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Distribution of Metals in Bottom Deposits in the Branches of Selenga River Delta

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Abstract—The paper reports newly obtained data on the granulometric and mineralogical composition of bottom deposits in branches in the Selenga River delta and on the distribution of metals in various granulometric fractions and along the length of an branch of the river in the delta. It was determined that carbonates precipitate as a solid phases in the Kharauz branch, the most copious stream in the delta, and the metals are concentrated in the sand fraction. The bottom deposits of the minor Kolpinnaya branch are characterized by the accumulation of Mn oxides of variable composition, a mixture of colloidal or poorly crystalline minerals (most commonly, pyrolusite). Most of the metals are concentrated in the pelite fraction.

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INTRODUCTION

Bottom deposits are important components of aquatic systems that largely control their states. Having a significant sorption capacity, bottom deposits (BD) can accumulate pollutants. Important characteristics of BD are their granulometric and mineral composition. Because of this, it is important to study natural and anthropogenic factors controlling the distribution of chemical elements, their accessibility to plants, and the ability of elements to pass into natural waters. The major- and trace-element composition of bottom deposits is largely controlled by the lithology and lithochemistry of the sediments and by their transformations by modern supergene processes and is a result of complicated sedimentation processes.

The delta of the Selenga River (Fig. 1) occupies much of the Ust'-Selenga depression southeast of Lake Baikal and is situated in its central, seismically most active and rapidly subsiding part [1, 2]. Its formation was controlled by the tectonic subsidence of the central part of the Baikal Basin and the compensating accumulation of terrigenous and organic material. The leading role in the origin and shaping of the Selenga River delta is played by tectonic activity, rising and lowering of the water level in Lake Baikal, the compaction of the grounds, the water mass of the river, its solid runoff, and the wind regime. The Selenga River, the major feeding stream of Lake Baikal, builds up its advancing delta with numerous river branches, lakes, islands, and a shore bar.

In its delta, the river separates into two major arms (Fig. 1), which remain communicating via minor branches over some distance downstream, with water flowing from the right-hand (northern) to the left-hand (southern) branch. The Galutai, Srednyaya, and Kolpinnaya minor branches part to the left from the right-hand branch, and two more branches, Severnaya and Srednii Peremoi, part from it 5–6 km farther downstream. One of the main branches of this group, Lobanovskaya, develops along the right-hand margin of the delta. Now much of the riverine runoff (50–55% in summer and up to 90% in winter) through the delta is still restricted to the left-hand margin of the Kharauz branch and to the Levoberezhnaya and Galutai branches. The most copious stream in the right-hand part of the delta is the Lobanovskaya branch, which carries up to 30% of the runoff in summer and approximately 10% in winter. The minor branches in the central part (Kolpinnaya and Srednyaya) account for about 3% of the total riverine runoff. These branches are usually frozen to the bottom from midwinter to spring, and the runoff through them practically stops [3, 4].

MATERIALS AND METHODS

We studied bottom sediments from the mouths of some branches of the Selenga River in its delta (control points Levoberezhnaya, Shamanka, Kharauz, Galutai, Srednyaya, Kolpinnaya, Severnaya, and Lobanovskaya) and their upper reaches, where they enter the delta (control points Murzino and Kabansk) (Fig. 1). The observation sites were classed into a left-hand riverside (Levoberezhnaya, Shamanka, Kharauz, and Galutai) of southwest direction, central part (Srednyaya, Kolpinnaya, and Severnaya) of western direction, and right-hand riverside (Lobanovskaya) of northeastern direction.

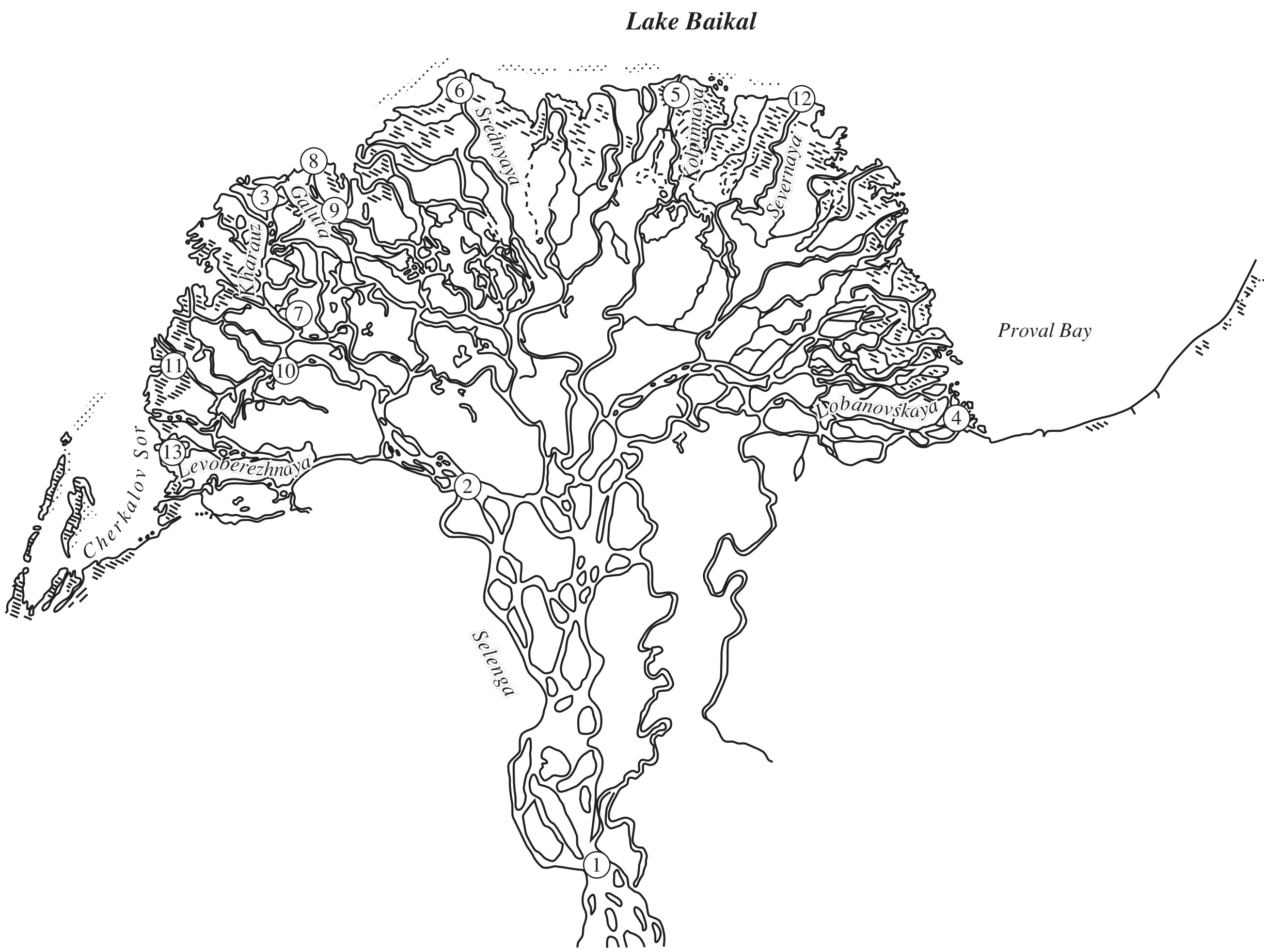

Fig. 1. Schematic map of the Selenga delta. (1) Selenga–Kabansk; (2) Selenga–Murino; (3) Kharauz branch, mouth; (4) Lobanovskaya branch, mouth; (5) Kolpinnaya branch, mouth; (6) Srednyaya branch, mouth; (7) Lake Zavernyaikha; (8) Galuta branch, mouth; (9) Galuta branch; (10) Selenga–Semenovskii Island; (11) Shamanka branch, mouth; (12) Severnaya branch, mouth; (13) Levoberezhnaya branch, mouth.

The experimental data were obtained by the authors mostly during joint fieldwork with researchers from the Institute of Limnology, Siberian Division, Russian Academy of Sciences. In 2001–2005, 278 BD samples (approximately 1.5 kg each) were collected at the Selenga delta. The samples were dried in air at temperatures of 22–25°C. For X-ray diffraction analyses, samples were pulverized in a mortar with a rubber pestle. The samples for granulometric analysis were screened into three fractions: (1) 0.25–0.1 mm, (2) 0.1–0.01 mm, and (3) <0.01 mm.

The mineralogical analysis of BD from the Selenga delta was carried out in compliance with conventional procedure [5, 6]. We analyzed the sand–siltstone fraction (0.25–0.01 mm), as having the most representative sets of terrigenous minerals, and the fine silt fraction (<0.01 mm), to identify the major clay and other fine-grained minerals. The sand–silt fractions of sediments were examined by the immersion method with the ultimate separation in heavy liquids (with a density of 2.9 g/cm^3) into a light and heavy subfractions, and the fine pelitic fractions were examined by physicochemical techniques (X-ray diffractions, thermal, and chemical analysis).

X-ray diffraction analysis was carried out on an Advance (Brucker) diffractometer with Cu–Kα. The concentrations of Fe, Mn, Pb, Cu, Zn, Cr, Cd, Co, Ni, Ca, and Mg were determined by atomic absorption spectrometry with flame atomization on a SOLAAR spectrophotometer. For flame atomization, we used an acetylene–air mixture. The precision of the method (evaluated by ten measurements of a standard with known metal concentrations) was 5–15% for various metals. The accuracy of the reported concentrations of elements (deduced from ten replicate measurements of a standard sample) was 2–3%. The Si concentrations were determined by the colorimetric method accurate to 2–3%. The concentrations of elements are reported for anhydrous BD masses.

GRANULOMETRIC COMPOSITION OF BOTTOM DEPOSITS

The delta BD were analyzed in compliance with the systematics for the deposits of water basins [7]. The deposits are dominated by three major granulometric fractions: sandy—more than 70% of the fraction 1.0–0.1 mm; silty—fraction 0.1–0.01 mm no more than 50–70%, fraction <0.01 mm 30–50%; and pelitic—fraction 0.1–0.01 mm 30–50%, fraction <0.001 mm 50–70%.

The granulometric composition of BD from the Selenga delta retain features of alluvial genesis. The granulometric distribution of the delta BD shows a general tendency toward a decrease in the grain size of the sediments down the branches. Seasonal variations in the granulometric composition of BD in the mouths of the branches are different.

In the period of winter mean water at the delta entrance, when the water velocity and discharge are at a minimum, the deposited particles belong predominantly to the sand–silt fraction. This is most clearly pronounced in the annual granulometric distribution of the BD material near the villages of Murzino and Kabansk (Fig. 2). At these sites, the transporting ability of the stream gradually diminishes, and this results in the intense deposition of coarse particles, which are dominated by the products of riverbed erosion and rewashing. At the exits from the branch mouths in the delta, the particles belong mostly to the silt and pelite fractions (Fig. 3). The periphery of the delta is characterized by a low relief. The branching of the river course results in a decrease in the transporting ability of the stream and weakening of riverbed processes. The accumulation activity of the branches, in which sand alluvium is deposited, also weakens. In the polygenetic BD sediment, sands become better sorted and finer grained.

During spring floods, the massive inflow of water erosion products and the high turbidity of the water leads to a drastic increase in the percentage of coarse-grained fraction. In summertime, which is characterized by the active aquatic vegetation, the sediments contain roughly equal amounts of sand, silt, and pelite fractions (Figs. 2, 3). This seems to be explained by the fact that the period of the intensified biological production of reed and other hydrophyte plants is characterized by the deposition of the bulk of the particulate matter, which is dominated by coarse-grained sand fractions. The predominance of fine-grained material in the BD at the exit from the branches in the central part of

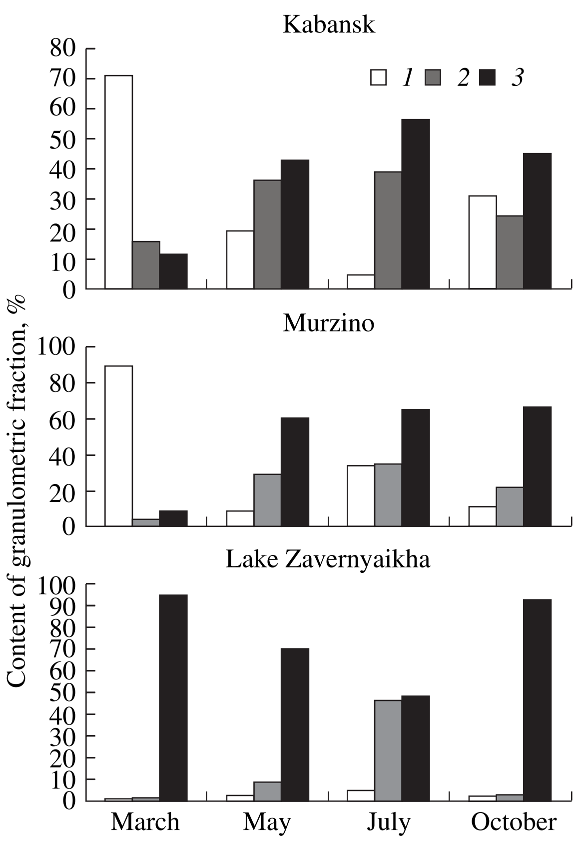

Fig. 2. Granulometric composition of bottom deposits at the Kabansk and Murzino villages and in Lake Zavernyaikha. Granulometric fractions: (*1*) 0.25–0.1 mm; (*2*) 0.1–0.01 mm; (*3*) <0.01 mm.

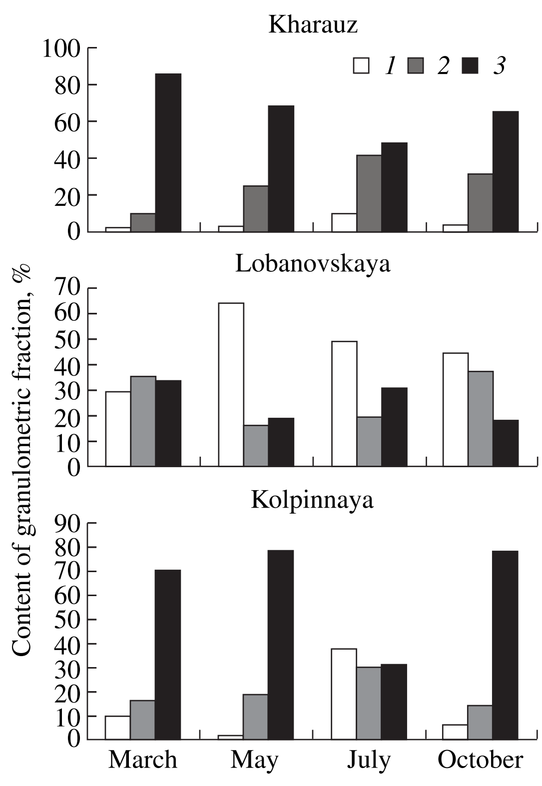

Fig. 3. Granulometric composition of bottom deposits of the Kharauz, Kolpinnaya, and Lobanovskaya branches. Granulometric fractions: (*1*) 0.25–0.1 mm; (*2*) 0.1–0.01 mm; (*3*) <0.01 mm.

the delta (Kolpinnaya, Srednyaya, and Severnaya) and its left-bank part (Kharauz, Galutai, and Levoberezhnaya) is related, first, to the transportation of silt–pelitic fraction for longer distances and, second, to the higher mobility of these fractions upon stirring. In the course of weathering, they behave according to the following scheme: transition to a mobile state—migration—secondary deposition. In sluggishly flowing watercourses in the central part and in Lake Zavernyaikha, the BD are dominated by silt–pelite fractions during all phases of the river regime (Figs. 2, 3).

The BD of the Lobanovskaya branch is dominated by sand fractions, regardless of the hydrological phase (Fig. 3). This can be explained by the effect of winds. The northeasterly wind (so-called Barguzin) in the Lobanovskaya branch induces (with an 18% repetitiveness probability) water inflow from Proval Bay. The backwater flow results in a decrease in the flow velocity in the branches and the intense deposition of the suspended material. The repetitiveness of the northwesterly winds is more than three times higher than that of the northeasterly winds, and this results in the intense deposition of the solid runoff within Proval Bay and in delta growth in the Lobanovskaya branch mouth.

MINERAL COMPOSITION OF THE BOTTOM DEPOSITS

The mineral composition of the bottom deposits depends on their granulometric composition, and this is confirmed by the results of our observations. An increase in the grain size of the BD of the sand fraction is coupled with an increase in the contents of minerals resistant to mechanical wearing and destruction. Most of these minerals have high densities. These are tourmaline, kyanite, sillimanite, amphiboles, and quartz. Correspondingly, the contents of such minerals as zircon, epidote, and feldspars decrease. The BD are virtually devoid of ore minerals, such as magnetite, ilmenite, pyrite, and marcasite. In analyzing the mineral composition of the BD, we distinguished the mouths of branches: Kharauz is the major watercourse; Lobanovskaya is the second largest stream; and Kolpinnaya is a minor stream.

The mineral composition of the BD indicates that the quartz contents of these deposits progressively increase from the upper reaches (Murzino and Kabansk) to their mouths. The amounts of plagioclase, amphiboles, pyroxenes, chromite, and garnets simultaneously decrease.

It is worth noting certain features of the X-ray diffraction patterns of the pelitic fraction from the Kharauz and Kolpinnaya BD (Figs. 4a, 4b). The X-ray diffraction patterns of these deposits show characteristic lines of rock-forming quartz, feldspars, and other minerals and lines of weathering products, such as illite, chlorite, and authigenic iron hydroxides. The X-ray diffraction pattern of the Kharauz BD (Fig. 4a) displays reflections of carbonates (at 3.03, 2.88, 2.128, and 1.873 Å), and the thermograms exhibit endo- and exothermal effects between 600 and 800°C, as is typical of calcite. The reflections at 4.16–4.37 Å in the pelite fractions of the BD are caused by iron hydroxides. In contrast to them, the X-ray diffraction pattern of BD from the Kolpinnaya branch (Fig. 4b) shows a relatively strong reflection corresponding to a spacing of 2.45 Å. This reflection is typical of quartz and of lepidocrocite γ-FeO[OH] and Mn oxides of the psilomelane group. The latter is a group of water-bearing Mn oxides of variable composition, a mixture of colloidal and poorly crystalline minerals, predominantly pyrolusite. After annealing at 500°C, the intensity of this reflection significantly decreases.

The BD from the mouth of the Kharauz branch, through which the bulk of the Selenga River runoff passes, is characterized by the formation of calcite owing to the mixing of the waters of the Selenga River and Lake Baikal and a shift of the carbonate equilibrium. The activation of water exchange leads to the saturation of the water relative to Ca carbonate. The shift in the carbonate equilibrium in response to a change in the physicochemical conditions brings about $CaCO_3$ precipitation in the form of a solid phase.

Thus, X-ray diffraction data indicate that active water exchange during the mixing of riverine and lacustrine waters leads to the accumulation of Ca carbonate in the BD (for example, in the mouth of the Kharauz branch), and more sluggish water exchange in minor branches (such as the mouth of the Kolpinnaya branch) is favorable for the accumulation of Mn and Fe hydroxides.

The pelite fraction from the mouth of the Lobanovskaya branch contains hornblende grains, which cause a characteristic reflection at 2.71 Å, but this reflection is absent from the diffraction patterns of the same fraction from the mouths of the Kharauz and Kolpinnaya branches.

DISTRIBUTION OF PRINCIPAL CHEMICAL COMPONENTS IN BOTTOM DEPOSITS

According to the distribution of elements in the granulometric spectrum of the BD of the Selenga delta, the elements can be classified into five groups. The first group comprises Si and Al, which are equally distributed through all fractions (Fig. 5), although their concentrations vary from site to site. As was mentioned above, the Si concentration increases from the upper reaches to mouths of the delta branches. This element is concentrated in the sand fraction because of the predominance of quartz. Its content in the pelite fraction is no lower (and sometimes even higher) due to the predominance of clay minerals. Because of this, Si is distributed practically evenly through all granulometric fractions of the delta sediments.

The second group comprises Ca and Mg. Their concentrations decrease with increasing particles sizes at

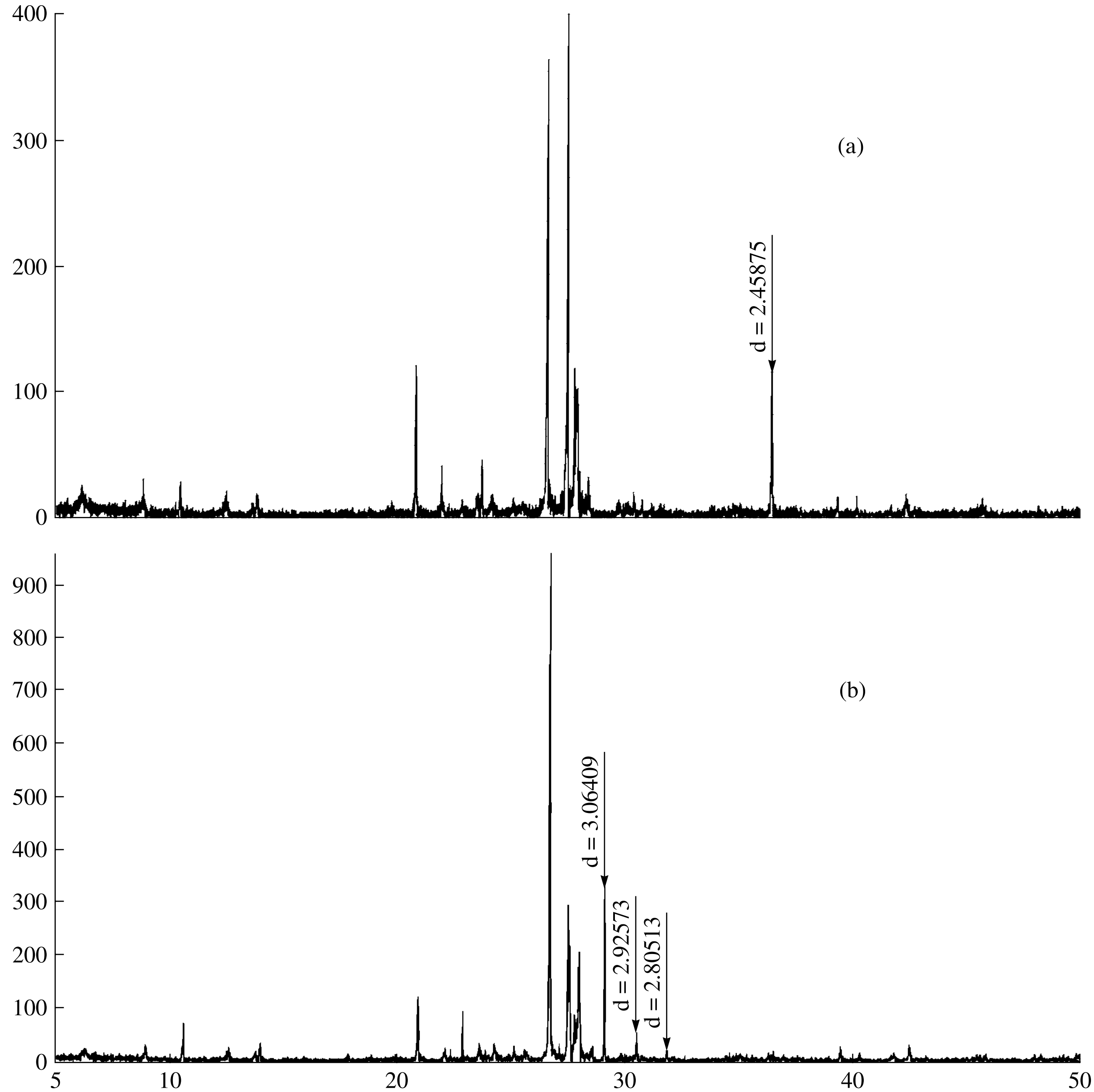

Fig. 4. X-ray powder diffraction patterns of the pelitic fraction of BD from (a) the Kolpinnaya and (b) Kharauz branches.

the entrance and outer margin of the delta (Fig. 5). The Ca concentrations of clay minerals (kaolinite, illite, and chlorite) are low. The CaO distribution is controlled by the presence of carbonate shells and their fragments, which are more abundant in the silt and pelite fractions.

The third group consists of basic elements carrying Fe and Mn. The fourth group includes Pb, Zn, and Cu, whose behavior is strongly dependent on the distribution of the third-group elements. Finally, the fifth group comprises Ni, Co, Cr, and Cd, which are contained predominantly in the fine fraction.

It is interesting to consider the behavior of the elements of the third, fourth, and fifth groups in the BD of the branches. Iron is accumulated in the sand fraction of the Kharauz branch, in the silt fraction of minor watercourses in the central part of the delta, and in the pelite fraction of the Lobanovskaya branch and in the upper reaches of the branches (Murzino and Kabansk). The Fe concentration usually systematically increases with decreasing grain size of the sediments. The Mn concentration shows a not so strong correlation with the granulometric composition of the BD, although the general tendency toward an increase in its content in finer sediments is quite obvious, except in the Kharauz branch. The BD in the Kharauz mouth contain Mn concentrated in the sand fraction, whereas the BD of all other exam-

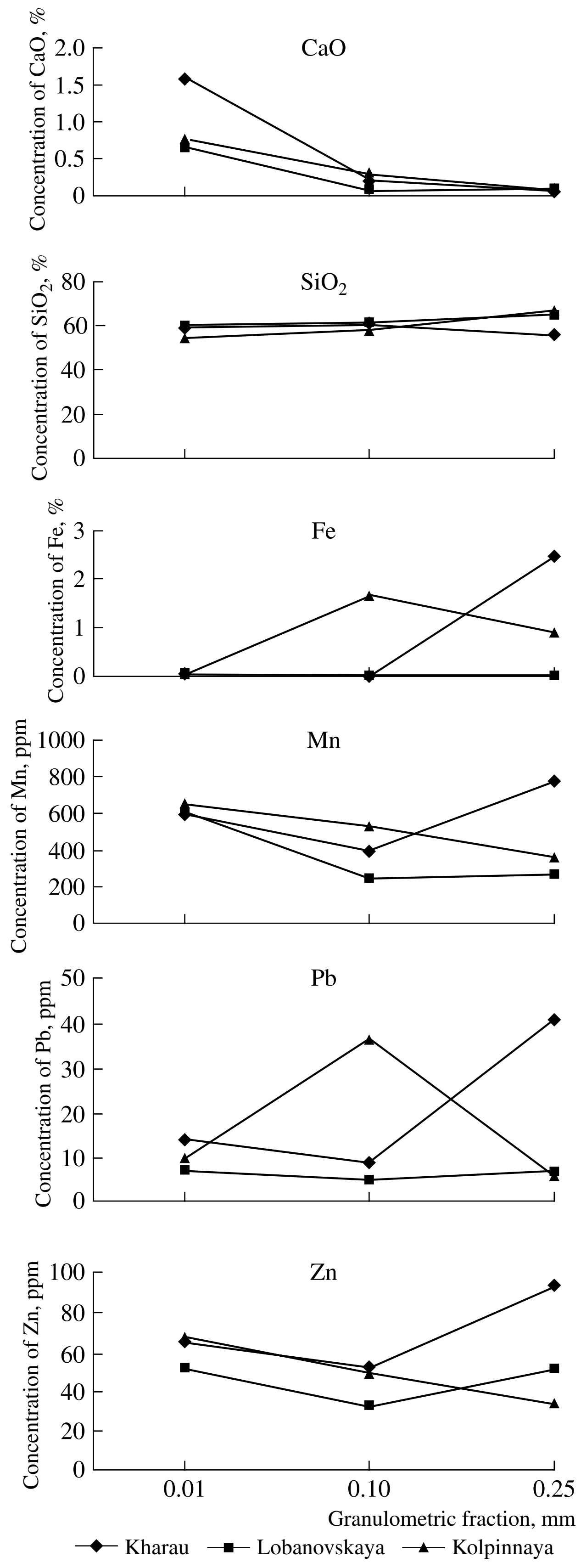

Fig. 5. Distribution of metals between granulometric fractions of sediments.

ined branches and the upper part of the delta contain this element in the pelite fraction (Fig. 5).

The distribution of Cu and Zn in granulometric fractions is analogous to the distribution of Fe and Mn. As was specified above, the BD of the Kharauz branch contain Mn and Fe in the sand fraction. The same fraction is the richest in Cu and Zn. The BD of the central part (Kolpinnaya and Srednyaya branches) and Lake Zavernyaikha contain these elements in the pelite fraction. In the Lobanovskaya branch, Cu enriches the pelite fraction, whereas Zn is equally distributed through all fractions and only weakly enriches the pelite fraction. In the upper reaches of the branches (delta entrance), Zn is concentrated predominantly in the silt fraction, and Cu is concentrated in the pelite fraction (Kabansk). Finally, at Murzino both elements are concentrated in the pelite fraction (Fig. 5).

The distribution of Pb is somewhat different, because its behavior is significantly affected by the Fe distribution in granulometric fractions. The highest Fe concentrations in the BD of the Kharauz branch are restricted to the sand fraction, which also concentrates Pb. In the BD of all of other examined branches in both the upper part of the delta and at the mouths, Pb predominantly enriches the silt and silt–sand fractions of the sediments (Fig. 5). In the Lobanovskaya branch, Pb is evenly distributed between all fractions with a weak enrichment of the sand and pelite fractions.

The highest Pb contents (37–41 ppm) in the silt–sand fractions of the Kharauz and Kolpinnaya mouths are higher than the maximum permissible concentration (MPC) for soils (33 ppm). The maximum concentrations of Cu (82–98 ppm) and Zn (99–110 ppm) in the pelite fraction of the central and right-bank parts and in the sand fraction of the Kharauz branch are 2–2.5 times higher than MPC for soils. The contents of the examined elements in various granulometric fractions are 1.5–2 times higher than the bulk contents of these elements reported in [8, 9].

The fifth group of elements (Cr, Co, Ni, and Cd) is distributed in the BD of the Kharauz branch roughly evenly in all fractions, with a weak increase in the sand fraction. In the BD of all other mouths and upper reaches of the branches, this group of elements is concentrated in the pelite fraction.

Proceeding from the results presented above, we revealed the main tendency in the behavior of trace elements: they are predominantly concentrated in two granulometric fractions—the finest pelite fraction and the coarse sand. The latter fact is explained by an increase in the thickness of Mn and Fe oxide films, which concentrate heavy metals. Pelite fractions are enriched in the metals because of sorption processes and the precipitation of Fe and Mn hydroxides on clay particles and because of the abrasion of films on coarser particles.

In the mouths of branches with active water exchange (Kharauz) and predominantly oxidizing conditions, the metals are selectively accumulated in the sand fraction. This fraction becomes enriched in Fe and Mn, which are followed by Pb, Cu, and Zn. The second group of metals (Cr, Co, Ni, and Cd) is practically equally distributed between all fractions, with slightly higher concentrations in the sand fraction. Thus, Fe and Mn largely predetermine the behavior of other elements.

In the mouths of minor branches (Kolpinnaya), sediments are rich in Mn and, to a lesser degree, Fe hydroxides. In these environments, Fe is concentrated in the silt fraction and Mn in the pelite fraction, with Pb following Fe and enriching the silt fraction and Zn, as Mn, concentrating in the pelite fraction. The behavior of Cu is characterized by an equal distribution between all fractions. The pelite fraction is also enriched in another group of metals: Cr, Co, Ni, and Cd.

Let us consider the variations in the distribution of basic elements (Ca, Mg, Na, and K) in the bottom deposits of the branches from their upper reaches to mouths (Fig. 6). Figure 6 demonstrates that, while the BD at Kabansk contain no more than 1.2% Ca, these deposits in the mouths of branches in the central part contain no more than 0.85% Ca, and the Lobanovskaya branch contains 0.74% Ca. The fraction <0.01 mm of the BD of the Kharauz deposit contains up to 1.6% Ca. The increase in the Ca content in the Kharauz branch is explained by the precipitation of Ca carbonate because of the oversaturation of the water with respect to this element. Hence, the Ca concentration in the BD of the branches decreases from the upper reaches of the branches to their mouth, with the only exception of the Kharauz branch.

The behavior of Mg differs from that of Ca. The maximum Mg contents are 0.7–0.9% in the upper reaches of the branches (Kabansk and Murzino) and increase to 1.0–1.17% in the mouths of the branches. The distribution of alkali elements is not contrasting, and their concentrations remain practically equal throughout the whole lengths of the branches.

The most drastic decrease in concentration in the BD of the branches over their lengths in the delta is characteristic of Fe. The Fe concentration in the BD at the delta entrance ranges from 4.5 to 7.9%, and the analogous value for the mouths decreases to 2.5% for the Kharauz branch, 1.7% for branches in the central part of the delta, 2.1% for the Lobanovskaya branch, and 2.6% for Lake Zavernyakha (Fig. 6).

Similarly to Fe, Mn is an important element in the geochemical processes, because Fe and Mn hydroxides can actively adsorb many trace elements. We revealed the following tendencies in the Mn distribution in the BD of the delta branches. The BD contain 0.2–0.3% Mn at Kabansk and only 0.04–0.06% at Murzino. In the mouths of branches at the outer margin of the delta, the Mn contents decrease to 0.04–0.077% (Fig. 6).

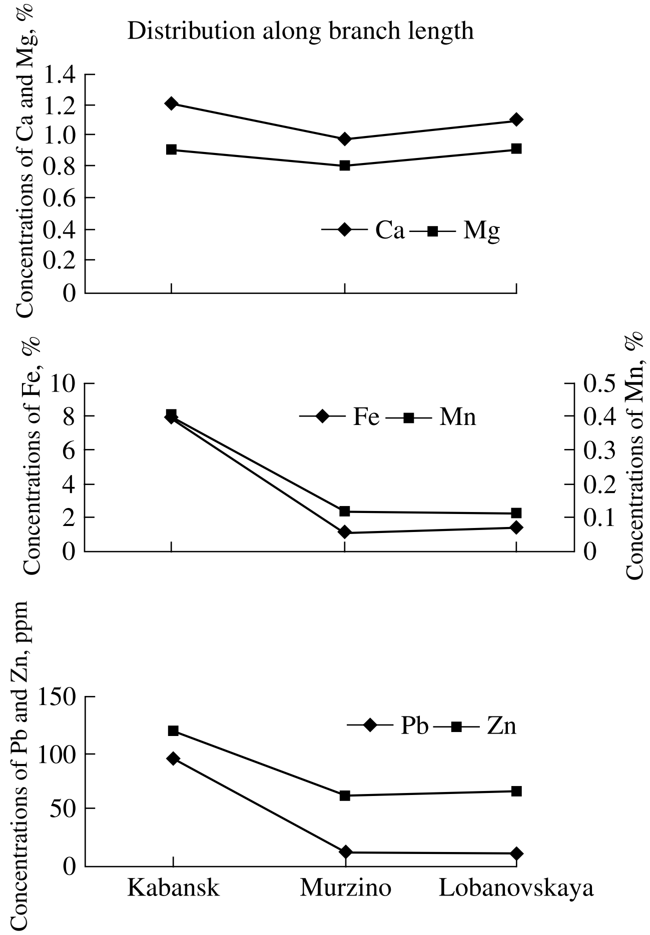

Fig. 6. Distribution of metals along branches in the Selenga River delta.

The Pb distribution shows a significant decrease in the concentrations only in the mouth of the Lobanovskaya branch. For example, while the Pb concentrations at Kabansk is equal to 33 ppm, these values at Murzino and in the mouth of the Lobanovskaya branch decrease to 8–12 ppm. At the same time, Pb contents in the mouth of the Kharauz branch and in branches in the central part of the delta are as high as 37–41 ppm (Fig. 6).

The Cu concentrations decrease in the BD in the delta. Whereas the maximum Cu concentrations in the granulometric fractions of the BD at delta entrance are 98 ppm, these concentrations decrease to 83 ppm in the Kharauz branch and to 47 ppm in other branches.

The most significant decrease in concentration along the course of the branches are typical of Zn and Cr. For example, the Zn content in the BD at the delta entrance is 99–119 ppm and decreases to 33–69 ppm at the outer margin of the delta. The Zn content in the sand fraction of the Kharauz branch is 94 ppm. The BD contain 82–87 ppm Cr at Kabansk and no more than 74 ppm at the exit from the delta.

The distribution of Ni, Co, and Cd in the BD shows no significant decrease in concentrations along the lengths of the branches.

CONCLUSIONS

1. Analysis of the granulometric composition of the deposits indicates that the BD of southwestern and western branches (branches in the left-bank and central parts) are dominated by the silt–pelite fraction. The deposits of the branches of northeastern direction (Lobanovskaya) contain mostly the sand fraction. This is likely explained by the fact that the Lobanovskaya branch enters into Poval Bay, where the mixing of riverine and lacustrine waters is more sluggish.

2. The silt fraction contains such weathering-resistant minerals as hornblende and actinolite, which are absent from the sand fraction. The pelite fraction of the BD of the Kharauz branch is characterized by the precipitation of carbonates, and the deposits of the Kolpinnaya branch contain water-bearing Mn oxides of variable composition.

3. The mouth of the Kharauz branch is characterized by an unusual distribution of the examined elements between granulometric fractions. Most of the metals are concentrated in the sand fraction in the BD of the mouth of the Kharauz branch but enrich the pelite and silt fractions in the deposits of all other branches.

4. The tendencies in the distribution of chemical elements in the delta highlight distinctive features of the sedimentation process. Along the lengths of the branches from their upper reaches to mouths, the BD become systematically depleted in most of the elements. The only exception is the Kharauz branch, which is characterized by the accumulation of Ca and, less significantly, Pb. The delta is characterized by the extensive branching and merging of its watercourses and by the active redistribution of runoff between branches. These factors result in a decease in the contents of chemical elements in the BD in the mouths of the branches.

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