

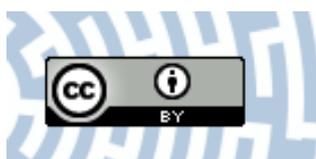


You have downloaded a document from
RE-BUŚ
repository of the University of Silesia in Katowice

Title: Composition and physico-chemical properties of bottom sediments in the southern part of the Bratsk Reservoir (Russia)

Author: Mariusz Rzętała, Victoria A. Babicheva, MArtyna A. Rzętała

Citation style: Rzętała Mariusz, Babicheva Victoria A., Rzętała Martyna A. (2019). Composition and physico-chemical properties of bottom sediments in the southern part of the Bratsk Reservoir (Russia). "Scientific Reports" Vol. 9 (2019), art. no 12790, DOI 10.1038/s41598-019-49228-4



Uznanie autorstwa - Licencja ta pozwala na kopiowanie, zmienianie, rozprowadzanie, przedstawianie i wykonywanie utworu jedynie pod warunkiem oznaczenia autorstwa.



UNIWERSYTET ŚLĄSKI
W KATOWICACH



Biblioteka
Uniwersytetu Śląskiego



Ministerstwo Nauki
i Szkolnictwa Wyższego

OPEN

Composition and physico-chemical properties of bottom sediments in the southern part of the Bratsk Reservoir (Russia)

Mariusz Rzetala¹, Victoria A. Babicheva² & Martyna A. Rzetala¹

The paper presents the results of studies of bottom sediments taken from the southern part of the Bratsk Reservoir. The following analyses have been conducted: trace element analysis, particle-size analysis as well as chemical analysis of water, hydrochloric acid and alkaline extracts for 18 samples of the bottom sediments. The granulometric analysis has identified the predominance of fine silt and silty-clayed sediments. The data on the content of trace elements in the bottom sediments of the Bratsk Reservoir is presented in comparison with their content in the natural environment of the Baikal region; the anomaly ratio was used to characterize the excess for trace elements. The chemical analysis of extracts has showed "saline contamination" of mud (silt), high concentration of carbonates in it, as well as the presence of mobile (free) forms of aluminum oxide. In this research, an attempt was made by using a correlation analysis to evaluate the impact of various physical and chemical characteristics of the bottom sediments, such as the content of clay fraction, organic carbon, carbonates, and water-soluble salts on the accumulation of trace elements.

The ecological state of the entire reservoir geosystem, as well as its individual components (water mass, bio-organisms, aquatic vegetation, sediments (bottom deposits)), depends on a number of natural and anthropogenic factors. As a result of contamination, the trace element content in all components of the geosystem can vary considerably¹⁻⁵. A dangerous trend in this case is the accumulation of toxic elements, such as heavy metals⁶⁻¹⁷. Most of them are biochemically active, are not subject to biodegradation and have the ability to accumulate intensively in such "comfortable" environment as bottom sediments^{18,19}.

The accumulation of trace elements in bottom sediments occurs along with complex physical and chemical mechanisms of absorption, which depend on the peculiarities of the composition, structure and properties of the sediment, as well as on the properties of the absorbed compounds^{20,21}. The accumulation might occur through interaction with the solid phase, following the mechanisms of ion exchange and complex formation with humic acids, adsorption by clay and other minerals, iron and manganese hydroxides, etc.^{22,23}. Therefore, the accumulation and distribution of trace elements is greatly influenced by different physical and chemical characteristics of the sediment, such as granulometric composition (particle-size distribution), particularly the content of silt (clay) fraction, the content of organic carbon, carbonates, water-soluble salts, and amorphous oxides²⁴. It is known that these components are involved in the formation of structural bonds of dispersive soils and, depending on the composition and amount, are able to weaken or strengthen these bonds, thus affecting the deformation and strength properties²⁵. These components also have a significant effect on the physical and chemical activity of the sediments. For example, elevated concentrations of organic carbon lead to a decrease in the content of inorganic carbon and hydrogen index and, as a consequence, to the change of oxidation-reduction potential, leading to the release of metals from the sediments into the aquatic environment²⁶. Due to the leaching of water-soluble compounds, the density of the texture of subsoils, their cohesive properties and permeability change. In the process of dissolution and leaching of salts, the composition of absorbed cations, which significantly affect the properties of sediments, may change²⁷.

¹University of Silesia, Faculty of Earth Sciences, Bedzinska 60, 41-200, Sosnowiec, Poland. ²Russian Academy of Sciences, Institute of Earth's Crust, Lermontova 128, 664033, Irkutsk, Russia. Correspondence and requests for materials should be addressed to M.R. (email: mariusz.rzetala@us.edu.pl)

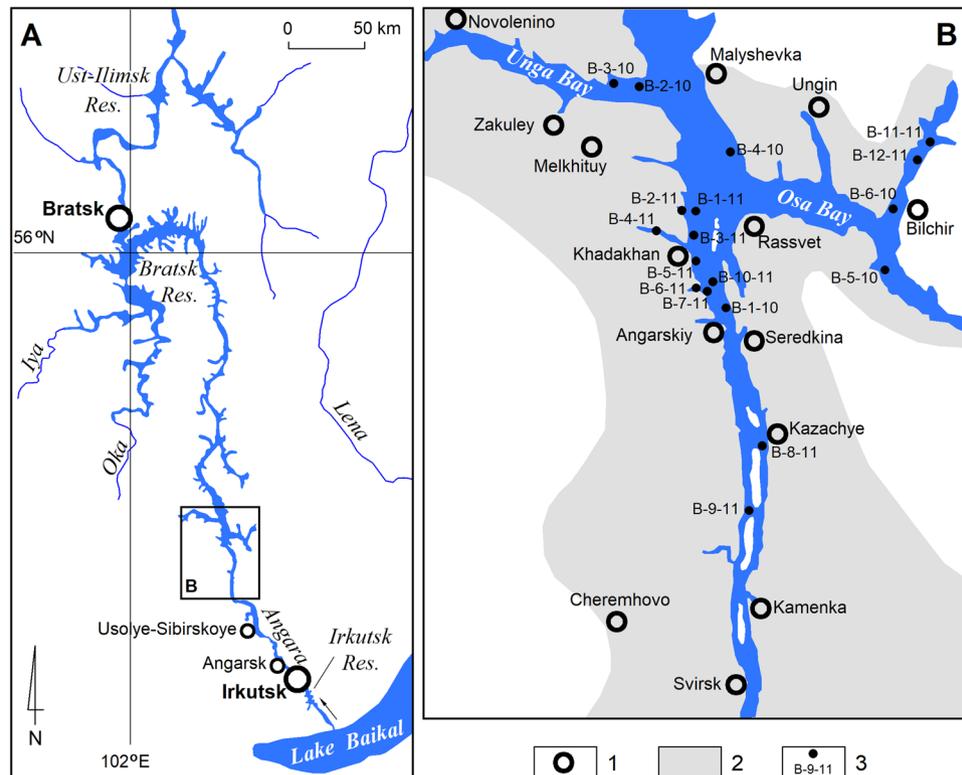


Figure 1. Layout of the study area: 1 – settlements; 2 – agricultural land: arable land, pastures, 3 – sediment sampling points with sample numbers.

The purpose of this study, based on the results of laboratory analyses of sediments taken from the south of the Bratsk Reservoir, is to identify possible existing relationship between such physical and chemical characteristics of the bottom sediments as the content of clay fraction, organic carbon, carbonates, water-soluble salts, amorphous oxides and accumulation of trace elements.

Study Area

The Bratsk Reservoir is the second in the cascade of three existing reservoirs on the Angara River and is the second largest (in terms of its volume – 170 km³) in the world. The body of water is located in the south of the Central Siberian Plateau and is elongated in meridional direction, from south to north, covering the steppe, forest-steppe and taiga landscape-climatic zones. Along with the erosion-denudation and structural-denudation relief, the presence of relic accumulative and accumulation-erosion terraces (of 10–20 m and 12–80 m heights respectively) that appeared in Quaternary, can be observed. Most accumulative river terraces have the common gently-sloping surface leveled out by denudation (some terraces were flooded after creation of the Bratsk Reservoir)²⁸. This reservoir is used mostly for energy purpose, which does not preclude its use for other purposes, such as for water supply, recreation, fisheries, water transport and timber floating. The Bratsk Reservoir has been operating for almost 50 years, since 1967²⁹.

The present exploration target is the southern part of the Bratsk Reservoir – from the transient region to the mouth of the Unginsk Creek. The width of the reservoir at the site under study varies from 1 to 7.5 km, an average of 3 km. The average depth is 9–10 m, the maximum depth is 30 m. This is the most developed part of the reservoir. There are several small towns on the shores with existing industries (Usolye-Sibirskoye – chemical industry, mechanical engineering; Svirsk – timber and woodworking industry; Cheremkhovo – coal-mining, timber and woodworking industry) and a large number of villages with well-developed agriculture³⁰ (Fig. 1). The territory belongs to the forest-steppe zone strongly affected by gully erosion³¹.

The Bratsk Reservoir is fed mainly by the Angara River flowing out of Lake Baikal. The rivers flowing into the reservoir on the site under study (the Irkut, Kitoi, Belaya, Ushakovka, Kuda, Osa) are of secondary importance here. The flowage of the Bratsk Reservoir is low, on average about 2/3 of its total volume. As a result, the speed of discharge currents in the Angara river bed is 6–10 cm/sec, and in the spreading of the stream it slows down to 2–5 cm/sec³².

The bedrock is Lower-Middle-Cambrian rock, consisting of dolomites, limestones, gypsum, anhydrite and carbonate breccias and Middle-Upper-Cambrian rock, which consist of marl, dolomite, argillites and aleuro-lite intercalations with thin gypsum lenses. The alluvial deposits are represented by sands – from fine- to medium-grained, with interbedded clay and loam, fine sandy loams, loams and gravels. The slopes and alluvium of river terraces are covered with deluvial (talus) clay loam and fine sandy loam of small thickness – 10–15 m³³.

Sampling and Analysis

Sediment samples were collected from 15 different locations of Bratsk Reservoir in 2010 and 2011 using a sediment core sampler operated from a boat. The sampler was submerged on a steel line using a hand-operated winch. In total 18 samples from a sediment layer of a thickness of about 10 cm were collected. Sampling depth varied from 2.5 m to 28.0 m.

The selected samples were dried to air-dry state *in vitro*, and then each sample was divided into 2 parts. After the homogenization process, one part was packed in a plastic bag and sent to ACTLABS (Activation Laboratories Ltd.) in Canada to be analyzed for the trace element contents. Laboratory analyses in 2010 were conducted using TD-ICP (total digestion-inductively coupled plasma) method with respect to Cu, Mo, Ni, Pb and Zn. A 0.25 g sample aliquot is digested with HClO₄-HNO₃-HCl-HF at 200 °C to fuming and is then diluted with aqua regia^{34,35}. This leach is partial for magnetite, chromite, barite and other spinels and potentially massive sulphides. The other trace element contents were determined using the INAA (instrumental neutron activation analysis) method. A 1 g aliquot is encapsulated in a polyethylene vial and irradiated with flux wires and an internal standard (1 for 11 samples) at a thermal neutron flux of $7 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. After a 7-day decay to allow Na-24 to decay the samples are counted on a high purity Ge detector with resolution of better than 1.7 keV for the 1332 keV Co-60 photopeak. Analysis results are given in ppm^{34,35}.

In 2011 analyses were conducted using the Aqua Regia – ICP/MS method. A 0.5 g sample is digested in aqua regia at 90 °C in a microprocessor controlled digestion block for 2 hours. Digested samples are diluted and analyzed by Perkin Elmer Sciex ELAN 6000, 6100 or 9000 ICP/MS^{34,35}.

Another part of each sample was analyzed in the Analytical Centre of the Institute of the Earth Crust (Irkutsk, Russia) using a special method developed for analysing clay and loessial soils²⁵. Clay and loess deposits are complex natural formations consisting of the primary particles and aggregates. The presence of aggregates affects the results of particle size (granulometric) analysis, as it reduces the content of fine particles and increases the content of coarse ones. This distorts the correct understanding of the massive material, the content of certain particles in it and its classification. The particle size analysis shows the limiting (extreme) dispersion, but in order to obtain information about the natural dispersion, it is necessary to know the number of secondary micro-aggregate particles. This method allows obtaining such information without isolating the micro-aggregate composition or performing additional micro-aggregate analysis of the soil. Namely, the granulometric analysis was made by pipette method, using 3 processes of specimen preparation³⁵: (1) aggregate process (shaking up of the specimen in water causes the destruction of coarse water-unstable aggregates); (2) the semi-disperse process (boiling of triturated specimen in presence of ammonia), and (3) disperse preparation (boiling of triturated specimen with sodium pyrophosphate leads to maximum destruction of aggregates). The semi-dispersed technique is a standard one and it is recommended for determining the particle size distribution of clay soils and for naming the sample within the framework of the classification.

By water, muriatic and alkaline extracts the components and structural bonds such as water soluble salts, carbonates, amorphous sesqui-oxides and mobile Al₂O₃ forms were determined. To a certain extent, water extract imitates the material composition of the soil solution, so it can help get an insight into the content and composition of the most mobile soil components that are more capable of migration. The principle of the water extraction method is the short-term (3 min.) interaction of a soil sample with distilled water, at the ratio 1:5. At the same time, the dissolution of readily-soluble salts occurs, while medium- and low-soluble salts are partially dissolve. Analysis of the extract begins with determining the carbonate and total alkalinity, as well as the pH of the extract, then the amount of dry residue is determined (the content of water-soluble salts is determined as the sum of anions and cations) after evaporation in a water bath. When analysing the hydrochloric acid extract, the contents of R₂O₃, SiO₂, CaO, MgO, Fe₂O₃, SO₃ as well as the loss on ignition and the value of the mineral insoluble residue are obtained. Then, using special coefficients, oxides are recalculated for the content of carbonate salts (CaCO₃, MgCO₃, FeCO₃) and their sum is determined, which characterizes the total carbonate content of the soil. Analysis of the alkaline extract allows us to determine the content of mobile Al₂O₃ forms^{25,36}.

The humus content was determined according to I.V. Tyurin's method based on the oxidation of carbon of organic matter by excess potassium bichromate. The oxidation occurs in a highly acidic medium and is accompanied by the reduction of hexavalent chromium to the trivalent. Excess bichromate in the solution after oxidation of organic matter is titrated with a solution of Mohr's salt. Based on the difference of potassium bichromate – before and after oxidation – the content of organic carbon in the soil is found³⁷.

Results and Discussion

The material composition of the bottom sediments at the site under study refers to the terrigenous genetic type. The terrigenous sediments are formed from detrital or pelitic (lutaceous) material, originating from the banks, due to various exogenous processes³⁸. As a result of mechanical differentiation under the action of waves, currents, underwater gravitational processes, etc., coarse deposits usually prevail in the area of submerged shoals: pebbles, gravel, and sand. With distance from the shoreline, they are replaced by fine sands and silts.

Granulometric analysis (particle-size distribution) of bottom sediments. The granulometric analysis of the sediments from the south of the Bratsk Reservoir has determined the predominance of fine silt and silty-clayed muds. The sediment received its name according to the particle-size distribution of the sample with semi-dispersed preparation. Figure 2 shows a batch of the ten most representative samples from the groups of finely-aleuritic (B-12-11, B-8-11, B-7-11, B-3-11, B-2-11) and aleuritic-clayed (B-11-11, B-6-11, B-5-11, B-4-11, B-5-10) silt³⁵. The particle-size distribution of each sample is presented in two versions of sample preparation: a – semi-disperse, and b – dispersed ones. The graphs demonstrate how the ratio of particle contents by fractions significantly changes towards the increased number of more micro-fine particles with maximum destruction of aggregates in the case of dispersed sample preparation.

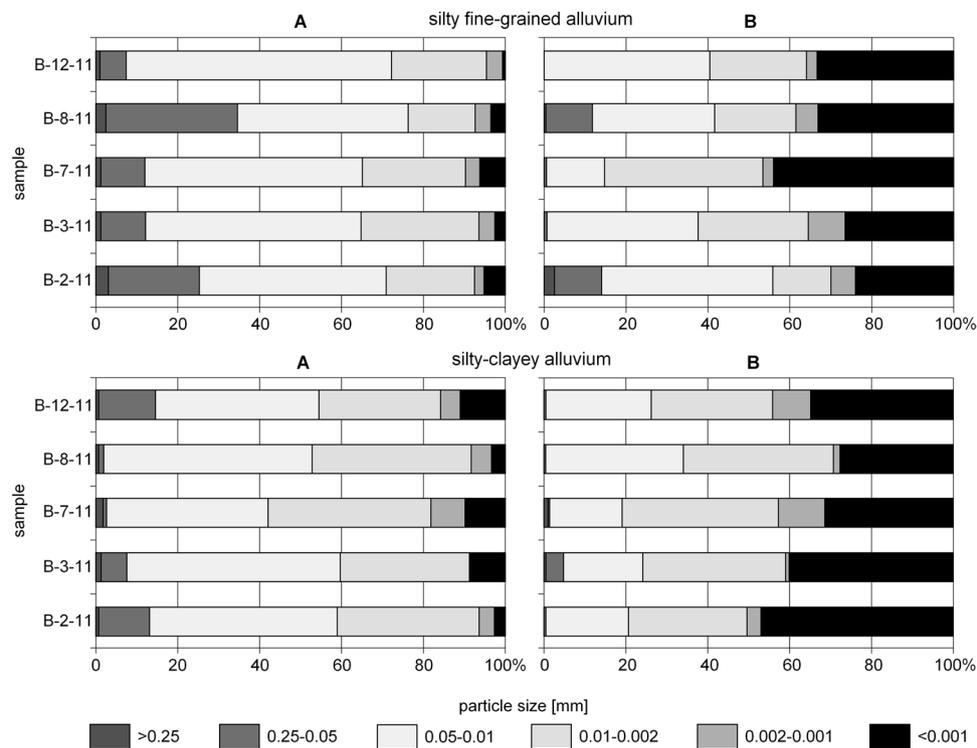


Figure 2. The particle contents in the Bratsk Reservoir sediment samples: (A) – semi-dispersed specimen preparation, (B) – dispersed specimen preparation.

In fine silt muds, the content of 0.05–0.01 mm fraction is mainly up to 50–70% (Fig. 2). The fractions of 0.25–0.05 mm and 0.010–0.002 mm have approximately the same ratio. The total content of silt with particle size of <0.01 mm does not exceed 40%. Aleuritic-clayey silts generally contain no more than 50% of 0.05–0.01 mm particle size (but when the dispersed sample preparation is used, their content decreases sharply several times in favor of fine-grained particles <0.001 mm in size), and more than 40% of clay particles <0.01 mm in size. The content of the sand fraction (>0.25 mm) in almost all samples does not exceed 1%.

Trace element composition of bottom sediments. The average, minimum and maximum trace element contents in the sediments from the south of the Bratsk Reservoir are presented in Table 1^{22,35,38–42}. As a rule, environmental assessment of the levels of content of chemical elements in the natural environments is carried out by comparing their actual concentrations versus regulatory (standardized) parameters. However, to date there are no regulatory requirements for the maximum permissible trace element concentration for the sediments in Russia. Therefore, in order to assess the quality of bottom sediments in the Bratsk Reservoir, Table 1 shows the values of percentage abundance (clarks) of trace elements in the earth's crust, according to Rudnick and Gao⁴², as well as the average trace element contents in the bedrock of the Baikal region^{22,39} and abyssal silt of Lake Baikal^{40,41} (for certain elements). The studies show that for such trace elements as Co, Cr, Cu, Mn, Ni, Pb, Th, V, Zn, the exceeding in the geochemical background of bedrock in the region is observed. It may be noted that the average trace element contents in the deep (abyssal) silt of Lake Baikal for the most part can be checked against the maximum contents in the bottom sediments of the Bratsk Reservoir or exceed them.

Thus, in order to determine the excesses of the aforementioned trace elements (Co, Cr, Cu, Mn, Ni, Pb, Th, V, Zn), anomaly ratio (AR) was used, which is calculated as the ratio of the content of a chemical element in the studied natural object to the geochemical background⁴³. So, the highest excess of the background (among the aforementioned) is recorded for Co, Ni and Zn (AR is 2.0–2.18). The average content of other elements exceeds the geochemical background less than 1.5 times.

Structure-forming components. According to the results of chemical analysis of aqueous extract, silts in the Bratsk Reservoir are characterized by varying degrees of salinity: from medium saline (Water-soluble salt contents, S_{ws} % range within 0.329–0.944%)³⁵ – to extremely highly saline (S_{ws} is up to 2.080%); the average value is 1.042% (Fig. 3). The salinity quality is predominantly of carbonate-sulfate type; it is caused by a high degree of water solubility of the chloride salts, which practically do not accumulate in the sediments.

The total content of carbonates in the sediments varies widely, from 15.08 to 31.32%³⁵, on average it is 24.36% (Fig. 4). $CaCO_3$ and $MgCO_3$ as prevail in the content of carbonate salts. According to Ryashchenko³⁸, the constant presence of $CaCO_3$ dominated carbonates is a regional feature of quaternary sediments (loessial and clayey soils) in the south of Eastern Siberia, as well as salinity, however, at a weaker level (S_{ws} varies within 0.06–0.42%)

Element	Content [ppm]			Percentage abundance in the Earth's crust ⁴² [ppm]	Average content in the natural environment of the Baikal region [ppm]		AR
	average	max	min		bedrock ^{22,39}	deep (abyssal) silt of Lake Baikal ^{40,41}	
Be	1.30	2.00	0.80	2.10	2.0	—	0.63
Co	18.10	28.00	12.20	17.30	9.0	19.00	2.01
Cr	95.30	176.00	45.10	92.00	80.0	120.00	1.19
Cs	2.70	5.00	1.11	4.90	6.2	5.00	0.44
Cu	31.30	44.00	15.70	28.00	29.0	—	1.08
La	28.30	41.90	14.30	31.00	35.2	58.00	0.80
Mn	717.60	1200.00	424.00	1000.00	685.0	945.00	1.05
Mo	0.80	2.09	0.35	1.10	8.3	1.40	0.10
Ni	68.00	97.00	45.30	47.00	32.0	84.00	2.12
Pb	13.80	19.00	8.18	17.00	11.0	19.00	1.25
Rb	42.60	100.00	16.00	84.00	42.80	80.00	1.00
Sc	10.70	20.30	4.70	14.00	11.00	13.00	0.97
Sr	140.40	250.00	45.00	320.00	210.0	320.00	0.67
Th	5.70	8.90	1.20	10.50	3.8	10.00	1.49
V	83.90	138.00	49.00	97.00	62.0	160.00	1.35
Y	18.00	29.00	11.50	21.00	22.5	—	0.8
Zn	89.50	108.00	62.80	67.00	41.0	88.00	2.18

Table 1. Trace element contents in the bottom sediments of the Bratsk Reservoir, versus their content in the natural environment of the Baikal region, as well as calculated anomaly ratio (AR). Explanation: (—) – data is not available.

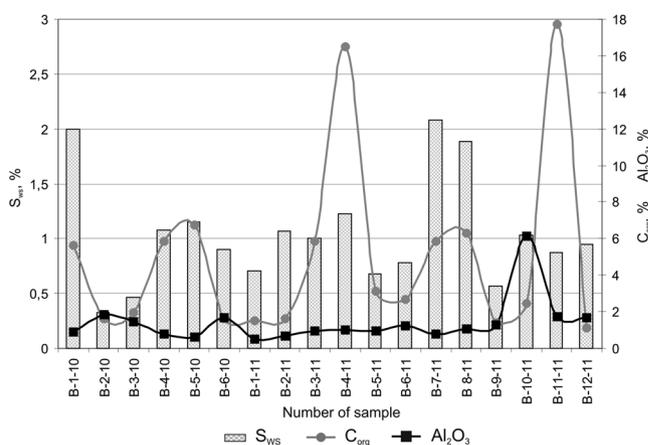


Figure 3. Total content of water-soluble salts (S_{ws}), humus (C_{org}) and mobile forms of aluminum oxide (Al_2O_3).

and predominantly of chloride-carbonate type. The so-called “saline contamination” of sediments in the Bratsk Reservoir might be technology-related and can be linked to the close proximity of industrial areas.

The content of mobile (free) forms of aluminum oxide (Al_2O_3), which plays the role of cement taking part in the formation of the sediment’s structural connections and contributing to the increased particle aggregation, is 0.48–6.13% (an average of 1.43%) (Fig. 3).

The humus content ranges within 1.14–17.70%, an average of 5.60% (Fig. 3). Based on the studies by Butakov⁴⁴, it was determined that the bulk organic carbon in the sediments of the Bratsk Reservoir accounts for humic acid. The proportion of organic carbon (C_{org}) in humic acids (both bound and free, in total) reaches 62%. This indicates a high degree of humification of the reservoir bottom sediments, which, in turn, suggests the allochthonous nature of the humic substance in the reservoir sediments.

Influence of physical and chemical characteristics of bottom sediments on the distribution of trace elements. Table 2 presents Pearson’s correlation coefficients between the contents of Co, Cr, Cu, Mn, Ni, Pb, Th, V, Zn (trace elements for which the excess of geochemical background of bedrock in the region was marked), such physical and chemical parameters as the content of pelitic (clayey) particles (<0.01 mm) in a

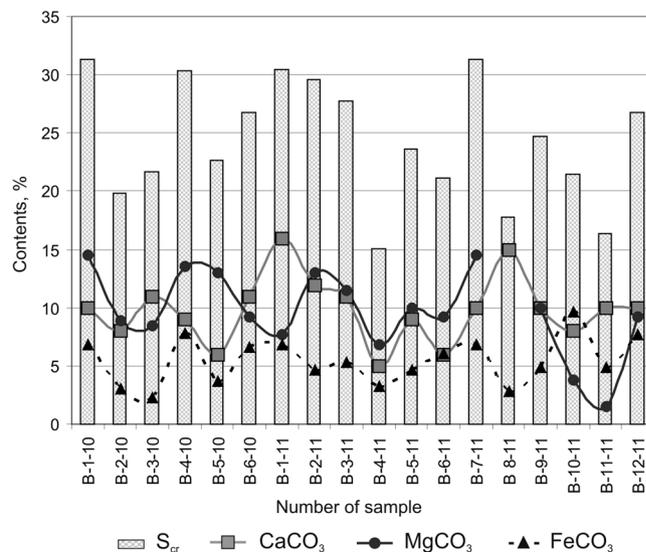


Figure 4. Composition of carbonate salts, total content of carbonates (S_{cr}).

sample with different variants of sample preparation, as well as the content of calcium and magnesium carbonates, organic carbon and water soluble salts.

Many studies have confirmed that particle-size distribution of sediments affects the transport and accumulation of high-density (heavy) metals in soils^{45,46}. Huang *et al.* have found that Cu, Ni and Mn showed a positive correlation with clay proportions because clay particles are more prone to adsorb heavy metals⁴⁷. In this study, the correlation analysis has also showed that the highest value in the accumulation of trace elements in the sediments is their dispersion, i.e., the content of particles <0.01 mm in size. Co, Cr, Cu, Ni, Pb and Zn demonstrated the most significant positive correlation in terms of the content of pelitic (clayey) particles in an aggregated state (r ranges from 0.597 (Pb) to 0.849 (Ni)). When semi-dispersed and dispersed sample preparation is used, i.e., when aggregates are destroyed, this correlation is weakened for most elements, as indicated by a decrease in the correlation coefficient. Thus, when semi-dispersed and dispersed sample preparation is used, only Co, Ni and Pb show the average degree of correlation ($0.5 < r < 0.69$) with the content of pelitic particles, while Cr, Cu and Zn show the moderate correlation ($0.3 < r < 0.49$).

The influence of organic matter on the accumulation of heavy metals in the sediments is insignificant. This is indicated by the correlation coefficients of the content of organic carbon and heavy metals in the sediments, varying from -0.313 to 0.459 (the exception is an inverse correlation of C_{org} with Th ($r = -0.686$)). The weak correlation between concentrations of heavy metals in the sediments containing organic matter in most cases suggests the secondary role of humic substance in the process of accumulation and migration of metals, and it is the evidence of predominantly terrigenous nature of the formation of trace-element composition of the bottom sediments in the Bratsk Reservoir.

The territory under study is intensively used for agricultural purposes. Farms tend to use large quantity of fertilizers (both mineral and organic ones) and pesticides to promote the acceleration of agricultural production. As numerous studies show, this practice often leads to the accumulation of trace such elements as Cr, Ni, Cu, Zn, As, Cd and Pb in soils^{45,48,49}. Soil erosion, being an important factor in the redistribution of soil in the reservoir, is probably the main mechanism by which the studied trace elements enter the bottom sediments of the reservoir⁵⁰.

The correlation analysis has showed a average negative correlation of the content of calcium carbonate $CaCO_3$ with Ni ($r = -0.524$), as well as a moderate negative correlation with such trace elements as Co, Cr, Cu, Pb and Zn. The content of magnesium carbonate $MgCO_3$ moderately positively correlates with such trace elements as Cr, Cu, Pb, V and Zn. Besides, there is a moderate negative correlation between the content of water soluble salts and S_{ws} and the content of Mn, Pb and V in the bottom sediments. Interestingly, metals are correlated with each other. A particularly strong positive correlation ($r > 0.70$) is observed between Co, Cr, Cu, Ni, Pb and Zn. Such a pronounced correlation might indicate that these trace elements have the same source of influent into the reservoir⁵¹. Mn is the least active in correlation with other trace elements (its correlation is generally very weak, $r < 0.19$). For Th and V, the correlation with other trace elements mainly varies from very low to moderate.

Thus, the correlation relations confirm the dependencies – both well-known and specific for the reservoir under study – between the analysed features of the bottom sediments. First of all, it is the relationship between particle size and the content of toxic metals, which can be attributed to the conditions of sedimentation of sediments in the reservoir. The accumulation of trace elements in finely dispersed sediments can be viewed as a manifestation of the purifying role, especially in the zone of a variable backwater of the reservoir, but also as an increasing threat of environmental pollution. Significant correlation coefficients of the content of most toxic trace elements in the samples under study suggest the complex nature of the influent of pollutants into bottom deposits.

Characteristic	Agg	SD	D	Co	Cr	Cu	Mn	Ni	Pb	Th	V	Zn	CaCO ₃	MgCO ₃	C _{org}
SD	0.850														
D	0.648	0.652													
Co	0.823	0.588	0.510												
Cr	0.598	0.420	0.417	0.828											
Cu	0.658	0.487	0.495	0.886	0.962										
Mn	0.287	0.593	0.442	0.093	0.003	-0.054									
Ni	0.849	0.561	0.567	0.956	0.873	0.887	0.071								
Pb	0.597	0.630	0.562	0.651	0.783	0.806	0.258	0.645							
Th	0.301	0.045	0.006	0.524	0.706	0.675	-0.402	0.556	0.434						
V	0.058	0.199	-0.039	0.386	0.479	0.501	0.065	0.261	0.406	0.066					
Zn	0.629	0.494	0.479	0.865	0.933	0.959	-0.001	0.855	0.776	0.505	0.608				
CaCO ₃	-0.654	-0.537	-0.400	-0.452	-0.409	-0.405	-0.021	-0.524	-0.456	-0.065	-0.156	-0.490			
MgCO ₃	-0.065	-0.067	0.046	0.282	0.442	0.414	-0.079	0.210	0.320	0.518	0.473	0.325	0.058		
C _{org}	0.194	0.288	0.459	0.033	-0.246	-0.094	0.223	-0.026	0.089	-0.686	0.022	0.058	-0.313	-0.497	
S _{ws}	-0.210	-0.396	0.178	-0.042	-0.261	-0.151	-0.334	-0.110	-0.304	-0.022	-0.334	-0.202	0.163	0.203	0.217

Table 2. Correlation matrix of the content of heavy metals in bottom sediments of the Bratsk Reservoir. Explanations: Agg – the content of pelitic particles (<0.01 mm) in samples with aggregate preparation; SD – the same, with semi-dispersed preparation; D – the same, with dispersed preparation.

Conclusions

1. Based on the results of the granulometric analysis, the sediments in the south of the Bratsk Reservoir are mainly represented by fine silt and silty-clayed muds with a high degree of fine particles aggregation.
2. The trace element composition of the bottom sediments includes a number of elements, the content of which exceeds the values of the geochemical background of the bedrock in the region: Co, Cr, Cu, Mn, Ni, Pb, Th, V, and Zn. Among these, the highest excess of the background is recorded for Co, Ni and Zn (AR 2.0–2.18), the average contents of other elements exceed the geochemical background less than 1.5 times.
3. According to the results of chemical analysis of extracts, the muds (silts) are characterized by various degrees of “saline contamination”, high concentration of carbonates, and the presence of mobile (free) forms of aluminum oxide. The wide ranges of variation of these indicators suggest technogenic pollution of certain water lots in the reservoir area.
4. The content of organic carbon in the samples also varies widely, and in some cases it reaches high values (up to 17.70%). The high degree of humification of the bottom sediments might indicate an external source of organic matter entering the reservoir. As shown by the correlation analysis, humic substance has the secondary role in the process of accumulation and migration of metals, and it is the evidence of predominantly terrigenous nature of the formation of trace-element composition of the bottom sediments in the Bratsk Reservoir.
5. The content of heavy metals in the reservoir sediments is controlled mainly through the dispersion of bottom deposits – the content of pelitic (lutaceous) particles (<0.01 mm) in the aggregated state. No significant correlation between the content of carbonates and water-soluble salts and the accumulation of trace elements under consideration has been identified. There is a strong direct relationship between many heavy metals, which indicates the same source of their influent into the reservoir.

References

1. Karadede, H. & Ünlü, E. Concentrations of some heavy metals in water, sediment and fish species from the Atatürk Dam Lake (Euphrates), Turkey. *Chemosphere* **41**, 1371–1376, [https://doi.org/10.1016/S0045-6535\(99\)00563-9](https://doi.org/10.1016/S0045-6535(99)00563-9) (2000).
2. Karadede-Akin, H. & Ünlü, E. Heavy metal concentrations in water, sediment, fish and some benthic organisms from Tigris River, Turkey. *Environmental Monitoring and Assessment* **131**(1–3), 323–337, <https://doi.org/10.1007/s10661-006-9478-0> (2007).
3. Trounova, V. A. & Sokolovskaya, I. P. Microelement content of the Novosibirsk reservoir bottom sediments as the reflection of its ecological state. *Nuclear Instruments and Methods in Physics Research A* **448**, 446–448, [https://doi.org/10.1016/S0168-9002\(00\)00234-5](https://doi.org/10.1016/S0168-9002(00)00234-5) (2000).
4. Rzetala, M. *et al.* Variations in the chemical composition of bottom deposits in anthropogenic lakes. *Polish Journal of Environmental Studies* **22**(6), 1799–1805 (2013).
5. Juracek, K. E. & Mau, D. P. Metals, trace elements, and organochlorine compounds in bottom sediment of Tuttle Creek Lake, Kansas, USA. *Hydrobiologia* **494**, 277–282, <https://doi.org/10.1023/A:1025447223154> (2003).
6. Diagonanolin, V., Farhang, M., Ghazi-Khansari, M. & Jafarzadeh, N. Heavy metals (Ni, Cr, Cu) in the Karoon waterway river, Iran. *Toxicology Letters* **151**, 63–68, <https://doi.org/10.1016/j.toxlet.2004.02.018> (2004).
7. Wang, H., Wang, C. X., Wang, Z. J. & Cao, Z. H. Fractionation of heavy metals in surface sediments of Taihu Lake, East China. *Environmental Geochemistry and Health* **26**(2), 303–309, <https://doi.org/10.1023/B:EGAH.0000039594.19432.80> (2004).
8. Carman, C. M., Li, X. D., Zhang, G., Wai, O. W. H. & Li, Y. S. Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China. *Environmental Pollution* **147**, 311–323, <https://doi.org/10.1016/j.envpol.2006.06.028> (2007).

9. Ochieng, E. Z., Lalah, J. O. & Wandiga, S. O. Analysis of Heavy Metals in Water and Surface Sediment in Five Rift Valley Lakes in Kenya for Assessment of Recent Increase in Anthropogenic Activities. *Bulletin of Environmental Contamination and Toxicology* **79**(5), 570–576, <https://doi.org/10.1007/s00128-007-9286-4> (2007).
10. Abraham, G. & Parker, R. Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environmental Monitoring and Assessment* **136**, 227–238, <https://doi.org/10.1007/s10661-007-9678-2> (2008).
11. Christophoridis, C., Dedepsidis, D. & Fytianos, K. Occurrence and distribution of selected heavy metals in the surface sediments of Thermaikos Gulf, N. Greece. Assessment using pollution indicators. *Journal of Hazardous Materials* **168**, 1082–1091, <https://doi.org/10.1016/j.jhazmat.2009.02.154> (2009).
12. Ongeri, D. M. K., Lalah, J. O., Wandiga, S. O., Schramm, K. W. & Michalke, B. Levels of Toxic Metals in Multisectoral Samples from Winam Gulf of Lake Victoria. *Bulletin of Environmental Contamination and Toxicology* **82**(1), 64–69, <https://doi.org/10.1007/s00128-008-9530-6> (2009).
13. Trujillo-Cardenas, J. L. *et al.* Speciation and Sources of Toxic Metals in Sediments of Lake Chapala, Mexico. *Journal of the Mexican Chemical Society* **54**(2), 79–87 (2010).
14. Baek, Y. W. & An, Y. J. Assessment of toxic heavy metals in urban lake sediments as related to urban stressor and bioavailability. *Environmental Monitoring and Assessment* **171**(1–4), 529–537, <https://doi.org/10.1007/s10661-009-1297-7> (2010).
15. Schenone, N. F., Avigliano, E., Goessler, W. & Cirelli, A. F. Toxic metals, trace and major elements determined by ICPMS in tissues of *Parapimelodus valenciennis* and *Prochilodus lineatus* from Chascomus Lake, Argentina. *Microchemical Journal* **112**, 127–131, <https://doi.org/10.1016/j.microc.2013.09.025> (2014).
16. Deng, L. *et al.* Variation and Accumulation of Sediments and Associated Heavy Metals Along Cascade Dams in the Mekong River, China. *Environmental Engineering and Management Journal* **16**(9), 2075–2087 (2017).
17. Han, L. F. *et al.* The spatial distribution, accumulation and potential source of seldom monitored trace elements in sediments of Three Gorges Reservoir, China. *Scientific Reports* **5**, Art. Number 16170, <https://doi.org/10.1038/srep16170> (2015).
18. Yousef, Y. A., Baker, D. M. & Hvitved-Jacobsen, T. Modeling and impact of metal accumulation in bottom sediments of wet ponds. *The Science of the Total Environment* **189**, 349–354, [https://doi.org/10.1016/0048-9697\(96\)05230-8](https://doi.org/10.1016/0048-9697(96)05230-8) (1996).
19. Romanov, A. S., Orekhova, N. A., Ignatyeva, O. G., Kononov, S. K. & Ovsyany, E. I. Influence of physico-chemical characteristics of the bottom sediments on the trace elements distribution by the example of Sevastopol bays (Black Sea). *Ekologiya Morya* **73**, 85–90 (2007).
20. Ghrefat, H. & Yusuf, N. Assessing Mn, Fe, Cu, Zn, and Cd pollution in bottom sediments of Wadi Al-Arab Dam, Jordan. *Chemosphere* **65**, 2114–2121, <https://doi.org/10.1016/j.chemosphere.2006.06.043> (2006).
21. Avila-Pérez, P., Balcázar, M., Zarazúa-Ortega, G., Barceló-Quintal, I. & Díaz-Delgado, C. Heavy metal concentrations in water and bottom sediments of a Mexican reservoir. *Science of the Total Environment* **234**, 185–196, [https://doi.org/10.1016/S0048-9697\(99\)00258-2](https://doi.org/10.1016/S0048-9697(99)00258-2) (1999).
22. Grebenshchikova, V. I., Lustenberg, E. Y., Kitayev, N. A. & Lomonosov, I. S. Geochemistry of the Baikal region environment (Baikal geoenvironmental test site) [in Russian]. (Geo, Novosibirsk, 2008).
23. Varshal, G. M., Velyukhanova, T. K. & Koshcheyeva, I. Y. Geochemical role of Humic acids in the migration of elements. In: *Humic Substances in the Biosphere* [in Russian]. (Nauka, Moscow, 1993).
24. Karnaukhova, G. A. Cyclicity of sedimentation and physical properties of the bottom sediments in artificial reservoirs. *Doklady Earth Science* **471**(2), 1230–1233, <https://doi.org/10.1134/S1028334X16120102> (2016).
25. Ryashchenko, T. G. Regional soil science (Eastern Siberia) [in Russian]. (IEC SB RAS, Irkutsk, 2010).
26. Mitropolsky, A. Y., Bezborodov, A. A. & Ovsyany, Y. I. Geochemistry of the Black Sea [in Russian]. (Naukova dumka, Kiev, 1982).
27. Lomtadze, V. D. Engineering Geology. Engineering Petrology [in Russian]. (Nedra, Leningrad, 1984).
28. Bratsk Reservoir. Engineering Geology of the territory [in Russian]. Odintsov M. M. (Eds). (Publishing House of the Academy of Sciences, Moscow, 1963).
29. Jagus, A., Rzetala, M. A. & Rzetala, M. Water storage possibilities in Lake Baikal and in reservoirs impounded by the dams of the Angara River cascade. *Environmental Earth Sciences* **72**(2) SI, 621–628, <https://doi.org/10.1007/s12665-014-3166-0> (2015).
30. Khak, V. A. & Kozyreva, E. A. Changes of geological environment due to the anthropogenic impacts: a case study of south of East Siberia, Russia. *Zeitschrift für Geomorphologie* **56**(2), 183–199, <https://doi.org/10.1127/0372-8854/2011/0064> (2012).
31. Mazaeva, O., Babicheva, V. & Kozyreva, E. Geomorphological process development under the impact of man-made reservoir operation, a case study: Bratsk reservoir, Baikal-Angara hydroengineering system, Russia. *Bulletin of Engineering Geology and the Environment*, <https://doi.org/10.1007/s10064-018-1428-x> (2018).
32. Ovchinnikov, G. I., Pavlov, S. C. & Trzhtsinsky, U. B. Change of geological environment in the zones of influence of the Angara-Yenisei reservoirs [in Russian]. (Nauka, Novosibirsk, 1999).
33. Logachev, N. A., Lomonosova, T. K. & Klimanova, V. M. Cenozoic Deposits of the Irkutsk Amphitheater [in Russian]. (Nauka, Moscow, 1964).
34. ActLabs. Available online, <http://www.actlabs.com>. (Accessed on 14 June 2016).
35. Babicheva, V. & Rzetala, M. A. Results of preliminary phase of study of bottom sediments composition in southern part of Bratsk reservoir: some physical and chemical characteristics. 15th International Multidisciplinary Scientific Geoconferences SGEM 2015. Science and Technologies in Geology, Exploration and Mining. Conference Proceedings, vol. I. Geology, Mineral Processing, Oil & Gas Exploration, pp 443–450 (2015).
36. Ryashchenko, T. G., Akulova, V. V. & Erbaeva, M. A. Loessial soils of Priangaria, Transbaikalie, Mongolia and northwestern China. *Quaternary International* **179**, 90–95, <https://doi.org/10.1016/j.quaint.2007.06.035> (2008).
37. Arinushkina, Y. V. Manual on chemical analysis of soil [in Russian]. (Moscow University Press, Moscow, 1979).
38. Ryashchenko, T. G. Lithogenesis and Engineering-Geological Evaluation of Quaternary Deposits (Eastern Siberia) [in Russian]. (Nauka, Novosibirsk, 1984).
39. Kitayev, N. A. & Grebenshchikova, V. I. Ore and rare chemical elements in the environment of the Baikal region (bed-rock, soil, bottom sediment) [in Russian]. Herald of ISTU, No. 8 (55), 40–46 (2011).
40. Vetrov, V. A. & Kuznetsova, A. I. Trace elements in the natural environment of Lake Baikal region [in Russian]. (Publishing House of the SB RAS, SPC of JIGGM, Novosibirsk, 1997).
41. Kuznetsova, N. A., Grosheva, Y. I. & Klimashevskaya, Z. A. Trace Elements in the sediments of Lake Baikal, In: *Monitoring status of Lake Baikal* [in Russian]. (Gidrometeoizdat, Leningrad, 1991).
42. Rudnick, R. L. & Gao, S. Composition of the Continental Crust. *Treatise on Geochemistry* **3**, 1–64, <https://doi.org/10.1016/B0-08-043751-6/03016-4> (2003).
43. Environmental Geochemistry [in Russian]. YU, Y., Sayet, B. A., Revich, Y. & Yanin, P. *et al.* (Eds). (Nedra, Moscow, 1990).
44. Butakov, Y. V. Metals in Humic Substances from the Bratsk Reservoir Bottom Sediments [in Russian]. Current Problems of Geochemistry – Proceedings of the Conference of Young Scientists (12–17 September 2011), Irkutsk. (Publishing House of V.B. Sochava, Institute of Geography SB RAS, Russia, 2011).
45. Duka, I., Shallari, S., Maçi, A. & Shehu, J. Heavy metal concentration and physico-chemical parameters in Koder Kamza soils. *Albanian J. Agric. Sci.* **14**(2), 157–161 (2015).
46. Song, J. Y. *et al.* The accumulation and redistribution of heavy metals in the water-level fluctuation zone of the Nuozhadu Reservoir, Upper Mekong. *Catena* **172**, 335–344, <https://doi.org/10.1016/j.catena.2018.08.027> (2019).

47. Huang, B. *et al.* Adsorption characteristics of Cu and Zn onto various size fractions of aggregates from red paddy soil. *J. Hazard Mater.* **264**, 176–183, <https://doi.org/10.1016/j.jhazmat.2013.10.074> (2014).
48. Alves, L. R., dos Reis, A. R. & Gratao, P. L. Heavy metals in agricultural soils: From plants to our daily life. *Cientifica* **44**(3), 346–361, <https://doi.org/10.15361/1984-5529.2016v44n3p346-361> (2016).
49. Wang, X. *et al.* Effects of Long-Term Fertilizer Applications on Peanut Yield and Quality and on Plant and Soil Heavy Metal Accumulation. *Pedosphere*, [https://doi.org/10.1016/S1002-0160\(17\)60457-0](https://doi.org/10.1016/S1002-0160(17)60457-0), in press (2017).
50. Ye, C., Li, S. Y., Zhang, Y. L. & Zhang, Q. F. Assessing soil heavy metal pollution in the water-level-fluctuation zone of the Three Gorges Reservoir, China. *J. Hazard. Mater.* **191**(1–3), 366–372, <https://doi.org/10.1016/j.jhazmat.2011.04.090> (2011).
51. Cheng, H., Liang, A. & Zhi, Z. Heavy metals sedimentation risk assessment and sources analysis accompanied by typical rural water level fluctuating zone in the Three Gorges Reservoir Area. *Environmental Earth Sciences* **76**(12), Article Number: 418, <https://doi.org/10.1007/s12665-017-6732-4> (2017).

Acknowledgements

We would like to thank the Editors and Referees for their kind comments and constructive criticism of our article. We would also like to thank the linguistic team for the linguistic corrections of the manuscript. The study was funded by a grant from the Polish National Science Centre.

Author Contributions

M.R., V.A.B. and M.A.R. conceived and planned the study. V.A.B. and M.R. conducted field work, provided samples. M.R., V.A.B. and M.A.R. analyzed the results and wrote the paper. All authors collaborated on manuscript editing at all stages.

Additional Information

Competing Interests: The authors declare no competing interests.

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2019