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Metals in the River Waters of Primorye

V. M. Shulkin[a], N. N. Bogdanov[a], and V. I. Kiselev[b]

[a] *Pacific Institute of Geography, Far East Division, Russian Academy of Sciences, ul. Radio 7, Vladivostok, 690041 Russia*
e-mail: shulkin@tig.dvo.ru

[b] *Far East Geological Institute, Far East Division, Russian Academy of Sciences, pr. Stoletiya Vladivostoka 159, Vladivostok, 690022 Russia*

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Abstract—New data are presented on the contents of Fe, Mn, Zn, Cu, Pb, Cd, and Ni in dissolved and particulate modes of occurrence in unpolluted or anthropogenically contaminated major rivers of Primorye. The background contents of dissolved metals are as follows: 0.1–0.5 μg/l for Zn and Ni, 0.3–0.7 μg/l for Cu, 0.01–0.04 μg/l for Pb and Cd, and 2–20 μg/l for Fe and Mn. Common anthropogenic loading (communal wastewaters) notably increases the dissolved Fe and Mn concentrations Industrial wastes lead to a local increase in the contents of dissolved metals in river waters by one to three orders of magnitude. The effect of hydrological regime is expressed most clearly in the areas of anthropogenic impact. The metal contents in the particulate matter are controlled mainly by its granulometric composition.

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INTRODUCTION

The chemical composition of river waters reflect the common natural–climatic features of a given region (the amount of atmospheric precipitates, temperature regime, and the type of vegetation) and certain conditions in its drainage system (rock composition, geomorphology, and the character of vegetation). In addition, river waters are affected by active (water consumption) and passive (wastewater disposal) anthropogenic loading, and their chemical, including trace-element, composition can serve as a good integral indicator of the effect of anthropogenic activity on the landscape.

The level of metal concentrations in rivers attracts attention because of the increasing anthropogenic effect and the possible toxicity of high contents of some metals for hydrobionts. The metal content in consumable waters is standardized in the form of maximum permissible concentrations (MPC) [1]. The quality of water for the needs of fish breeding and fishing is standardized in the form of the contents of dissolved metal species, and that for industrial and domestic waters, in the form of total contents of all modes of occurrence of a metal. In addition, metals can be used as tracers of many biogeochemical and migration processes. However, the accurate quantification of dissolved metal species, which is typically equal to about 10^{-9} g/l in natural waters, continues to remain a serious chemical–analytical problem. At present, the main errors are related to sampling and preliminary treatment of water samples [2–4]. Therefore, in spite of significant efforts and certain success, much data on the content of dissolved species of such metals as Zn, Cd, Pb, and Mn in river waters, including rivers in Primorye, remain controversial [5, 6]. It should be noted that the problem of the precise determination of metal content in the river waters is also acute in other countries [3, 7].

This paper is aimed at (1) the characterization of metal contents (Fe, Mn, Zn, Cu, Pb, Cd, and Ni) in river water and particulate matter from typical rivers in Primorye based on the results recently obtained by modern techniques preventing pollution during sampling and preparation; (2) the analysis of water flows in Primorye affected by diverse anthropogenic impact to estimate the degree and character of anthropogenic effect on trace element composition of river waters; and (3) the assessment of the possible effect of hydrological regime on the metal contents in the river water and particulate matter.

MATERIALS AND METHODS

The samples were collected during the ice-free period in 2002–2004 in Primorye rivers variably affected by anthropogenic loading, including the major rivers of the region: Tumannaya, Razdol'naya, and Ussuri (Fig. 1). The town of Ussuriisk, the second largest urban area in Primorye, is located in the middle reaches of the Razdol'naya River. It should be noted that 30% of the Razdol'naya River run-off is from the People's Republic of China. To reveal the role of seasonal factors, the Razdol'naya River was sampled three times in different hydrological regimes: from summer low water with a debit of 22.5 m^3/s to high water with a debit of 123 m^3/s, at an average long-standing river debit of 70.9 m^3/s [8]. As an example of water flow strongly polluted by industrial discharge, we studied

Fig. 1. Schematic map of the study area and the sampling sites of water and particulate matter.

the Vtoraya Rechka river, draining one district of Vladivostok. As background contents, we used the data on small rivers of southwestern Primorye, which drain thinly populated forested mountainous drainage systems.

Samples were taken and filtered in situ using a MasterFlex™ pump and an AquaPrep600™ filter with pore size 0.45 μm. The filtrates were acidified with HNO_3 to pH 2 and isolated from dust by a double plastic cover. Nonfiltered samples were simultaneously taken to extract suspension.

In the laboratory, particulate matter was extracted by filtration through preliminarily weighted Nucleopor filters with a pore size of 0.45 μm. When the amount of particulate matter was determined, the filters with it were decomposed by a $HF–HClO_4$ mixture to deter-

Table 1. Results of the analysis of bottom sediment standard BCSS-1. Fe in %; other metals, in µg/g; *n* is the number of determination

	Fe	Cd	Pb	Zn	Cu	Ni	Mn
Certificate	3.29 ± 0.1	0.25 ± 0.04	22.7 ± 3.4	119 ± 12	18.5 ± 2.7	55.3 ± 3.6	229 ± 15
Actual, *n* = 5	3.17 ± 0.15	0.24 ± 0.02	24.1 ± 2.1	97 ± 8	17.3 ± 1.5	53.8 ± 2.0	212 ± 12

Table 2. Content of dissolved metals (µg/l) in the river waters of Primorye and in some other rivers with a different level of anthropogenic loading

River	*N*	Fe	Mn	Zn	Cu	Pb	Cd	Ni
Tumannaya R.*	6	75.3 / 29–124	115 / 46–246	1.14 / 0.05–1.76	1.82 / 1.42–2.33	0.14 / 0.03–0.40	0.030 / 0.004–0.084	0.73 / 0.6–0.9
Background**	6	11.5 / 8.21	5.6 / 2.0–11.5	0.21 / 0.11–0.39	0.44 / 0.28–0.68	0.037 / 0.02–0.07	0.025 / 0.015–0.04	0.14 / 0.02–0.48
Razdol'naya R.*	12	23.7 / 3.7–48.5	14.9 / 8.2–26.8	0.36 / 0.08–0.90	1.27 / 0.76–1.44	0.02 / 0.01–0.07	0.012 / 0.003–0.03	0.8 / 0.6–0.9
Rivers of the Ussuri Basin***	20	59.6 / 5.4–242	19.7 / 2.1–80.5	0.22 / 0.02–0.83	1.05 / 0.67–1.42	0.03 / 0.01–0.07	0.005 / 0.002–0.009	0.61 / 0.37–1.5
Vtoraya Rechka R.	4	41.0 / 2.3–146	27.3 / 0.3–88.1	3.6 / 0.6–10.1	2.2 / 0.4–3.8	0.019 / 0.01–0.03	1.13 / 0.03–3.17	2.23 / 0.3–4.97
Lena R. [10]		36	–	0.35	0.60	0.083	0.005	0.27
Delaware R. [12]		–	–	11.8	2.33	0.27	0.17	4.29

Note: * Lower reaches.
** Rivers of the southwestern Primorye.
*** Including the Khanka Lake Basin.
N is the number of samples, numerator is the average value, denominator is the range, (–) data are absent.

mine the metal contents by atomic absorption spectrophotometry (AAS). The dissolved metals were concentrated by extracting in a DDTK–Na–$CHCl_3$ system [9]. The extent of extraction of the dissolved ionic species of these metals by this technique was repeatedly examined experimentally by the "input–found" method and accounted for 85–95%. The $CHCl_3$ extracts were decomposed by heating and dissolved in 2% HNO_3, in which metal contents were determined by AAS on a Shimadzu 6800 analyzer (Fe, Mn, Zn, Cu, and Ni) equipped with a flame ionization detector and on a Shimidazu 6800G analyzer using furnace atomization (Pb and Cd).

The accuracy of metal content measurements in particulate matter was controlled by blanks and systematic analyses of the BCSS-1 standard decomposed in the same manner as the particulate matter was (Table 1). The determination of Pb and Cd contents by furnace atomization was additionally controlled by methods of standard additions, whose precision was no worse than 80–85%. In addition, to test the measurement accuracy of dissolved metal species, parallel aliquots of some oxidized filtrates were analyzed by ICP-MS on an Agilent apparatus. Unfortunately, the sensitivity of IP-MS was insufficient to determine reliably the contents of dissolved Pb, Cd, and Fe species, but data on Mn, Zn, Cu, and Ni show satisfactory agreement between AAS after concentration and ICP-MS analyses.

RESULTS AND DISCUSSION

Data on the concentration of dissolved metals in river waters of Primorye in summer to autumn from 2000 to 2004, as well as in some other rivers, are shown in Table 2. In spite of the broad scatter of these data, the level of dissolved metal concentrations in weakly polluted mainly mountainous rivers of southwestern Primorye was determined as follows: 0.1–0.5 µg/l for Zn and Ni, 0.3–0.7 µg/l for Cu, 0.01–0.04 µg/l for Pb and Cd, and 2–20 µg/l for Fe and Mn. In the larger Ussuri and Razdol'naya plain rivers, which drain economically developed areas but are unaffected by strong and

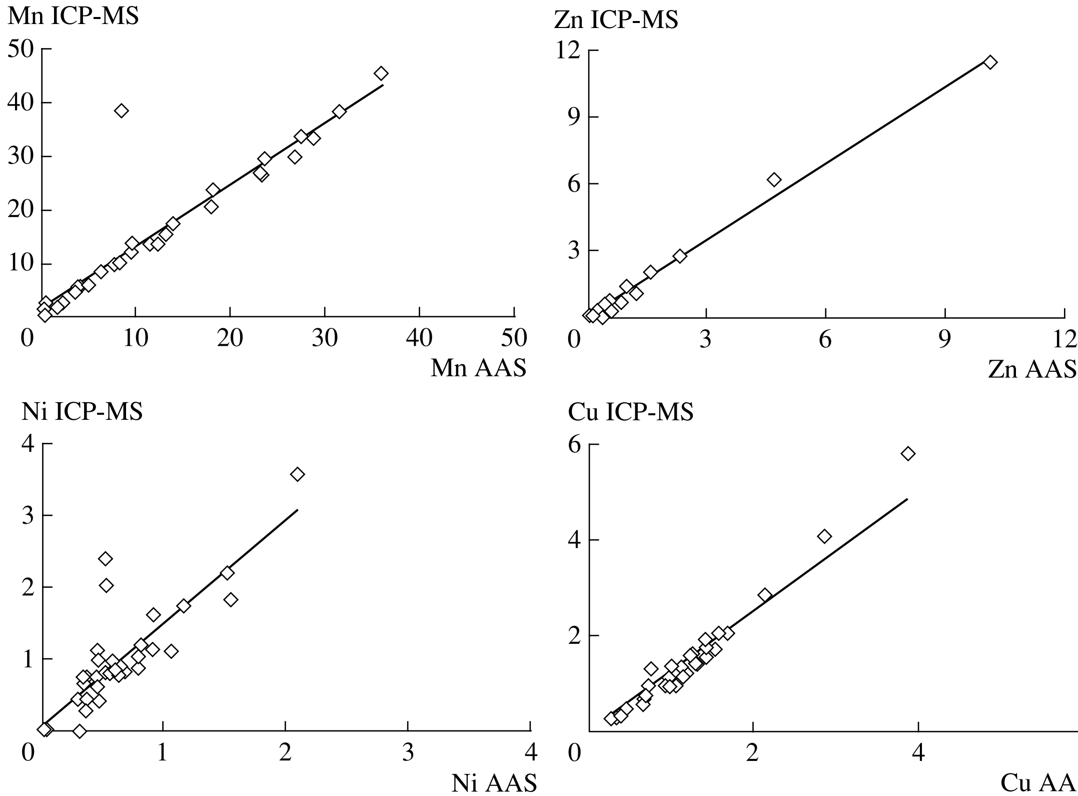

Fig. 2. Content of dissolved metals (μg/l) in river waters of Primorye by ICP-MS without preliminary concentration (*x* axis) and by the AAS method (*y* axis).

specific industrial impact, the concentrations of dissolved Zn, Pb, and Cd show no significant variations beyond the direct influence of anthropogenic wastes, though the Cu and Ni contents show a double increase, while the concentrations of Fe and Mn increase by factors of 5–7. This is consistent with data reported for such rivers as Lena [10] or Mississippi [11]. The Tumannaya River can be ascribed to the same group, but its Zn, Pb, and Cu contents are higher by factors of 2–5, while the average Mn content is 20 times lower than in the background rivers and 10 times lower than in the Ussuri River (Table 2). Since pollution in the drainage system of the Tumannaya River in the People's Republic of China is one order of magnitude higher than that in Russian Primorye, the increase in the contents of dissolved metals is probably related to the general increase in the anthropogenic loading.

The most distinct relations between hydrological regime and chemical composition were detected for basic ions and total mineralization, which is proportional to an easily and reliably measurable parameter: the water conductance (electrical conductance). An increase in the water amount of a river is accompanied by a decrease in the water mineralization and conductance (Fig. 3a). The salinity of waters of the Razdol'naya River increases in the area of the strongest anthropogenic impact at the town of Ussuriisk. The lower the total debit of the river, the higher the anthropogenic loading (Fig. 3a).

No unambiguous relations exist between the contents of dissolved metals and the hydrological regime in the upper and lower reaches of the Razdol'naya River, in areas with relatively low anthropogenic loading (Figs. 3b, 3c, 3d, 3f). However, in the middle reaches of the river, the influence of the run-off from the town of Ussuriisk (R5) distinctly depends on the hydrological regime: at a low water debit in the river, the anthropogenic increase in the contents of dissolved Zn and Mn in the Razdol'naya River is more significant (Figs. 3b, 3c). This correlation is absent for dissolved Pb, Cu, and Cd (Figs. 3d, 3e, 3f), which suggests that the flux of the dissolved metals with run-off from the town of Ussuriisk is insignificant. However, the contents of dissolved Cd, and especially, Pb increase in the upper reaches of the river, which is especially notable at a low water debit (Fig. 3e). In the absence of known pollution sources upstream of the town of Ussuriisk, an additional flux of dissolved Pb can be introduced from the territory of the People's Republic of China. An additional flux of Cd is presumably caused by Russian sources, because the maximum concentrations are distant from the boundary (Fig. 3f).

The concentration levels of dissolved metals in the water flows receiving industrial wastes is controlled by

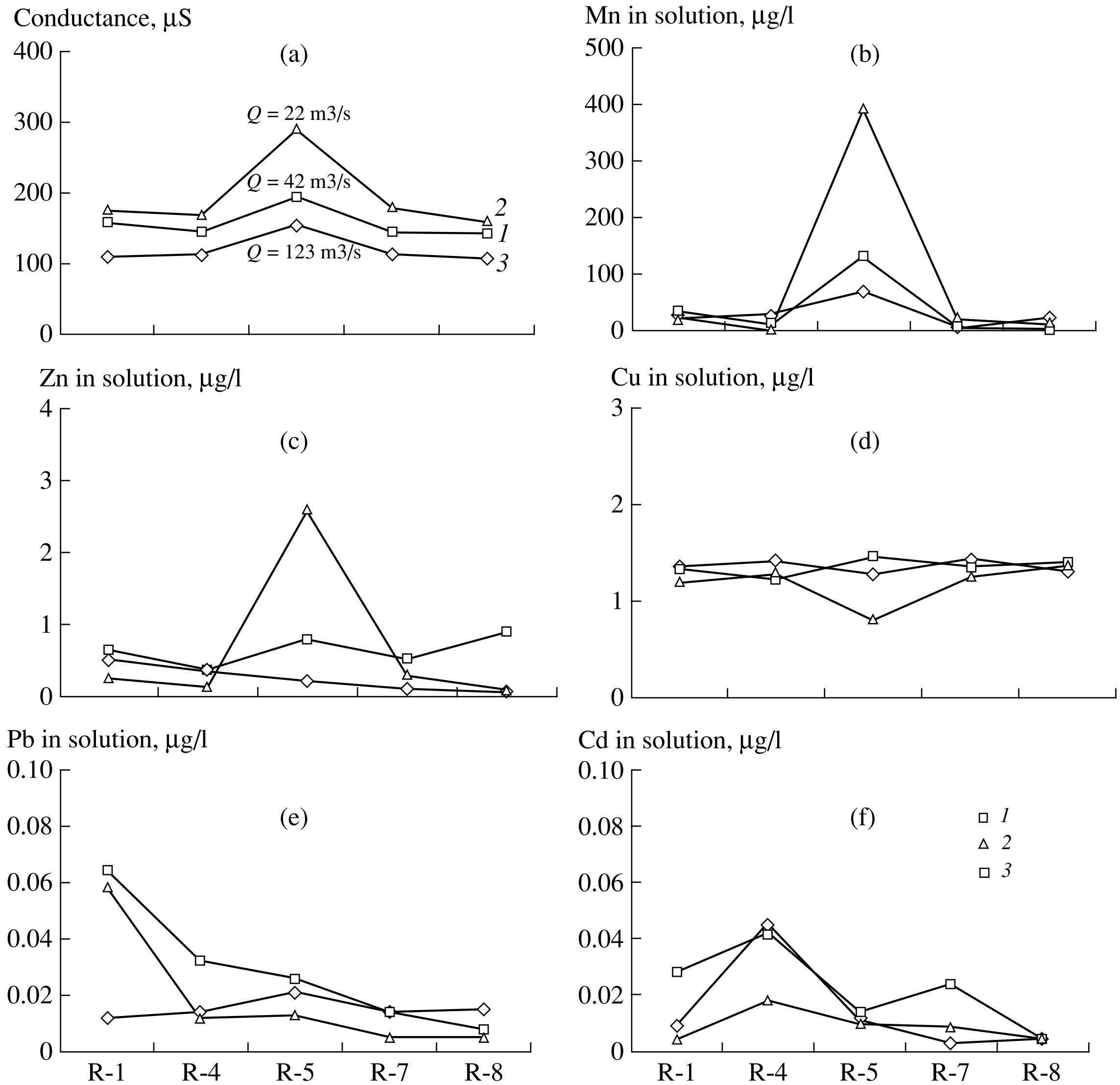

Fig. 3. Change in (a) the conductance and (b–f) the concentrations of dissolved metals in the Razdol'naya River from its upper reaches (st. R-1) to lower reaches (st. R-8) at different hydrological regimes: (*1*) June 2003, debit $Q = 42$ m^3/s; (*2*) September 2003, debit $Q = 22$ m^3/s; (*3*) July 2004, debit $Q = 123$ m^3/s. Station R-5 is located near the wastewaters output of the town of Ussuriisk.

their character. The Vtoraya Rechka River in the town of Vladivostok, to which wastes from machine plants having galvanic lines are discharged, demonstrates a 100-fold increase in dissolved Cd, a 10- to 15-fold increase in Zn and Ni, and only a 2-fold increase in Cu, while the contents of dissolved Fe, Mn, and Pb show no significant deviations from the level of the Razdol'naya or Ussuri rivers. The contents of dissolved metals in the upper reaches practically do not differ from the background ones (Table 2, Fig. 4a). In the lower reaches, the Vtoraya Rechka River receives communal wastes, which cause an insignificant decrease in the anomalies of dissolved Cd, Cu, and Ni, whereas the contents of dissolved Fe, Mn, and Zn continue to increase (Fig. 4a). The pollution of the Vtoraya Rechka River by dissolved metals approaches the level observed in the Delaware River, one of the most polluted rivers in the United States [12], and the Cd content even exceeds it. Another example of a river affected by a specific anthropogenic load in Primorye is the Rudnaya River, which drains an area with a well-developed ore mining industry. Owing to this, the concentration of dissolved Zn is higher in it by a factor of up to 100, while the Pb, Cd, Mn increase by a factor of 10, and Cu shows a double or triple increase [5, 13].

The metal migration in river waters is characterized by a significant role of particulate matter, i.e., metals are transported mainly in the suspended rather than dissolved mode. The role and behavior of particulate modes of metal occurrence can be characterized based on data on the content of metals in suspension con-

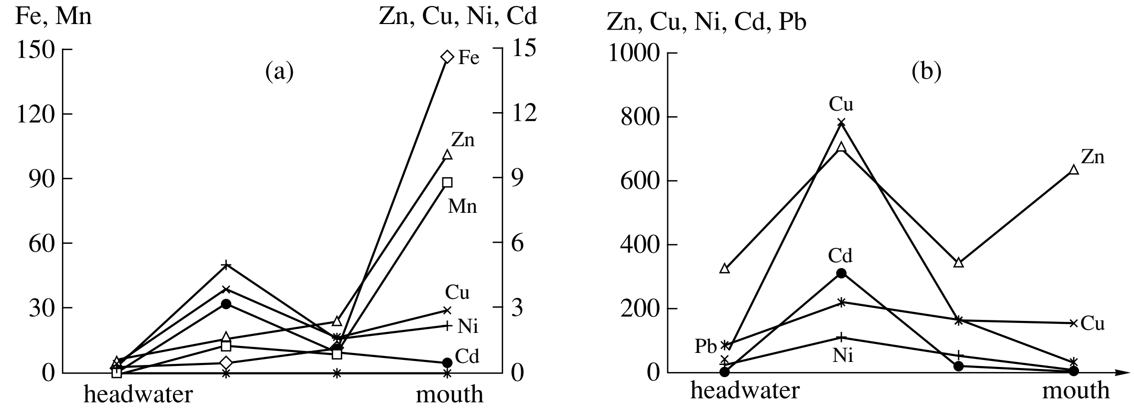

Fig. 4. Variations in the contents of dissolved metals, μg/g (a) and the contents of metals in particulate matter, μg/g (b) in the Vtoraya Rechka River (Vladivostok) from headwaters to the mouth, October 2004.

tained in a unit volume of water (μg/l) or on the metal content per unit weight of suspension (μg/g).

Table 3 presents the concentration levels of the particulate modes of metals in the major rivers of Primorye (Razdol'naya, Ussuri, and Tumannaya rivers), as well as in the weakly polluted rivers of southwestern Primorye at mean-weighted suspension concentration, while Fig. 5 demonstrates the proportions between the dissolved and particulate modes in the balance of metals. Evidently, in spite of the broad variations in the content of particulate metal modes, the total fluxes of most metals transported by rivers are dominated by these. Only nonpolluted rivers with low turbidity (less than 5–10 mg/l) demonstrate the predominance of dissolved modes for Cd and Cu, equal concentrations of dissolved and particulate modes for Mn and Zn, and the predominance of particulate Pb and Fe modes (Fig. 5). The predominance of particulate modes in metal migration becomes evident for plain rivers with high contents of particulate matter or during their high-water periods (Fig. 5). Practically in all of the rivers, metals form the following succession according to increasing of their particulate modes during migration: Cd < Cu < Mn < Zn < Pb < Fe, regardless of the particulate matter contents.

Unlike the content of the particulate modes of metals calculated for unit volume μg/l and, therefore, proportional to the amount of particulate matter in water (its turbidity), the specific metal content in particulate matter as calculated per unit weight of particulate matter (μg/g) depends not as strongly on the hydrological regime during sampling and more distinctly characterizes the anthropogenic impact and/or the geochemical specialization of the drainage area. Table 4 demonstrates the average values of and variations in the metal contents in the particulate matter of Primorye rivers. With the exception of the anomalous Vtoraya Rechka River, the average metal contents in the riverine particulate matter are similar, though the Pb and Cu contents in the particulate matter from the Tumannaya River are 1.5–2 times higher. At the same time, the trace-element composition of the riverine particulate matter is highly variable. The main natural factor affecting the metal contents in the particulate matter is its granulometric composition, which is, in turn, controlled by the content of particulate matter, coarser grained at high water and finer at low water. Correspondingly, in the absence of strong anthropogenic impact, the metal contents in particulate matter at low turbidity must be higher and,

Table 3. Contents of particulate modes of metals (μg/l) in some rivers of Primorye with average contents of particulate matter (mg/l)

River	Particulate matter	Fe	Mn	Zn	Cu	Pb	Cd
Tumannaya*	124	7576	494	17.6	6.90	8.08	0.056
Razdol'naya*	73	3464	121	7.6	2.0	2.14	0.018
Ussuri	27	1542	51.2	3.55	0.73	1.06	0.017
Background**	9.6	454	12.8	1.43	0.33	0.24	0.007

Notes: * Lower reaches.
** Background is the river of southwestern Primorye.

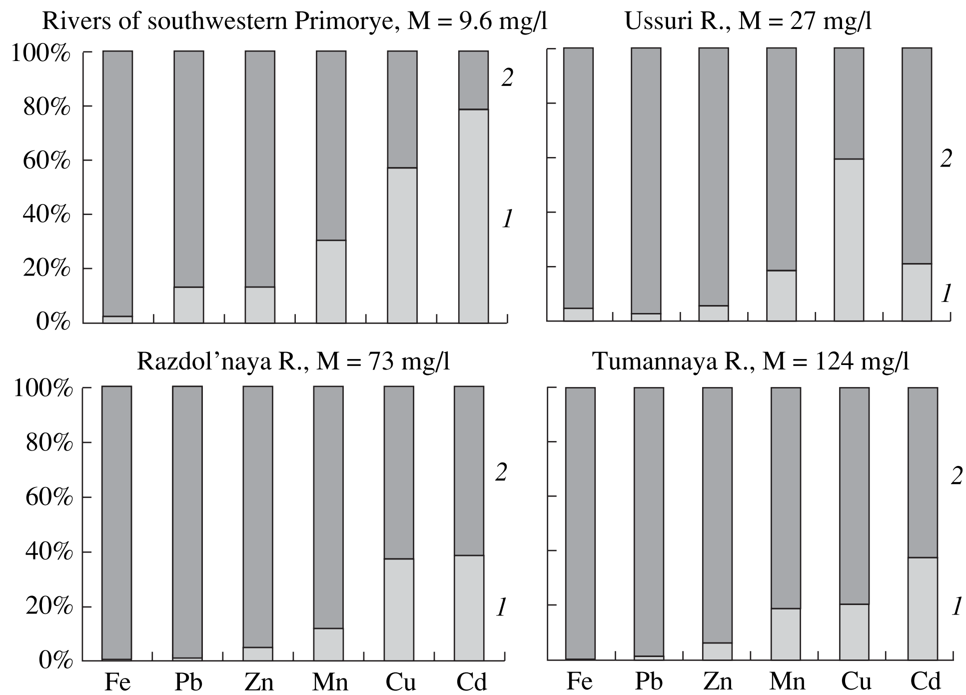

Fig. 5. Proportions of (*1*) dissolved and (*2*) particulate modes of metal migration in the typical rivers of Primorye at the average level of the particulate matter content, M, mg/l.

at high waters, lower. This tendency was already noted for Primorye rivers [5] and is confirmed by our data.

The analysis of variations in the metal contents in the particulate matter of the Razdol'naya and other rivers of Primorye shows (Table 4) that natural variations in the granulometric composition of the particulate matter and characteristics of the drained watershed could be accompanied by the following change in the contents of metals (in μg/g): from 80 to 140 for Zn, from 18 to 42 for Cu, from 15 to 98 for Pb, from 0.08 to 0.87 for Cd, and from 34 to 77 for Ni at Fe and Mn contents from 2.77 to 8.93 and from 320 to 5700 μg/g, respectively. The average metal contents in the particulate matter of the Razdol'naya and Ussuri rivers are close to those in particulate modes from the lower reaches of the Lena and Mississippi rivers [11, 14]. Metal contents higher than the indicated value unambiguously indicate an additional anthropogenic flux of metals into the river.

The metal content in the particulate matter in the river areas modified by a mild anthropogenic impact (for example, the Razdol'naya River near the town of Ussuriisk) increases (Fig. 6). The extent of anthropogenic impact of such "spot" sources depends on the hydrological regime: with an increase in the water debit in a river, the metal content in its particulate matter downstream of the discharge site of anthropogenic wastes significantly decreases (Fig. 6) due to dilution by nonpolluted natural material. As was mentioned previously [15], the Zn, Pb, and Cd contents in the particulate matter in the upper reaches of the Razdol'naya River increase, especially at a low water debit (Fig. 6), which presumably reflects the anthropogenic impact on the drainage system within the People's Republic of China. The Pb content reaches in this case 150 μg/l, while that of Cd is 2 μg/l, which exceeds the natural level for particulate matter content in this region. For Cd and Pb, the anthropogenic nature of this increase is confirmed by the increase in the dissolved modes (Fig. 3e, 3f).

A significant decrease in the metal content in particulate and dissolved modes in the lower reaches of the Razdol'naya River (Figs. 3, 6) indicates that the river can efficiently purify itself.

The trace-element composition of the particulate matter in water flows affected by industrial wastes (Rudnaya and Vtoraya Rechka rivers) is determined by their economic specialization. In particular, the Rudnaya River, whose catchment area includes draining the middle part of Sikhote Alin with its well-developed ore mining industry, demonstrates an increase in the Zn, Pb, and Cd concentrations in the riverine particulate matter by 1.5–2 order of magnitude as compared to the background contents [13, 16]. The Vtoraya Rechka River in the town of Vladivostok receives wastes from machine-building and galvanic facilities in its middle reaches and communal wastes near the mouth. Correspondingly, the particulate matter in the upper reaches of the river bears metal concentrations at the background level, while those in the middle reaches show an increase by factors of 5–7 in the Pb, Ni, and Zn concentrations, by a factor of 20 in Cu, and by a factor of 1000

Table 4. Metal contents in the particulate matter of Primorye rivers and some other rivers with different levels of anthropogenic loading

River	N	Fe	Mn	Zn	Cu	Pb	Cd	Ni
Tumannaya*	6	6.12 / 4.32–7.72	3992 / 947–10014	142 / 122–162	56 / 33–100	65 / 33–128	0.45 / 0.04–0.77	37 / 23–48
Background**	6	4.73 / 3.60–6.44	1335 / 816–1719	149 / 118–176	34 / 26–39	25 / 12–48	0.71 / 0.53–0.97	36 / 22–62
Razdol'naya*	12	5.38 / 3.5–7.63	1529 / 717–3605	116 / 65–164	32 / 23–42	42 / 21–98	0.35 / 0.08–0.91	54 / 34–77
Rivers of the Ussuri River basin***	20	5.78 / 3.55–8.93	1866 / 1027–4511	128 / 87–191	26 / 18–34	41 / 26–67	0.56 / 0.19–0.87	43 / 27–49
Vtoraya Rechka River	4	4.27 / 1.05–6.77	1921 / 271–2522	504 / 342–709	287 / 45–784	125 / 31–220	84.8 / 2.41–312	48 / 8–109
Mississippi R. [11]		4.5–5.5	1620	130	38	33	0.41–0.9	45
Lena R. [14]		5.5	1243	180–217	26–39	31–37	0.14–1.42	24–37
Shel'da R. [17]		–	–	540–1133	125–192	125–132	6.3–12.7	33–67

Notes: * Only lower reaches.
** Suspension from rivers of southwestern Primorye.
*** Including the Khanka Lake basin. N is the number of samples, numerator is the average value, denominator is the concentration range, Fe in %, other metals, in µg/g.

for Cd. Toward the mouth of the Vtoraya Rechka River, the Ni and Pb contents in the particulate matter decrease to the background level, whereas those of Cu and Zn remain elevated (5-fold increase), as also is the Cd concentration, which is higher by one order of magnitude (Fig. 4b). The extent of particulate matter pollu-

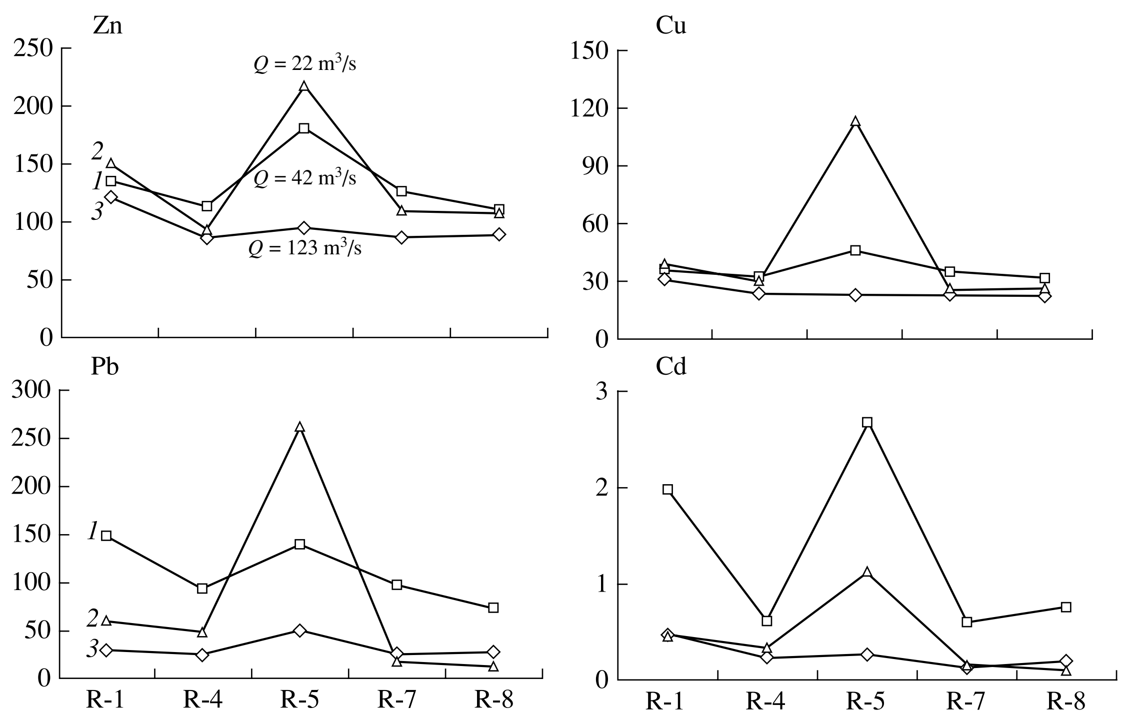

Fig. 6. Variations in the content (µg/g) of chalcophile elements in the particulate matter of the Razdol'naya River (st. R-1) to the lower reaches (st. R-8) at different hydrogeological regimes (symbols are shown in Fig. 3).

tion in the Vtoraya Rechka River is equal to that in the Scheldt River, one of the most polluted rivers in Europe [17], and is even higher for Cd.

CONCLUSIONS

The accurate determination of the background concentrations of metals in river waters is of decisive significance for the correct assessment of anthropogenic impact on water flows. The minimum background levels of dissolved metals are observed in Primorye rivers that drain forested, mountainous, and thinly populated watersheds and account for 0.1–0.5 μg/l for Zn and Ni, 0.3–0.7 μg/l for Cu, 0.01–0.04 μg/l for Pb and Cd, and 2–20 μg/l for Fe and Mn. Plain rivers with a high degree of total anthropogenic impact but without significant specific pollution (Razdol'naya and Ussuri rivers) contain two times more dissolved Cu and Ni, and five to seven times more dissolved Fe and Mn. With increasing anthropogenic impact, the contents of dissolved Zn, Pb, and Cu can reach two to five background levels, and those of Mn can be 20 times higher than the background (Tumannaya River). In the water flows affected by industrial wastes, enrichment in dissolved metals depends on the specialization of wastes and can reach 2–3 orders of magnitude.

The influence of the hydrological regime on the content of dissolved metals in the river waters of the Primorye, as illustrated by the Razdol'naya River, is distinctly seen in the areas modified by significant anthropogenic loading. In the middle reaches of the river affected by wastes of the town of Ussuriisk, the increase in the water debit leads to the dilution of the anthropogenic contribution and a decrease in the anthropogenic anomaly of dissolved Zn and Mn. The effect of wastes on the the contents of dissolved metals already significantly weakens 5 km downstream. However, only 40 km downstream, the Zn and Mn contents decrease to the level observed above the town of Ussuriisk. In the upper reaches of the Razdol'naya River, the additional flux of dissolved Pb from the territory of the People's Republic of China is also most significant at a low water debit and is fairly rapidly equalized.

The level of metal content in the particulate matter of the Primorye rivers unaffected by specific industrial loading is close to the world's average data. The observed natural variations are caused primarily by the variations in granulometric composition and account for 80–140 μg/g for Zn, 18–42 μg/g for Cu, 15–98 μg/g for Pb, 34–77 μg/g for Ni, and 0.08–0.87 μg/g for Cd at Fe and Mn contents in the particulate matter from 2.77 to 8.93% and from 320 to 5700 μg/g, respectively. Metal content higher than the aforesaid suggest an additional anthropogenic flux of metals into the river.

The usual anthropogenic impact (mainly communal wastes), results in an increase in Zn, Cu, Pb, Cd, and Ni in the particulate matter by factors of 1.5–3 relative to the natural one. The extent of enrichment depends on the hydrological regime, reaching a maximum at low waters and a minimum at high waters. Regardless of the hydrological regime, the anthropogenic effect on the trace-element composition of the particulate matter of the Razdol'naya River is equalized over a distance of 5–10 km.

The effect of industrial wastes on the metal content in the river particulate matter depends on its specialization. In particular, water flows mixing with galvanic wastes show a 5- to 20-fold increase in the Pb, Ni, Zn, and Cu concentrations, and a three-order of magnitude increase for Cd. The effect of ore mining is accompanied by one to two order increase Pb, Zn, and Cd concentrations.

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