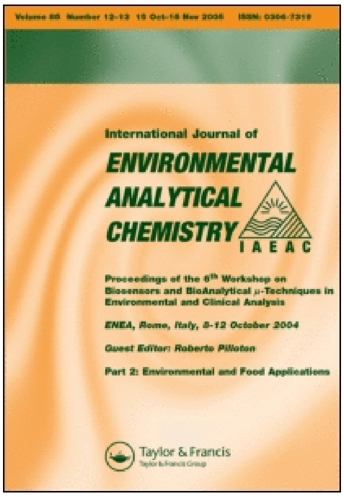

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Ultra-thin window electron probe microanalysis of suspended particles in tributaries of Lake Baikal, Siberia

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Fluvial suspended particles along with dissolved substances in riverine waters are valuable for understanding the processes in the watershed. Data on the chemical composition of suspended particles in the tributaries of Lake Baikal, Siberia are scarce and obtained mainly by regular techniques. Application of low-Z electron probe microanalysis with subsequent cluster analysis of the results appeared to specify the chemistry of different groups of suspended particles. Results obtained show that all the particles may be divided into three groups: (1) mineral, (2) organic, and (3) mixed. Contribution of these groups into the total composition of suspended sediments was evaluated. According to abundances of the particle groups, two categories of the rivers have been distinguished. Both chemical and mineralogical differences in suspended particles between two categories of Baikal tributaries are discussed. They are mainly conditioned by natural landscape features and the land use on the watersheds.

Keywords: Low-Z electron probe microanalysis; Suspended sediments; Lake Baikal; Tributaries

1. Introduction

Suspended particulate sediments as well as the substances dissolved in fluvial waters are important inquiry subjects for understanding the processes occurring on the watershed. The composition of suspended particles is mainly a result of physical processes whereas that of aqueous phase is mainly formed by chemical interactions with the solid phase. There is an enormous number of publications devoted to surface water chemistry but much less on the composition of suspended particles. Most of such data are obtained using routine analytical destructive and nondestructive techniques like flame emission/absorption analysis, mass spectrometry, X-ray fluorescence, etc. At present, few authors applied conventional EPMA with subsequent cluster analysis to chemical examination of single particles in suspended and bottom

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sediments. This method was used to analyze individual particles of suspended materials in Onondaga Lake (New York) by D.L. Johnson *et al.* [1]. B.T. Hart *et al.* [2] characterized colloidal and particulate matter in Magela creek system in Norhtern Australia. V.M. Dekov *et al.* [3] studied chemical composition of bottom sediments and suspended matter of the Nile river. In some studies, the EPMA-based mineralogy reconstructions were attempted [4, 5].

Data on the composition of suspended particles in Lake Baikal and its tributaries are scarce. There are more than 300 tributaries entering Lake Baikal, however except the highest content of suspended particles in the Selenga River (10–20 and even more than $20\,\mathrm{mg\,L^{-1}}$ in some seasons) only in large tributaries (the Rivers Barguzin, Upper Angara, Turka) the concentration of suspended particles is around $2\,\mathrm{mg\,L^{-1}}$. In most other rivers, especially the mountain ones, there is very low content of suspended sediments; therefore it is not easy to study their composition. In 1963, G. Patrikeeva [6] published the first data: she investigated the particulate phosphorus in fluvial waters of Southern Baikal tributaries. N. Sudakova [7] and E. Tarasova [8, etc.] studied organic constituents, mainly the content of organic carbon, in suspended particles of Baikal tributaries. In 1977, L. Vykhristuyk [9] firstly reported the data on particulate Si, Ca, Fe, Mn, and Ti in 17 Baikal tributaries. The mineralogy of suspended sediments in Baikal tributaries was shortly presented by V. Shevchenko with co-authors [10]. About ten years ago, when more sensitive instrumental methods became available, more extensive studies of the chemical composition of suspended riverine particles were started [11, 12]. However, the data are still scarce, and some authors prefer to calculate the composition of suspended riverine particles by mathematical modeling [13] or to use data on bedrocks composition [14] instead of those obtained directly by examination of particles suspended in fluvial waters. The only EPMA data and simple reconstruction of suspended particles mineralogy in Lake Baikal tributaries have been presented by Jambers and Van Grieken [15]. The chemical composition of different types of particles was not quantified in the paper, because measurements were performed by the conventional EPMA (with $7\,\mu\mathrm{m}$ Be window in front of the X-ray detector) and using element relative X-ray intensities instead of the concentrations as the output data. The weight contribution of different particle types into the total weight of suspended sediments was not evaluated too, since carbon could not be measured with a conventional detector and thus the organic phase could not be estimated. Additionally the procedure of mineralogy reconstruction was not perfect. The present study aims to apply ultra-thin window EPMA capable of quantifying low-Z elements as whole with subsequent cluster analysis. This will allow quantifying results and improving the procedure of mineralogy reconstruction.

2. Experimental

2.1. *Sampling*

Thirteen water samples from eight Baikal tributaries (figure 1) were collected during a sampling campaign in July 1996. The rivers Selenga, Upper Angara, and Barguzin are the largest Baikal tributaries contributing annually about 66% of the total water inflow [16]. The contribution of the Rivers Snezhnaya, Solzan, Slyudyanka, Utulik, and

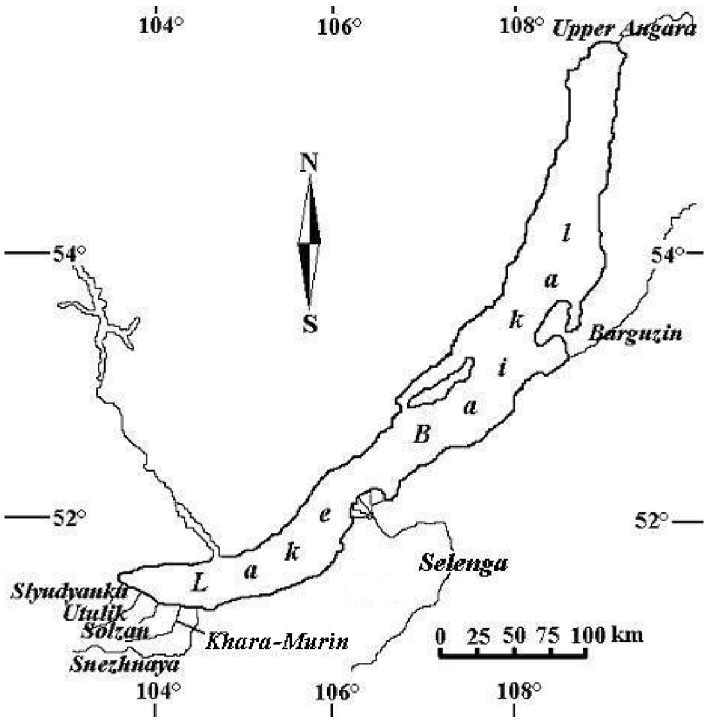

Figure 1. Map of Lake Baikal basin showing locations of major rivers.

Khara-Murin inflowing into Southern Lake Baikal from the Khamar-Daban Ridge is much lower. The Snezhnaya is the most full-flowing river among small rivers listed above.

From 0.3 to 3.9 L of fluvial waters were run through 0.45 µm pore acetate membrane filters, 47 mm in diameter (D-3354 Dassel, Germany). After filtering, the samples on filters were air dried for 1–2 days at room temperature and stored in airtight Petri dishes.

2.2. *Analytical procedures*

The particulate matter on the filters was re-suspended in water and then deposited on a silver foil by a pipette. Samples prepared in this way were analyzed by a JEOL 733 electron probe microanalyser (JEOL, Tokyo, Japan) equipped with an ultra-thin window Oxford Si(Li) detector. One hundred particles were analyzed in each sample. Due to small size of the majority of deposited particles, the measurements were done manually with an accelerating voltage of 10 keV and a beam current of 1 nA. To avoid beam damage of the particles, the sample holder was cooled by liquid nitrogen during measurement [17]. Such conditions are suitable to analyze low-Z analytes starting from C.

The characteristic X-ray spectrums obtained by EPMA were evaluated by non-linear least squares fitting using the AXIL program (Analysis of X-ray spectra by Iterative Least squares) [18]. The semi-quantitative elemental composition of the particles was calculated with an iterative approximation method based on the Monte Carlo simulations [19].

Using the results obtained, the analyzed particles were classified by the Hierarchical Clustering Analysis (HCA) [20]. In this way, the particles were divided into different clusters accordingly to their compositional similarity.

2.3. *Data processing and simple mineralogy reconstruction*

The different particle clusters within the sample have different abundances and densities. To obtain the data on bulk chemistry of the sample we assume for simplicity the density of organic phase to be close to 1. In this case, the densities of mixed and mineral particles are conventionally assumed to be 1.5 and 2.5, respectively.

To evaluate the bulk chemical composition of suspended sediments, the abundance of mixed and organic particles (clusters) was divided by the corresponding factor (1.5 or 2.5) and the sum of new abundances normalized to 100%. Then, the element contents corresponding to each cluster were multiplied with new cluster abundances, and the values obtained were summarized within each sample. Since the diameter of most particles (about 90%) was within a narrow 0.7–1.5 µm range, it was not taken into consideration during calculation procedure.

Mineralogy was reconstructed on the base of ratios between the elements. The basic principles of preliminary grouping of mineral particles are given in table 1. The elements Si, Al, and Fe were taken as a matrix, whereas the sum of Na, K, Mg and Ca was considered as an indicative constituent.

To determine the average mineral stoichiometry, a more complicated procedure was applied. As the first step, the carbon was not considered and the total content of elements was normalized to 100%. In the second step, the molar equivalents (ME) of elements were calculated: the oxide percentage was divided by its molar mass. At the next step, the obtained coefficients were normalized to the number of oxygen atoms in structural cell of the corresponding mineral according to table 1. It is necessary to keep in mind that the "mica" we measured may actually be a mixture of different stratiform aluminosilicates. Thus a precise identification is not invariably possible using this approach.

Table 1. The principles of simple mineralogy reconstruction based on the element composition of suspended particles.

Mineral	Indicative constituents	Matrix	Structural cell
Amphiboles	Me* > 10%	Si 20–35%	$[(OH)_2 \mid Si_8O_{22}]^{13-}$
		Al 10–25%	
Mica	Me < 10%	Fe 2–15%	$[(OH)_2 \mid (AlFe)Si_3O_{10}]^{5-}$
Feldspars	Me < 15%	Si 30–35%	$[AlSi_3O_8]^-$
		Al 10–15%	$[Al_2Si_2O_8]^{2-}$
Silicon oxide	Me + Al + Fe < 3%	Si > 42%	$Me_xSi_yO_2$
SiO_2-rich residues**	Me + Al + Fe < 10%	Si < 40%	$Me_xSi_yO_2$ or $(Me_xO_y + SiO_2)$

*$Me_xO_y = (Na + K + Mg + Ca)$.

**Intermediate weathering products or SiO_2 aggregates.

3. Results and discussion

In all samples studied, the particle size ranges from 0.4 to 3.6 µm; however, as it was mentioned above, most particles are within a narrower range (0.7 to 1.5 µm). Majority of mineral particles have a regular shape whereas the shape of organic particles is often irregular. No chemical composition dependence on particle size and shape was observed.

Based on their element composition, all the particles can be divided into three groups: (1) mineral, (2) organic, and (3) mixed particles. The chemical composition of different particles is shown in table 2. In the first group, the particles consist mainly of at least three lithophile elements: O, Si, and Al. The carbon content is less than 8%. In the second group, carbon (36–41%) and oxygen (48–56%) absolutely prevail over the other elements, whereas the silicon is absent or rather negligible. The third group is by 11–17% composed of carbon and by 51–63% of oxygen; the rest falls to the other elements. The important feature of organic particles is their enrichment (up to 3.5 times) with Ca and Mg as compared to the first and the third particle groups (table 2).

Table 2. Chemical composition of different particles in Baikal tributaries measured by EPMA, % per particle group.

	Na	K	Mg	Mn	Ca	Fe	Al	Si	C	O	
Object	(%)										Abundance
Mineral											
Selenga	1.9	1.8	0.3	–	1.2	1.7	10.6	31.2	4.0	47.3	92.0
Barguzin	2.0	1.2	1.3	–	2.2	3.9	10.7	28.9	3.6	46.3	71.8
Snezhnaya	–	0.7	0.9	–	1.4	5.1	9.0	30.2	7.5	45.2	72.8
Average	1.3	1.2	0.8	–	1.6	3.6	10.1	30.1	5.1	46.3	78.9
Up. Angara	–	–	–	–	2.0	–	9.1	34.3	6.6	48.0	53.1
Slyudyanka	–	–	–	–	–	–	9.8	34.7	7.2	48.3	63.3
Utulik	–	–	1.0	–	1.0	1.9	6.4	35.1	7.3	47.3	53.0
Khara-Murin	–	–	–	–	–	–	–	43.5	6.8	49.7	40.0
Average	–	–	0.3	–	0.7	0.5	6.3	36.9	7.0	48.3	52.3
Organic											
Barguzin	–	–	2.8	–	2.8	1.9	3.1	2.1	36.6	50.9	9.3
Snezhnaya	–	–	1.7	–	2.6	–	1.4	1.0	39.3	54.1	21.8
Average	–	–	2.2	–	2.7	0.9	2.2	1.5	37.9	52.5	15.6
Up. Angara	–	–	1.3	4.8	4.3	2.8	–	1.0	36.8	49.0	15.0
Solzan	–	1.0	2.0	0.8	3.5	6.6	0.5	–	36.9	48.8	60.9
Slyudyanka	0.8	0.5	2.4	–	5.8	–	0.8	0.3	38.0	51.5	36.7
Utulik	–	–	0.6	–	2.0	–	0.8	0.5	40.6	55.6	17.4
Khara-Murin	0.5	0.6	1.3	–	2.7	–	0.3	–	40.2	54.5	28.8
Average	0.3	0.4	1.5	1.1	3.7	1.9	0.5	0.4	38.5	51.9	31.8
Mixed											
Selega	–	–	2.2	–	–	20.9	2.5	3.8	15.5	55.2	8.0
Barguzin	–	–	1.5	2.0	2.9	6.5	2.7	6.5	17.3	60.5	19.0
Snezhnaya	–	–	1.5	1.5	2.1	–	5.2	10.0	16.8	62.9	5.4
Average	–	–	1.8	1.2	1.7	9.1	3.5	6.8	16.5	59.6	10.8
Up. Angara	–	–	1.7	–	2.3	14.4	4.4	12.4	11.1	53.8	32.0
Solzan	–	0.6	0.6	–	1.7	14.9	4.5	11.8	11.7	54.2	39.1
Utulik	–	–	0.5	–	1.7	24.9	3.0	6.4	12.4	51.1	29.6
Khara-Murin	–	1.0	1.5	–	1.3	4.1	5.6	15.4	12.5	58.7	31.2
Average	–	0.4	1.1	–	1.7	14.6	4.4	11.5	11.9	54.4	33.0

Examination of single particles shows that suspended sediments in the Rivers Selenga, Barguzin and Snezhnaya contain 92%, 72% and 73% of mineral particles, respectively (table 2). The Rivers Upper Angara, Solzan, Slyudyanka, Khara-Murin, and Utulik contain from 40% to 63% of such particles. Thus, based on abundances of mineral particles in riverine suspended sediments, two categories of the rivers can be distinguished: (1) those containing $>72\%$ of mineral particles and (2) those containing $<63\%$ of mineral particles. One can see that in large rivers (except the Upper Angara) suspended sediments are mainly represented by mineral particles, whereas in small rivers organic and mixed particles comprise a substantial share of the suspended matter. In general, the larger the watershed, the higher a share of arable lands, the higher is the percentage and diversity of mineral substances in fluvial suspended sediments.

Data obtained (tables 2 and 3) show that the chemical composition of specified particles (mineral, organic or mixed) is different in all the samples studied. However, mostly the group of predominant particles in the sample stipulates the difference in bulk chemistry between the first and the second categories of rivers. In contrast to small rivers, the suspended particles in the Rivers Selenga, Barguzin, and Snezhnaya are enriched in Na, K, Mn, Al, and Si (table 3). Comparison between bulk chemistry (Sum lines in table 3) of suspended particles in this category of rivers and the chemical composition of different particle groups (lines Mineral, Organic and Mixed) show that all these elements, except Mn, are mostly incorporated into mineral phase.

Suspended particles in the second category of rivers are enriched in organic substance, which is their major constituent, as compared to the first category of tributaries. Table 3 is vertically structured to show decreased contribution of mineral particles and increased contribution of organic particles from top to the bottom. Suspended sediments in small rivers are also slightly enriched with Fe associated to a greater extent with the mineral phase of mixed particles compared to suspended sediments in large rivers containing Fe mostly in mineral particles (table 3). The prevalence of organic substance in suspended particles of these rivers may be due to both landscape/land use and surface geology. There are the landscapes of mountain taiga in this area, in which the carbon is a widespread element because of unmanaged dense vegetation that covers the watersheds. Vegetation cover also strongly protects the soil from erosion.

The concentrations of Mg and Ca in fluvial suspended sediments are the same in large and small tributaries (table 3). In small tributaries, these elements are mostly associated with organic particles, whereas in large tributaries they are associated with mineral phase. Most probably in small rivers organic particles are represented by Ca-Mg salts of humic acids, absorption complexes, and partly decomposed plant residues.

The differences in chemistry of mineral phase are conditioned by quantitative and qualitative differences in mineralogical composition of samples (table 4). In the first category of rivers, the mineral particles and mineral part of the mixed particles in fluvial suspended sediments mainly consist of feldspars, amphiboles and micas, whereas in the second category of rivers micas and silicon oxide represent most of the mineral particles. Amphibole-like minerals were surmised to be present only in the mixed particles. Since the mineral phase in these particles is probably tightly coupled with organic substance, we are unable to give the exact composition of mineral fraction.

To assess integrally the possible differences in watershed geochemistry, the total bulk chemistry data were normalized to aluminum (table 5). These are the abundance

Table 3. The contribution of different groups of particles into bulk chemistry of suspended sediments, % per sample.

	Na	K	Mg	Mn	Ca	Fe	Al	Si	C	O	
Object	(%)										Abundance
Rivers with predominance of mineral particles in suspended sediments											
Selenga											
Mineral	1.8	1.6	0.2	–	1.1	1.6	9.8	28.7	3.7	43.5	92.0
Organic	–	–	–	–	–	–	–	–	–	–	–
Mixed	–	–	0.2	–	–	1.7	0.2	0.3	1.2	4.4	8.0
Sum	1.8	1.6	0.4	–	1.1	3.3	10.0	29.0	4.9	47.9	100.0
Barguzin											
Mineral	1.5	0.8	0.9	–	1.6	2.8	7.6	20.8	2.6	33.2	71.8
Organic	–	–	0.3	–	0.3	0.2	0.3	0.2	3.4	4.7	9.3
Mixed	–	–	0.3	0.4	0.6	1.2	0.5	1.2	3.3	11.5	19.0
Sum	1.5	0.8	1.5	0.4	2.4	4.2	8.4	22.2	9.3	49.4	100.0
Snezhnaya											
Mineral	–	0.5	0.7	–	1.0	3.7	6.5	22.0	5.5	32.9	72.8
Organic	–	–	0.4	–	0.6	–	0.3	0.2	8.6	11.8	21.8
Mixed	–	–	0.1	0.1	0.1	–	0.3	0.5	0.9	3.4	5.4
Sum	–	0.5	1.1	0.1	1.7	3.7	7.1	22.7	14.9	48.1	100.0
Average	1.1	1.0	1.0	0.2	1.7	3.7	8.5	24.6	9.7	48.5	
Rivers with predominance of organic and mixed particles in suspended sediments											
Utulik											
Mineral	–	–	0.5	–	0.5	1.0	3.4	18.6	3.9	25.1	53.0
Organic	–	–	0.1	–	0.4	–	0.1	0.1	7.0	9.6	17.4
Mixed	–	–	0.1	–	0.5	7.4	0.9	1.9	3.7	15.1	29.6
Sum	–	–	0.8	–	1.4	8.4	4.4	20.5	14.6	49.9	100.0
Upper Angara											
Mineral	–	–	–	–	1.1	–	4.8	18.2	3.5	25.5	53.1
Organic	–	–	0.2	0.7	0.6	0.4	–	0.1	5.5	7.4	15.0
Mixed	–	–	0.5	–	0.7	4.6	1.4	4.0	3.6	17.2	31.9
Sum	–	–	0.7	0.7	2.4	5.0	6.3	22.3	12.6	50.0	100.0
Slyudyanka											
Mineral	–	–	–	–	–	–	6.2	21.9	4.5	30.6	63.3
Organic	0.3	0.2	0.9	–	2.1	–	0.3	0.1	13.9	18.9	36.7
Mixed	–	–	–	–	–	–	–	–	–	–	–
Sum	0.3	0.2	0.9	–	2.1	–	6.5	22.1	18.5	49.5	100.0
Khara-Murin											
Mineral	–	–	–	–	–	–	–	17.4	2.7	19.9	40.0
Organic	0.1	0.2	0.4	–	0.8	–	0.1	–	11.6	15.7	28.8
Mixed	–	0.3	0.5	–	0.4	1.3	1.7	4.8	3.9	18.3	31.2
Sum	0.1	0.5	0.8	–	1.2	1.3	1.8	22.2	18.2	53.9	100.0
Solzan											
Mineral	–	–	–	–	–	–	–	–	–	–	–
Organic	–	0.6	1.2	0.5	2.2	4.0	0.3	–	13.3	38.8	60.9
Mixed	–	0.2	0.2	–	0.6	5.8	1.8	4.6	4.6	21.2	39.1
Sum	–	0.8	1.4	0.5	2.8	9.8	2.0	4.6	17.9	60.0	100.0
Average	0.1	0.3	0.9	0.2	2.0	4.9	4.2	18.3	16.4	52.7	

rows obtained for particulate elements in the first (1) and the second (2) categories of tributaries, respectively:

$$(1)\ \mathrm{Mn} < \mathrm{K} = \mathrm{Na} < \mathrm{Mg} < \mathrm{Ca} < \mathrm{Fe} < \mathrm{Si};$$

$$(2)\ \mathrm{Na} = \mathrm{Mn} < \mathrm{K} < \mathrm{Mg} < \mathrm{Ca} < \mathrm{Fe} < \mathrm{Si}.$$

Table 4. Chemical composition of mineral particles, % per particle, and their abundance in suspended sediments of Baikal tributaries, % per sample.

Sample	Na	K	Mg	Ca	Fe	Al	Si	O	Formula	Particle abundance (%)
	(%)									
Selenga		8.5	1.2	1.2		10.6	30.8	47.6	$Ca_{0.08}Mg_{0.14}K_{0.59}Al_{1.05}Si_{2.95}O_8$	19.9
	5.0			2.4		12.9	30.6	49.1	$Ca_{0.16}Na_{0.57}Al_{1.25}Si_{2.84}O_8$	36.6
					7.6	15.3	28.6	48.5	$Fe_{0.50}Al_{2.07}Si_{3.70}O_{10}(OH)_2$	22.0
							46.7	53.3	SiO_2	13.6
Barguzin	4.0			2.4		13.6	30.6	49.4	$Ca_{0.15}Na_{0.45}Al_{1.31}Si_{2.83}O_8$	37.5
		3.3	3.6	2.7	10.6	10.1	25.0	44.7	$Ca_{0.27}K_{0.33}Mg_{0.59}Fe_{0.75}Al_{1.47}Si_{3.51}O_{10}(OH)_2$	26.5
					0.8	1.9	44.5	52.7	$Fe_{0.01}Al_{0.04}Si_{0.96}O_2$	7.8
Snezhnaya				2.1		2.0	43.6	52.3	$Ca_{0.03}Al_{0.04}Si_{0.95}O_2$	27.5
					1.8	17.0	30.6	50.6	$Fe_{0.11}Al_{2.19}Si_{3.80}O_{10}(OH)_2$	19.7
		2.1	2.9	1.9	14.4	12.4	22.5	43.9	$Ca_{0.19}K_{0.21}Mg_{0.48}Fe_{1.03}Al_{1.85}Si_{3.21}O_{10}(OH)_2$	25.6
Up. Angara				2.1		9.8	36.7	51.4	$Ca_{0.03}Al_{0.23}Si_{0.81}O_2$	53.1
Slyudyanka						10.6	37.4	52.1	$Al_{0.24}Si_{0.82}O_2$	63.3
Utulik			1.9	1.9	3.6	11.8	31.5	49.4	$Ca_{0.16}Mg_{0.27}Fe_{0.23}Al_{1.56}Si_{4.00}O_{10}(OH)_2$	30.9
							46.7	53.3	SiO_2	22.1
KharaMurin							46.7	53.3	SiO_2	40.0

Table 5. Al-normalized chemical composition of suspended particles in Baikal tributaries.

River	Na	K	Mg	Mn	Ca	Fe	Si
Selenga	0.2	0.2	–	–	0.1	0.3	2.9
Barguzin	0.2	0.1	0.2	–	0.3	0.5	2.6
Snezhnaya	–	0.1	0.2	–	0.2	0.5	3.2
Average	0.1	0.1	0.1	–	0.2	0.4	2.9
Solzan	–	–	0.2	–	0.3	1.9	4.7
Slyudyanka	–	–	0.1	0.1	0.4	0.8	3.6
Up. Angara	–	–	0.1	–	0.3	–	3.4
Utulik	0.1	0.3	0.5	–	0.6	0.7	12.2
Khara-Murin	–	0.4	0.7	0.2	1.4	4.8	2.3
Average	–	0.1	0.2	0.1	0.5	1.2	4.4

Taking into account the magnitude of values, the only real difference between these two rows lies in the Na position. This may probably reflect higher forestation of small rivers watersheds compared to that of large tributaries and consequently lower erosion, which serves as a source of Na-rich minerals. The same may be the reason for presumably lower particulate Al content in small rivers (table 3) that leads to higher particulate Me/Al ratios for most elements in these tributaries compared to large ones (table 5). Our data on the element concentrations are in agreement with those reported by Callender and Granina (7) obtained using direct current plasma AES for three major Baikal tributaries: the Rivers Selenga, Upper Angara, and Barguzin (table 6). To make the comparison possible, we converted the element concentrations to those of oxides.

4. Conclusion

Electron microscopy coupled with X-ray microanalysis is a universal tool for studying the geochemical processes at the single particulate level. Application of the ultra-thin

Table 6. Comparison of the results obtained in present study and the data by L. Granina and E. Callender (1997).

Source	Na_2O	K_2O	MgO	MnO	CaO	Fe_2O_3	Al_2O_3	SiO
	(%)							
				Selenga				
Present study	2.6	2.1	0.7	–	1.6	5.1	20.5	67.4
Granina & Callender	2.1	2.1	2.1	0.2	2.7	6.4	12.5	49.5
				Upper Angara				
Present study	–	–	1.7	1.3	4.7	9.9	16.4	66.1
Granina & Callender	1.2	1.3	1.4	0.2	2.9	11.7	8.9	33.4
				Barguzin				
Present study	2.5	1.3	3.1	0.6	4.2	7.6	20.3	60.4
Granina & Callender	1.6	1.6	2.1	0.3	3.6	7.5	10.0	39.5

window EPMA with subsequent HCA allowed us to distinguish different groups of the particles suspended in fluvial waters and to obtain data on their chemical composition without complicate sample pretreatment. This is of great importance for the investigation of fluvial suspended sediments in the Baikal region, characterized by extremely low concentrations of suspended particles in the most rivers. Small masses (micrograms) of suspended particles collected on the filters demand extremely sensitive techniques to be reliably studied. Semi quantitative determination of low-Z elements such as C and O gives the unique opportunity to distinguish organic and inorganic phases and to evaluate the contribution of different groups of particles to the bulk chemistry of suspended sediments.

Based on their element composition, all the particles studied were divided into three groups: (1) mineral, (2) organic, and (3) mixed. According to abundances of the particle groups, two categories of Baikal tributaries have been distinguished. There are more than 72% of mineral particles in suspended sediments of the first category tributaries, whereas, in the second category of rivers, the suspended sediments contain less than 63% of mineral particles. Percentage of different particles causes a difference in the chemical composition of suspended sediments among the rivers. The aluminum normalization procedure shows such difference to be the most pronounced for Na. As a result, we suggest that natural landscape features and land use of watersheds may be of great importance for the chemical and mineralogical composition of suspended sediments in Lake Baikal tributaries.

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References

[1] D.L. Johnson, J. Jiao, S.G. DosSantos, *Environ. Sci. Technol.*, **25**, 736 (1991).

[2] B.T. Hart, G.B. Douglas, R. Beckett, A. Van Put, R.E. Van Grieken, *Hydrological Processes*, **7**, 105–118 (1993).

[3] V.M. Dekov, Z. Komy, F. Araujo, A. Van Put, R. Van Grieken, *Sci. Total Environ.*, **201**, 195 (1997).

[4] W. Jambers, A. Smekens, R. Van Grieken, V. Shevchenko, V. Gordeev, *Colloids Surf., A*, **120**, 61 (1997).

[5] W. Jambers, V. Dekov, R. Van Grieken, *Mar. Chem.*, **67**, 17 (1999).

[6] G.I. Patrikeeva, *Gidrohimicheskie Issledovaniya Ozera Baikal*, pp. 120–143, Akad. Nauk SSSR, Moscow (1963).

[7] N.D. Sudakova, *Operativnye informatsionye materialy*, **1**, 73 (1973). [In Russian.]

[8] E.N. Tarasova, A.I. Mescheryakova, *Sovremennii Gidrohimichekii Regim Ozera Baikal*, p. 142, Nauka, Novosibirsk (1992). [In Russian.].

[9] L.A. Vykhristyuk, *Lithologiya i poleznye iskopaemye*, **1**, 54 (1977). [In Russian.]

[10] V. Shevchenko, Yu. Anockhin, T. Prokhorova, *Baikal Kak Prirodnaya Laboratoriya Dlya Globalnih Izmenenii*, pp. 82–83, LISNA, Irkutsk (1994). [In Russian.]

[11] E. Callender, L. Granina, *Limnol. Oceanogr.*, **42**, 148 (1997).

[12] L. Granina, U. Tomza, R. Arimoto, A. Grachev, M. Granin, *Nucl. Instrum. Methods Phys. Res., Sect. A*, **448**, 419 (2000).

[13] S.A. Kashik, I.K. Karpov, I.S. Lomonosov *et al.*, *Dokl. RAN*, **362**, 353 (1994). [In Russian.]

[14] I.S. Lomonosov, V.S. Antipin, T.K. Lomonosova, A.E. Gapon, *Rus. Geol. Geoph.*, **42**, 268 (2001). [In Russian.]

[15] W. Jambers, R. Van Grieken, *Environ. Sci. Technol.*, **31**, 1525 (1997).

[16] A.N. Afanas'ev, *Vodnie resursi i vodnii balans basseina ozera Baikal*, p. 297, Nauke, Novosibirsk (1976). [In Russian.]

[17] A. Worobiec, J. de Hoog, J. Osan, I. Szaloki, C.U. Ro, R. Van Grieken, *Spectrochim. Acta, Part B*, **58**, 479 (2003).

[18] B. Vekemans, K. Janssens, L. Vincze, F. Adams, P. Van Espen, *X-Ray Spectrom.*, **23**, 278 (1994).

[19] J. Osan, I. Szaloki, C.U. Ro, R. Van Grieken, *Mikrochim. Acta*, **132**, 349 (2000).

[20] I. Bondarenko, B. Treiger, H. Van Malderen, R. Van Grieken, P. Van Espen, *Spectrochim. Acta, Part B*, **51**, 441 (1996).