

Geochemical Features of the Quaternary Deposits of the Irkutsk's Reservoir Zone under Technogenic Conditions

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Abstract: The article considers the some geochemical characteristic of the loesslike and bottom sediments of the area Novo-Razvodnoy of the Irkutsk's reservoir. Main objectives of this research are to determine contents of trace elements (V, Cr, Co, Ni, Cu, Zn, Ga, Pb, As, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Nd) and major elements (CaO, TiO₂, MnO, Fe₂O_{3(total)}) in the investigated samples by X-ray fluorescence analysis method (XRF), to establish the trace elements distribution dynamics on the lateral profile of the area Novo-Razvodnoy, to reveal the pollution degree of the studied sediments and to calculate the specific geochemical coefficients Rb/Sr and Ca/Sr in the studied sediments. As a result of the studies, it is established that the dried part of the coastal shallows experiences the higher technogenic load in comparison with other considered zones of the lateral profile. This fact was confirmed by the maximum content of As (12 mg kg⁻¹) exceeding by 6 times the established value of the maximum permissible concentrations in soils (MPC) and the maximum calculated values of pollution load index (PLI) and geoaccumulation index (I_{geo}) for arsenic.

Key words: Technogenesis, XRF analysis, trace elements distribution dynamics, pollution.

1. Introduction

The loess loams can change their microelemental composition under technogenic conditions. Thus, in the contact zone of land with the waters of the Irkutsk's reservoir abrasion of the loess loams, forming the beach scarp, and their redeposition within the coastal zone of the reservoir occur. As a result, certain changes are noted in microelemental composition of the loess loams which came into the type of bottom sediments [1].

Recently, an increase in the technogenic load occurs both at the expense of industrial wastewater, and due to pollution by household waste of coastal areas, since the water protection zone has many bays near which numerous recreation centers are located.

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2. Objects

The samples of the loesslike and bottom sediments of the lateral profile of the area Novo-Razvodnoy are selected as objects of study.

The lateral profile is divided into blocks: first is the beach scarp (the starting material submitted by loess loams); second is the dried part of the coastal shallows (it is formed by the blurred and redeposited loess loams during the high water level in the reservoir in autumn); third is the water edge; fourth is the underwater part of the coastal shallows.

Fig. 1 shows the dried part of the coastal shallows and the abrasion beach scarp folded by dealluvial loess loam during of low water level in the Irkutsk's reservoir (52°14'12" N and 104°19'18" E).

Also, you can see a large amount of household waste scattered in the dried part of the coastal shallows. The transfer of wastes into the water will occur at a higher water level in the reservoir.

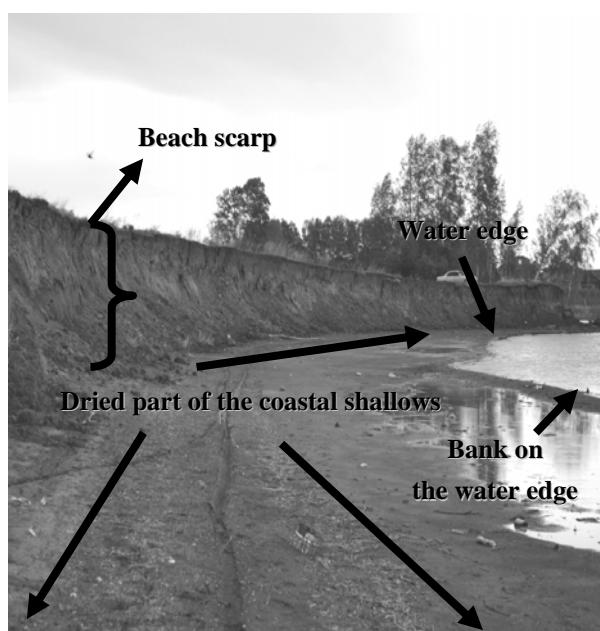


Fig. 1 The dried part of the coastal shallows and the abrasion beach scarp folded by dealluvial loess loam in the area Novo-Razvodnoy of Irkutsk's reservoir (June of 2013, the low water level in the reservoir).

3. Research Method

3.1 X-Ray Fluorescence Analysis (XRF)

Determining the contents of major and trace elements in the studied samples was carry out by XRF. A simple, rapid and nondestructive Wavelength Dispersive X-ray Fluorescence Spectrometry (WDXRFS) was developed for the determination of different elements in the rocks, soils and sediments [2]. All measurements were performed in a vacuum condition using a WDXRF spectrometer S8 TIGER (Bruker AXS, Germany). Detailed information about the WDXRF-spectrometer features can be found elsewhere [3]. This instrument is equipped with a 4 kW power X-ray tube with a rhodium anode and a beryllium window of 75 μm thickness.

The selection of material for the analysis was carried out by the quartering method. The selected samples were powdered manually in an agate mortar. For the elimination of a particle aggregation during the milling process a few drops of an ethyl hydroxide of high purity were added. The prepared samples were pressed into tablets on a boric acid base with a diameter of 40 mm using the HERZOG HTP 40

semiautomatic press (Germany) with a pressure of 100 kN.

The prepared samples weighing 1 ± 0.0001 g were used for the determination of concentrations of CaO, TiO_2 , MnO, $\text{Fe}_2\text{O}_{3(\text{total})}$, V, Cr, Co, Ni, Cu, Zn, Ga, As, Pb, Ce, Ba, La and Nd. The samples weighing 5 ± 0.0001 g were applied for the determination of Rb, Sr, Y, Zr and Nb. In the latter case, to enhance the emitting layer in the sample the binder (wax) in the ratio of 5:1 was added before the process of tableting. These methods are described detail in the work [4].

In most cases, the spectrum lines of the K-series were used as the most intensive for determining the elements, with the exception of Pb, Ba, La, Ce and Nd, which were determined using the L-series lines.

Measurement time of the analytical line and the background from each element was 60–100 s and 30–60 s, respectively. Processing the X-ray spectra, numerical peak separation, and the correction of the matrix effects were performed using the software SPECTRA^{plus} [5] linked to the equipment.

The detection limits of all trace elements vary from 2 to 5 mg kg^{-1} . For CaO, TiO_2 , MnO, and $\text{Fe}_2\text{O}_{3(\text{total})}$ the detection limits increase (15–30 mg kg^{-1}).

3.2 Methods of Contamination Assessment in the Studied Samples

In this study, geoaccumulation index (I_{geo}) and pollution load index (PLI) were calculated to assess the toxic elements contamination levels in studied samples. Also, comparative analysis was performed between obtained concentrations of the toxic elements (V, Cr, Co, Ni, Cu, Zn, Pb, As) and the established values of the maximum permissible concentrations in soils (MPC) [6-9].

3.2.1 Geoaccumulation Index (I_{geo})

The geoaccumulation index (I_{geo}) is used in the assessment of contamination by correlation of the levels of the toxic elements contents to background levels. Originally bottom sediments are used [10, 11]. It was calculated using the equation:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right), \quad (1)$$

where C_n represents the measured concentration of the toxic element and B_n is the geochemical background value of this element in bottom sediments of the Baikal region [6]. For arsenic the established value (MPC) (2 mg kg^{-1}) [6] was used.

The following classification is given for geoaccumulation index: practically unpolluted (< 0), unpolluted to moderately polluted (0–1), moderately polluted (1–2), moderately to strongly polluted (2–3), strongly polluted (3–4), strongly to extremely polluted (4–5) and extremely polluted (> 5) [10, 12].

3.2.2 Pollution Load Index

The calculation of PLI was carried out taking into account the values of ratios (C_f) of obtained concentration of all the toxic elements in studied samples to the background contents of these elements in the continental crust. Author used upper continental crust (UCC) [13]. For arsenic the established value was used from work [14]. PLI was determined using the equation:

$$PLI = (C_{f1} \times C_{f2} \times C_{f3} \times \dots \times C_{fn})^{1/n}, \quad (2)$$

where n is the number of toxic elements.

The pollution levels were divided into four degree: no pollution ($PLI < 1$), moderate pollution ($1 < PLI < 2$), heavy pollution ($2 < PLI < 3$), and extremely heavy pollution ($3 < PLI$) [15].

4. Result and Discussions

4.1 Major and Trace Elements

The XRF analysis results indicated that the CaO, TiO₂, MnO and Fe₂O_{3(total)} concentrations in studied samples of the sediments vary in the ranges (in %): 1.93–3.33, 0.948–1.127, 0.093–0.126, 7.121–8.831, respectively. It should be noted that MnO and Fe₂O_{3(total)} are characterized by high values of the cation exchange capacity. They are the centers of certain chemical elements localization [16]. Among considered oxides Fe₂O_{3(total)} is the leader. On the lateral profile the maximum concentration of Fe₂O_{3(total)} is observed in the dried part of the coastal shallows. The minimum concentration of Fe₂O_{3(total)} is noted on the water edge. Some increase in this oxide concentration is observed in the underwater part of coastal shallows. Higher contents of CaO (3.33%), MnO (0.126), and TiO₂ (1.127) are noted in the sediments of the underwater part of coastal shallows in contrast to the deposits of whole territory of shallows.

Table 1 presents the mean concentrations (mg kg^{-1}) of trace elements in the studied samples on the lateral profile. All investigated sediments are characterized by the elevated contents of Ba, Zr, and As.

The analysis of trace elements concentrations shows some increase in V, Cr, Ni, and Cu concentrations (within 15%) in the dried part of the coastal shallows in contrast to their concentrations in original material represented by the loess loams. Near the water edge this increase disappears.

Reduction in contents of Cr, Co, Zr, La and some increase in the concentration of Zn occur on the water edge. The sediments of the underwater part of the coastal shallows are more saturated by chemical elements

Table 1 Mean concentrations (mg kg⁻¹) of V, Cr, Co, Ni, Cu, Zn, Ga, Pb, As, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Nd in the studied samples on the lateral profile.

Elements	The beach scarp	The dried part of the coastal shallows	The water edge	The underwater part of the coastal shallows
V	135 ± 5	143 ± 6	140 ± 5	150 ± 6
Cr	125 ± 5	143 ± 7	120 ± 5	180 ± 9
Co	20 ± 0.5	20 ± 0.6	14 ± 1.2	19 ± 0.9
Ni	64 ± 4	70 ± 3.5	70 ± 3.5	68 ± 3
Cu	33 ± 0.5	36 ± 0.8	34 ± 0.9	32 ± 0.7
Zn	75 ± 3	71 ± 2	77 ± 2.8	76 ± 2.6
Ga	16 ± 0.8	15 ± 1.1	15 ± 0.9	15 ± 1.1
Pb	19 ± 0.9	20 ± 1.2	19 ± 0.5	19 ± 0.8
As	9.0 ± 0.8	11 ± 0.5	8.8 ± 1.2	9.3 ± 0.8
Rb	76 ± 3.2	87 ± 3.1	79 ± 2.5	77 ± 3.1
Sr	220 ± 8	203 ± 7	220 ± 7	240 ± 8
Y	28 ± 1.5	29 ± 0.8	28 ± 1.2	35 ± 0.8
Zr	305 ± 5	330 ± 5	230 ± 6	550 ± 8
Nb	12 ± 0.8	13 ± 0.6	13 ± 0.6	14 ± 0.5
Ba	660 ± 10	650 ± 10	670 ± 9	670 ± 9
La	39 ± 1.1	40 ± 1.6	37 ± 1.5	43 ± 1.3
Ce	77 ± 2.5	78 ± 3.5	69 ± 2.8	89 ± 3
Nd	29 ± 1.2	32 ± 2.0	30 ± 1.1	39 ± 1.8

Confidence intervals were computed at the confidence level $p = 0.95$ and the number of the measurements $n = 6$.

than in the dried part and on the water edge. In this area the maximum concentrations of V, Cr, Sr, Y, Zr, Ba, La, Ce, and Nd are established. The sediments of the water edge are characterized by same high content of Ba. On the lateral profile changes in the contents of Pb, Ga, and Nb are not observed.

Particular attention is given to the distribution of the toxic elements (V, Cr, Co, Ni, Cu, Zn, Pb, and As) in studied samples of sediments. The V, Cr, Co, Ni, Cu, Zn, Pb, and As concentrations vary in the following ranges (mg kg⁻¹): 130–150, 120–180, 14–22, 62–75, 30–39, 66–77, 18–20, 8–12, respectively. Despite the fact that the arsenic concentrations take the last place in contrast to the contents of V and Cr, the comparison of the obtained data on the As contents with the maximum permissible concentrations (MPC) shows the increase in the established values by 4 and 6 times, respectively [6].

At two points of the dried part of coastal shallows the maximum content of As (12 mg kg⁻¹) is established. These two points are located in 40 m and 60 m from the beach scarp, respectively.

The higher concentrations of Cr are established in the dried part of coastal shallow in 20 m from the beach scarp (150 mg kg⁻¹) and in underwater part (180). Also, these contents of Cr exceed the value of MPC by 1.5 and 1.8 times, respectively [7].

Fig. 2 shows the result of the comparison of the mean concentrations of toxic trace elements with the maximum permissible concentrations (MPC).

Perhaps, high concentrations of arsenic are associated with elevated contents of Fe₂O₃(total) because in previous studies the samples with high concentrations of iron (11.360–19.620%) were characterized by high concentrations of arsenic (18–38 mg kg⁻¹) [17]. One of the reasons of the high concentrations of Cr is related to high contents of this toxic element in the bedding rocks. So, within the Baikal research zone, the identified maximum concentration of chromium in bedding rocks is 4,000 mg kg⁻¹ [7]. But authors do not exclude the influence of technogenic pollution on the concentration of toxic elements in studied sediments on the lateral profile.

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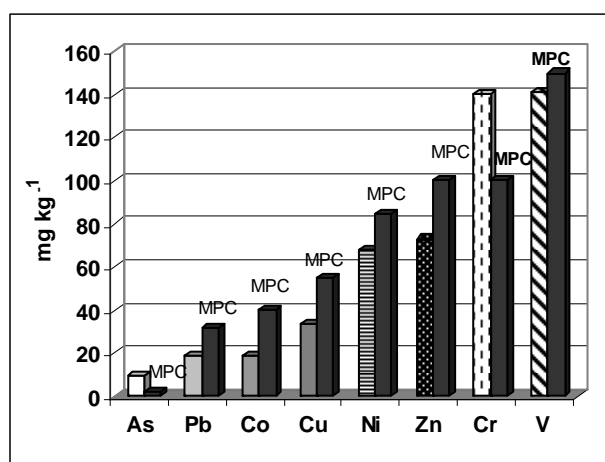


Fig. 2 The mean concentrations of toxic elements and values of the MPC for these elements.

However, contents of V, Zn, Ni, Cu, Co, and Pb do not exceed the established values (MPC) [6-9].

4.2 Geoaccumulation Index (I_{geo}) and Pollution Load Index (PLI) in the Studied Samples on the Lateral Profile

In most cases, the calculated values of the geoaccumulation index (I_{geo}) are less than zero (< 0). Arsenic values I_{geo} vary from > 1 (the beach scarp, the water edge, the underwater part of the coastal shallows) to 2 (the dried part of the coastal shallows). The results of I_{geo} analysis indicate that the studied samples are practically uncontaminated by V, Cr, Co, Ni, Cu, Zn, and Pb, while these samples are moderately polluted by As.

The values of PLI belong to $1 < PLI \leq 2$ category which means that studied samples are moderately polluted by V, Cr, Co, Ni, Cu, Zn, Pb and As. On the beach scarp values of PLI vary from 1.46 to 1.52. In the dried part of the coastal shallows values of PLI change from 1.49 to 1.68. On the water edge and in the underwater part of the coastal shallows values of PLI are 1.46 and 1.60, respectively. Maximum value (1.68) is established in the dried part of the coastal shallows at point which located in 60 m from the beach scarp.

4.3 Geochemical Coefficients

During the investigation of various geological processes, including the process of sedimentation, different geochemical coefficients are applied widely [18-20].

Author analyzed the distribution of values of the Rb/Sr and Ca/Sr for studied samples on the lateral profile.

The Rb/Sr indicator characterizes of weathering intensity [21]. The rubidium does not form its own minerals. Usually, this chemical element is part of the rock-forming minerals enriched of potassium, such as feldspars and mica, while the strontium accumulates in carbonates and calcium-rich minerals such as hornblende, plagioclase and picrite [22]. Calcium-rich minerals break down more easily than potassium-rich minerals [23]. In the process of chemical weathering, strontium is leached from minerals much easier than rubidium. The different behaviors between Rb and Sr can be used to determine the intensity of chemical weathering [24].

The values of this indicator vary from 0.29 to 0.42 for the beach scarp. The values of Rb/Sr change from 0.30 to 0.51 for the dried part of the coastal shallows. The values of Rb/Sr for the water edge and the underwater

part of the coastal shallows are 0.36 and 0.32, respectively. In most cases, the obtained values are similar to the value of Rb/Sr of upper continental crust (UCC, 0.32) [25].

At two points of the dried part of the coastal shallows maximum value of Rb/Sr (0.51) is connected to lower concentrations of CaO (1.93%) and Sr (180 mg kg⁻¹) in studied sediments. Moreover, these investigated sediments are characterized by a higher content of Fe₂O_{3(total)} (8.691–8.831%). These two points are located in 40 m and 60 m from the beach scarp, respectively.

The values of Ca/Sr change from 77 to 98 for the beach scarp. The values of this indicator vary from 77 to 80 for the dried part of the coastal shallows. The values of Ca/Sr for the water edge and the underwater part of coastal shallows are 100 and 99, respectively. It should be noted that the obtained values are less than the value of Ca/Sr of upper continental crust (UCC, 120).

5. Conclusions

As a result of the study, some general features of studied sediments were established. All sediments are characterized by the elevated contents of Fe₂O_{3(total)}, Ba, Zr, and As.

The sediments of the underwater part of the coastal shallows are characterized by the maximum contents of CaO, TiO₂, MnO, V, Cr, Sr, Y, Zr, La, Ce, and Nd.

It is established that the dried part of the coastal shallows experiences the higher technogenic load in comparison with other considered zones of the lateral profile. This fact was confirmed by the maximum content of As (12 mg kg⁻¹) exceeding by 6 times the established value of MPC and the maximum calculated values of pollution load index (PLI) and geoaccumulation index (I_{geo}) for arsenic.

The actions should be taken to clean the dried part of the coastal shallows and the entire coastal area, since there is the hazard of water pollution in the Irkutsk's reservoir.

Analysis of the calculated values distribution of the Rb/Sr indicator allowed identifying the intensity of chemical weathering on the lateral profile.

In most cases, the calculated values of Ca/Sr are less than 100. The obtained concentrations of Sr in the studied samples of sediments are much lower than its content in the earth's crust (340 mg kg⁻¹) [14]. Perhaps, it is connected to the intensive migration of strontium.

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