

Article

Role of Gravitational Processes in the Migration of Heavy Metals in Soils of the Priolkhonye Mountain-Steppe Land-Scapes, Lake Baikal: Methodology of Research

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Abstract: The study object of this work is the soils of the Priolkhonye mountain-steppe landscapes. This research is performed at the Priolkhonye test site. Annual monitoring for exogenous geological process activity is conducted there. This research aims to study the influence of gravitational geological processes (landslides) on the migration of heavy metals, which are introduced into soil as a result of human agricultural activity. A methodology for the geoecological monitoring of soils based on an assessment of their contamination level by anthropogenic heavy metals, and a transfer mechanism throughout whole migration path (field–landslide–coast) is proposed. The following steps were taken to solve this problem: isolating a fine-grained fraction (<100 µm); determining the Hg, Cd, Pb, and Cu concentrations using wavelength dispersive X-ray fluorescence and atomic absorption spectroscopies, as well as total organic carbon (TOC) content using UV-Vis spectrophotometry; computing various geochemical indices; and describing the migration path of these heavy metals and TOC. The monitoring results showed that these pollutants migrate to the coastal zone as a result of landslides activation. The soil contamination level is increased which can cause negative toxic effects in coastal ecosystems, and could rise to a dangerous level for humans. Thus, the observed changes in the indices and TOC values allow us to assess the geoecological state of the study area; namely, the periods of landslide activity and the supply of these pollutants to the coastal zone.

Keywords: gravitational geological processes; landslides; geoecological monitoring; coastal zone; coastal ecosystem; anthropogenic heavy metals; WDXRF; total organic carbon; geochemical indices; migration of heavy metals

1. Introduction

The Priolkhonye Region is one of the intensively developed territories of the Baikal Region and belongs to the federal state budgetary institution, the "Pribaikalye Preserve" [1]. Nowadays, tourist and recreational development of Priolkhonye is intensive and constantly expanding, especially on Olkhon Island. Olkhon Island is the biggest island of Lake Baikal and a part of Baikal National Park, which is included on the list of UNESCO World Heritage Sites [2]. Human-caused impacts on the Priolkhonye Region can be divided into two following periods: agricultural (1935–2005), which occurred in the past, and tourist and recreational, which began in 2005 and continues to the present day [3]. Currently, Olkhon Island is the most visited area of Lake Baikal. Such a long impact of human activities on Olkhon soil cover activated a certain type of exogenous geological processes, which appeared as the formation of unique relief forms. At the same time, the geoecological subcomponent of the environment, namely, the anthropogenic, is getting

worse [4–7]. Over the last twenty years, this anthropogenic impact has increased by several times and has given rise to the activation of exogenous geological processes and the accumulation of pollutants in recreational-use areas [7–9].

The study area is the catchment basin of Bayan-Shungen Bay, which is included in the Priolkhonye test site for the annual monitoring of activity of exogenous geological processes. Within this catchment basin there is an agricultural field, used during the period of 1935–2005, and, within its coastal zone, seasonal unorganized camping tourism has been developed. This territory is complicated by gravitational processes of different types, such as landslides, debris, diluvial drift, etc. The slope of the catchment basin is composed of clay and loamy soils with inclusions of rubble and sand lenses. The deformed slopes have clearly outlined, trough-shaped cirques with benches that are up to 1–2 m high. Annual morphometric measurements were performed using a leveling survey for the last seven years; moreover, in 2000, these measurements were carried out as a part of a complex monitoring of the exogenous geological processes at the Priolkhonye test site. Analysis of the data obtained showed that the dynamics of gravitational processes were only observed in the lower and thalweg parts of the coast. The abrasion process in this area has little activity [5].

The main factor in the formation of the climate of the study area, and the entire Priolkhonye, is a pronounced change in the atmospheric circulation system during warm and cold periods, as well as an increased inflow of solar radiation to the surface. The average annual precipitation is 180 mm, which is the absolute annual minimum for the coast of Lake Baikal. Approximately two thirds of this amount of moisture fall during the three summer months (June–August). In January–March, the monthly amount of rain does not exceed 5 mm, so there is usually no snow cover [10]. Usually, atmospheric precipitation falls as local rain with an intensity of 30–40 mm/h. Precisely, such rain precipitation can activate most of the gravitational processes, which are hazardous geological processes. This is confirmed by the data obtained over the past six years on the amount of atmospheric precipitation in the area, as well as an analysis of space images taken in the years in which the greatest amount of atmospheric precipitation fell. However, when comparing the harm to human health derived from exogenous process activation and geoecological deterioration, environmental contamination by pollutants comes to the foreground. Heavy metals and potentially toxic elements cannot be organoleptically recognized, can accumulate in soil cover for a long time, and can migrate in soil cover along the current of soil moisture and thus cause contamination of soils and sediment in reduced relief elements such as ravines, balks, etc., and, as a consequence, in the coastal zone of Lake Baikal [11,12]. To address this issue, the catchment basin of Bayan-Shungen Bay was chosen because it is the most dynamic zone for material transfer.

In summary, this research aims to study the influence of gravitational geological processes (landslides) on the migration of heavy metals and total organic carbon (TOC) supplied to soil as a result of agricultural human activity. A methodology for the geoecological monitoring of soils based on an assessment of their contamination levels by anthropogenic heavy metals, such as Hg, Cd, Pb, and Cu, is proposed. We emphasize that the findings of the relationships between landslides and heavy metals and TOC are the novelty of this study.

The specific objectives of the study are the following: (i) determining the heavy metal concentrations of Hg, Cd, Pb, and Cu, as well as TOC in fine-grained fractions ($<100\ \mu\text{m}$) of soils by using wavelength dispersive X-ray fluorescence (WDXRF) and atomic absorption (AA) spectroscopies, as well as UV-Vis spectrophotometry; (ii) assessing the level of heavy metal contamination of soils, examined using various geochemical indices, including the contamination factor (C_f), contamination degree (C_d), normalized enrichment factor (EF), pollution load index (PLI), and geoaccumulation index (I_{geo}); (iii) evaluating the distribution of anthropogenic heavy metals in the field, landslide, and coastal zones of the catchment basin; (iv) observing the transfer of heavy metals and TOC from the field to the

coastal zone of the catchment basin; (v) studying the contribution of gravitational geological processes to the migration and accumulation of these pollutants and TOC in the coastal zone of Bayan-Shungen Bay; and (vi) validating the application of the proposed research methodology for geoecological and geodynamic monitoring.

2. Materials and Methods

2.1. Field Description and Experimental Design

Administratively, Olkhon Island is a part of the Irkutsk Region of Priolkhonye with its center located at Khuzhir Village; it is at latitude $53^{\circ}14'36''$ N and longitude $107^{\circ}28'31.3''$ E (Figure 1). The catchment basin of Bayan-Shungen Bay was divided into three landscape zones (Figures 1 and 2): a field zone, including the agricultural field and ground road system (S1 and S2 sites); a landslide zone, including the main scarp, landslide benches, and sliding tongue (S3–S6 sites); and a coastal zone, including the beach and coastline (S7 and S8 sites). A total of 80 soil samples from the three landscape zones were collected from the catchment basin in the following way: samples for multi-element analysis were collected in the autumn–winter period of 2020 and samples for the determination of TOC were collected in the autumn–winter period of 2014–2020, during annual monitoring of landslide processes. Ten samples were collected from each site (S1–S8) using the classic envelope method [13] with a step of 10–50 m. This distance depended on the form of relief.

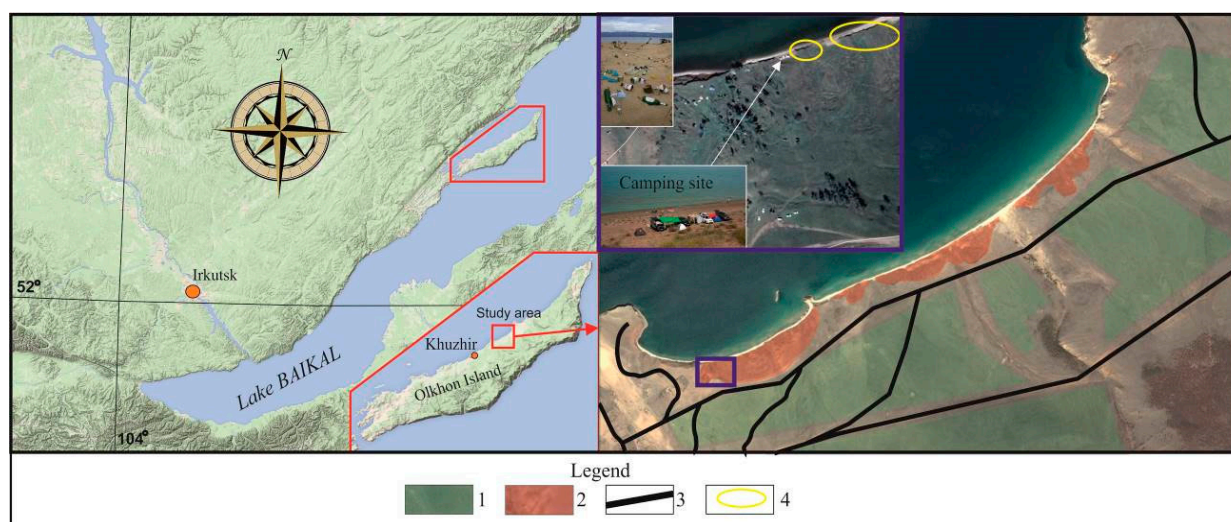


Figure 1. The study area: 1—field; 2—landslide; 3—modern ground road; 4—sliding tongue.

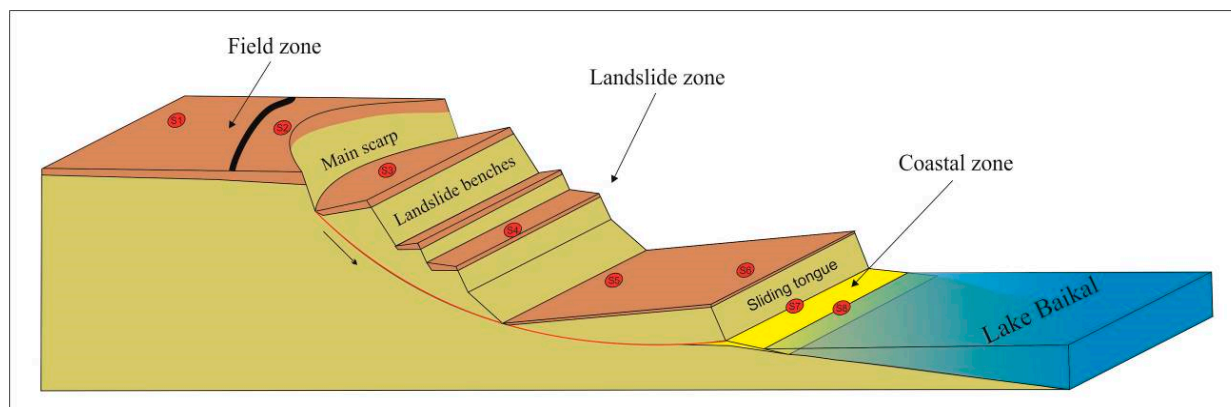


Figure 2. Scheme of the studied area in the catchment basin of Bayan-Shungen Bay. Locations of sampling sites (S1–S8) are also reported.

It is known that heavy metals accumulate in the surface horizon at a depth of approximately 0–15 cm, and that this indicator shows an ecological imbalance in the environment [12,14,15]. In accordance with [12,15], all soil samples were collected from the first 15 cm using a stainless-steel spade. Each sample was prepared as a composite sample, consisting of five subsamples. Afterwards, they were sealed in polyethylene bags and kept under natural wet conditions during fieldwork. The samples were transported to our laboratory for further analysis.

2.2. Analytical Methodology

2.2.1. Flowchart of the Analytical Methodology

The flowchart of the analytical methodology (AM) is presented in Figure 3. The main steps of the methodology are described below in detail. The collected samples were air dried at an ambient temperature for 72 h and were then placed in an oven at 110 °C until they reached a constant weight. Afterwards, soil samples were carefully crushed, ground in an agate mortar, and sieved using a 250-mesh sized sieve before performing analyses. An Analysette 22 NanoTec laser particle-size analyzer (FRITSCH, Idar-Obershtein, Germany) verified that the sample particles were smaller than 63 µm.

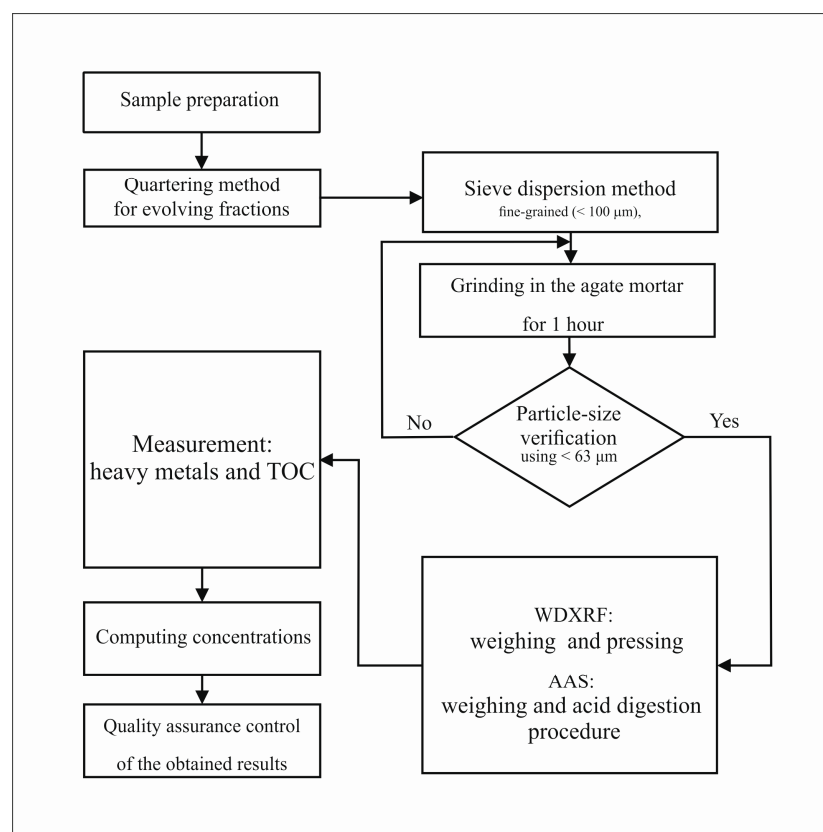


Figure 3. Flowchart of the analytical methodology (AM) adopted in this study.

WDXRF analysis of Cu and Pb. All soil samples for WDXRF analysis were prepared in accordance with [16]. For the determination of Pb content, each powdered soil sample (5 ± 0.001 g) and wax (1 ± 0.001 g) that was used as a binding agent were weighed using an AB-series analytic balance (St. Petersburg, Russia). Then, these components were mixed and thoroughly shaken for two minutes. For the determination of Cu content, each powdered sample (5 ± 0.001 g) was also weighed using the analytic balance. All the powdered samples were pressed into tablets with a diameter of 30 mm using a HERZOG HTP-40 (Maschinenfabrik GmbH & Co. KG, Osnabruck, Germany) semiautomatic press with a pressure of 100 kN and with boric acid as the bottom material. The measurements of Pb

and Cu intensities were carried out using a WDXRF-spectrometer (S8 TIGER, Bruker AXS, Germany) [17].

Figure 4 presents the X-ray spectra for the analytical CuK_α - and PbL_β - lines of the certified reference material (CRM) of SGR-1b (green river shale) and the reference material (RM) of SDPS-3 (soddy-podzolic soil), measured in the RbK_α – FeK_α wavelength range, from 26 to 60 2θ degrees. The measurements were carried out using the following conditions: 50 kV operating voltage, 50 mA current, a $\text{LiF}(200)$ crystal, a collimator with an angle aperture of 0.17° , a scintillation counter, measurement time of the CuK_α line was 60 s, background of 30 s, measurement time of the PbL_β line was 100 s, and a background of 60 s.

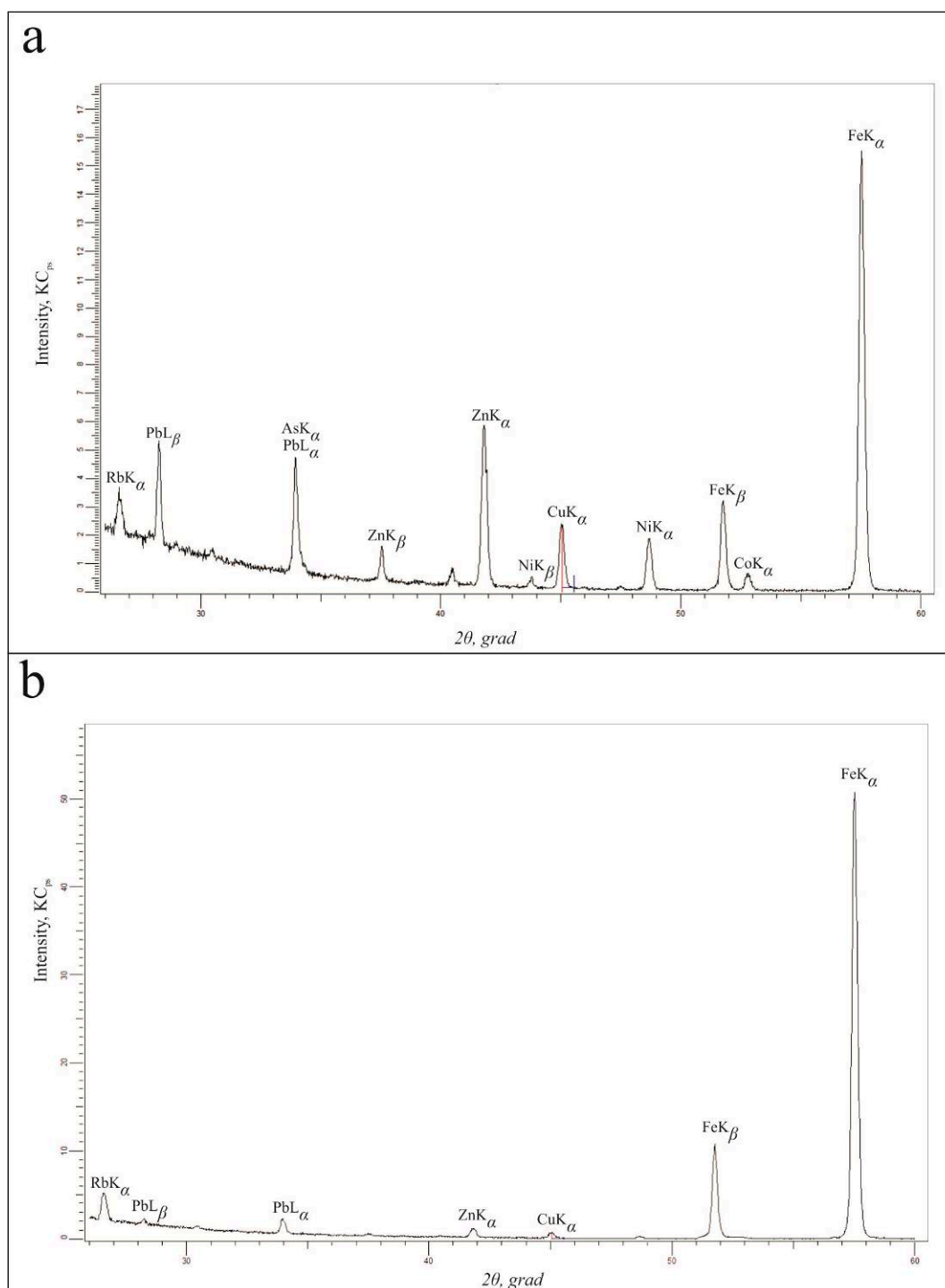


Figure 4. X-ray spectra of the SDPS-3 RM (a) and the SGR-1b CRM (b) in RbK α – FeK α wavelength range from 26 to 60 2 θ degree.

For the assessment of element concentrations, the overlap of spectral lines was taken into account using the SPECTRA^{plus} software [18] linked to the equipment. The certified values of the Cu and Pb contents (in mg kg^{−1}) were 260 and 250, respectively, for the SDPS-3 RM, and were 66 and 38, respectively, for SGR-1b CRM. As seen in Figure 4, the RbK α line may affect the PbL β line because the K α line intensity is higher than the L β -line intensity by about 4–5 times; the NiK β line may also affect the CuK α line. Thus, the influence of these lines on the analytical signal intensities of CuK α - and PbL β - lines should be taken into account.

Calibration curves were constructed using the twenty RMs and CRMs of soils, sediments, and shales. Values of the element concentrations in all these reference materials vary within a wide range, from 8 mg kg^{−1} to 240 mg kg^{−1} for Cu, and from 3 mg kg^{−1} to 280 mg kg^{−1} for Pb. The matrix correction method using fixed α -coefficients of SPECTRA^{plus} software was employed.

AAS determination of Hg and Cd. The Hg content was determined in the solid sample using the direct flameless method with a subsequent determination of atomic Hg using an atomic absorption analyzer (RA-915M) with an RP-91C add-in device (Lumex®, Russia). The determination of Hg content was conducted in accordance with the certified method—Federal Preservation Regulation Document (FPRD) [19]. To determine the Cd content, all samples were digested using concentrated acids (HNO₃, HCl, HClO₄) after pre-ignition of solids (weight of sample of 1 g, stepwise heating to 600 °C, with 50 °C steps) according to Church [20]. Then, the resulting solutions were brought to a volume of 10 mL by adding 1M HNO₃ (brand A, nitric acid of high purity) [21]. The content of Cd in the digested samples was determined by AAS using a Solar M6 spectrometer with a Zeeman and deuterium background correction system (Thermo Electron, USA). All the measurements were performed according to the certified method—M-MVI-80-2008 [22].

This work involved equipment located at the Center for Geodynamics and Geochronology, Institute of the Earth's Crust, Siberian Branch of Russian Academy of Sciences (IEC SB RAS), Irkutsk, Russia, and at the Analytical Center for Multi-Elemental and Isotope Researches, V.S. Sobolev Institute of Geology and Mineralogy, SB RAS (Novosibirsk, Russia).

TOC determination. The TOC method is a classic type of analysis in soil science [23–25]. Determination of TOC concentration in soil samples was carried out by using UV-Vis spectrophotometry according to the Tyurin method in the modification of CRIASA (Central Research Institute of Agrochemical Services for Agriculture) [26]. Note that the Tyurin method was improved according to the existing laboratory procedures: (i) within 1 hour, the samples were gradually heated on a stove in flasks with a volume of 100 mL at a temperature of 94–98 °C and achieved low boiling; (ii) photometry was carried out by using an UV-Vis spectrophotometer—GENESYS 10S (Thermo Fisher Scientific, Waltham, MA, USA); (iii) the accuracy of TOC determination was verified using the classical Walkley and Black titration method in the laboratories of the IEC SB RAS and Vinogradov Institute of Geochemistry, SB RAS (Irkutsk, Russia).

This method is based on the oxidation of organic matter with a solution of K₂Cr₂O₇ in sulfuric acid and subsequent determination of Cr³⁺, which is related to the content of organic matter: $3C + 2K_2Cr_2O_7 + 8H_2SO_4 = 2Cr_2(SO_4)_3 + 2K_2SO_4 + 8H_2O + 3CO_2$.

Each representative sample powder of 3 ± 0.001 g was weighed using an analytic balance and thoroughly ground in an agate mortar, then sieved through a woven sieve with 0.25-mm holes.

Preparation of 0.4 N dichromate solution. Finely ground K₂Cr₂O₇ weighing 40.0 ± 0.1 g was dissolved in 1 L of distilled water. Then, 1 L of concentrated H₂SO₄ was added to this solution in aliquots of 100 mL at an interval of 10–15 min.

Preparation of the reducing solution — 0.2 N Mohr's salt solution. $(\text{NH}_4)_2\text{SO}_4 \times \text{FeSO}_4 \times \text{H}_2\text{O}$ weighing 80.0 ± 0.1 g was dissolved in 1 L of distilled water and 20 mL of concentrated H_2SO_4 was added to this solution.

Analysis process. The sample weight of 0.5 ± 0.001 g was selected on the basis of the analytical data obtained in previous studies [7,27] and their supposed TOC concentrations. The loss on ignition (LOI) was preliminarily determined in accordance with [28].

Each soil sample was placed in a 100 mL flask. Then, 10 mL of dichromate solution was added dropwise at the same rate; small funnels were inserted in the flask, which played the role of a reflux refrigerator. Next, the suspension was gently shaken and heated on an electric stove for 1 hour at a temperature of 94–98 °C without boiling. Afterwards, the flasks were cooled, and 40 mL of water was added to each. Then, these suspensions were thoroughly mixed and left for a while for solid particles to settle, until complete clarification of the solution.

The next step was to prepare seven reference solutions, in which the mass of TOC was in the range from 0 to 10.3 mg, in accordance with the recommendations given in [26]. In the prepared reference solutions, the mass of TOC was equivalent to the volume of the reducing agent in the reference solution. The absorbance of the prepared solutions was determined at a wavelength of 590 nm by the GENESYS 10S equipment (Thermo Fisher Scientific, USA) using a quartz cell with a length of 10 mm.

2.2.2. Quality Assurance Control

The quality assurance control of the Hg, Cd, Pb, and Cu, and TOC determinations using XRF, AAS, and spectrophotometry was carried out using CRMs, such as SGR-1b (green river shale), SCo-1 (cody shale), Jlk-1 (lake sediment powder), JSd-1 (stream sediment powder), and RMs, namely, SSK-1 (grey carbonaceous soil), SSK-2 (industrial soil), SDPS-1 (background soil), SDPS-2 (industrial soil), SDPS-3 (soddy-podzolic soil), SKP-1 (krasnozem), ZUK-1 (coal ash powder), and BIL-1 (silt powder) [29–32]. Statistical processing of the XRF, AAS, and UV-Vis spectrophotometry results was conducted in accordance with [33,34].

For the XRF analysis, the instrumental limit of detection (ILD) values were the following: 0.8 mg kg^{-1} for Cu and 1.5 mg kg^{-1} for Pb. Note that the LOD values for these elements were higher than the ILD values: 1.4 mg kg^{-1} for Cu and 2.1 mg kg^{-1} for Pb. Repeatability of the XRF was tested, as defined in [35]. The repeatability test showed that the relative standard deviation (RSD) values were acceptable and did not exceed 5%, indicating high stability of the measurements. The accuracy of the Pb and Cu determinations in the samples examined was verified by measuring the SGR-1b and Jlk-1 CRMs. Comparison of the achieved results indicated that the obtained data showed a good agreement with the reference values. The relative percentage difference (RPD) values between the certified and measured concentration values for Pb and Cu were found to be satisfactory and ranged between 94% and 103%.

For the AAS, the limit of detection (LOD) values were as follows: for Hg, $0.01 \text{ } \mu\text{g g}^{-1}$; for Cd, $0.5 \text{ } \mu\text{g g}^{-1}$; for TOC, 0.017 wt%. The standard deviation (SD) values for Hg did not exceed 20% ($p = 0.95$) for concentrations in the range of 5×10^{-7} to 2.5×10^{-2} wt% (specified by producer). For AA analysis, all RMs (SDPS-3, SSK-1, SKP-1, etc.) and samples were diluted with specpure Al_2O_3 . The RSD values for Cd and TOC did not exceed 30%, which is admissible for analytical results of soil and sediment samples [22,26]. The RPD values for the Cd and TOC concentrations were found to be satisfactory and within the range of 86% to 104%.

The accuracy of the AAS and UV-Vis spectrophotometry results was verified by measuring the SDPS-3, SSK-1, SCP-1, BIL-1, and ZUK-1 RMs. Agreement between the certified and the obtained values was in the range of 10–25 % at a $p = 0.95$ confidence probability. Figure 5 shows the TOC calibration curve, as well as reference materials (RMs) ZUK-1 (coal ash powder) and BIL-1 (silt powder) [29] with certified values of TOC at 1.33

and 2.24 wt%, respectively. Comparison of the achieved results indicated a good agreement with the reference values.

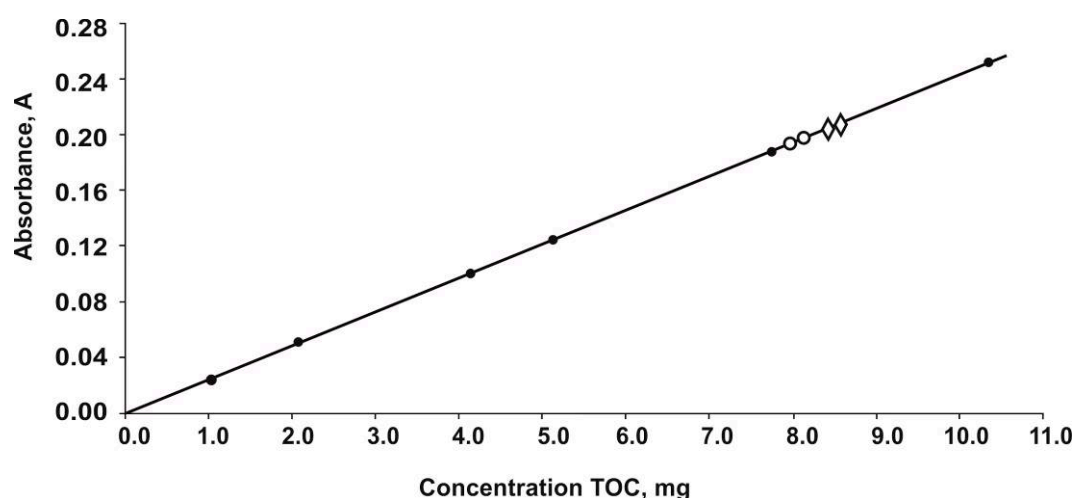


Figure 5. TOC calibration curve. Note: ● – calibration solutions; ○ – ZUK-1 RM; ◇ – BIL-1 RM.

Afterwards, processing of the obtained results was carried out. Mass fraction of TOC (in wt%) was calculated from the expression:

$$X = \frac{m \cdot K}{m_1} \cdot 100\%, \quad (1)$$

where m is the mass of TOC in the sample analyzed (in mg), which is determined from the calibration curve; K is the correction coefficient for the concentration of the reducing agent; and m_1 is the mass of the sample analyzed (in mg).

2.3. Data Processing

There are dozens of works devoted to assessing the level of soil pollution by heavy metals [14,36–44]. In this study, five geochemical indices, the contamination factor (C_f), contamination degree (C_d), normalized enrichment factor (EF), pollution load index (PLI), and geoaccumulation index (I_{geo}) were applied to completely assess the level of soil contamination by heavy metals (Hg, Cd, Pb, Cu) and their possible sources.

The C_f factor is widely used to evaluate the potential ecological risk of pollutants in soils [37,44]; it was defined as the ratio of average heavy metal concentrations (C_i) in the top horizon (depth ~15 cm) at the S1–S8 sites to the regional background values (C_n^i) [45]. The values of the C_f factor were computed from the following equation [46,47]:

$$C_f^i = C^i / C_n^i. \quad (2)$$

In accordance with [46], C_f is categorized into four classes: $C_f < 1$ (low contamination level), $1 \leq C_f < 3$ (moderate contamination level), $3 \leq C_f < 6$ (considerable contamination level), and $6 \leq C_f$ (very high contamination level).

The C_d of the environment was assessed as the sum of all contamination factors (C_f^i) for all the examined elements [46]:

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

With this approach, C_f accounts for the pollution of a single element according to the concentration background, while the C_d value is applied to assess the total soil pollution

within all the studied sites. Four classes were recognized [46]: $C_d < 8$ (low degree of contamination), $8 \leq C_d < 16$ (moderate degree of contamination), $16 \leq C_d < 32$ (considerable degree of contamination), and $32 \leq C_d$ (very high degree of contamination).

The level of contamination and possible sources of heavy metals are effectively assessed by computing the EF factor. EF is a normalization method proposed by Simex and Helz [48] to evaluate metal contents. For our purpose, Fe was chosen as the most appropriate soil constituent for normalization because the constituent should be associated with finer particles. Moreover, Fe was applied to reduce the metal variability caused by grain size and mineralogy in this study. The EF for each metal is defined as follows [49]:

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

where $(C_{Metal}/C_{Fe})_{Sample}$ is the ratio of metal and Fe contents in the soil sample, $(C_{Metal}/C_{Fe})_{Background}$ is the ratio of metal and Fe contents of the regional background. According to Sutherland [50], the EF factor is used to classify the soils into five categories: $EF < 2$ (deficiency to minimal enrichment), $2 < EF < 5$ (moderate enrichment), $5 < EF < 20$ (significant enrichment), $20 < EF < 40$ (very high enrichment), and $EF > 40$ (extremely high enrichment). However, in agreement with Zhang and Liu [51], the values of $0.5 \leq EF \leq 1.5$ denote that the enrichment of trace metals is basically of crustal origin, whereas an $EF > 1.5$ suggests that the source of the metals is more anthropogenic.

The PLI method was proposed by Tomlinson [52] to assess the overall level of heavy metal pollution. The PLI index is computed using the following expression:

$$PLI = (C_{f1} \times C_{f2} \times C_{f3} \times \dots \times C_{fn})^{1/n}, \quad (5)$$

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 divided in four grades according to [53]: $PLI < 1$ (no pollution), $1 < PLI < 2$ (moderate pollution), $2 < PLI < 3$ (heavy pollution), and $3 < PLI$ (extremely heavy pollution).

The I_{geo} index was introduced by Muller [54] to define heavy metal pollution in sediments and soils by comparing current concentrations with preindustrial levels. The I_{geo} index is expressed as follows:

$$I_{geo} = \log_2(C_n / 1.5B_n), \quad (6)$$

where C_n is the measured concentration of element n in the soil sample, B_n is the regional background value of element n in the study area [45], and the constant 1.5 allows analysis of the natural content fluctuations of a substance in the environment and detection of small anthropogenic influences [11]. Seven classes based on the I_{geo} index were recognized [55]: $I_{geo} \leq 0$ (practically uncontaminated), $0 < I_{geo} < 1$ (uncontaminated to moderately contaminated), $1 < I_{geo} < 2$ (moderately contaminated), $2 < I_{geo} < 3$ (moderately to heavily contaminated), $3 < I_{geo} < 4$ (heavily contaminated), $4 < I_{geo} < 5$ (heavily to extremely contaminated), $5 < I_{geo}$ (extremely contaminated).

3. Results and Discussion

Multielement analysis of soils of Olkhon Island using XRF spectrometry has been carried out since 2016 [6,27,56,57]. In our work [27], we proposed XRF spectrometry as a convenient and powerful method for the determination of major and minor amounts of rock-forming (Na_2O , MgO , Al_2O_3 , SiO_2 , P_2O_5 , K_2O , CaO , TiO_2 , MnO , $Fe_2O_{3(tot)}$) and trace (F, Stot, V, Cr, Co, Ni, Cu, Zn, Ga, Pb, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Nd) elements in solid environmental samples. Different landscapes, where different types of soils developed,

such as mountain dark-chestnut, chestnut (Kastanozems), and sod-podbur (Retisols) [58] were considered. As a result of studying natural and anthropogenic loads on these types of soils, we detected pollutant elements, such as Hg, Cd, Pb, and Cu, which may cause negative prolonged toxic effects in ecosystems and directly harm human health [7]. For this purpose, we developed a methodology for assessing the geoecological state of territories using geochemical indices (C_f , C_d , EF, PLI, and I_{geo}) [7].

Compared to a previous study [7], in this paper, the results of assessing the distribution of heavy metals and contamination level of the soils examined in the fine-grained fraction (<100 μm), as well as the migration of these heavy metals and TOC from the field zone of the catchment basin to the coastal zone are considered in detail. In addition, the possible sources of these heavy metals are discussed, as well as the role of gravitational processes on the migration and accumulation of these pollutants and TOC.

3.1. Distribution of Anthropogenic Heavy Metals in Soils in Comparison with Guideline and Background Values

The distribution of Hg, Cd, Pb, and Cu in the soil samples of the fine-grained sand fraction (<100 μm), according to the three investigated zones, including eight sampling sites (S1–S8) (Figure 2), are discussed. To assess the level of the heavy metal concentrations in the examined soils, guideline values for Hg and Pb were taken from the Russian Guide for soil quality [59], and values for Cd and Cu were from the Canadian Council of Ministers of the Environment (CCME) [60]. The regional background values for Hg, Cd, Pb, and Cu were taken from [45].

3.1.1. Field Zone

The order of median heavy metal concentrations (in mg kg^{-1}) in the soil samples for the field zone (S1 and S2 sites, Figure 2) was the following: Cu (45) > Pb (20) > Cd (0.21) > Hg (0.12). The determined concentrations of Hg, Cd, Pb, and Cu were in the following ranges (in mg kg^{-1}): 0.015–0.126, 0.18–0.34, 3.50–30.0, and 33–78, respectively. These elements showed moderate variability, except Hg, for which it was higher, with concentrations increasing towards the S2 site.

The comparison of the obtained Hg, Cd, Pb, and Cu concentrations for the soil samples with their regional background values showed that all the concentrations are significantly higher than their background values, except for Cu. The median concentration of Pb (20 mg kg^{-1}) was twice the regional background (10 mg kg^{-1}), the median concentration of Cd (0.21 mg kg^{-1}) exceeded the background value (0.16 mg kg^{-1}) by 1.3 times, and, moreover, the median concentration of Hg (0.12 mg kg^{-1}) was higher than its background value (0.02 mg kg^{-1}) by six times. The median concentration of Cu (45 mg kg^{-1}) did not exceed the background value (48 mg kg^{-1}) but was close to it. According to [59,60], the median values of all the investigated heavy metal concentrations do not exceed their guideline values (concentration/guideline value) (in mg kg^{-1}): Pb (20/32), Cd (0.21/1.4), Hg (0.12/2.1), and Cu (45/63).

3.1.2. Landslide Zone

The order of median heavy metal concentrations in the soil samples for the landslide zone (S3–S6 sites, Figure 2) was the following (in mg kg^{-1}): Cu (48) > Pb (19) > Cd (0.20) > Hg (0.13). The determined concentrations of Hg, Cd, Pb, and Cu were in the following ranges (in mg kg^{-1}): 0.022–0.155, 0.16–0.29, 3–25, and 34–75, respectively. These elements showed a moderate variability, except Hg, which showed a higher variability, its concentration, increasing towards the S6 site.

Similar to the field zone, comparing the obtained Hg, Cd, Pb, and Cu contents for the soil samples with their regional background values indicated that all the heavy metal concentrations were significantly higher than their background values, except for Cu. The median concentration of Pb (19 mg kg^{-1}) was twice the regional background (10 mg kg^{-1}),

the median concentration of Cd (0.20 mg kg^{-1}) exceeded the background value (0.16 mg kg^{-1}) by 1.25 times, and, moreover, the median concentration of Hg (0.13 mg kg^{-1}) was higher than its background value (0.02 mg kg^{-1}) by 6.5 times. The median concentration of Cu (48 mg kg^{-1}) did not exceed the background value (48 mg kg^{-1}) but was a boundary value. According to [59,60], the median values of all heavy metal concentrations did not exceed their guideline values (concentration/guideline value) (in mg kg^{-1}): Pb (19/32), Cd (0.20/1.4), Hg (0.13/2.1), and Cu (48/63).

3.1.3. Coastal Zone

For convenience, the coastal zone, including the beach (S7 site, Figure 2) and the coastline (S8 site, Figure 2), are discussed separately. The order of median heavy metal concentrations for the S7 site was the following (in mg kg^{-1}): Cu (50) > Pb (19) > Hg (0.14) > Cd (0.051). The determined concentrations of Hg, Cd, Pb, and Cu were in the following ranges (in mg kg^{-1}): 0.037–0.160, 0.012–0.140, 7.4–26.0, and 35–60, respectively. All these elements showed a large variability, especially in the case of Hg and Cd. The Hg concentration was increasing towards the S8 site, whereas the Cd concentration was decreasing.

The order of median heavy metal concentrations for the S8 site was the following (in mg kg^{-1}): Cu (37.5) > Pb (15.7) > Hg (0.15) > Cd (0.046). The determined concentrations of Hg, Cd, Pb, and Cu were in the following ranges (in mg kg^{-1}): 0.049–0.158, 0.012–0.082, 8.9–23.0, and 25–68, respectively. All these elements showed large variability, especially in the case of Hg. The Hg concentration increased, whereas the Cd concentration significantly decreased compared with sites S1–S6.

Comparing the obtained Hg, Cd, Pb, and Cu contents for the soil samples in the S7 site with their regional background values indicated that all the concentrations were significantly higher than their background values, except for Cd. The median concentration of Pb (19 mg kg^{-1}) was twice the regional background (10 mg kg^{-1}), the median concentration of Cu (50 mg kg^{-1}) was higher than the background value (48 mg kg^{-1}), and, moreover, the median concentration of Hg (0.14 mg kg^{-1}) was higher than its background value (0.02 mg kg^{-1}) by seven times. The median concentration of Cd (0.051 mg kg^{-1}) was lower than the background value (0.16 mg kg^{-1}) by 0.3 times. According to [59,60], the median values of all the heavy metal concentrations did not exceed their guideline values (concentration/guideline value) (in mg kg^{-1}): Pb (19/32), Cd (0.051/1.4), Hg (0.14/2.1), and Cu (50/63).

The comparison of the obtained Hg, Cd, Pb, and Cu contents for the soil samples in the S8 site with their regional background values indicated that all the concentrations were significantly higher than their background values, except for Cd and Cu. The median concentration of Pb (15.7 mg kg^{-1}) was higher than the regional background (10 mg kg^{-1}) by 1.5 times, the median concentration of Hg (0.15 mg kg^{-1}) was higher than the background value (0.02 mg kg^{-1}) by 7.5 times. The median concentration of Cu (37.5 mg kg^{-1}) was lower than the background value (48 mg kg^{-1}), the median concentration of Cd (0.046 mg kg^{-1}) was lower than the background value (0.16 mg kg^{-1}) by 0.3 times. According to [59,60], the mean median values of all the investigated heavy metal concentrations did not exceed their guideline values (concentration/guideline value) (in mg kg^{-1}): Pb (15.7/32), Cd (0.046/1.4), Hg (0.15/2.1), and Cu (37.5/63).

In summary, the distribution of the investigated heavy metals in all the discussed zones indicated a trend towards a slight increase in Hg content from the field (S1 and S2 sites) toward the coastal zone (S7 and S8 sites), whereas the Cd content decreased significantly going toward the coastline (S8 site). Note that the increased concentrations of all metals retained a migration pathway from S1 to S6 sites and changed only starting at the coastal zone (S7–S8 sites). Such an increase in the Hg, Cd, Cu, and Pb concentrations along this pathway indicated that these metals migrated from the S1 to S6 sites without participation of surface runoff, in which there is a loss of concentration. In this case, loss of the Cd and Pb concentrations starting from the S8 site occurred due to the influence of wave currents. Based on the fact that gravitational processes occur between the field and coastal

zones, in this study, we aimed to investigate their supposed role in the migration of the examined pollutants.

3.2. Assessment of Soil Pollution Level

Following the experimental results obtained in a previous study [7], the fine-grained fraction ($<100\ \mu\text{m}$) of the soil samples was studied using ecological and geochemical indices (C_f , C_d , EF, PLI, and I_{geo}).

The C_f values were computed by applying Equation (2). The order of the mean C_f for all the heavy metals in the field zone (S1 and S2 sites) was $\text{Hg} (6.30) > \text{Pb} (1.58) > \text{Cd} (1.53) > \text{Cu} (0.86)$. The order of the mean C_f in the landslide zone (S3–S6 sites) was $\text{Hg} (5.83) > \text{Cd} (1.32) > \text{Pb} (1.42) > \text{Cu} (0.84)$. The order of the mean C_f in the coastal zone (S7 site) was $\text{Hg} (6.29) > \text{Pb} (1.76) > \text{Cd} (0.32) > \text{Cu} (1.20)$. The order of the mean C_f in the coastal zone (S8 site) was $\text{Hg} (6.71) > \text{Pb} (1.38) > \text{Cd} (0.30) > \text{Cu} (1.30)$. The maximum values of C_f were those for Hg in all sites, indicating pollution in the environment, even if the Hg concentration was always below the guideline values. High C_f values were observed for Cd (1.53 and 1.32) at sites S1–S6 and for Pb (1.58, 1.42, and 1.76) in the S1–S7 sites, as well as for Cu (1.20 and 1.30) in the S7 and S8 sites, which provided evidence of a moderate contamination level in the soils examined [46]. According to Equation (3), the mean C_d value for all zones equals 58.02, denoting a very high degree of environmental pollution [46], despite none of the median values of concentrations of the studied heavy metals being above their guideline values.

The assessment of the contamination load for individual sites of all the studied zones (PLI index, Equation (5)) indicated a moderate contamination level in the environment, according to [52].

The mean EF values for all the studied zones were as follows: $\text{Hg} (7.06) > \text{Pb} (1.74) > \text{Cu} (1.12) > \text{Cd} (1.03)$. The highest EF values for Hg occurred in sites S1–S2 (10.35), S7 (6.35), and S8 (6.78), indicating that the investigated soils classified as significantly enriched [49]. The high EF values for Cd occurred at sites S1–S2 were equal to 2.38, indicating that the soils were classified as moderately enriched [49]. In accordance with Equation (4), the EF values obtained for Hg, Cd, and Pb were in the range of 1.5–10.35, which suggests a possible anthropogenic source for these heavy metals. The EF values for Cu occurred in the range of 0.41–2.87 for all sites. This suggests both a possible crustal origin (weathering product) and an anthropogenic source. According to [7], we suggest that there might be various possible sources of Cu. As is obvious from the obtained results, the C_f value of Cu starts to rise in the coastal zone (S7 and S8 sites, Figures 1 and 2). As can be seen from Figure 1, unofficial seasonal camping takes place on the coastal territory, which is the area that is exposed to landslides. Aerial images show garbage left by tourists in the coastal zone. This could be one of the reasons for the occurrence of pollutants, such as Pb, Hg, Cd, and Cu, and others in the soil and an increase in their concentrations.

The I_{geo} values ranged from 1.70 (S1 and S2 sites) to 2.06 (S8 site) for Hg (mean of 1.85) and from -0.36 to 0.10 for Pb (mean of 0.18). The other trace metals, i.e., Cu and Cd, showed negative values of I_{geo} . According to the classes recognized in [55], all zones (S1–S8 sites) could be considered to be moderately contaminated by Hg, and only the S7 site (coastal zone, beach) could be considered not-to-moderately polluted by Pb. Moreover, the highest I_{geo} value for Hg was 2.06, which may suggest that the concentration of this metal has been significantly impacted by anthropogenic activities.

Finally, consistent with the obtained results, the contamination level of the study area by the investigated heavy metals does not exceed the moderate level, except for Hg, which ranged from moderate to considerable levels. Note that the Hg content increased in the coastal zone (C_f value equal to 6.71). This metal tends to accumulate in soils and sediments for a long time and may directly harm human health if people come into contact with it [42].

Presumably, anthropogenic sources of Hg and Cd could include inherited pollution from phosphoric fertilizers [7] applied to agricultural soils. Moreover, heavy metal-containing insecticides, which were also applied to agricultural soils in the past, could have caused heavy metals pollution [61]. As discussed above, the content and pollution level of Pb increased towards the coastal zone (S7 site) (Figure 2). As is evident from a detailed space image from 2019, many tourists used the area as an unofficial camping site. Moreover, the existing road system and traffic nearby might contribute to the increase in Pb concentration. Afterwards, this concentration insignificantly decreases towards the coastline (S8 site) due to coastal currents.

3.3. Migration of Heavy Metals and TOC

It was proposed to consider the transfer routes of the heavy metals discussed throughout these studied zones. Such information is very important for monitoring the geoecological state of the environment, because these heavy metals belong to the Groups 1–3 toxic chemicals according to World Health Organization classifications, IARC [62].

The increased concentration of Hg was retained throughout all migration pathways and increased in the coastal zone (S7 and S8 sites). Indeed, in this zone there is an accumulation of Hg. High Cd content is also retained throughout a migration pathway from the field to the coastal zone. Afterwards, Cd is carried away along the coastline influenced by the wave flow and migrates together with the coastal current. Lead in agricultural soils usually originates from mineral fertilizers [14], which were used to fertilize the fields in the past [7]. As described above, a high Pb concentration remains throughout the migration pathway from the field to the coastal zone (S7 site), where the concentration increases. Afterwards, Pb concentration insignificantly decreases, influenced by the wave flow. It is not possible to observe migration of Cu, since no sources of metal entry in the field and landslide zones were identified. However, the highest concentrations of Cu were found in the coastal zone (S7 and S8 sites), which might suggest an influx of this metal from the camping area as a result of tourist and recreational activities [7,14]. TOC migration can be traced only from the landslide zone (S3–S6 sites), where it is formed as a result of wetting slopes and a large amount of vegetation, to the coastal zone (S7 and S8 sites). Afterwards, TOC is carried away by wave flow and migrates together with the coastal current, and is discussed below.

3.4. Role of Gravitational Processes in Migration and Accumulation of Heavy Metals and TOC

As discussed above, we suggest the following transfer mechanism of the heavy metals examined throughout all migration pathway: field—landslide—coast. The possible anthropogenic sources of Hg, Cd, and Pb arise in the field zone, whereas, the source of Cu mainly originates in the coastal zone (camping area). The increased values of the Hg, Cd, and Pb concentrations remain throughout all migration paths, while they decrease only in the coastal zone. On the other hand, Cu content shows an increasing trend only in the coastal zone.

In this study, the amount of atmospheric precipitations and TOC concentration in the coastal zone were analyzed for the autumn–winter periods from 2014 to 2020. In these periods, the freezing of the coastal edge of the bays began before the formation of the ice cover [58]. It was noted that the increase in TOC concentration corresponds to the years with the highest amount of precipitations (Figure 6), which activated landslide processes. As a result of the movement of landslide, the tongue is transferred to the beach zone, and, afterwards, the landslide mass is eroded under the influence of intense waves (storms) in the autumn–winter period. Figure 6 shows traces of material entry to the coastal zone in years with significant TOC content for this area (2014 and 2019).

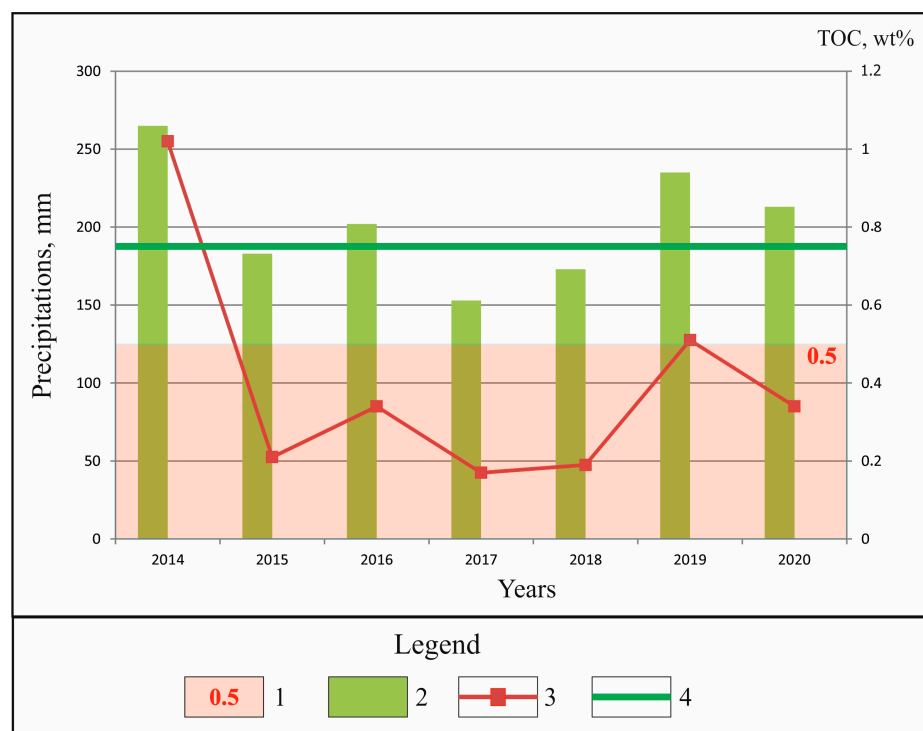


Figure 6. Dependence of the annual amount of rain precipitations on the concentration of TOC in the soil samples. Legend: 1—landslide stability zone; 2—rain precipitation; 3—the TOC concentration in wt%; 4—the borderline value of mean annual amount of precipitation.

As a result of this monitoring, we found that a TOC value $\geq 0.5\%$ in the coastal zone indicated that landslides activated in that year. This means that TOC is a marker of occurred movement of rock masses to the beach zone. This type of landslide is called solifluctional [4]; that is, the movement of landslide masses is similar to a travelling belt at an airport, which transfers material from one place to another without changing its chemical composition. This is evidenced by the constant values of the Hg, Cd, Pb, and Cu concentrations via the migration pathway: field—landslide—coast. It is a reminder that the Cd and Cu concentrations start to decrease only in the coastal zone due to wave current activities.

The results of this study showed that it is dangerous to have human activities on the beach in places where landslides might occur because high concentrations of heavy metals can be found in transported soils and sediments. Indeed, the presence of significant concentrations of heavy metals can cause negative toxic effects in coastal ecosystems.

3.5. Methodology for Geoecological and Geodynamic Monitoring of Soils

In this study, we attempted to address the problem of heavy metal pollution, as well as migration and accumulation of anthropogenic heavy metals and TOC in the coastal ecosystem of Olkhon Island in Lake Baikal. During the research, we discussed a possible role of landslide processes in soil mass displacement via the pathway: field—landslide—coast. We proposed the following complex methodology for geoecological and geodynamic monitoring.

Figure 7 shows the flowchart of the complex methodology for geoecological and geodynamic monitoring. As shown in Figure 7, the analytical methodology (AM) is included.

The presented methodology is convenient for studying territories where gravitational processes are likely to occur.

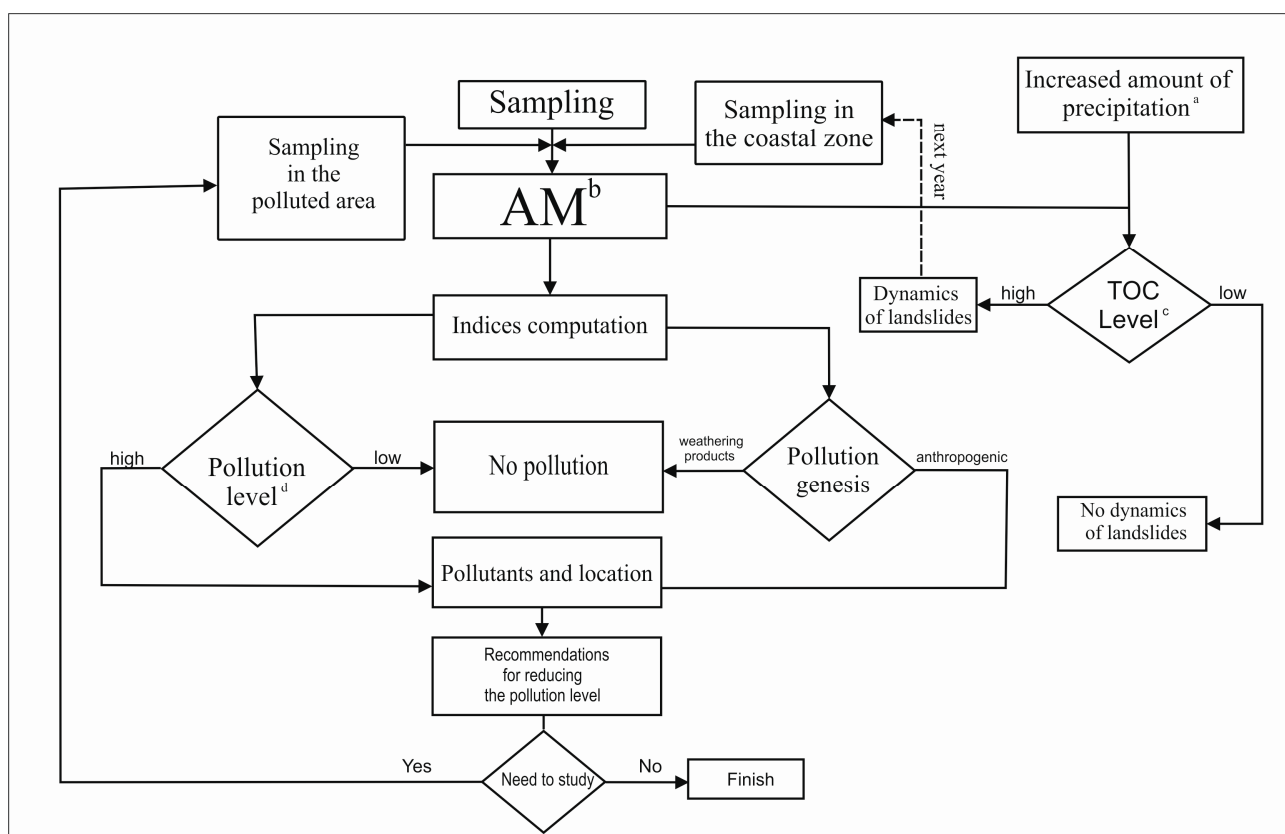


Figure 7. Flowchart of the complex methodology for the geoecological and geodynamic monitoring. Note: a—determining the dependence of the amount of rain precipitations on the TOC content; b—analytical methodology (AM); c—computing the TOC content; d—determining ranges of contamination applying geochemical indices.

4. Conclusions

This research investigated the Hg, Cd, Pb, Cu, and TOC concentrations in a fine-grained fraction ($<100\ \mu\text{m}$) of soils using XRF, AAS, and UV-Vis spectrophotometry. The level of anthropogenic heavy metal contamination of the soils examined in three zones, such as field, landslide, and coastal areas, was assessed using various geochemical indices. The possible sources of Hg, Cd, Pb, and Cu were defined as anthropogenic, including tourist and recreational activities, the existing road system and traffic nearby, inherited pollution of agricultural soils from phosphoric fertilizers and insecticides. The level of environmental hazard in the coastal ecosystem as a result of an increase in the concentration of the heavy metals studied in the soil was discussed. Specifically, the mean Cd value for all zones equals 58.02, denoting a very high degree of environmental pollution, despite none of the median values of concentrations of the studied heavy metals being above their guideline values. At the same time, the assessment of the contamination load for individual sites of all the studied zones using the PLI index indicates a moderate contamination level of the environment. In addition, it is worth paying attention to the higher variability of Hg in comparison with other studied metals, as well as an increase in its concentration from $0.015\ \text{mg kg}^{-1}$ to $0.160\ \text{mg kg}^{-1}$ toward the coastal zone. Note that all the discussed anthropogenic metals must be monitored annually because the pollution level of these pollutants could rise to a dangerous level.

As a result of a TOC concentration monitoring, it was found that a TOC value $\geq 0.5\%$ in the coastal zone indicates that a landslide activated in that specific year. This means that TOC could be considered as a marker of the occurred movement of landslide material to the beach zone. The transfer of the material occurred from one place to another without changing its chemical composition. This is evidenced by the constant values of Hg, Cd,

Pb, and Cu concentrations via the migration pathway: field—landslide—coast. The complex analytical and geochemical flowchart for geoecological and geodynamic monitoring presented in Figure 7 could be an useful tool for studying territories where gravitational processes may occur.

Additional research activities are foreseen for the next few years to monitor the concentrations of the anthropogenic heavy metals, as well as assess their contamination levels in soils and sediments in accumulative shores of Olkhon Island and Lake Baikal. The problem of migration and accumulation of anthropogenic heavy metals and TOC in coastal ecosystems of Olkhon Island and Lake Baikal, as well as the relationships between heavy metals, TOC, and gravitational processes remains relevant. This problem needs focused and continuous attention.

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