Assessment of metal pollution and subsequent ecological risk in the coastal zone of the Olkhon Island, Lake Baikal, Russia

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HIGHLIGHTS

- Relationships between the particle size of sands and their elemental composition were studied.
- Determination of Hg, Cd, As, Pb, Cr, Co, Ni, Cu, Zn was performed by X-ray fluorescence and atomic absorption spectrometry.
- Heavy metals pollution was from moderate to significant level for Hg, As, Cd, Pb, and Cu.
- The geochemical indices showed that the Hg, Cd, Pb, Cu sources were more likely to be anthropogenic.
- The Pearson correlation analysis indicated high positive correlations between Pb and Hg, As, Cd.

GRAPHICAL ABSTRACT
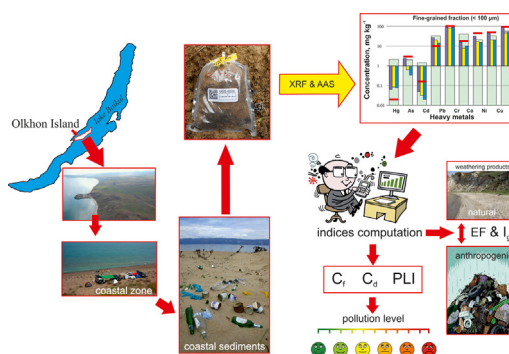
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ABSTRACT

Olkhon Island is the largest island in Lake Baikal and a part of Baikal National Park, Russia. The first objective of this study is to establish relationships between the particle size of accumulating sediments and their elemental composition, as well as the concentrations of heavy metals (Hg, Cd, As, Pb, Cr, Co, Ni, Cu, and Zn). The second goal is to completely assess the contamination level and to identify the possible sources of heavy metals using geochemical indices, including enrichment (EF) and contamination (C_f) factors, contamination degree (C_d), geoaccumulation index (I_{geo}), and pollution load index (PLI). The results obtained are summarized as follows. Heavy metal pollution in the coastal zone of Olkhon Island ranged from moderate to significant levels for Hg, As, Cd, Pb, and Cu. The EF and I_{geo} indices showed that Hg, Cd, Pb, and Cu sources were more likely to be anthropogenic, whereas the As, Cr, Co, Ni, and Zn sources were similar to crustal sources. Thus, Hg, Cd, and Pb are the main pollutants in the study area and pose high ecological risks. Pearson correlation analysis indicated high positive correlations between Pb and Hg (0.741), As and Cd (0.730), and Cd and Pb (0.803), and strong positive correlations among Cr, Co, Ni, Cu, Zn and Fe. This can reflect the same source and migration pathway, either crustal or anthropogenic. However, it does not indicate that Cr, Co, Ni, and Zn have anthropogenic origins because these metals are linked with Fe—Mn deposits. These findings could contribute to a more effective investigation of relationships between heavy metals and their sources. We emphasize that Hg, Cd, and Pb could rise to dangerous levels. These reliable results allow us to use our study as a model for studies relating to heavy metal contamination in different areas.

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1. Introduction

In recent years, the problem of heavy metal pollution has attracted critical attention worldwide due to the increase in human activities such as industrial, traffic, agricultural, and tourism activities (Bhuiyan et al., 2010; Wei and Yang, 2010; Li et al., 2014; El Zrelli et al., 2015; Zhang et al., 2017; Zhang et al., 2018; Al-Absi et al., 2019; Rinklebe et al., 2019). Heavy metals have become important pollutants in the environment. The relevance of this problem is obvious due to their nondegradable nature, since during migration, heavy metals can only change their level of concentration, location, and form. These pollutants can accumulate in soils and sediments for a long time during which human bodies can come in contact with the contaminated beach sand and seawater (Qu et al., 2014; Liu et al., 2018; Kim and Choi, 2019; Chandrasekaran et al., 2020). The intense influence of industry and tourism gives rise to a considerable change in the ecological state of the coastal zone of water bodies around the world (Gonzalez-Macias et al., 2006; Zhang et al., 2019; Liu et al., 2020). According to the data obtained in the 1980s, 70% of the world's coast is suffering changes due to high anthropogenic pressure (Bird, 1987). In addition, the study of the influence of human activity on biota and humans is becoming relevant. These problems are studied by using ecological toxicology, namely, the impact of toxic substances on ecosystems and their circulation in the environment.

Currently, the American Chemical Agency (CAS) of the American Chemical Society (ACS) has registered more than 166 million organic and inorganic chemical substances (CAS, 2020a; CAS, 2020b) (https://www.cas.org/support/documentation/chemical-substances). From this list of pollutants, the most dangerous are heavy metals that often occur on beaches, such as Pb, Cd, Hg, and Zn (Ozturk et al., 2015; Vivas et al., 2006); moreover, their accumulation in the environment is very rapid. Pollution of coastal zones caused by toxic metals is mainly from natural and anthropogenic activities. Natural sources include geological weathering of rocks that bear ores (Ross, 1994), weathering of coal mine spoils (Dang et al., 2002), fires and volcanic eruptions (Seaward and Richardson, 1990). Anthropogenic sources include different industrial processes, such as smelting and mining of metal ores that produce wastes containing heavy metals (Lalah et al., 2008; Rodriguez et al., 2009), agriculture (Liu et al., 2013) and tourism (Kim and Choi, 2019).

Lake Baikal is a unique natural water body, in which approximately 20% of the world's reserves and more than 80% of Russian reserves of surface fresh water are contained (Berkin et al., 2009; http://whc.unesco.org/en/list/754). In 1996, Lake Baikal was included in the list of UNESCO World Heritage Sites. In 2006, the government of the Russian Federation approved the boundaries of the Baikal natural territory (Fradkov, 2006). Olkhon Island is the largest island in Lake Baikal and a part of Baikal National Park, Russia. Currently, the area around the lake is used for economic and recreational purposes. Until 2014, twelve specially protected areas operated near Lake Baikal, which are now combined into two federal state units, namely, "Pribaikalye Preserve" and "Podlemorye Preserve" (Donskoy, 2013). Currently, Olkhon Island is a major tourist center and the most visited area in Lake Baikal. More than 100 thousand tourists visit Olkhon Island annually, and this number is increasing annually. In this regard, the anthropogenic load on the island has increased significantly, and as a result, the supply of toxicants to the environment, especially to the coastal zone, has also increased. This has led to an increase in the number of unauthorized garbage dumps, which were eliminated only in 2013 (http://baikal-info.ru/na-baykalskom-ostrove-olhone-nakonec-ubrali-svalku-kotoraya-sushchestvovala-okolo-30-let). However, the debris was removed only from the surface. Full soil reclamation has not been performed. This indicates that the pollutants remaining in the soil layer still have an impact on the environment. Pollutants can accumulate in the sediments of the coastal zone for a long time, and it is very difficult to remove them in a short period of time (Yaqin et al., 2008). It directly affects the physical and chemical properties of the beach sand. Moreover, they directly harm human health

through polluted beach sand and sediments if human bodies come into contact with them (Chandrasekaran et al., 2020). Further assessment of the degree and level of heavy metal contamination by determining the toxic concentrations in the beach sand is required. For our study, we chose the coastal zone because it is the most dynamic zone for material transfer, both in terms of mechanics and geochemical migration of chemical elements.

In summary, the problem of heavy metal pollution in the world and Olkhon Island in the Baikal region specifically remains unresolved and has relevance. There is a lack of comprehensive research on heavy metals, namely, Hg, Cd, As, Pb, Cr, Co, Ni, Cu, and Zn, in beach sand and their contamination level and subsequent ecological risk in the Olkhon Island coastal zone. Thus, this study aims to attract the attention of people from different countries to this existing problem.

The objectives of this study are the following: (i) determining the heavy metal concentrations, such as Hg, Cd, As, Pb, Cr, Co, Ni, Cu, and Zn, in various fractions of beach sand by using X-ray fluorescence (XRF) and atomic absorption (AA) spectrometry; (ii) establishing the relationship between particle sizes of various fractions of beach sand and sediments and their elemental composition; (iii) assessing the degree and level of heavy metal contamination in the Olkhon Island coastal zone using various geochemical indices such as contamination factor (C_f), contamination degree (C_d), normalized enrichment factor (EF), pollution load index (PLI), and geoaccumulation index (I_{geo}); and (iv) identifying the possible sources (natural/anthropogenic) of the heavy metals and interelemental relationships using the EF and I_{geo} methods and statistical analysis.

2. Materials and methods

2.1. Description of the study area

Geographically, the shores of Olkhon Island have two main sides: a northwestern side, washed by the waters of the Maloe More Strait; and a southeastern side, interacting with the main water area of Lake Baikal (Fig. 1). The coastline is 225 km long. The natural mechanisms and long time for the formation of the coast of Olkhon Island are more similar to sea and oceanic mechanisms than to lake ones (Galaziy and Parmuzin, 1975). The coast formed under the influence of wind waves, geological structures, climatic conditions, exogenous processes and fluctuations of the lake level. Waves are the primary factor. The intensity of the impact on the coastal zone from waves and wave currents depends, on the one hand, on the wind and level regimes and, on the other hand, on the geological structure of the coastline and the degree of saturation of clastic material (Pinegin, 1975). These conditions have determined the formation of erosive types of shores on Olkhon Island, the length of which is 220.5 km, which is more than 98% of the length of the island coastline. The remaining 2% of the coast of Olkhon Island is represented by accumulating shores. However, living zones, tourists, and agricultural activities are located on the accumulating shores.

The study area is located on the coast between the villages of Kharansy and Khalgay and spans latitudes 53°13′20.9″N–53°15′23.3″N and longitudes 107°25′06.5″E–107°31′42.7″E (Fig. 2 a, b, c), where seasonal unorganized camping tourism is developed (Fig. 2 c), from which much garbage is left (Fig. 2 b). In general, this load is insignificant since volunteers clean the coast during the spring–autumn period. However, sediments of the coastal zone accumulate not only garbage debris but also heavy metals, which include both natural (Ross, 1994) and anthropogenic toxicants (Rodriguez et al., 2009; Liu et al., 2013) that migrate from the entire catchment area together with surface and groundwater (Il'in, 1991). Thus, geoecological assessment of beach sediments is indicative since it reflects the state of not only the coastline but also the entire territory of the catchment area adjacent to it.
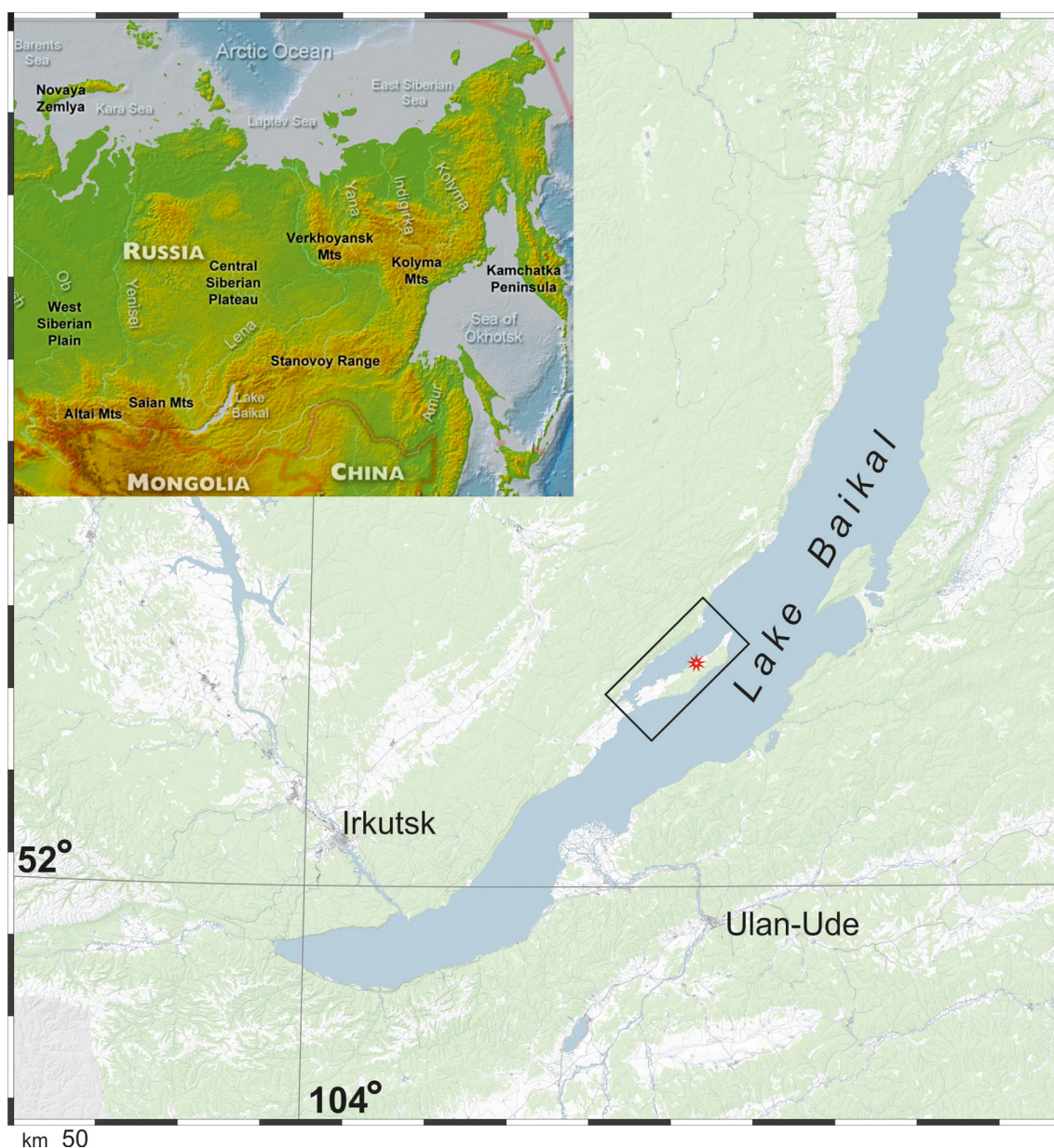
Fig. 1. Study area showing sample locations.

2.2. Sampling

The study area is located at latitude 53°14′36″N and longitude 107°28′31.3″E. The beach area connects with the mouth of the catchment basin, where aeolian relief is developed in the thalweg. From the point of view of landscape conditions, this area is the most convenient for organizing unofficial camping since the rest of the area is exposed to landslides. Within this coastal zone, three transverse profiles (A, B, and C) were placed at a distance of 1 km from each other, and material was sampled at three key points on the beach: coastline, front, and shore ledge (Fig. 2 a). Note that profile B is in the thalweg zone and does not have a ledge zone. Five samples were collected from each zone in all profiles by using the envelope method with a step of 1 m. Thus, a total of 40 surface beach sand samples in three profiles (A, B, C) were collected from the beach area of Bayan-Shungen Bay in August 2020, Olkhon Island, Lake Baikal, Russia.

It is known that heavy metals accumulate in the surface horizon at a depth of approximately 15 cm, and it is an indicator that shows an ecological imbalance in the environment (Il'in, 1991; Chernykh, 1995;

Kuz'min, 2005; Wei and Yang, 2010; Gao et al., 2016). All beach sand samples were collected at a depth of 15 cm using a stainless steel spade. All 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 samples were transported to our laboratory for further analysis.

2.3. Analytical methodology

The flowchart of the analytical methodology is presented in Fig. 3. The main steps of the methodology are described below in detail. The collected samples were air dried at ambient temperature for 72 h and then placed in an oven at 110°C until they reached a constant weight (Fig. 3). Afterwards, various plant residues were removed from the selected material using tweezers. The quartering method was applied for evolving fractions from the collected sand samples (see Fig. 3). After the end of the quartering process, three fractions were isolated from ¼ (one-fourth) of the quartered sample material using 2000 and
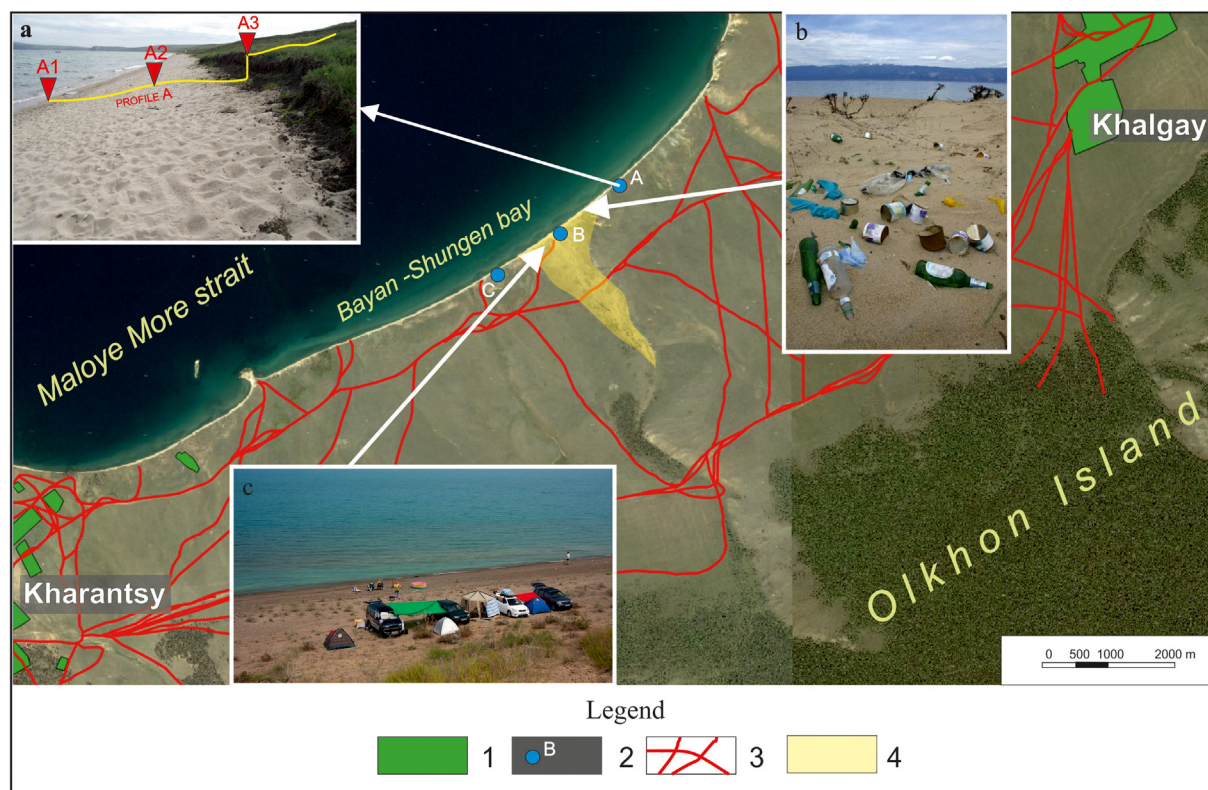
Fig. 2. The study area: a – example of the cross profile (A); b – different types of trash left by tourists in the camping area; c – seasonal unorganized camping. Legend: 1 – village territories; 2 – three profiles discussed (A, B, C); 3 – modern ground road system; 4 – aeolian field.

100 μm sieves, as well as a total sample. We obtained three fractions (see Fig. 3): a coarse fraction (10–2 mm), which contained bedrock; a medium-grained fraction (2 mm–100 μm), which could contain an anthropogenic, as well as the natural, component; and a fine-grained fraction (< 100 μm), which was a product of both physical and chemical destruction of the larger fractions and could contain an anthropogenic, as well as the natural, component. An Analysette 22 NanoTec laser particle-size analyzer (FRITSCH, Germany) verified that the sample particles were less than 63 μm in size. The verification indicated that the particle size of the sand fraction was as low as 63 μm. The next step was the weighing procedure (Fig. 3).

All samples for X-ray fluorescence (XRF) analysis were prepared in accordance with Industrial Standard, 2005. Prepared samples were pressed in tablets with a diameter of 30 mm using a HERZOG HTP-40 (Germany) semiautomatic press with a pressure of 100 kN. The measurement of the Pb, Cr, Co, Ni, Cu, and Zn intensities was conducted using a wavelength dispersive (WD) XRF-spectrometer S8 TIGER, Bruker AXS, Germany (Service Manual, 2007). Processing the X-ray spectra and correction of the matrix effects were performed using SPECTRA^{plus} software (SPECTRA^{plus}, 2008) linked to the equipment (Table 1). As shown in Table 1, the comparison indicated that the SD values obtained by applying the fixed alpha coefficients were less than the SD values achieved without matrix correction by 1.3–5.4 times.

The contents of total Hg in the solid samples were determined by using the direct flameless method with subsequent determination of atomic Hg by atomic absorption spectrometry (AAS) on an RA-915 M analyzer with an RP-91C add-in device (Lumex®, Russia). Determination of Hg content was conducted in accordance with the certified method – Federal Preservation Regulation Document (FPRD) (FPRD, 2013).

To determine the Cd and As contents, decomposition of the samples was performed by using the method of wet digestion of mineral acids (HNO$_3$, HCl, and HClO$_4$) (Fig. 3) with preignition of solids (stepwise heating to 600 °C, with 50 °C steps) according to Church (1981). Then,

the resulting solutions were brought to a 10 ml aliquot of 1 M HNO$_3$ (ultraclear). The contents of Cd and As in the digested samples were determined by using an AAS using a Solar M6 spectrometer with a Zeeman and deuterium background correction system (Thermo Electron, USA). All measurements were performed according to the certified method M-MVI-80-2008 (M-MVI-80-2008, 2008).

The WDXRF spectrometer S8 TIGER, laser particle-size analyzer Analysette 22, and HERZOG HTP-40 semiautomatic press are located at the Center for Geodynamics and Geochronology, Institute of the Earth's Crust (IEC), Siberian Branch of the Russian Academy of Sciences (SB RAS) (Irkutsk, Russia). The AAS equipment is located at the Analytical Center for Multielemental and Isotope Research, V.S. Sobolev Institute of Geology and Mineralogy (IGM), SB RAS (Novosibirsk, Russia).

Quality assurance control of the Cd, Hg, As, Pb, Cr, Co, Ni, Cu, and Zn determinations by using the WDXRF and AAS (Fig. 3) was performed using certified reference materials (CRMs), such as SGR-1b (green river shale), SCo-1 (cody shale), JLk-1 (lake sediment powder), and JSd-1 (stream sediment powder), and reference materials (RMs), namely, SSK-1 (gray carbonaceous soil), SSK-2 (industrial soil), SDPS-1 (background soil), SDPS-2 (industrial soil), SDPS-3 (soddy-podzolic soil), SKP-1 (krasnozem), and OOKO303 (carbonaceous background silt) (Govindaraju, 1994; Catalog of Reference materials, 2013; USGS, 2020; GSJ, 2020) (Tables 2 and 3).

Statistical processing of the XRF and AAS results was performed in accordance with the recommendations given at a 95% confidence interval (Magnusson and Örnemark, 2014; Barwick, 2016). The ILD values are less than 1 mg kg^{-1} for Pb, Co, Ni, Cu, and Zn, and 2.3 mg kg^{-1} for Cr. The limits of detection (LODs) were as follows: for Hg, 0.01 μg g^{-1}; for Cd, 0.5 μg g^{-1}; and for As, 0.1 μg g^{-1}.

The repeatability of the WDXRF was tested as defined in Margui et al. (2005) and Cherkashina et al. (2017). The repeatability test showed that the relative standard deviation (RSD) values were acceptable and did not exceed 5%.
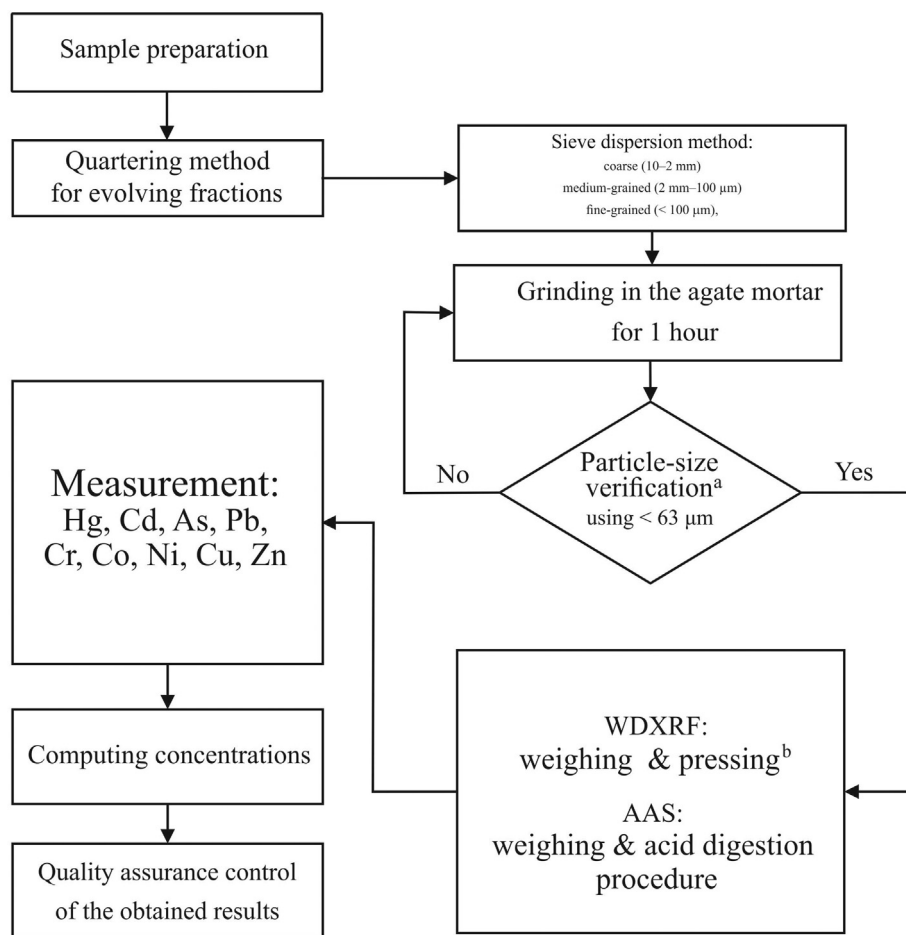
Analytical methodology

Fig. 3. Flowchart of the analytical methodology. Note: a – laser particle-size analyzer Analysette 22 NanoTec, FRITSCH, Germany; b – HERZOG HTP-40 (Germany) semiautomatic press.

The SD values for Hg did not exceed 20% ($p = 0.95$) for concentrations in the range from $5\ 10^{-7}$ to $2.5\ 10^{-2}$ wt% (specified by producer). All CRMs, RMs and samples were diluted with specpure Al_2O_3. The RSD values for Cd and As did not exceed 35%, which is admissible for the analytical results of the soil and sediment samples (M-MVI-80-2008, 2008). The relative percentage difference (RPD) for Cd and As was found to be satisfactory and within the interval from 86% to 104%. The accuracy of the AAS results is presented in Table 3. Agreement between the certified and obtained values was in the range of 10–25% at a p = 0.95 confidence probability.

The accuracy of the Pb, Cr, Co, Ni, Cu, and Zn determinations in the samples examined was verified by measuring the SGR-1b (green river shale, United States Geological Survey) and JLk-1 CRMs (see Table 2). As shown in the table, a comparison of the results indicated that the data show good agreement with the reference values. The RPD values between the certified and measured concentration values for all elements were found to be satisfactory and ranged between 94% and 104%. This indicates that the results are within the detectable range of the certified values.

Table 1
Calibration data obtained for the sediment and soil matrices.

Elements	Number of the CRMs and RMs	Calibration range, mg kg^{-1}	Line overlap correction	Influence coefficients (alpha-correction)	SD[a], mg kg^{-1}	
					I[b]	I[c]
Pb	19	11.34–979.30	–	CaK_α, SiK_α	–	3
Cr	25	4.3–2000	VK_α, MnK_α	CaK_α, TiK_α, FeK_α	27	5
Co	20	2–106	FeK_α	SiK_α, VK_α, MnK_α	5	3
Ni	20	4.4–2240	RbK_α	SiK_α, CaK_α, FeK_α	22	14
Cu	25	8–240	NiK_α	CaK_α, FeK_α	9	7
Zn	20	10–610	CuK_α	CaK_α	21	9

[a] Standard deviation.
[b] Without correction of the matrix effects.
[c] With accounting of the matrix effects (alpha-correction).

Table 2
The accuracy of the Pb, Cr, Co, Ni, Cu, Zn determinations in beach sand samples by XRF.

Elements	SGR-1b CRM (green river shale)		JLk-1 CRM (lake sediment powder)	
	C_{XRF}[a]	$C_{certified}$[b]	C_{XRF}	$C_{certified}$
Pb	ND[c]	38 ± 4	46 ± 2.4	43.7 ± 1.3
Cr	33 ± 0.5	30 ± 2	ND	69. ± 4.3
Co	13 ± 0.4	12 ± 0.6	ND	18.1 ± 1.2
Ni	24 ± 2	29 ± 3	ND	35.95 ± 2.5
Cu	64 ± 3	66 ± 4	ND	61.35 ± 3.8
Zn	72 ± 2	74 ± 2.5	ND	151.5 ± 5.6

[a] Obtained concentrations of the metals (mg kg^{-1}) for CRM: mean ± SD, $n = 5$.
[b] Certified concentrations of the metals (mg kg^{-1}) for CRM: mean ± SD, $n = 5$.
[c] This concentration is not measured.

Table 3
The accuracy of the As, Hg, Cd determinations in beach sand samples by AAS.

Elements	SDPS-3 RM (soddy-podzolic soil)		SSK-1 RM (gray carbonaceous soil)		SKP-1 RM (krasnozem)	
	C_{AAS}[a]	$C_{certified}$[b]	C_{AAS}	$C_{certified}$	C_{AAS}	$C_{certified}$
As	ND[c]	70 ± 20	ND	13 ± 5	10 ± 3	13 ± 5
Hg	0.31 ± 0.01	0.35 ± 0.06	ND	0.025 ± 0.007	ND	0.08 ± 0.03
Cd	ND	4 ± 1	0.10 ± 0.03	0.12 ± 0.03	ND	0.12 ± 0.03

[a] Obtained concentrations of the metals (mg kg^{-1}) for RM: mean $\pm$ SD, n = 5.
[b] Certified concentrations of the metals (mg kg^{-1}) for RM: mean $\pm$ SD, n = 5.
[c] This concentration is not measured.

2.4. Data processing

There are dozens of studies in the literature devoted to assessing the level of soil and sediment pollution by heavy metals (Coskun et al., 2006; Dragovic et al., 2008; Yaqin et al., 2008; Lin et al., 2016; Zhang et al., 2017; Li et al., 2017; Gholizadeh and Patimar, 2018; Zhang et al., 2019; Al-Absi et al., 2019; Rinklebe et al., 2019; Chandrasekaran et al., 2020; Liu et al., 2020). In this study, five geochemical indices, including the enrichment factor (EF), contamination factor (C_f), contamination degree (C_d), geoaccumulation index (I_{geo}) and pollution load index (PLI), were applied to completely assess the degree and level of contamination and to identify the possible sources of heavy metals.

2.4.1. Contamination factor (C_f) and contamination degree (C_d)

The assessment of the level and degree of contamination in the sand samples examined was conducted using the contamination factor (C_f) for a single element and contamination degree (C_d). C_f is widely used to evaluate the potential ecological risk of pollutants in sediments (Saraee et al., 2011; Lin et al., 2016). It was defined as the ratio of the heavy metal average concentrations (C^i) in the top horizon (depth ~ 15 cm) at three profiles to the regional background values (C_n^i) (Hakanson, 1980; El Zrelli et al., 2015):

$$C_f^i = C^i / C_n^i \qquad (1)$$

The regional background values for Hg, Pb, Cr, Co, Ni, Cu, and Zn were taken from Grebenshchikova et al. (2008). For As and Cd, these values were computed taking into account the Clarke number of the lithosphere of Vinogradov (1957). In accordance with Hakanson (1980), C_f is categorized into four classes.

The C_d of the environment was evaluated as the sum of all contamination factors for all elements examined (Hakanson, 1980):

$$C_d = \sum_{i=1}^{9} C_f^i \qquad (2)$$

With this approach, C_f accounts for the pollution of a single element according to the concentration requirement, and the C_d value is applied to compute the total soil and sediment pollution within the profiles studied. Four classes were recognized (Hakanson, 1980).

2.4.2. Pollution load index (PLI) method

The pollution load index (PLI) method was proposed by Tomlinson et al. (1980) to assess the overall level of heavy metal pollution (Tomlinson et al., 1980). The PLI index is computed as follows:

$$PLI = \left(C_{f1}^i \times C_{f2}^i \times C_{f3}^i \times \ldots \times C_{fn}^i \right)^{1/n}, \qquad (3)$$

where C_f^i is the contamination index of heavy metals and n is the number of species involved in the assessment of heavy metals. This method is convenient for assessing the pollution load for individualized sites by expressing the concentrations of all individual elements under consideration. The pollution levels were classified into four grades (Liu et al., 2013).

2.4.3. Enrichment factor (EF) analysis

The level of contamination and possible sources of heavy metals are effectively assessed by computing the enrichment factor (EF). The EF is a normalization method proposed by Simex and Helz (Simex and Helz, 1981) to evaluate metal contents. Al, Fe, Mn, total organic carbon (TOC), and grain size were chosen as the most appropriate sediment constituents for normalization. For our purpose, the constituent should be associated with finer particles. To reduce the metal variability caused by grain size and mineralogy, Fe was used in this study. Thus, the EF for each metal is defined as follows (Ergin et al., 1991):

$$EF = \frac{(C_{Metal}/C_{Fe})_{Sample}}{(C_{Metal}/C_{Fe})_{Background}}, \qquad (4)$$

where $(C_{Metal}/C_{Fe})_{Sample}$ is the ratio of metal and Fe contents in the sample and $(C_{Metal}/C_{Fe})_{Background}$ is the ratio of metal and Fe contents of the regional background (Grebenshchikova et al., 2008; Kuz'min, 2005). According to Sutherland (2000), the EF is categorized into six classes.

2.4.4. Geoaccumulation index (I_{geo}) method

The geoaccumulation index (I_{geo}) was introduced by Muller (1969) to define heavy metal pollution in sediments and soils by comparing current concentrations with preindustrial levels. The I_{geo} index is expressed as follows (Muller, 1969):

$$I_{geo} = \log_2(C_n / 1.5 B_n), \qquad (5)$$

where C_n is the measured concentration of element n in the beach sand sample, B_n is the regional background value of element n in the study area (Grebenshchikova et al., 2008), and the constant 1.5 allows analysis of the natural content fluctuations of a substance in the environment and detection of small anthropogenic influences (Yaqin et al., 2008). Seven contamination categories based on the I_{geo} index were recognized (Muller, 1969; Wei et al., 2009).

3. Results and discussion

3.1. Distribution of heavy metals in beach sand taking into account their granulometric composition

Information about the Hg, Cd, As, Pb, Cr, Co, Ni, Cu, and Zn concentrations in the three fractions (10–2 mm, 2 mm–100 μm, and <100 μm) from the beach sand samples is presented in Table 4. This table exhibits the variations in the elemental composition depending on the particle size of the three grain size fractions of sand from profiles A, B, and C. As is obvious from Table 4, trace metal contents showed large variability, especially in the case of Cr and Zn in all sand fractions. Other elements showed moderate variability except Hg in the composite samples and coarse sand fraction in the B and C profiles, as well as Cd in the composite samples in the A and C profiles. Furthermore, the fine-grained fraction (<100 μm) in all profiles examined is characterized by higher concentrations of heavy metals compared with the composite sample and coarse (10–2 mm) and medium-grained (2 mm–100 μm) fractions. Al-Abdali et al. (1996) noted that positive correlations

Table 4
Concentrations of heavy metals in beach sand samples obtained by XRF and AAS.

Elements	Concentration ranges (mg kg^{-1}), n = 15 Profile A	Concentration ranges (mg kg^{-1}), n = 10 Profile B	Concentration ranges (mg kg^{-1}), n = 15 Profile C	SD
Composite sample				
Hg	0.010–0.025	0.01[a]	0.01[a]	0.0053
As	0.69–5.10	0.44–1.30	0.16–1.30	1.57
Cd	0.016–0.018	0.01–0.12	0.07–0.027	0.04
Pb	14–23	14.5–16.3	14–17	2.88
Cr	36–80	24–51	19–94	26.17
Co	4.5–15.0	3.1–6.7	2.7–11.0	4.29
Ni	10–37	7.4–18.0	7.2–21.0	9.78
Cu	15–37	15–17	13–18	7.67
Zn	14–73	11–18	8–31	21.11
Coarse sand fraction (10–2 mm)				
Hg	0.010–0.017	0.01	0.01	0.0025
As	0.58–4.60	0.28–0.48	0.36–10.0	3.41
Cd	0.001–0.067	0.019–0.088	0.024–0.026	0.028
Pb	5.7–25.0	7–14	11–15	5.89
Cr	68–204	29–116	15–89	60.83
Co	1.95–15.0	1.99–5.50	1.97–22.0	6.06
Ni	8.9–33.0	7–12	5.4–38.0	12.42
Cu	20–41	16–19	17–31	8.51
Zn	18–79	11–14	12–28	22.21
Medium-grained sand fraction (2 mm–100 μm)				
Hg	0.010–0.049	0.02–0.07	0.010–0.014	0.022
As	0.27–13.0	0.59–0.61	0.33–0.60	4.43
Cd	0.017–0.081	0.012–0.069	0.024–0.082	0.028
Pb	9–23	10.5–15.0	8.9–16.3	4.62
Cr	25–72	29–45	16–1.3	28.22
Co	1.98–10.0	2.1–6.9	1.97–14.0	4.13
Ni	6.3–26.0	6.5–13.0	6.7–17.2	6.69
Cu	16–33	15.7–16.4	14–19	5.91
Zn	9.7–59.0	12–17	13–27	16.35
Fine-grained sand fraction (< 100 μm)				
Hg	0.064–0.085	0.018–0.160	0.037–0.051	0.043
As	0.34–2.40	0.37–0.56	0.65–13.0	4.36
Cd	0.020–0.049	0.012–0.066	0.053–0.140	0.041
Pb	14–26	7.4–25.0	15–23	6.4
Cr	80–87	84–94	46–123	24.6
Co	7.7–15.0	8.3–16.0	11–30	8.0
Ni	15–31	16–27	13–67	17.63
Cu	20–45	23–28	30–60	13.94
Zn	45–89	53–59	29–164	42.02

SD, standard deviation.
[a] No variations.

existed between the increase in metal concentration and decrease in grain size (Gonzalez-Macias et al., 2006; Nowrouzi and Pourkhabbaz, 2014).

The mean order of elemental concentrations in the composite samples for all profiles is the following: Cr (50.75) > Zn (25.0) > Cu (18.38) > Ni (17.33) > Pb (16.38) > Co (6.55) > As (1.30) > Cd (0.040) > Hg (0.012). The distribution of the heavy metals in the composite beach sand samples collected from each of the A, B, and C profiles compared with the fine-grained fraction (<100 μm) is shown in Fig. 4. The guideline values for Hg, As, Cd, Pb, Ni, Cu, and Zn were taken from the Russian Guide (Onishchenko, 2006), and values for Cr and Co were used from the Canadian Guide – Canadian Council of Ministers of the Environment (CCME) (CCME, 2007) due to the absence of their values in the Russian Guide. As shown in Fig. 4, the metal contents in the composite samples in all profiles are lower than the guideline and regional background values except Pb in the A, B, and C profiles and As in the A profile. Distribution of the trace metals indicates a trend towards increasing elemental contents from coastline to shore ledge. Fig. 4 shows the increase in metal contents in the fine-grained sand fraction in all profiles compared with the composite sample. The contents of Pb and Hg in all profiles and As in the C profile are higher than their background values. In addition, the distribution of trace metals shows

a trend towards increasing elemental contents from coastline to shore ledge except Hg in the A profile. Hg content in the A profile increases from the shore ledge to the coastline. According to the particle size rule, sediments with smaller grain sizes are more likely to absorb heavy metals (Borg and Jonsson, 1996). This is a very important factor in research on the geochemical behavior of heavy metals in beach sediments. The accumulation of heavy metals in beach sand may occur due to a direct discharge of large amounts of domestic sewage from resorts and villages situated near the coast of Lake Baikal. Note that the heavy metals have the ability to be sorbed by various polymeric materials. In addition, the coastal zone accumulates toxicants that migrate from the catchment basin along with surface water. These and other possible reasons for the accumulation of heavy metals in the coastal zone beach sand of Olkhon Island will be discussed below.

3.2. Assessment of heavy metal pollution

According to Borg and Jonsson (1996) and our experimental results, sediments with smaller grain sizes (<100 μm) are more likely to absorb heavy metals. Let us consider the results of assessing the pollution level of the sediments in the fine-grained fraction (< 100 μm) obtained using ecological and geochemical indices.

3.2.1. C_f and C_d indices
The C_f index was studied for each metal in the beach sand samples in profiles A, B, and C. The C_f values were computed using Eq. (1). The applied method of the contamination factor assesses the enrichment in metals in relation to the background concentrations of each metal in the sediment samples. The order of the mean C_f was Hg (3.51) > Pb (1.87) > Cr (1.17) > Co (0.92) > As (0.88) > Zn (0.76) = Cu (0.76) > Ni (0.60) > Cd (0.35). The maximum values of C_f were 4.45 and 3.77 for Hg in profiles A and B, respectively, as shown in Fig. 4, which indicates a considerable pollution level in the environment. High C_f values were observed for Pb (from 1.62 to 2.0) in all profiles and 2.30 for Hg, 1.72 for As, and 1.27 for Co in the C profile (Fig. 5), which provided evidence of a moderate contamination level in the samples examined (Hakanson, 1980). The C_d value for all described profiles was calculated using formula Eq. (2) and equals 83.06, which denotes a very high degree of environmental pollution (Hakanson, 1980).

3.2.2. PLI method
To assess the overall level of pollution across all profiles examined, Eq. (3) was applied. The order of the PLI indices for all profiles was C (1.17) > A (0.74) > B (0.68). This demonstrates that the C profile was moderately polluted, whereas the A and B profiles were not polluted (Tomlinson et al., 1980). In addition, we suggest that assessment of pollution level in relation to anthropogenic and natural origin sources of the elements should be considered in combination with the distribution of toxic elements along the coastal zone. In this case, we can see the following order: shore ledge (1.40) > front (0.81) > coastline (0.49). The PLI values for profile C (1.17) and shore ledge (1.40) were higher than 1 (Liu et al., 2013), suggesting that trace metals, which presumably have an anthropogenic origin, accumulated in the shore ledge of the coastal zone and that there was no input from the coastline and frontal zones.

Thus, geochemical assessment of beach sediments by using the PLI method is indicative, as it reflects the state of not only the coastal zone but also the adjacent area (catchment basin) as a whole. The coastal zone accumulates toxicants that migrate along the catchment basin with surface water. In addition, the increased content of toxic elements in the C profile indicates that the transfer of elements occurs due to coastal currents.

3.2.3. EF method
For each metal, the EF index was assessed by Eq. (4). The mean EF values for the A, B, and C profiles were as follows: Hg (4.67) > Pb
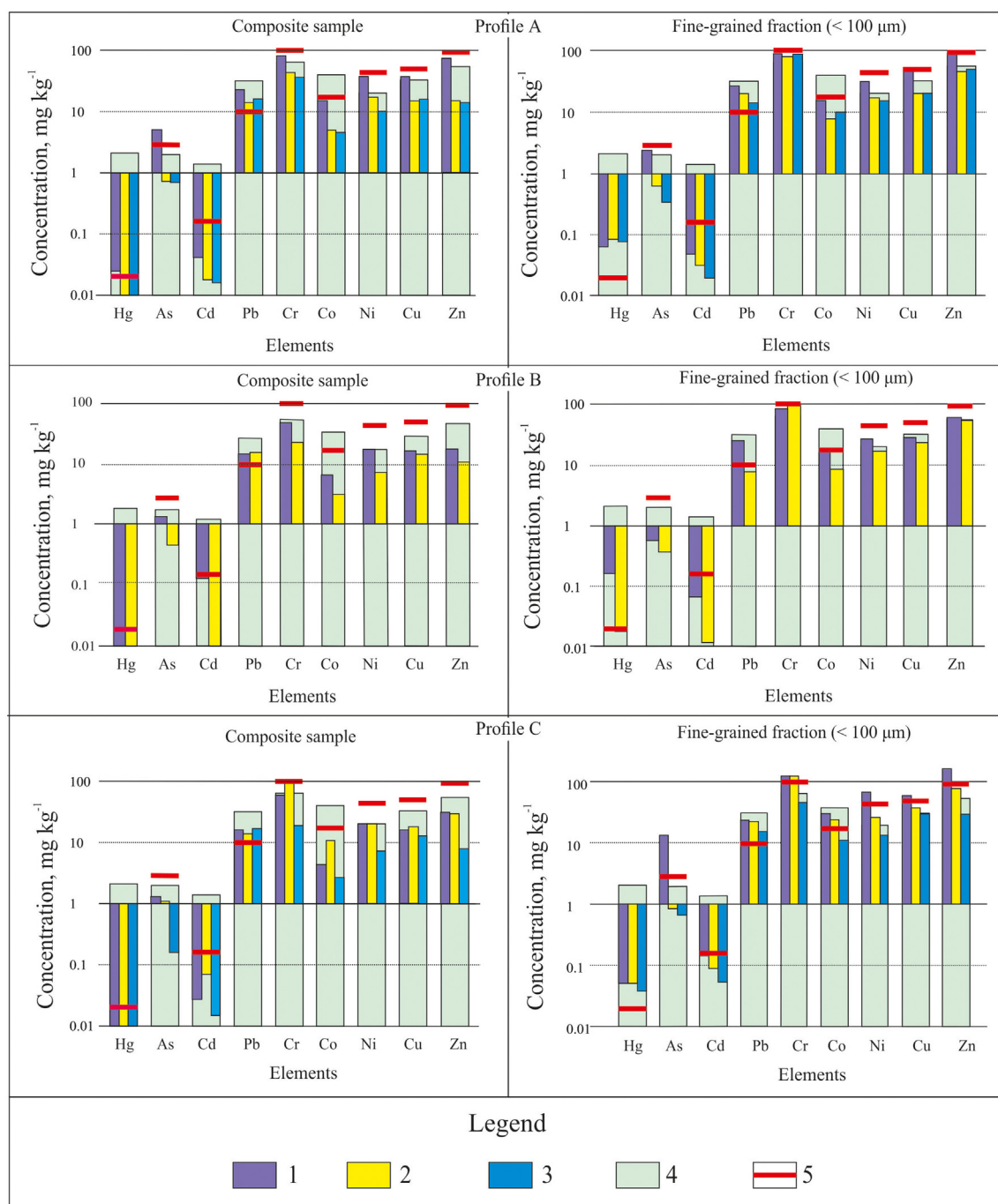
Fig. 4. Distribution of heavy metals in beach sand samples at A, B, C profiles: A – in composite sample; B – in fine-grained fraction (< 100 μm). Legend: 1 – shore ledge; 2 – front; 3 – coastline; 4 – guideline values; 5 – regional background values.

(3.49) > Cr (1.38) > Cu (1.10) > Co (0.97) > Zn (0.87) > Cd (0.80) > Ni (0.79) > As (0.46). As shown in Fig. 6, the highest EF values for Hg occurred in profiles A (6.0; 7.5), B (11.1), and C (7.2), and for Pb in the C profile (9.2); therefore, the sediments were classified as significantly enriched (Sutherland, 2000). Consistent with Zhang and Liu (2002), the values of 0.5 ≤ EF ≤ 1.5 denote that the enrichment of trace metals is basically of crustal origin (weathering product), whereas an EF > 1.5 suggests that the source of the metals is more anthropogenic. Thus, the EF values obtained for Hg, Cd, Pb, and Cu were in the range of 1.6–11.1, which indicates a possible anthropogenic origin for these metals.

The EF values for As, Cr, Co, and Zn in the A, B, and C profiles and partially for Cd and Cu in the A and B profiles vary within the interval from 0.1 to 1.9. This corresponds to a minimal enrichment in the sand samples examined. In addition, the EF values for Pb in profiles A and B are in the range of 2.2–3.5, which shows a moderate enrichment of this element.

The distribution of the toxic elements along the coastal zone is as follows: coastline (1.88) > front (1.75) > shore ledge (1.0). The main toxicants are Hg (11.1) in the B profile and Pb (3.5 and 9.2) in the B and C profiles, respectively. This corresponds to our assumption that the input of heavy metals into the coastal zone is a result of surface runoff, which flows into the thalweg zone of the catchment basin and further into the frontal zone. Toxic elements are influenced by coastal wave-breaking process impacts and migrate to the coastline. Furthermore, metals are transferred with the fine-grained fraction along the frontal zone and accumulate in the cape part of the gulf.
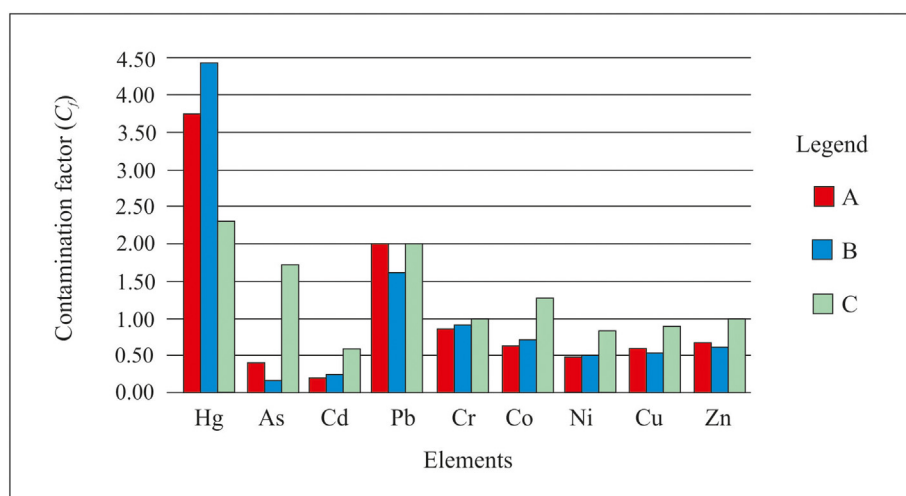
Fig. 5. The contamination factor (C_f) computed for single trace metal in the beach sand samples at A, B, C profiles.

3.2.4. I_{geo} method

The I_{geo} method is successfully applied for the definition of pollution intensity from heavy metals in a given environment (Ergin et al., 1991). The I_{geo} values ranged from 0.303 to 2.415 for Hg (mean of 0.930) and from −1.019 to 0.794 for Pb (mean of 0.249). Other trace metals have negative values of I_{geo}. According to the classification level (Wei et al., 2009), Hg is considered to have none to moderate pollution in the B (0.8) and C (0.6) profiles, as well as Pb in the A (0.4) and C (0.4) profiles (Fig. 7). As shown in Fig. 7, Hg is considered to be moderately polluted in the A (1.3) profile. This indicates that the beach sands examined are uncontaminated to moderately contaminated by Hg and Pb. Moreover, the high I_{geo} value for Hg was 1.3, which may suggest that this metal has been significantly impacted by anthropogenic sources.

Finally, for metal accumulation, an increase in Hg, Cd, As, Pb, Co, and Cu concentrations implies an enhancement of their mobility. Cd, Pb, Co, and Cu are mutually linked with Fe and Mn (Alloway, 1995). On Olkhon Island, there are more than seven deposits containing Fe and Mn ores, which were used in the past as a material for obtaining ferroalloys (Konopatskii, 1982). The EF and I_{geo} indices showed that the Hg, Cd, Pb, and Cu sources were more likely to be anthropogenic, whereas the

As, Cr, Co, Ni, and Zn sources were similar to crustal sources (weathering products). Presumably, anthropogenic sources of Cd and Hg could include nickel-cadmium batteries, as well as inherited pollution from phosphorus fertilizers, insecticides, pesticides, discharge of sewage, combustion of rubbish, traffic emissions, and other anthropogenic activities (Alloway, 1995; Zhang and Wong, 2007; Wei and Yang, 2010; Cherkashina et al., 2017; Zhang et al., 2017; Zhang et al., 2018; Al-Absi et al., 2019; Gu et al., 2021). Note that cadmium belongs to the Group 1 toxic chemicals according to World Health Organization classifications (IARC, 2018). A high C_f value equal to 1.72 for As in the C profile may indicate an agricultural impact from the past, namely, the usage of arsenic fertilizers (Cherkashina et al., 2017). Thus, the possible sources of the heavy metals discussed can be of various natures. It is necessary to study them, especially in regard to As and Cu.

Pesticides belong to a class of organometallic compounds that are very hazardous in the environment, namely, they pollute water bodies, soil and air (Volgina et al., 2009). The authors note that pesticides, due to their high biological activity, gradually accumulate from simpler organisms to more complex organisms when circulating in the environment.

In accordance with previous studies (Borg and Jonsson, 1996; Dou et al., 2013) and our results, the fine-grained fraction (< 100 μm) in the sediments sorbed heavy metals such as Hg, Cd, As, Pb, Co, and Cu. This result indicates that fine-grained sediments may be a good carrier for trace metals and a marker for tracking the dynamics of accumulative processes.

Thus, the acceptable results from the EF and I_{geo} methods indicate that Hg, Cd, and Pb are the main pollutants in the study area.

3.2.5. Accumulation of mercury and lead in the coastal zone

One of the main ways that heavy metals, including Hg and Pb, enter an environment is by their sorption byproducts that are made of polymeric material, namely, plastic bottles and plastic containers for shampoos that are resistant to degradation and decomposition (Holmes et al., 2012; Antunes et al., 2013). This material enters the coastal zone together with natural material (sand, clay, and sandy loam) as a result of accumulative processes. An alternative source of heavy metal input is extreme atmospheric precipitation falling over the territory of coastal catchment basins and entering the beach area along with surface runoff (Il'in, 1991).

As discussed above, Pb is linked with Fe and Mn ore deposits and therefore may have a crustal origin due to weathering or accumulative processes. Pb may migrate along with the current soil moisture and may cause pollution of groundwater and sediments in reduced relief elements. On the other hand, Pb has significant enrichment in beach sediments, which indicates its anthropogenic origin, presumably due to its
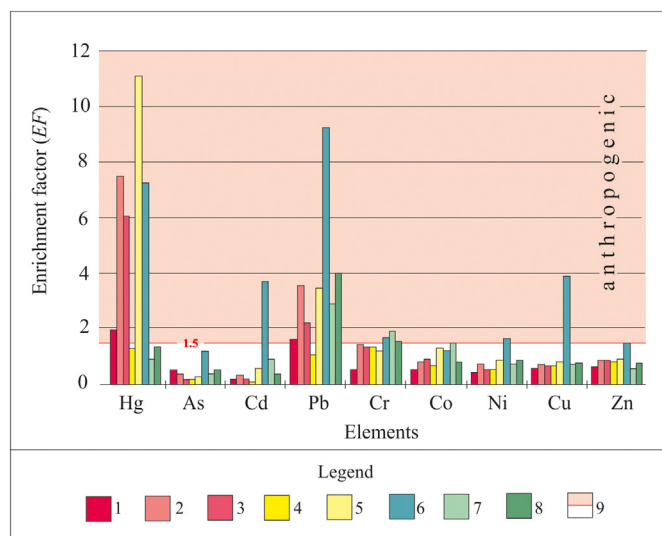

Fig. 6. The normalized enrichment factor (EF) computed for each trace metal in the beach sand samples at A, B, C profiles. Legend: A profile: 1 – shore ledge; 2 – front; 3 – coastline. B profile: 4 – coastline; 5 – front. C profile: 6 – coastline; 7 – front; 8 – shore ledge. 9 – anthropogenic origin of metal (EF > 1.5).
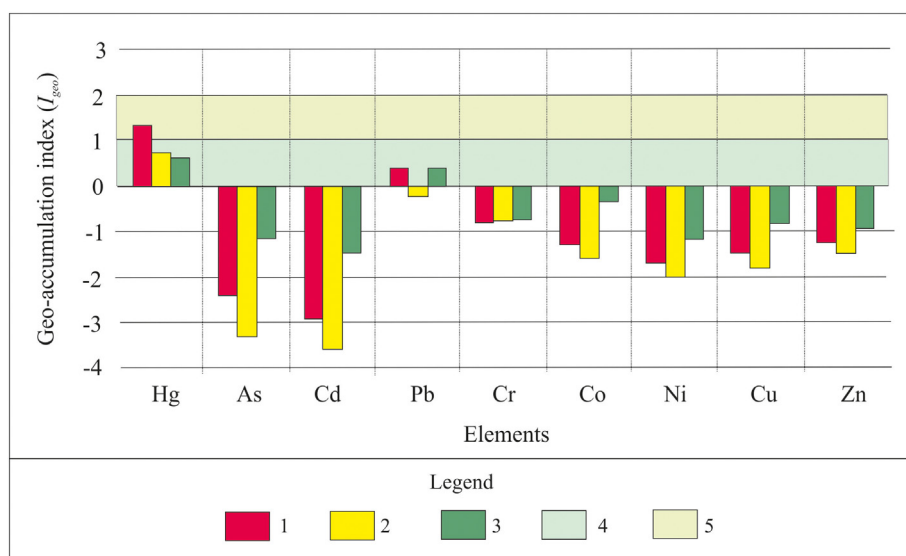
Fig. 7. Geo-accumulation index (I_{geo}) computed for each trace metal in the beach sand samples at A, B, C profiles. Legend: Profiles: 1 – A; 2 – B; 3 – C. Categories of I_{geo} index: 4 – uncontaminatd to moderately contaminated ($0 < I_{geo} < 1$); 5 – moderately contaminated ($1 < I_{geo} < 2$).

use in the production of insecticides and fertilizers (Alloway, 1995), and is derived from sewage sludge and illegal landfills (Wei and Yang, 2010). The mean values of the Pb content in soils and sediments in the Baikal region are within the interval from 11.0 to 11.6 mg kg^{-1}, and the average value of Pb in benthal deposits is 13.2 mg kg^{-1} (Grebenshchikova et al., 2008).

Hg content values in Baikal water range from 0.0007 to 0.0023 mg kg^{-1} (Grachev, 2002); in soils in the Baikal region, it ranges from 0.0169 to 0.029 mg kg^{-1} (Grebenshchikova et al., 2008); and in benthal deposits, the average value is equal to 0.063 mg kg^{-1} (Helety et al., 2007). We suggest that Hg concentrations (0.010–0.160 mg kg^{-1}) in the beach sands that were examined, as well as the EF and I_{geo} results, are more likely to be from anthropogenic sources in their origin. This assumption is also confirmed by the fact that there are no rocks associated with Hg in the territory of Olkhon Island.

3.2.6. Correlation analysis

To identify the relationship between trace metals in the beach sand, Pearson correlation analysis (PCA) was applied to the data. Interelemental relationships provide information about heavy metal sources and pathways (Dragovic et al., 2008; Magiera et al., 2018; Chandrasekaran et al., 2020). The Pearson correlation coefficient defines the strength of a linear relationship between any two variables on a scale from −1 (perfect inverse relationship) through 0 (no relationship) to +1 (perfect positive relationship) (Chandrasekaran et al., 2020). According to the obtained values (Table 5), high positive correlations between Pb and Hg (0.741), As and Cd (0.730), and Cd and Pb (0.803) are observed. Strong correlations between metals such as Cr, Co, Ni, Cu, and Zn associated with iron

and iron monosulfide (Goldschmidt, 1954) are statistically significant (see Table 5). This indicates that these elements were derived from similar sources and similar migration pathways, either crustal or anthropogenic (Bhuiyan et al., 2010; Zhang et al., 2019). However, it does not indicate that Cr, Co, Ni, Cu, and Zn have anthropogenic origins because these metals could have come from crustal sources (weathering products and linkages with Fe—Mn deposits).

The main sources of lead in the soil are atmospheric deposition, both local in nature and transboundary transfers as a result of the activities of industrial enterprises, thermal power plants, and mining (Il'in, 1991; Chernykh, 1995; Vodyanitskii, 2013). However, the source of Pb in agricultural soils mainly originates from mineral fertilizers, especially phosphoric fertilizers (Wei and Yang, 2010). The fact that there are no industrial enterprises within a radius of more than 100 km from Olkhon Island is consistent with Pb soil pollution resulting from agricultural use in the past (Pellinen et al., 2016).

3.3. Debate about heavy metal pollution on Olkhon Island

In this study, we attempted to raise the problem of heavy metal pollution in the coastal zone of Olkhon Island in Lake Baikal. During the study, we were able to obtain new data on the concentrations of heavy metals examined in the sediments, to discuss possible sources of the pollutants entering the environment and to assess possible ecological risks.

The last major studies related to pollution of the Olkhon Island environment by heavy metals were conducted by Russian scientists prior to 2005. The study by Kuz'min (2005) presented data on some trace elements found in the soils of Olkhon Island, such as Fe, Mn, Ba, Sr, Cu, Co, Cr, Ni, V, and Pb. This study found an increase in the concentrations of Cu, Co, Cr, Ni, and V with an increase in the concentration of Fe. We agree with this study. There is a certain geochemical dependence of the concentrations of these elements with iron. In turn, we identified additional pollutants, such as Hg and Cd, as well as increased Pb concentrations compared with data from Kuz'min (2005). In the case of Pb content, we do not agree with Kuz'min, who confirmed that Pb content in the soils was less than 10 mg kg^{-1}. The concentrations of all elements studied were measured before 2005, when the sensitivity of XRF and AA devices was very low. Moreover, as noted above, garbage dumps in the island territory were eliminated only in 2013. This became one of the reasons for the emergence of new pollutants in the soil and an increase in their concentrations.

Table 5
Pearson correlation coefficients between the elemental compositions of beach sands.

	Hg	As	Cd	Pb	Cr	Co	Ni	Cu	Zn
Hg	1.000								
As	0.011	1.000							
Cd	0.355	0.730	1.000						
Pb	0.741	0.533	0.803	1.000					
Cr	0.019	0.418	0.258	0.205	1.000				
Co	0.159	0.747	0.882	0.617	0.578	1.000			
Ni	0.200	0.904	0.745	0.603	0.671	0.859	1.000		
Cu	−0.060	0.907	0.798	0.546	0.394	0.873	0.859	1.000	
Zn	0.073	0.836	0.564	0.457	0.820	0.789	0.952	0.788	1.000

Thus, although the ecological risks of the heavy metals studied are relatively low, some heavy metals can sometimes cause negative toxic effects in coastal ecosystems (Zhang et al., 2017). We agree with this statement and believe that if the problem of pollution on Olkhon Island in Lake Baikal regarding heavy metals is not thoroughly investigated, then an ecological catastrophe may occur in the future.

4. Conclusion

This study investigated the concentrations of elements and determined the relationships between particle size of accumulated sediments and their elemental composition, pollution level and possible sources of nine heavy metals in beach sand on the coast of Olkhon Island, Lake Baikal. The authors presented new results regarding the ecological and geochemical state of Bayan-Shungen Bay, Olkhon Island.

The results from assessing the pollution levels in the fine-grained fraction ($< 100\ \mu m$) of beach sand were as follows. Based on regional background values and the results from various indices, PC analysis showed that heavy metal pollution on the coast of Olkhon Island, Lake Baikal, was at moderate to significant levels for Hg, As, Cd, Pb, and Cu. Elements such as Co, Cr, Zn, and Ni, and partially for Cd and Cu, were minimally enriched. The EF and I_{geo} indices showed that sources of Hg, Cd, Pb, and Cu were more likely to be anthropogenic; whereas, sources of As, Cr, Co, Ni, and Zn were likely to be crustal (weathering products). The possible sources of heavy metals can be of various natures. It is necessary to study them, especially in regard to As and Cu.

Thus, geochemical assessment of beach sediments is significant and topical because it reflects the state of the coastal zone, as well as the adjacent area (catchment basin) as a whole. The coastal zone accumulates toxicants that migrate from the catchment basin along with surface water.

In accordance with our results, the fine-grained fraction in the sediments sorbed heavy metals such as Hg, Cd, As, Pb, Co, and Cu. These results indicate that fine-grained sediments may be a good carrier for trace metals and a marker for tracking the dynamics of accumulative processes. Although the ecological risks from the heavy metals examined are relatively low, some heavy metals may sometimes cause negative toxic effects in coastal ecosystems. We should give special attention to the main pollutants that were revealed in this study, such as Hg, Cd, and Pb, in future studies concerning the Baikal region. The pollution level of the pollutants could rise to a dangerous level.

In summary, we should continue this research in the future to determine the relationships between heavy metals and their sources. The assessment of all accumulative shores of Lake Baikal is also planned.

CRediT authorship contribution statement

Vadim Pellinen: Conceptualization, Methodology, Software, Data curation, Writing – original draft, Visualization, Investigation, Funding acquisition. **Tatiana Cherkashina:** Methodology, Software, Data curation, Validation, Writing – original draft, Investigation. **Marya Gustaytis:** Methodology, Software, Data curation, Validation, Writing – original draft, Investigation.

Declaration of competing interest

This research was carried out in the absence of any commercial and financial relationships. We declare no conflict of interest.

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