF}	^e C _{certified}
Cr	25	4.3–2000	VK _α , MnK _α	CaK _α , TiK _α , FeK _α	27	5	33 ± 0.5	30 ± 2.0
Co	20	2–106	FeK _α	SiK _α , VK _α , MnK _α	5	3	13 ± 0.4	12 ± 0.6
Ni	20	4.4–2240	RbK _α	SiK _α , CaK _α , FeK _α	22	14	24 ± 2.0	29 ± 3.0
Cu	25	8–240	NiK _α	CaK _α , FeK _α	9	7	64 ± 3.0	66 ± 4.0
Zn	20	10–610	CuK _α	CaK _α	21	9	72 ± 2.0	74 ± 2.5

^aStandard deviation.

^bWithout correction of the matrix effects.

^cWith accounting of the matrix effects (alpha-correction).

^dObtained concentrations of the metals (mg kg⁻¹) for the CRM SGR-1b: mean ± SD, *n* = 5.

^eCertified concentrations of the metals (mg kg⁻¹) for the CRM SGR-1b: mean ± SD, *n* = 5.

[18]. The values of the ILDs for the elements determined were assessed in compliance with [19]. The ILD values for Co, Ni, Zn are less than 1 mg kg^{-1} , and for Cr – 2.3 mg kg^{-1} .

The accuracy of the Cr, Co, Ni, Cu and Zn determinations in the samples studied was checked by measuring the SGR-1b CRM (Green River Shale) produced by the United States Geological Survey. Comparison of the achieved results (see Table 1) indicated that the data obtained show a good agreement with the reference values. A relative percentage difference (RPD) between the certified and measured concentration values was found to be satisfactory and ranged between 82% and 110%.

The As, Cd and Pb contents were obtained by AASSolaar M6 (Thermo Electron, USA) equipped with an automatic sample introduction system for unattended operation. This equipment is located at the Center for Multielement and Isotopic Studies, V.S. Sobolev Institute of Geology and Mineralogy (IGM), SB RAS (Novosibirsk, Russia). All measurements were performed accordingly the certified method – M-MVI-80-2008 [20].

The contents of Hg in the samples examined were measured by flameless AAS on a RA-915 M mercury analyser (Lumex®, Russia) with a PYRO-951 + pyrolysis attachment. The technical attributes of the instrument allow avoiding special pretreatment of solid samples. The SDPS-3 RM (sod-podzol-silt soil) certified for heavy metals and mercury has been applied for calibration this spectrometer and checking the quality of analyses. The determination of the Hg content in the studied samples was conducted in accordance with the certified method – Federal Preservation Regulation Document (FPRD) [21]. The measurement time of each sample was 100 s. The SD values were no more 20% ($p = 0.95$) for concentrations in the range from $5 \cdot 10^{-7}$ to $2.5 \cdot 10^{-2} \text{ wt.}\%$ (specified by producer). Standards and samples were diluted with specpure Al_2O_3 .

The digestion procedure of the samples for the AAS was conducted in a mixture of inorganic acids such as HF, HNO_3 , HCl with pre-ignition of solids (stepwise heating to 600°C , with 50°C steps) according to [22]. The analytical quality control of the As, Pb and Cd contents by AAS was carried out using the CRMs of soils such as 2709a (San Joaquin Soil) and 2711a (Montana Soil II) produced and certified by the National Institute of Standards and Technology (NIST, US Department of Commerce).

The relative standard deviation of the AAS measurement for As, Cd and Pb does not exceed 35%, which is admissible for the analytical results of the soil, ground and sediment samples [20]. The RPD values are within the interval from 86% to 104%. The LOD values for the As, Cd and Pb determinations were assessed as twice the standard deviation of the blank solution measured 10 times with 5 s integration time. The values of the obtained LODs for As, Pb and Cd are less than 0.1 mg kg^{-1} . The accuracy of the elements determined was checked using the 2410a CRM (Montana Soil I).

2.3. Data processing

Dozens of works devoted to assessing the level of the soil and sediment pollution by heavy metals [23–27].

To study heavy-metal retention in the stepper soil samples and to perform the preliminary assessment of the environmental risk, normalised enrichment factor (EF), contamination factor (C_f), degree of contamination (C_d) and pollution load index (PLI) were computed.

The enrichment factor (EF) for each metal determined in the soil samples was calculated by dividing its ratio to the normalising (reference) element (Fe) by the same ration found in the chosen baseline [28]:

$$EF = \frac{(C_{Metal}/C_{Fe})_{Sample}}{(C_{Metal}/C_{Fe})_{Background}} \quad (1)$$

In this expression, the regional background value of iron (Fe) was taken from [29]. The measurement of the Fe intensity was performed using the XRF spectrometer and its content in the studied samples was computed by the SPECTRA^{plus} software. In this study, iron was used as the reference element due to the following reasons: (1) geochemistry of Fe is similar to that of some trace metals; (2) iron natural concentration vary within the interval from 3% to 5% that is close to the Clark of the lithosphere [29] and tends to be uniform. Five contamination categories are recognised on the basis of the EF such as [30]: deficiency to minimal enrichment ($EF < 2$), moderate enrichment ($2 < EF < 5$), significant enrichment ($5 < EF < 20$), very high enrichment ($20 < EF < 40$), extremely high enrichment ($EF > 40$).

The assessment of the soil contamination was carried out using the contamination factor (C_f) for a single element and contamination degree (C_d). The C_f factor was defined as the ratio of the heavy metal mean concentrations in the topsoil horizon (15 cm) at five profiles to the regional background. The C_f factor evaluates the enrichment in metals in relation to the background concentrations of each metal in soils. The C_f index was expressed as [31]

$$C_f = \frac{C_{metal}}{C_{background}}, \quad (2)$$

where C_{metal} and $C_{background}$ are concentrations of the element in the soil sample and the background value of the element, respectively. The C_f calculation is identical to the EF calculation, except the fact that the CFs do not normalise concentrations against the normalising element (Fe). The regional background values for Hg, Pb, Cr, Co, Ni, Cu, Zn for the calculation were taken from [6], and for As and Cd from [9]. The C_f accounts for the contamination of single elements. To describe the contamination factor, we used the following ranges [31]: $C_f < 1$ (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 contamination degree (C_d) of the environment was evaluated as the sum of all contamination factors for all elements examined [31]:

$$C_d = \sum_{i=1}^9 C_f^i \quad (3)$$

With this approach, the contamination factor C_f^i accounts the pollution of single elements according to the concentration requirement, and C_d -value is applied for the computing total soil pollution within the profiles studied. Four classes were recognised accordingly [31]. These classes are the following: $C_d < 8$ (low degree of

contamination), $8 \leq C_d < 16$ (moderate degree of contamination), $16 \leq C_d < 32$ (considerable degree of contamination), $32 \leq C_d$ (very high degree of contamination).

To assess the overall level of the soil pollution across all profiles examined, the pollution load index (PLI) was calculated as [32]:

$$PLI = (C_{f1} \times C_{f2} \times C_{f3} \times \dots \times C_{fn})^{1/n} \quad (4)$$

where n is the number of elements. PLI is a simple and convenient method for the evaluation of level of heavy metal contamination, namely, this one assesses the pollution load for individualised sites by expression the concentrations of all individual elements under our consideration. The pollution levels were divided in four grades accordingly [33]: no pollution ($PLI < 1$), moderate pollution ($1 < PLI < 2$), heavy pollution ($2 < PLI < 3$) and extremely heavy pollution ($3 < PLI$).

3. Results and discussion

3.1. Distribution of the heavy metals in the stepper soils

We considered the concentrations and the distribution of the heavy metals in the soils across the sampling site. The Hg, As, Cd, Pb, Cr, Co, Ni, Cu, Zn concentrations in the soil samples vary in the following ranges (Table 2).

The guideline values for Hg, As, Cd, Pb, Ni, Cu, Zn were taken from the Russian Guide [10], and values for Cr and Co were used from the Canadian Guide [11] due to the absence of its values in the Russian Guide. Figure 2 demonstrates the distribution of the heavy metals in the soils examined from each of five key profiles (A, B, C, D, E). So, as it can be seen from Figure 2, the highest concentrations of Zn (223 mg kg^{-1}), Ni (98 mg kg^{-1}), Cr (182 mg kg^{-1}), Co (62 mg kg^{-1}) and Cu (78 mg kg^{-1}) at profile C were significantly higher than their guideline values. The probability level is equal to 0.45. The highest values of the regional background concentrations were occurred for Hg (except A, B, C, E), As (except A, B, E), Pb (except A, D, E), Cr (except A, B, E), Co (except E), Cu (except A, B, D, E), Zn (except B, E). However, negligible exceedance of the regional background values was occurred for As (D profile), Pb (B profile), Co (B profile) and Zn (B profile).

Table 2. Ranges of the obtained concentrations, contamination and enrichment factors for the soils examined at five profiles.

Element	Ranges of concentrations (mg kg^{-1})	Ranges of contamination factor (C_f)	Ranges of enrichment factor (EF)
Hg	0.015–0.026	0.75–1.30	0.93–2.02
As	1.4–6.0	0.5–2.1	0.7–3.0
Cd	0.18–0.34	1.1–2.1	1.58–2.98
Pb	3.5–30.0	0.4–3.0	0.49–4.20
Cr	86–182	0.9–1.9	1.23–2.60
Co	15–62	0.9–3.6	1.24–5.11
Ni	46–98	1.1–2.3	1.50–3.19
Cu	33–78	0.7–1.6	0.96–2.28
Zn	87–223	1.0–2.5	1.34–3.43

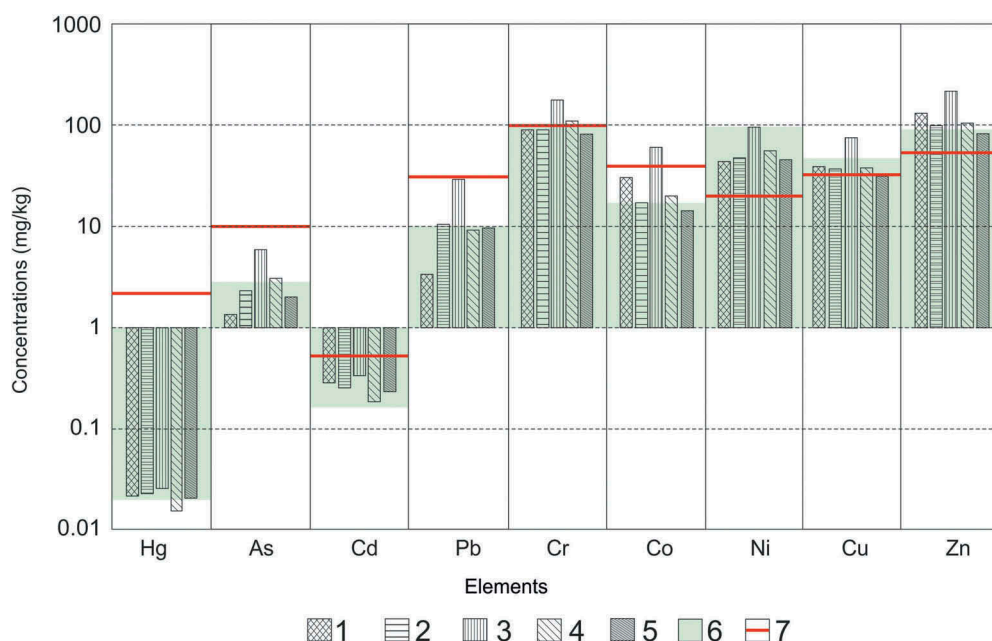


Figure 2. Distribution of the heavy metals in the soils examined of the Olkhon Island: 1–5 – A, B, C, D, E profiles, respectively; 6 – the regional background concentrations for the toxic elements; 7 – the guideline values for the toxic elements.

3.2. Indices for the pollution assessment

The heavy metal pollution and the preliminary environmental risk of the stepper soils were assessed using various indices such as EF, C_f , C_d and PLI.

3.2.1. Enrichment factor (EF)

The EF for each metal was assessed by the equation (Eq. 1). The EF ranges for the elements examined are presented in Table 2. The mean EF values for all five profiles were the following: Co (2.44) > Cd (2.24) > Zn (2.04) > Ni (1.96) > Pb (1.80) > Cr (1.63) > Hg (1.56) > As (1.51) > Cu (1.35). Along with that, the highest EF values for Co, Cd, Zn occurred at profile C and classified the soil as moderate polluted [30]. Cd (2.24), Co (2.44) and Zn (2.04) were the highest average EF values, which indicated the anthropogenic origin of these metals. The maximum EF was 5.11 for Co at profile C, as seen from Figure 3, whereas the mean EF for all profiles was equal to 1.84. So, it is classified the soil as significant contaminated according to [30]. It shows that the area was the subject of the agricultural impact in the past, namely the usage of arsenic or phosphate fertilisers, which is associated with the intensive agriculture practices. The EF values for A, B, D and E profiles vary within the interval from 1.05 to 2.64 (see Figure 3). It corresponds to a minimal and moderate contamination of the soils examined. The maximum EF for Hg was 2.02 at B profile, as it indicated in Figure 3, whereas the average EF was equal to 1.56, and we suggested that the Hg source was more likely to be natural and classified the soil as minimally contaminated [30].

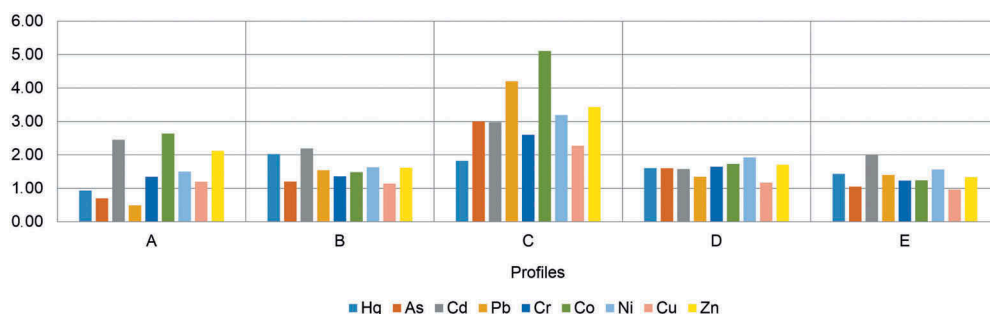


Figure 3. The normalised enrichment factor (EF) computed for each metal in the soils examined at five profiles.

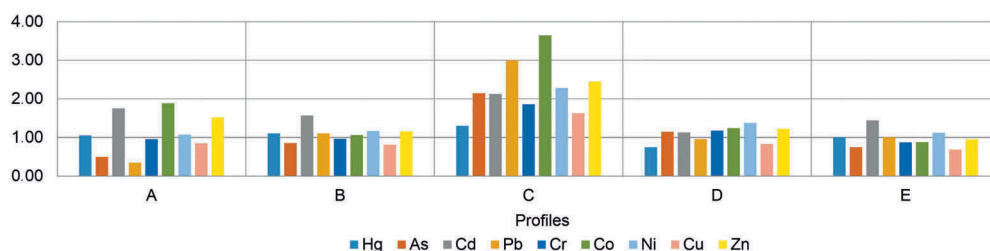


Figure 4. The contamination factor (C_f) computed for single toxic element in the soils examined at five profiles.

3.2.2. Contamination factor (C_f) and degree of the contamination (C_d)

The C_f was studied for each metal in the soil samples at all five profiles. The C_f values were calculated using Equation (2). The C_f ranges for the elements examined were the following (Table 2). The used method of the contamination factor (C_f) assesses the enrichment in metals in relation to the background concentrations of each metal in soils. The order of the mean C_f was Co (1.74) > Cd (1.60) > Zn (1.46) > Ni (1.40) > Pb (1.28) > Cr (1.17) > As (1.10) > Hg (1.04) > Cu (0.96). The maximum C_f was 3.6 for Co and 3.0 for Pb at profile C, as it can be seen from Figure 4, and indicates considerable pollution level of the environment. The high C_f values were 2.5 for Zn and 2.3 for Ni at profile C (Figure 4), which give evidence of moderate contamination level of the soils examined [31].

The C_d value for all described profiles was calculated using the formula (Eq. 3) and is equal to 11.75, which denotes moderate degree of the pollution level of the environment [31].

3.2.3. Load pollution index (PLI)

To assess the overall level of the soil pollution across all profiles examined, Equation 4 was used. The order of the PLI for all profiles was C (2.18) > D (1.08) > B (1.07) > A (1.05) > E (1.02). It is demonstrated that C profile was heavily polluted; A, B, D and E profiles were moderately polluted in accordance with [32]. The obtained results provide a simplified way of comparing soil quality between different profiles.

Finally, to metal accumulation, increasing the Co, Cd, Pb, Zn, Ni concentrations implies enhanced their mobility. As is known, these metals are mutually linked and with Fe and Mn as well [34]. In the Olkhon Island, there are more than seven deposits of Fe and Mn ores, which were used in the past as a material for the obtaining ferroalloy [35]. The EF and C_f factors showed that the Cd, Co, Ni, Zn sources were more likely to be anthropogenic, whereas the As, Cu, Cr, Pb sources were similar to be the crustal (weathering product). In addition, it is suggested that the Hg source was more likely to be natural and classified the soil as minimally contaminated.

Generally, the overall contamination indices based on the C_d and PLI confirmed the results obtained applying the EF and C_f factors.

4. Conclusions

The application of the contamination and enrichment factors, and overall contamination indices allowed us to reveal elevated concentrations of some toxic elements in the stepper soils of the Olkhon Island such as Co, Cd, Pb, Zn, Ni. The obtained results have the following important implications:

- (1) On the basis of the mean enrichment factor (EF), the soils examined were classified as minimally contaminated with Hg, Ni, Pb, Cr, As, Cu in A, B, D, E profiles, and also moderately polluted with Co, Cd, Zn in C profile. The evolved highest EF values for Co, Cd, Zn indicated the anthropogenic origin of these metals. However, in some cases, the soils were significantly polluted with Co (5.11) and moderately polluted with As (3.0), Pb (4.20), Ni (3.19) in C profile. The Hg source was more likely to be natural and classified the soil as minimally contaminated.
- (2) Relying on the mean contamination factor (C_f), the soils studied were classified as moderately contaminated with Co, Cd, Zn, Ni, Pb, Cr, As, minimally contaminated with Hg, Cu in all profiles. Moreover, the degree of the contamination (C_d) equals to 11.75 for the mean metal contents in all profiles explains indicated moderate pollution level of the environment.
- (3) The pollution load index (PLI) for all profiles denoted that C profile was heavily polluted; A, B, D and E profiles were moderately polluted. Increasing the Co, Cd, Pb, Zn, Ni concentrations implies enhanced their mobility.

Thus, the applied indices are good tools to evaluate the pollution level of the soils examined and also to address monitoring studies.

Summarising the foregoing, this research presents the primary data of the heavy metal contents of the soils examined and the assessment pollution level. We emphasise that an important role is played by the increase of the human-caused impact on the island landscapes. The work performed relates to a regional research and it is a part of a large study of the current ecological and geochemical state of a territory included in the UNESCO World Heritage Site. Future studies will be related with considering distribution of the heavy metal contents in plants to assess the ecological state of the Olkhon area. The Co, Cd, Pb, Zn, Ni inputs in the studied soils should also be controlled to minimise pollution effects for plants, groundwater, and as a consequence for the human.

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Disclosure statement

No potential conflict of interest was reported by the author.

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