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WATER QUALITY AND PROTECTION: ENVIRONMENTAL ASPECTS

Concentration and Distribution of Major Macro- and Microelements in Surface Waters in the Altai

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Abstract—The macroelement (HCO_3^-, SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, $Na^+ + K^+$, as well as NO_3^-, NO_2^-, and PO_4^{3-}) and microelement (As, Cd, Cr, Cu, Co, Fe, Mn, Ni, Pb, Zn, and V) composition of natural waters in different physiographical provinces of the Altai have been studied and characterized. It has been found that the concentrations of dissolved forms of metals in the waters of the examined rivers generally do not exceed the MAC_{wm}, though in some cases, they exceed the world averages and depend on the features of water nourishment of rivers and the concentrations of mineral salts in water. A considerable portion of metals in Altai surface waters has been found to be transported as a component of suspension, though the specific concentration of metals in suspension decreases with increasing water turbidity. The effect of the structure and properties of the soil cover on the drainage basins of various physiographic provinces of the Altai on surface water chemistry is most distinct in the case of macrocomponents and typomorphic elements (Fe, Mn, Ca), as well as under anthropogenic impact on the watershed.

Keywords: surface waters, watershed, water chemistry, microelements, major macroions, dissolved forms, suspended forms, Altai

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INTRODUCTION

The present-day scientific approach to studying hydrological and hydrochemical processes in natural waters implies the recognition of water objects as a component of geographic landscape. When studying the formation mechanisms of the quality of natural surface waters, the researcher has to take into account that their chemistry is governed by geomorphological and lithological features of drainage basins and the composition and properties of soils and soil-forming rocks and closely related with the zonal features of soil formation and the extent of anthropogenic load onto the environment and superaqual landscapes. The study should be focused not only on the river channel or lake bed alone, but also on the relationship between the water body or stream and its drainage basin.

A vast body of field data on the concentrations of heavy metals in natural waters has been accumulated by now [10, 14, 17, 31]. The fundamental works for assessing the migration of chemical elements in water are the studies of V.I. Vernadsky [4] and A.I. Perel'man [19]. The authors of [16] believe that the microelement composition of continental water is worst known among natural objects. The effect of soil cover structure and the biogeochemical status of drainage area on the physicochemical composition of surface waters is also rarely mentioned in the literature.

The objective of this work is to study the concentrations and distributions of macro- and microelements in the water–suspended matter system in surface waters of the Altai, taking into account the biogeochemical features of river drainage basins in different physiographic provinces. Examined in this work are small and medium rivers of the Northern, Northeastern, Eastern, Northwestern, and Pre-Altai provinces of the Altai [26], as well as the major types of soils of accumulative and transaccumulative landscapes and their drainage areas.

In the Northern Altai, major tributaries of the Katun R. in its lower reaches, i.e., the rivers of Sema (and its tributary—the Muna R.) and Chemal, as well as the Edigan and Elekmonar were studied. More detailed studies were focused on the tributary of the Katun R.—the Maima R. and its tributaries—the rivers of the medium-mountain (Biryulya, Saidys, Imerya) and low-mountain (Malaya Siul'ta, Ulala) belts. The rivers of the Charysh basin (Belaya, Inya, Sosnovka, and Maralikha) were studied in the Northwestern Altai province; and the Alei R. was studied in the Pre-Altai province (Fig. 1).

Since the hydrochemical features of surface waters are determined, primarily, by the peculiarities of the landscape–biogeochemical conditions on the drainage areas, we will consider the governing factors of

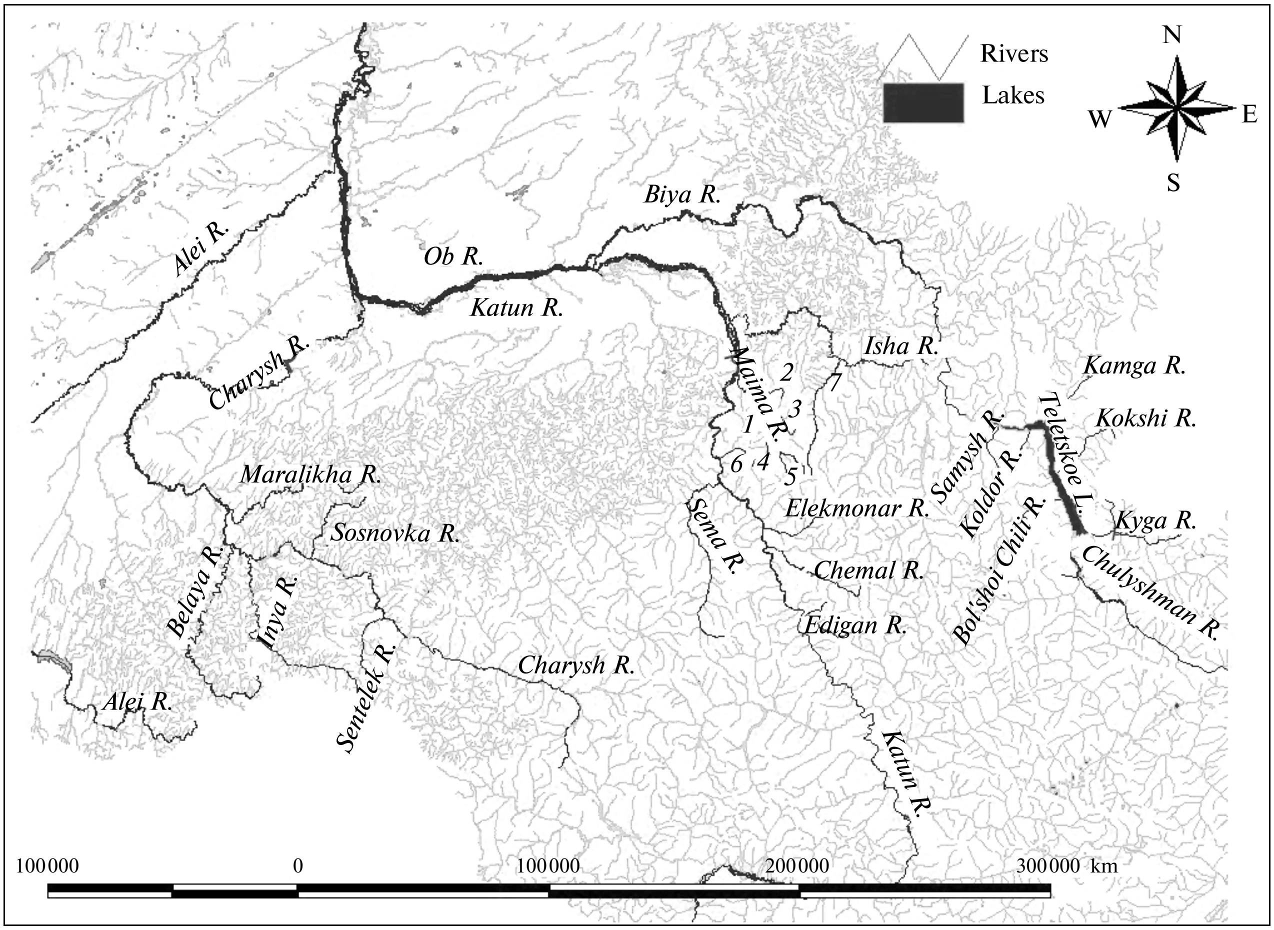

Fig. 1. Study objects—streams and water bodies in Pre-Altai, Northwestern, Northern, and Northeastern provinces of the Altai. Rivers: (1) Malaya Siul'ta R., (2) Ulala, (3) Saidys, (4) Biryulya, (5) Imerya, Sema ((6) Muny), Isha ((7) Malaya Isha).

their formation in the basins of individual model rivers. The Northeastern Altai is the warmest and wettest province [26]. In its part near Teletskoe Lake, medium-mountain flat-topped areas, occupied by cedar-fir forests with mountain-forest brown and permafrost-taiga soils alternate with vast, partially swampy depressions. The hydrological regime of Teletskoe Lake is determined by a considerable effect of the drainage basin—the ratio of water area to drainage area is 1 : 90 (for the Baikal, it is 1 : 17 [24]). The anthropogenic load onto the landscapes of the taiga near Lake Teletskoye is not very high. Low-mountain landscapes with black high-grass forests on mountain–forest gray soils dominate in the northwestern part of the Northeastern Altai Province (the rivers of Isha and Malaya Isha), depressions are occupied by river valleys or bogs [20, 26].

Accumulative and piedmont dry-steppe plains with common and southern black earths, mostly ploughed, dominate in the landscape structure of the Alei R. basin (Northwestern Altai and Pre-Altai Province). In addition, the landscapes of the Alei R. watershed experience considerable anthropogenic load from industrial urban areas, functioning and abandoned mining and processing plants, which serve as sources of uncontrollable and long-term supply of heavy metals into the environment in the river basin [21].

The medium-size mountains in the central Northern Altai are covered by mixed birch–aspen and fir–aspen forests (the upper reaches of the Biryulya and Saidys rivers), while larch park forests on black-earth-like soils dominate in the southern part of the province (Sema R.). A quarter of the province area is under steppes and steppe meadows on podzolized and leached black earths; considerable areas here are ploughed or used as hayfields or pastures (Maima R. basin). In their lower reaches, the rivers of the Northern Altai drain landscapes, which are mostly subject to the effect of agriculture.

Water samples were taken at the mouthparts of rivers during summer low-water period of 2007 and during spring flood of 2010, according to [8, 9]. The samples were taken into clear polyethylene vessels, filtered through a membrane filter, preserved by HNO_3 (2 mL per 0.5 L) according to procedure [18], and transported in dark containers.

Table 1. Mean concentration of major cations and anions, mg/kg, and pH in river waters in different Altai provinces (given above the line is the mean ± error of the mean, below the line is the coefficient of variations, %; here and in Tables 2–4, bold typed are maximal values)

CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	NO_3^-	NO_2^-	P-PO_4^{3-}	pH
Northern Altai									
1.4 ± 0.2 / 54	**179** ± 20 / 40	5.6 ± 0.4 / 24	4.5 ± 0.3 / 21	**29** ± 3 / 36	**12** ± 2 / 67	**1.6** ± 0.2 / 46	**0.031** ± 0.018 / 208	0.035 ± 0.002 / 24	7.1 ± 0.1 / 3
Northeastern and Eastern Altai									
<3	82 ± 7 / 31	4.8 ± 0.2 / 17	4.8 ± 0.3 / 25	16 ± 2 / 48	6.5 ± 1.9 / 102	0.8 ± 0.1 / 36	<0.003	0.023 ± 0.002 / 37	7.1 ± 0.1 / 4
Northwestern and Pre-Altai provinces									
6.3 ± 1.7 / <3–15	**182** ± 30 / 52	**9.6** ± 3.1 / 102	**6.3** ± 1.8 / 91	**22** ± 4 / 62	**15** ± 1 / 78	0.9 ± 0.3 / 108	**0.050** ± 0.020 / 137	0.044 ± 8 / 56	**7.7** ± 0.2 / 6

The macroion composition of surface water and aqueous extracts from soils (1 : 5) was determined by standard procedures with titrimetric completion [1]. The concentration of mineral nitrogen-containing substances and phosphates was determined with photo-colorimetric completion; water pH was determined by potentiometry.

The concentrations of microelements (As, Cd, Cu, Fe, Mn, Ni, Zn, Pb, Cr, Co, and V) were determined in the Chemical Analytical Center, IWEP SB RAS by atomic-absorption spectrometry with the use of electrothermal atomization on SOLAAR M-6. The instruments were calibrated against standard SSS solutions; the correctness of determinations was checked with the use of addition technique.

The statistical processing of data was based on standard methods [13] and included the evaluation of arithmetic mean, error of the mean ($\bar{x} = \frac{\sigma}{\sqrt{n}}$, where σ is the standard deviation, n is sample size), geometric mean, the coefficient of variation (Cv, %), and the correlation coefficient (r).

The ecological assessment of the concentrations of elements in water bodies and streams was based on their comparison with the world-averaged concentrations of the elements in river water [10] and their Clarkes in soils (for suspended forms), according to Beus [3]; water pollution was assessed by comparing with MAC_{wm} [5].

RESULTS AND DISCUSSION

According to the authors' results, the surface waters of Pre-Altai, Northwestern, Northern, and Northeastern Altai provinces refer to the class of fresh hydrocarbonate–calcium waters. The total water mineralization generally increases from high-mountain and medium-mountain rivers with mixed and snow–glacial nourishment to waters of low-mountain rivers with predominantly mixed and rain nourishment. The total salt content never exceeds 700 mg/L, and the variation of this characteristic within individual physiographic areas is insignificant (Cv < 40%), while variation of the concentrations of various cations and anions, especially, water-soluble mineral phosphorus (in the form of phosphates), nitrates, and nitrites is more significant.

The main feature in the runoff formation of small rivers is its close relationship with the biogeochemical properties of the basin landscape. Note that the concentrations of HCO_3^- and Cl^-, Ca^{2+}, and Mg^{2+}, as well as P as phosphates, N as nitrites and, especially, nitrates, in the rivers of the Northeastern Altai, which mostly drain mountain-forest taiga landscapes, are much less than those in rivers flowing over areas with higher agricultural development, i.e., Northern and Northwestern Altai (Table 1). The total water mineralization in the rivers of the Northern (381 ± 40 mg/L, Cv = 38%) and Northwestern (446 ± 70 mg/L, Cv = 51%) Altai is, on the average, twice as large as that of rivers of the Northeastern Altai (184 ± 20 mg/L, Cv = 28%).

Note that waters of rivers in steppe and forest–steppe areas in the Pre-Altai, Northwestern, and Northern Altai provinces contain more Ca^{2+} (its concentration is highest in the waters of the Maima and Alei rivers, reaching 48 mg/kg), which is determined by the wide occurrence in the provinces of soils with a pronounced carbonate horizon—common and southern black earths as well as mountain–forest black-earth-like soils of park larch forests (in the Northern Altai). The relatively low concentrations of Ca^{2+} in river water in Northeastern Altai correlate with its low concentrations in the soils of mountain–forest taiga landscapes.

In different physiographic provinces of the Altai, in summer, when biogeochemical processes are most pronounced and the surface and within-soil hydrochemical runoff is considerable, soil cover is among

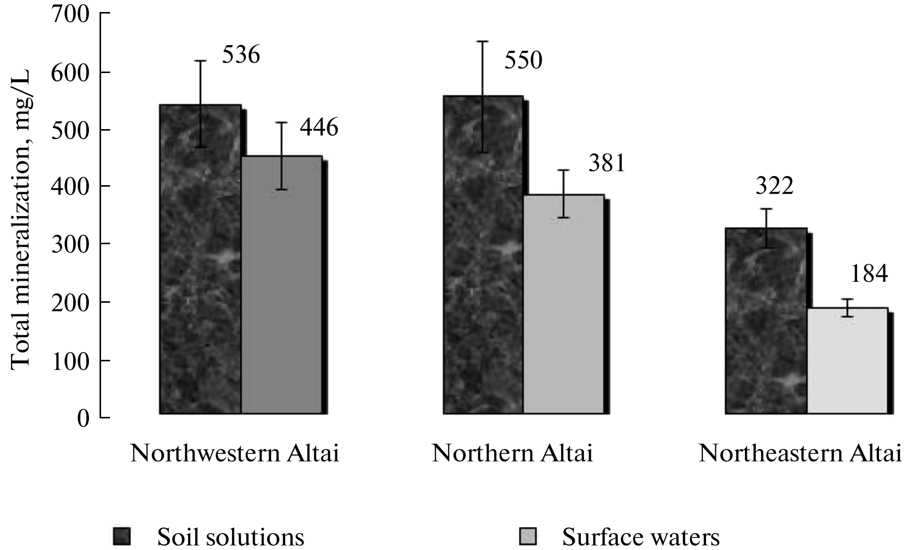

Fig. 2. Relationship between the ionic composition of surface waters and the total salt content, mg/L, of aqueous extracts from soils of accumulative landscapes in watersheds of rivers in different physiographic provinces of the Altai.

the leading factors in the formation of the ionic composition of surface waters.

This can be illustrated by the example of interaction between the total water mineralization and the sum of salts in watershed soils. For instance, the mean total concentration of water-soluble macroelements in the main types of soils of accumulative and transaccumulative landscapes in the Northern (550 ± 96 mg/kg) and Northwestern (536 ± 75 mg/kg) Altai is much higher than that in the soils of the Northeastern Altai (322 ± 34 mg/kg). Accordingly, waters of the rivers of Northeastern Altai, which drain soils lower in HCO_3^{2-}, Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, and Na^+, also show the least total mineralization (Fig. 2).

The surface waters of the examined part of the Altai show ecologically low (relative to Clarke concentrations) [10] dissolved forms of Cu, Fe, Mn, Zn, Co, and Pb (Table 2).

The concentration of dissolved Cu forms varies from 0.4 to 15.0 μg Cu/L, their maximal and minimal concentrations differing by a factor of 37; however, Cu concentration is in excess of its Clarke (7 μg Cu/L) [10] only in 15% of samples (mostly in river waters of the Northwestern Altai). For comparison, the concentration of Cu in water of the Selenga R. basin (Transbaikalia) varied from 0.7 to 9.0 μg Cu/L [11], while in the rivers of the northern East European Plain, the upper boundary of the most likely range of Cu concentration reaches 27.40 μg Cu/L [25].

The maximal concentration of Pb in surface waters of the examined Altai provinces differs from its minimal concentration by a factor of 13. In 15% of cases (mostly in rivers of the Northwestern Altai), Pb concentration is in excess of the world-averaged value of 1 μg Pb/L [10].

The concentration of Zn in Altai surface waters varies from <4 to 52 μg Zn/L, and only in 20% of samples, it exceeds its mean concentration in world rivers (20 μg Zn/L) by a factor of 1.5–2.5. For comparison, Zn concentration in water of the mouth part of the Ural R. in May 2003 reached 36 μg Zn/L [2]. In the water of the Volga Delta in 1995–2006, Zn^{2+} concentration varied from 11.7 to 13.5 μg Zn/L [29], though, according to [12], its mean concentration in Volga water in July 2005 was 25 μg Zn/L.

By Cr concentration, the examined streams in the Altai can be divided into two groups. The first group (2/3 of all samples) includes the tributaries of the lower reaches of the Katun R., which are of typically mountain character (Chemal, Edigan, Elekmonar), as well as the rivers of the Northwestern and Pre-Altai provinces and features low Cr (its concentration never exceeds the Clarke concentration of 1 μg Cr/L [10]). The second group includes the rivers of the Northeastern Altai and the basin of the Maima R. (Northern Altai) with appreciably higher Cr concentration—from 5 to 9 μg Cr/L, which corresponds to the concentration of this element in the Ob water in its middle and lower reaches [30].

The concentration of dissolved V forms in the rivers of the examined Altai provinces does not exceed the world mean (1 μg V/L) in 75% of samples, while in other 25%, its concentration varies from 2 to 5 μg/L.

Overall, the concentration of dissolved Ni in river water in the examined Altai provinces varies from 1 to 25 μg Ni/L and, in 82% of cases, it is appreciably higher than the values given in [10, 12]. Thus, in the rivers of the northern Russian Plain, Ni concentration corresponding to 50% occurrence was 2–7 μg Ni/L, its maximal values reached 13 μg/L; however, concentrations 1.3 times greater than the MAC were recorded

Table 2. Concentrations of soluble forms of microelements in surface waters of different physiographic provinces of the Altai, μg/L

Streams, water bodies	Cd	Cu	Fe	Mn	Ni	Pb	Cr
1. Northern Altai							
Range	0.03–1.1	0.3–11	130–340	1–5	1.0–25	0.3–2	0.1–9
Mean ± error of the mean	0.32 ± 0.10	2.4 ± 0.8	239 ± 17	3 ± 0.4	7 ± 2	0.8 ± 0.1	5 ± 1
Katun basin, lower part, down to the Maima mouth							
Sema R. (left tributary)	0.1	2	290	2	**25**	1	0.4
Muny R. (left tributary)	0.1	5	290	3	13	1	0.5
Chemal R. (right tributary)	0.04	1	200	1	3	0.1	0.1
Edigan R. (right tributary)	0.3	3	270	1	6	0.3	0.3
Mean ± error of the mean	0.12 ± 0.03	3 ± 0.4	256 ± 11	2 ± 0.3	**10** ± 2	0.6 ± 0.1	0.3 ± 0.04
Maima R. basin							
Maima R. (source)	0.03	0.3	190	2	1	0.3	6
Malaya Siul'ta R.	0.3	0.9	220	5	2	1	7
Biryulya R.	1.1	1.4	340	3	4	1	8
Maima R. (mouth)	1	**11**	150	5	6	2	7
Mean ± error of the mean	0.45 ± 0.12	2 ± 1	228 ± 20	4 ± 0.3	4 ± 0.7	1 ± 0.1	**7.5** ± 0.2
2. Southern part of the Northeastern Altai and the Eastern Altai, Lake Teletskoye basin							
Range	<0.01–0.1	0.4–3.0	150–310	0.6–11	1.0–20	0.1–3.0	5–7
Mean ± error of the mean	0.06 ± 0.01	1.1 ± 0.2	214 ± 13	3 ± 1	5 ± 2	0.5 ± 0.2	**7** ± 3
Kyga R. (eastern tributary)	0.1	0.8	230	1	6	0.4	7
Kokshi R. (eastern tributary)	0.1	1	230	0.7	3	0.1	7
Koldor R. (western tributary)	0.03	0.8	150	1	4	0.1	6
Chulyshman R.	<0.01	0.7	200	4	3	0.1	7
L. Teletskoye	0.07	0.9	220	4	1	0.1	5
Northwestern Altai and Pre-Altai Province							
Range	0.04–2	2–15	2–60	1–9	2–16	0.5–4	0.1–3
Mean ± error of the mean	**0.58** ± 0.17	**7** ± 1.3	24 ± 6	2.5 ± 1	7.2 ± 1.6	**1.4** ± 0.4	0.8 ± 0.4
Charysh R. (upper reaches)	0.3	3	7	1	3	0.5	0.1
Maralikha R.	0.5	2	19	9	12	**2**	0.8
Inya R.	0.3	11	60	1	5	0.5	0.2
Charysh R. (mouth)	0.9	15	35	3	16	1	0.1
Alei R. (upper part)	0.6	5	25	2	6	1	3
Alei R. (near mouth)	**2**	**9**	40	2	10	**3**	0.1
MAC_{wm} [5]	1	1000	300	100	20	10	50

in some years [25]. According to the authors' results, Ni concentration in the Sema R. (25 μg Ni/L) exceeds MAC_{wm} (20 μg Ni/L) and that in the Isha R. approaches this value (20 μg Ni/L).

The concentration of dissolved forms of Fe and Mn in the rivers of the examined Altai area does not exceed the world-averaged values (670 μg Fe/L and 10 μg Mn/L [10]). Fe concentration varies from 2 to 580 μg/L, and that of Mn—from 1 to 11 μg/L. Note that the Ob water at the mouths of its tributaries shows an appreciably higher concentration of those microelements [30]. Thus, at the Ket R. inflow, Fe content of water reaches 1742 μg/L and that of Mn reaches 19.5 μg Mn/L; at the Vakh R. mouth, we have 1468 μg Fe/L and 10.1 μg Mn/L; and in IrtyshR. water, 863 μg Fe/L and 19.5 μg Mn/L [30]. The mean concentration of dissolved Mn in Volga delta water in July 2005 was 31 μg Mn/L [12], which is higher than the maximal values in water of Ob basin rivers, whereas the mean concentration of Fe (293 μg Fe/L) was comparable with its concentration in water of Altai rivers.

Water-soluble Cd in rivers of Altai provinces occurs in amounts often in excess of the world mean for surface waters (0.2 μg Cd/L). In 41% of samples, its concentration is in excess of 0.3 μg Cd/L [10], and in 15% of samples, it varies from 0.6 to 2 μg Cd/L. The large proportion of water samples with Cd concentration in excess of the world mean may be due to its biogeochemical properties: Cd belongs to the group of elements ranking second in terms of the rate of involvement in water migration with K_i = 10.63 (according to V.V. Dobrovol'sky). For comparison, Cd concentration in Ural R. water (at its inflow into the Caspian Sea) in winter does not exceed the standard value; its mean value over 1994–2004 averaged 0.75 μg Cd/L, though Cd concentration in spring flood water can reach 2.4 μg Cd/L [2].

Note that the concentration of dissolved forms of microelements in the rivers of the Western Altai and Pre-Altai provinces are higher than in other examined provinces: the concentrations of Cu and Ni in river water in the province reaches 16 (Charysh R.); Pb reaches 4 (Sosnovka R.), V reaches 5, and Cd reaches 0.6–2.0 μg/L (Alei R.). These rivers have mostly rain nourishment; therefore, microelements here are more intensely leached from soils [15].

One more cause for the rivers of the Northwestern Altai (which have the majority of their drainage areas in low-mountain steppe and forest–steppe landscapes), as well as the Alei R. (its drainage basin consists mostly of plain steppe landscapes) to show higher concentration of dissolved metal forms is the higher water mineralization. Under the condition of higher mineralization, the distribution of metals in water depends on complex formation, rather than sorption processes. The formation of strong (mostly chloride) complex compounds of metals with mineral component of waters keeps metals in water mass and intensifies the processes of their desorption from the surface of particles in suspension and bottom sediments [14, 17, 31]. Therefore, in waters of rivers in the Northwestern Altai and Piedmont Province with higher total concentrations of mineral salts (on the average, 409 ± 67, Cv= 51%), the concentration of dissolved metals, except for Fe and Cr, was appreciably higher than that in the rivers of Northeastern Altai with low total water mineralization. The more mineralized surface waters of the rivers of Charysh with tributaries and Alei show much lesser concentration of dissolved Fe (on the average, 42 μg/L) compared with the surface waters of the Northern and Northeastern Altai, where mean Fe concentrations reach 238 ± 17 (Cv = 25%) and 222 ± 14 μg Fe/L (Cv = 21%), respectively.

With the total concentration of major macroions in river water in the examined Altai provinces up to 0.2 mg/L, the concentration of dissolved Fe was found to vary from 60 to 230 μg/L (mostly in the rivers of the southern Northeastern Altai). At the concentrations of major salts from 0.2 to 0.5 mg/L, Fe concentration varies from 19 to 340 μg Fe/L; and, when the total water mineralization exceeds 0.5 mg/L, the concentration of dissolved Fe in the Altai surface water drops to 2–290 (on the average, 88 ± 54) μg/L.

A reverse dependence of dissolved Fe concentration on the total water mineralization was also mentioned by other authors. Thus, studies in the middle and northern parts of the Gulf of Ob [23] showed that brackish waters feature a process of the transfer of Fe compounds from water into dissolved forms. With the total water mineralization of up to 1 mg/L, the concentration of dissolved Fe in water in Gulf of Ob in summer 2010 averaged 78.04 μg/L; at the mineralization of 1 to 10 g/L, it averaged 85.36 μg Fe/L; and at mineralization from 10 to 20 g/L, 25.32 μg Fe/L. The losses of dissolved Fe in the zone of mixing of fresh and salt water is the consequence of coagulation, taking place at an increase in water mineralization [23] with the formation and subsequent precipitation of floccules of oxihydrates and organic compounds of Fe [6].

The biogeochemical situation in the drainage basins of rivers in steppe landscapes facilitates Fe and Mn transfer into low-solubility compounds. Under oxidation conditions and in alkaline environment, those metals are known to occur mostly in a low-solubility form, the major portion of them being transported in suspension. Therefore, at low concentration of dissolved forms of Fe and Mn, the concentrations of their suspended forms in waters of the Northwestern and Pre-Altai provinces are higher, and those in Alei R. water are maximal (9250 μg Fe/L and 590 μg Mn/L).

Higher concentrations of dissolved forms of Fe and Mn were observed in surface waters in the northwestern part of the Northeastern Altai. Water of the Isha R. shows the concentrations of water-soluble Fe reaching 580 μg Fe/L, and that of Mn of 11 μg Mn/L. The rivers of this province drain landscapes of black taiga with acid soils, which are overmoistened in some places, or swampy dark-gray forest soils under manganese-loving vegetation, where the conditions for formation of migrating forms of Fe and Mn are optimal [10, 15]. Thus, the concentration of dissolved Fe in waters of the rivers examined by the authors in Altai provinces is determined by the landscape structure of the drainage area; it increases from the rivers draining mostly steppe landscapes of accumulative and piedmont plains with grassland steppes with southern and common black earth (Alei R., 30 ± 3 μg Fe/L), as well as from rivers of steppe and forest-steppe medium- and low-mountain landscapes (Charysh R. and its tributaries 49 ± 22 μg Fe/L) to rivers in predominantly high-, medium-, and low-mountain landscapes with light and dark coniferous mixed forests on dark gray forest soils (Maima R. and its tributaries, 228 ± 20 μg Fe/L), mountain–taiga cedar–fir (rivers of Lake Teletskoye basin, 214 ± 13 μg Fe/L), cedar–larch forests (the lower reaches of Katun R. and its tributaries, 256 ± 11 μg Fe/L) on mountain–taiga and mountain–forest brown soils, as well as black taiga (Isha R. and its tributaries, 435 ± 59 μg Fe/L) on dark gray and sod-podzol soils.

The concentrations of dissolved metal forms in river waters of the Northern Altai Province varies most significantly (Table 2) on watersheds with various nourishment character and landscape–geochemical conditions. However, it can be noted that the water of Maima R. tributaries, which are mostly of flat character (the rivers of Imerya and Ulala) show the concentrations of dissolved forms of Cd, Cu, Cr, as well as Mn and Pb appreciably higher than those in waters of typical mountain rivers (Chemal, Edigan, Elikmonar).

The concentrations of water-soluble forms of metals in Altai surface waters do not exceed the sanitary–hygienic (relative to MAC_{wm}) characteristics. An exception is Alei R. (Northwestern Altai), which mostly drains agricultural and mountain–mining landscapes. The concentration of dissolved forms of Cd in its water (2 μg/L) is twice as large as MAC_{wm}. This is due to the anthropogenic pollution of landscape components in river basin—the application to agricultural lands of phosphorus fertilizers, containing Cd as an admixture, as well as the entry into the environment of toxic material containing heavy metals from the surface of tailings of the Altai MPC (on the left bank of a tributary of Alei R.) [21].

Mobile forms of metals also enter the environment when a watershed experiences anthropogenic impact. Therefore, the dependence of the concentration of technophilic Cd in surface waters in the examined Altai provinces on its concentration in the soils of transaccumulative watersheds was most considerable. Thus, the highest concentration (0.58 ± 0.17 μg/L) of water-soluble Cd in river waters of the the Northwestern Altai corresponds to its highest concentration (1.85 ± 0.51 μg/kg) in the soils (Fig. 3) that experience heavier anthropogenic load. The hydrochemical runoff from the Northern Altai watersheds, where soils are polluted by previously applied Cd-containing phosphorus fertilizers, is an additional source of this element for surface waters of the province. The least concentration of soluble Cd was recorded in aqueous extracts from the soils and in waters of the Northeastern Altai (1.30 ± 0.31, 0.06 ± 0.01 μg/kg soil, respectively).

River waters of the Northeastern Altai, which mostly drain medium-mountain–forest landscapes with cedar–fir forests on mountain–taiga and mountain–forest brown soils, shows the following series of the ratios of dissolved forms of metals to their total concentrations: Cr > Zn ⩾ Co > Fe > Ni > V > Mn > Cd > Cu > Pb. In rivers of this province, the dissolved Zn and Cr account for more than 80% of their total concentrations, Co, Fe, and Ni, for more than 60%. For comparison, in water of Amur R., which mostly drains landscapes of mixed forests, Zn also migrates mostly in the form of dissolved compounds [28], though, according to estimates in [27], Cu is more soluble in waters of Primor'e, its concentration (as well as those of Br and I) exceeds 90%. In rivers of the Northeastern Altai, Cd is mostly transported as a component of suspension, as also was the case with the majority of examined waters of the Ob in its middle and lower reaches [30].

The distribution of metals is radically different in the water–suspension system in rivers of Northwestern Altai and Pre-Altai Province. The best soluble here are Cd (on the average, $64 \pm 4\%$ of soluble forms in the total concentration) and V ($57 \pm 7\%$), whereas Co, Fe, Cr, and Mn migrate in the rivers of those provinces mostly as components of suspension, the share of their soluble forms in the total concentration in water never exceeds 30%. The ratio of soluble to suspended forms of Cu and Pb in waters of those provinces is often 1 : 1. The distribution of Zn and Ni in the abiotic components of rivers in the Northwestern Altai is ambiguous, though the share of soluble forms of those microelements in their total concentration is more than 50%. For comparison, in Ural R. water near its inflow into the Caspian Sea, up to 75% of the total Cd concentration also occurs in dissolved form, while the dissolved forms of Zn and Ni account for not more than half of their total concentrations [2]. Waters of Ob River in its middle and lower reaches transports Co mostly as a component of suspension, while Ni (as well as in the Altai rivers, studied by the authors), along with Cu and Cr, migrate mostly in the dissolved form [30].

The mass ratios of soluble compounds and solid suspensions in river runoff is believed to depend on the character of terrestrial vegetation—the more widespread on the watershed are stable forest phytocenoses, preventing mechanical erosion of soil, the lesser is the amount of suspension exported with surface and subsurface runoff [10]. Indeed, IN waters of the rivers of the Northeastern province, which watersheds feature greater abundance of forest landscapes, the total concentration of suspended matter (turbidity) is appreciably less (from 1.2 to 18 mg/L) than those in the rivers of the Northern (3.6–130 mg/L) and Northwestern Altai and Pre-Altai Province (1.4–500 mg/L) (Fig. 4).

The concentration of microelements in suspensions in the rivers of examined Altai provinces varies widely (Table 3), obeying mostly lognormal distribution. Variations in the concentrations are maximal for Zn (200 times) and Cd (100 times) and minimal for Fe (6 times), and V (8 times).

The concentrations of Cd, Cu, Pb, and Ni (the geometric mean) in suspended matter in the Altai rivers (mg/kg), according to the authors' results, was much higher than the world average [22] (Table 3). Note that the excess for Cd, Cu, and Pb was recorded in 82, 79, and 60% cases, respectively.

The suspended matter in rivers is not mechanically crushed rock material, but the result of its transformation [10], a measure of which can be taken to be the ratio of the mean concentration of an element in river suspension to its Clarke in continental Earth crust (K_r). Some researchers believe [22] that the concentration of microelements in river suspensions corresponds to their concentrations in clays and clay shales and only

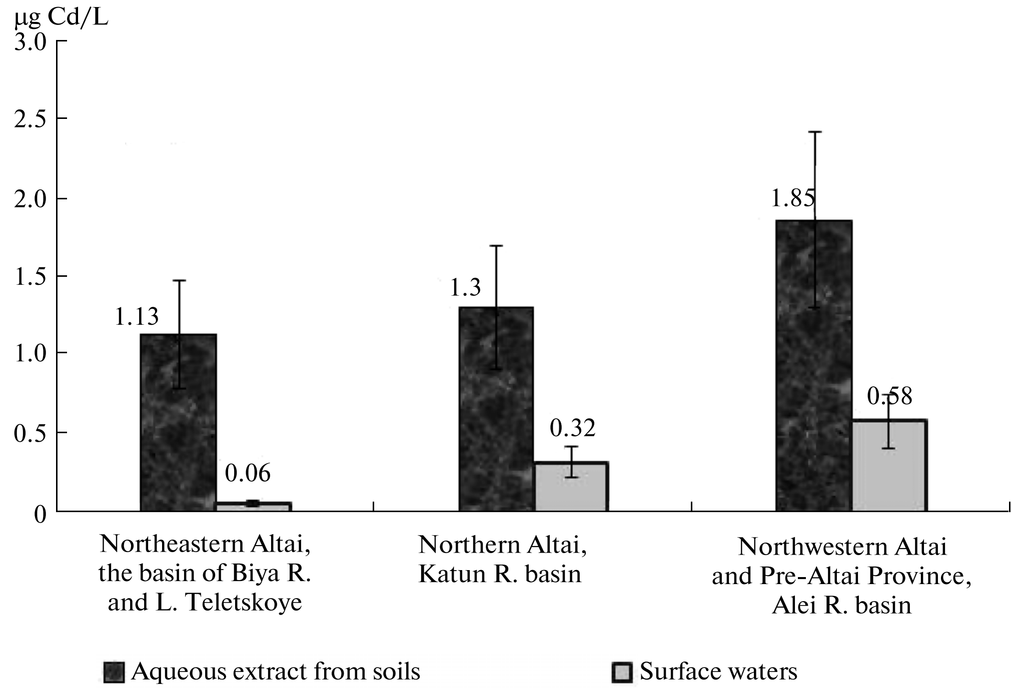

Fig. 3. Mean concentration of soluble cadmium in surface waters and soils in different physiographic provinces of the Altai.

slightly differs from their concentrations in soils and in the upper part of the continental crust [22]. However, according to [10], heavy metals show an intense increase in the concentrations in suspension relative to Clarke concentrations.

The largest excess of the Clarke concentration was recorded for Cd. The excess for Cu, Ni, Pb, and Zn varies within 10–20; and that for Cr and Co, within 2–4. The concentrations of Fe and Mn in suspensions in the rivers of the examined Altai provinces is in general agreement with their concentration in the Earth crust (Table 4).

The suspended matter in the Northern Altai rivers show higher concentrations of Cd and Zn; Cu is more abundant in that in the Northwestern Altai and Pre-Altai Province, and Fe, Ni, and Pb, in rivers of the Northeastern Altai. The suspensions of the rivers in the examined Altai provinces are very similar in terms of Cr content (Table 4; Fig. 4a).

The examined water bodies and streams in Altai provinces show an inverse relationship between the

Table 3. Variation–statistical parameters of metal concentrations in suspended matter in the Altai rivers in June 2007, mg/kg ($n = 33$; Lim is variation limits; $X_m \pm x$ is the arithmetic mean and its error; X_{geom} is geometric mean; n.d. means no data available)

Element	Lim	$X_m \pm x$	Cv	X_{geom}	Suspensions in world rivers [22]
Cadmium	0.7–79.2	**21.1** ± 3.2	89	14.1	3.2
Chromium	14–189	**108** ± 7	40	108	n.d.
Cobalt	3.1–27.4	**17.5** ± 1.0	33	18.3	n.d.
Copper	45.3–1016	**345** ± 45	76	310	98
Iron	18001–76829	**31140** ± 2240	42	31695	77900
Manganese	53–2693	**710** ± 99	81	532	1650
Nickel	66–1698	**509** ± 75	86	444	76
Lead	14–467	**193** ± 23	69	160	3.2
Zinc	6.6–1395	**535** ± 93	102	287	343
Vanadium	44.7–138	**80** ± 4	28	83.5	n.d.

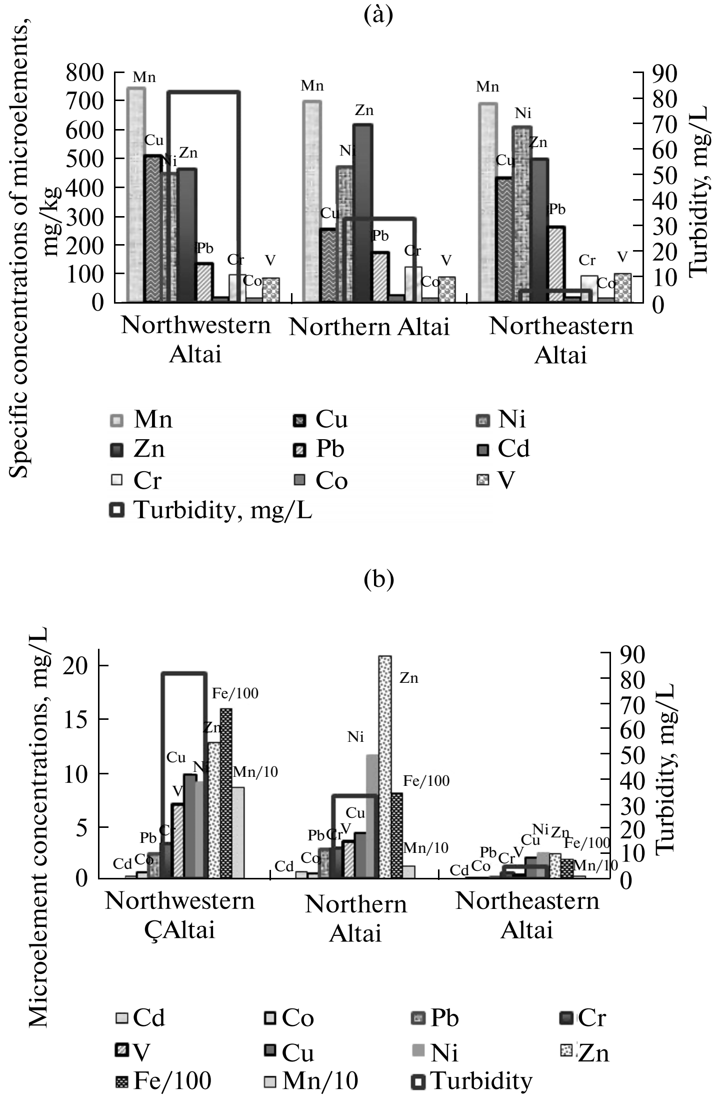

Fig. 4. Qualitative and quantitative characteristics of the concentrations of suspended forms of metals in surface waters of different physiographic provinces of the Altai: (a) metal concentrations in suspended matter of Altai rivers, mg/kg; (b) concentration of suspended form of metals in surface waters of Altai rivers, μg/L.

amount of suspension in the water body and its qualitative characteristic (the specific concentration of metals): a decrease in the total concentration of suspension in water is accompanied by an increase in the proportion of fine fractions with greater area of actively adsorbing surface, leading to an increase in its saturation with metals. The coefficients of correlation between water turbidity and metal concentrations in suspension for Northern Altai rivers are 0.78 for Cr, 0.78 for Cu, 0.68 for Pb, and 0.58 for Fe; the same coefficients for Northeastern Altai rivers are 0.60 for Cd, 0.66 for Cu, and 0.70 for Pb; and those for the rivers of the Northwestern Altai and Pre-Altai Province are 0.64 for Co and 0.63 for Cr (with a significance level of 5%) [13].

The coefficient K_r for the material of suspended matter as compared with the Earth crust was calculated with the use of Clarke concentrations according to A.A. Beus [3]. By the values of K_r, for groups of elements can be identified in the suspensions in Altai rivers: (1) those with K_r values close to 1 (Fe, Mn, V); (2) those with concentrations in river suspensions 2–4 times greater than the respective Clarke (Cr and Co); (3) those with K_r varying from 11 to 32 (Cu, Zn, Pb, and Ni); (4) those with concentrations in river suspension more than 100 times greater than their Clarke (Cd).

The export of considerable masses of heavy metals fixed on disperse weathering products is a mechanism of preservation of terrestrial living matter from excessive masses of such elements [10]. With the concentra-

Table 4. Arithmetic mean ± error of the mean for microelement concentrations in suspensions of rivers in different physiographic provinces of the Altai, mg/kg (above the line), and the ratio of the mean concentration of the element in suspension to its Clarke in the Earth crust (K_r, below the line) (according to A.A. Beus [3])

Cd	Cr	Co	Cu	Fe	Ìn	Ni	Pb	Zn	V
Northern Altai									
27.0 ± 5.4	125 ± 12	17.6 ± 1.3	256 ± 42	34 492 ± 4222	700 ± 200	472 ± 284	175 ± 32	**620** ± 170	92 ± 6
169	3.7	2.4	12	1	1	18	11	12	1
Northeastern Altai									
17.2 ± 3.2	93 ± 11	17.3 ± 1.4	435 ± 73	**39 510** ± 7979	692 ± 143	**609** ± 216	**262** ± 39	499 ± 136	101 ± 26
108	2.9	2.4	20	1	1	23	16	10	1
Northwestern Altai									
18.3 ± 7.6	99 ± 16	17.3 ± 3.5	**511** ± 195	25 195 ± 2174	747 ± 156	447 ± 141	137 ± 53	465 ± 180	85 ± 15
115	2.7	2.4	23	0.7	1	17	9	9	1

tion of dissolved Cd forms (and element of the 1st hazard class) in Altai rivers in excess of its MAC, the highest K_r values may be a manifestation of this mechanism and a sign of the process of removal of excessive concentration of the metal from biological turnover. The same can be said about Fe in water of the Northeastern Altai—the high concentration of its soluble forms in the soils and soil solutions in this province is compensated for by the transition of Fe in river water into an insoluble state (Table 4).

The territorial differences between the examined Altai provinces in terms of surface water chemistry are more pronounced in terms of the quantitative characteristics of the concentrations of insoluble metals in water (in μg/L), rather than in terms of the qualitative characteristic of river suspensions (by the specific concentration of metals in 1 mg/kg) (Fig. 4). The concentrations of suspended forms of metals in the rivers of the Northeastern Altai are appreciably less than that in the rivers of the Northwestern and Northern Altai. The waters of the rivers of the Northwestern and Pre-Altai provinces show on the average appreciably higher total concentration of suspension and insoluble forms of Fe (up to 9250 μg Fe/L), Mn (up to 590 μg Mn/L), Cu (up to 26 μg Cu/L), and V (up to 49 μg V/L); while the rivers of the Northern Altai, those of Zn (up to 114 μg Zn/L) and Ni (up to 35 μg Ni/L).

For comparison, in waters of the Ob basin (in its middle and lower reaches), the concentration of suspended form of Fe never exceeds 2039 μg Fe/L; that of Mn, 89.6 μg Mn/L; the concentrations of Cu and Zn, according to [30], is an order of magnitude less than those in the waters of the examined Altai rivers.

The situations when both characteristics of the suspended form of the metal—the quantitative (μg/L) and the qualitative (mg/kg)—suggest its higher concentration, were observed for Cd in the rivers of most agriculturally developed areas: the Alei (Northwestern Altai), Maima, Biryulya, Imerya (Northern Altai). In the same rivers, the concentrations of soluble forms of Cd were also the highest (from 0.7 to 2 μg/L).

The comparison of the chemistry of river suspensions in different hydrological periods suggests that the concentrations of metals in suspended matter is much greater in summer than during spring flood (Fig. 5). The point is that the fine fraction, which dominates in the suspended matter during summer low-water period, is more saturated with heavy metals because of its greater sorption capacity. During the floods, the physical processes in water mass dominate over the biogeochemical ones; therefore, aggregates that are much coarser, though less saturated with chemical elements, are involved in water migration. In this case, the amount of suspension in water flow due to the presence of coarse particles increases several times, but the concentration of microelements in it is not high in this period.

CONCLUSIONS

The total mineralization of surface waters in the examined provinces of the Altai does not exceed 700 (with an average of 352) mg/L, increasing from high-mountain rivers, which have snow–glacial nourishment, to low-mountain rivers, which mostly have rain nourishment.

The concentrations of dissolved forms of microelements in the Altai rivers do not exceed the MAC_{wm} (except for Cd in the rivers of Alei and Biryulya and Ni in Sema R.), and, generally, only 20% of water samples show them to be in excess of the world averages, while the concentrations of metals in suspended matter in the Altai rivers is higher than their Clarke concentrations in soils and mean concentrations in world rivers.

With an increase in the total water mineralization, the concentration of dissolved forms of the majority of microelements (except for Fe) in the Altai rivers also increases.

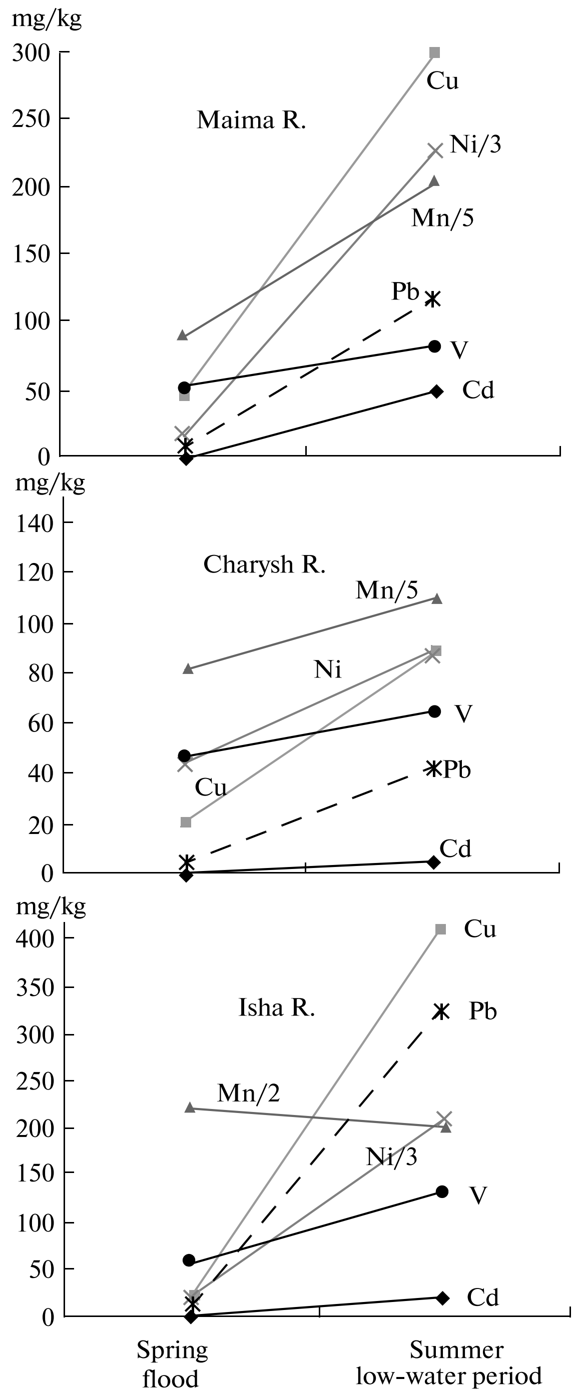

Fig. 5. Metal concentrations in suspended matter in rivers of different provinces of the Altai.

The differences between surface water chemistry in different Altai provinces are more pronounced for dissolved typomorphic elements (Fe, Mn, Ca), reflecting the contrast of biogeochemical conditions on watersheds.

The effect of landscape–geochemical conditions on the surface water chemistry in physiographic provinces of the Altai in summer is most distinct (1) for macrocomponents; (2) for dissolved forms of typomorphic chemical elements (Fe, Mn); (3) under anthropogenic impact on the watershed.

A decrease in the turbidity of the Altai surface waters is accompanied by an increase in the specific concentration of metals in suspension (mg/kg); low concentration of suspended form of metals (μg/L) is typical of waters with low turbidity.

The concentration of insoluble forms of metals in river waters in different Altai provinces (in μg/L—a quantitative characteristic) is more differentiated than the concentration of elements in suspension (in mg/kg—a qualitative characteristic of suspended matter of rivers).

Compared with the period of spring flood, the concentration of metals in suspended matter during summer low-water period is appreciably higher due to the predominance of fine fractions with large sorption capacity in the suspension in summer.

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